

 УНИВЕРЗИТЕТ У БАЊОЈ ЛУЦИ

 UNIVERSITY OF BANJA LUKA

 ТЕХНОЛОШКИ ФАКУЛТЕТ

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XIII CONFERENCE OF CHEMISTS, TECHNOLOGISTS AND ENVIRONMENTALISTS OF REPUBLIC OF SRPSKA

PROCEEDINGS

Banja Luka, October 30th 2020 REPUBLIC OF SRPSKA, B&H





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XIII CONFERENCE OF CHEMISTS, TECHNOLOGISTS AND ENVIRONMENTALISTS OF REPUBLIC OF SRPSKA

BOOK OF PROCEEDINGS

Banja Luka, October 30th 2020 REPUBLIC OF SRPSKA, B&H

XIII CONFERENCE OF CHEMISTS, TECHNOLOGISTS AND ENVIRONMENTALISTS OF REPUBLIC OF SRPSKA BOOK OF PROCEEDINGS

Publisher: University in Banjaluka, Faculty of Technology

Editorial board: Borislav Malinović, PhD, dean

Design and computer processing Goran Vučić, PhD BSc Branka Ružičić MSc Đorđe Vujčić

Website: https://savjetovanje.tf.unibl.org/

CIP - Каталогизација у публикацији Народна и универзитетска библиотека Републике Српске, Бања Лука 66(082)(0.034.2) 661:663/664(082)(0.034.2) 663 677(082)(0.034.2) 655(082)(0.034.2) 502(082)(0.034.2) CONFERENCE of Chemists, Technologists and Environmentalists of Republic of Srpska (13; Banja Luka; 2020) Book of Proceedings [Elektronski izvor] / XIII Conference of Chemists, Technologists and Environmentalists of Republic of Srpska, Banja Luka, October 30th 2020 ; [[editorial board Borislav Malinović]. - Onlajn izd. - El. zbornik. - Banja Luka : University in Banjaluka, Faculty of Technology = Tehnološki fakultet, 2021 Sistemski zahtjevi: Nisu navedeni. - Način pristupa https://savjetovanje.tf.unibl.org/. - Êl. (URL): publikacija u PDF formatu opsega 305 str. - Nasl. sa naslovnog ekrana. - Opis izvora dana 23.02.2021. ISBN 978-99938-54-90-6 COBISS.RS-ID 130974465

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Ministry of Scienctific and Technological Developmnet Higher Education and Information Society of the Republic of Srpska



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International Scientific Conference "XIII Conference of Chemists, Technologists and Environmentalists of Republic of Srpska"

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XIII Conference of Chemists, Technologists and Environmentalists of Republic of Srpska

GENERAL AND APPLIED CHEMISTRY

Original scientific article

SORPTION OF DICLOFENAC FROM AQUEOUS SOLUTION TO TEMPO OXIDIZED CELLULOSE

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Abstract

Pharmaceutically active compounds represent a large class of water pollutants. The most commonly detected pharmaceutically active compound in aqueous recipients is diclofenac. There are several methods for removing these compounds, and one of the most commonly used is sorption. Different materials are used as sorbents. The sorption of pharmaceutically active compounds into polysaccharides is determined by the type of polysaccharide and the method of its modification, as well as the structure of the drug itself. In this work, samples of selectively oxidized cellulose with 0.057 mmol/g COOH and 0.0845 mmol/g CHO (sample-OC1) and 0.063 mmol/g COOH and 0.0875 mmol/g CHO (sample-OC2) were used as polysaccharide sorbent. They were obtained by oxidation of the cellulose using TEMPO reagent for 2 hours at a temperature of 25±1°C. Sorption of diclofenac was performed from an aqueous solution of concentrations $c=1,5\cdot10^{-3}$ and $3,0\cdot10^{-3}$ mol/L at a temperature of 25±1°C for 48 hours. The amounts of bound drug were determined spectrophotometrically at a wavelength of $\lambda_{max} = 276$ nm. The maximum amount of bound drug after 24h was 0.0465 mmol/g OC (from solution $c=3.0\cdot10^{-3}$ mol/L, on a sample OC2). The paper studies the possibility of using a TEMPO oxidized cellulose for sorption of diclofenac. Also, the paper studies influence of the content of COOH and CHO groups and the sorption properties of OC, the concentration of diclofenac solution and the duration of sorption on its sorption.

Keywords: TEMPO-oxidized cellulose, diclofenac-K, sorption of diclofenac.

Introduction

The content of pollutants in drinking water is constantly increasing (Jeirani et al., 2017). Among the most common pollutants are pharmaceutically active compounds (PhAC). PhACs have been detected at different concentrations in wastewater as well as in surface water (Salgado et al., 2010). Of the pharmaceutically active compounds, diclofenac most commonly occurs as a contaminant and may be in the form of the sodium or potassium salt as well as in the form of diethylamine (Zhang et al., 2008). Diclofenac belongs to the antipyretic (non-opioid) analgesics, ie it belongs to the group of non-steroidal anti-inflammatory and antirheumatic drugs (NSAIDs) according to the ATC classification. It is one of the most commonly used analgesics in this group. In addition to analgesic action, it shows anti-inflammatory, antirheumatic and antipyretic action (Phillips & Currier, 2004). Structurally, diclofenac or 2 - [(2,6-dichlorophenyl) amino] phenyl] acetate (Figure 1) is an aminophenylacetic acid derivative.

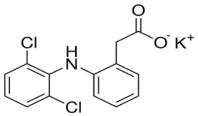


Figure 1. Chemical structure of diclofenac

The use of diclofenac in doses over 150 mg per day leads to organ damage and such concentrations may have a latent toxicity (Hickey et al., 2001). It is most commonly found in hospital and wastewater of the pharmaceutical industry (Gadipelly et al., 2014). Concentrations above 1 mg/L are toxic, because diclofenac is deposited in the tissues of living organisms and shows a cumulative effect. For these reasons, it is important to remove diclofenac from wastewater, so as not to increase its concentration in recipients.

Several ways of removing pharmaceutically active compounds from water have been developed, such as by membranes, biological treatments, flotation, various oxidation processes as well as sorption (Guo et al., 2017). Removal of PhACs by sorption has been the most researched. For this purpose, materials such as aluminosilicates (Kaur & Datta, 2014), carbon materials (Jeirani et al., 2017), metal oxide nanoparticles (Sestito et al., 2019), polymers (Bajpai & Bhowmik, 2010), natural polysaccharides such as chitin and chitosan (Lu et al., 2020) and cellulose derivatives (Ares et al., 2019; Raicopol et al., 2019).

According to the available literature, TEMPO oxidized cellulose has been used as a sorbent for the sorption of dyes (Široký et al., 2011) and heavy metals (Zhang et

al., 2006) but has not been used so far for the sorption of diclofenac or PhACs in general.

The aim of this work was to obtain oxidized cellulose with good sorption properties that could be used as a sorbent in wastewater treatment from diclofenac. The water retention and moisture sorption abilities were examined to determine the sorption capacity of the obtained cellulose. Also, the influence of the content of COOH and CHO groups, as well as the chemical structure of diclofenac and the duration of sorption on the sorption of diclofenac and the chemistry of drug binding was examined.

Materials and Methods

Materials

Cellulose (100%) was used as the material for TEMPO oxidation. Diclofenac in the form of potassium salt ($C_{14}H_{11}C_{12}NO_2K$) from Amoli Organics PVT LTD, India, molecular weight M = 334.23 g/mol, obtained from wholesale in the form of white powder as a pure active substance, was used for the preparation of the sorption solution.

TEMPO oxidation

Oxidized cellulose was obtained according to the method described in the literature (Saito & Isogai, 2004). The oxidation was performed with TEMPO reagents weighing 0.1124 and 0.1873 g. The amount of added NaBr for oxidation was 10 times higher than the added TEMPO reagent and 13% NaClO was added in an amount of 0.5 ml. During the oxidation period, the pH is maintained between 10 and 11 by adding 0.5M NaOH. The modification was performed at a temperature of $25\pm1^{\circ}$ C for 2 hours.

Characterization of oxidized cellulose

The content of carboxyl groups was determined by the Ca-acetate method (Kumar & Yang, 2002). Samples weighing 0.5 g of previously defibrillated cellulose are immersed in 30 ml of 0.25M Ca-acetate and 50 ml of distilled water and remain in solution for 1 h with stirring. Of the total 80 ml, 30 ml is taken for titration with 0.01M NaOH with phenolphthalein as indicator. The result is expressed as mmol/g cellulose and the content of carboxyl groups is determined by the formula:

$$COOH = \frac{\frac{80}{30} \cdot 0.01 \text{M} \cdot \text{V}(\text{NaOH}) \cdot \text{F}(\text{NaOH})}{\text{m}}$$
(1)

The content of aldehyde groups was determined in such a way that first the aldehyde groups were selectively oxidized to carboxyl groups by the sodium chlorite method (Kumar & Yang, 2002). Samples weighing 0.5 g are immersed in

10 ml of 2% sodium chlorite. The pH=3 is adjusted with 0.1M acetic acid. The samples are then placed in a dark place for 72 hours at room temperature. When aldehyde groups are selectively oxidized to carboxyl groups, the content of COOH groups is determined by the method described above. (2)

Moisture sorption was determined by gravimetric method by drying 1 g of material in a laboratory dryer to constant weight and calculating the moisture content. Moisture content is expressed in %, and is calculated according to the formula:

$$\Delta m = \frac{mp - mk}{mp} \cdot 100 \tag{3}$$

The water retention value of the determination is a standard method based on the determination of the amount of water that the tested samples can absorb and retain after immersion in distilled water for 1 h and after centrifugation for 5 min at 500 rpm. The value of water retention is expressed in %, and is calculated according to the formula:

$$w = \frac{mk - mp}{mp} \cdot 100 \tag{4}$$

FTIR spectra of OC and DC samples with bound diclofenac were recorded on an FTIR-BRUKER spectrophotometer, Tensor 27 (USA), in the range 4500-500 cm⁻¹, using an ATR PLATINUM module with a resolution of 4 cm⁻¹ and 16 scans.

Sorption of diclofenac-K

Binding of analgesic to oxidized cellulose was performed under static conditions. Samples of an oxidized bandage weighing 1 g are immersed in 200 ml of an aqueous solution of diclofenac, concentration $c=1.5 \cdot 10^{-3}$ and $c=3 \cdot 10^{-3}$ mol/l at a temperature of $25\pm1^{\circ}$ C for 24 hours. Spectrophotometric measurement of the amount of drug in the solution was performed after 5, 15, 30 min, and after 1, 2, 24 and 48 hours. A Perkin Elmer spectrophotometer model Lambda 25 (USA) was used, and the measurement was performed at the characteristic wavelength for diclofenac at λ max 276 nm.

Results and discussion

TEMPO oxidation of cellulose fibers oxidizes primary hydroxyl groups (at position C-6) and we obtain oxycellulose (OC) with different content of carboxyl and aldehyde groups.

The content of carboxyl and aldehyde groups in untreated samples of cellulose (NT) and oxidized cellulose (OC1 and OC2) is shown in Table 1 and can be seen to increase with increasing amount of added TEMPO reagent.

Sample	Content of carboxyl groups, mmol/g OC	Content of aldehyde groups, mmol/g OC
NT		
OC1	0.057	0.0845
OC2	0.063	0.0875

Table 1. Content of carboxyl and aldehyde groups for NT, OC1 i OC2

In TEMPO oxidized cellulose fibers, the presence of aldehyde groups is a consequence of unconverted aldehyde intermediates on C-6 to carboxyl groups (the oxidation process does not take place to the end).

During TEMPO oxidation, the structure of pores and crystallinity also changes, which affects the sorption characteristics, which can be characterized by moisture sorption and the ability to retain water. Sorption characteristics are used to assess the reactivity of cellulose.

Moisture sorption is the interaction between fibers and moisture by the formation of hydrogen bonds that are formed between the hydroxyl groups of cellulose and water molecules. Table 2 shows the moisture sorption values for NT and samples OC1 and OC2.

Sample	Moisture sorption, %	Water retention value, %
NT	5,8	19,7
OC1	6,5	113,6
OC2	12,7	127,9

Table 2. Moisture sorption and water binding values for NT, OC1 i OC2

Moisture sorption for starting unmodified cellulose fibers is 5.8%. From the results shown in Table 2, an increase in the value of moisture sorption with an increase in the content of COOH and CHO groups (ie, an increase in the content of TEMPO reagents), which can be explained by the destruction of cellulose in the reaction surface layer of fibers.

With the change of the supramolecular structure of the fiber, as a consequence of oxidation, the amount of water retention also changes. The values of water binding to NT and samples OC1 and OC2 are shown in Table 2. From the obtained results it can be seen that in sample OC2 has a higher ability to bind water than sample OC1. This increase occurs due to the introduction of hydrophilic carboxyl groups and morphological changes (from fibrillar form to short fragments).

The sorption results (Figure 2) show that the OC2 sample bound a slightly higher amount of diclofenac and that the amount of bound diclofenac increases with time and the concentration of the solution from which the sorption is performed.

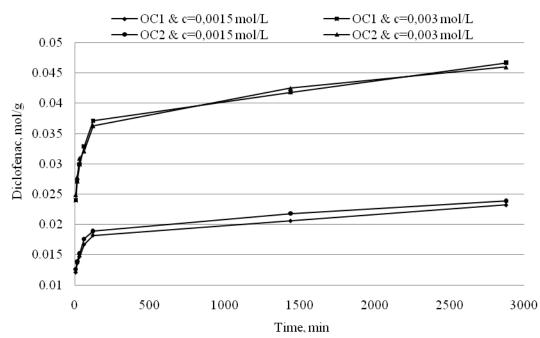


Figure 2. Amount of bound diclofenac to OC1 and OC2 and solution concentration $c=1.5\cdot10^{-3}$ and $c=3\cdot10^{-3}$ mol/l

The chemical structure of diclofenac and conformational flexibility allow it to bind via multiple chemical bonds to OC. Through the secondary amino group, it can build ionic bonds with COOH groups as well as Schiff bases with CHO groups of oxidized cellulose (Sailović et al., 2018). Through the carboxyl group, it can build dimers with COOH OC groups (Rodić Grabovac et al., 2017). Benzene rings can generate Van der Wals interactions with OH groups (π -H interactions) and glucose OC units (π - π interactions) (Saito & Isogai, 2004).

In addition to the ability to bind to multiple bonds, TEMPO oxidized cellulose binds less diclofenac than commercial activated carbon (Lach & Szymonik, 2020), aluminosilicates (Kaur & Datta, 2014), chitosan (Liang et al., 2019), and cigarette butts (Abu-Danso et al., 2019).

Expressed in percentages, 36.67 and 36.99% of the drug binds to OC1 and OC2 samples, respectively from solution $c=1.5 \cdot 10^{-3}$ as well as 9.35 and 9.22% of drug to OC1 and OC2 samples, respectively from solution $c=3 \cdot 10^{-3}$.

A higher percentage of bound drug from a solution of lower concentration (36,67-36,99%) can be explained by the filling of reactive centers and the impossibility of binding an absolutely larger amount of drug from a solution of higher concentration. On the FTIR spectrum (Figure 3) there is a decrease in the peak for the carbonyl group (at 1740 cm⁻¹) because the oxidized cellulose from the form with free carboxyl groups is converted into the form of potassium salt, during OC sorption in diclofenac-potassium solution.

This is also confirmed by the position of the peaks in the spectrum for the carboxylate anion at 1600cm^{-1} and the peaks in the range $1350-1450 \text{cm}^{-1}$. (Zhbankov, 1966)

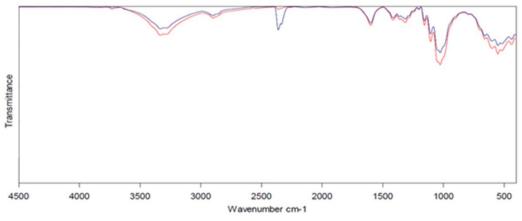


Figure 3. FTIR spectrum OC with bound diclofenac

Conclusion

Two oxidized cellulose samples with 0.057 mmol/g COOH and 0.0845 mmol/g CHO (sample-OC1) and 0.063 mmol/g COOH and 0.0875 mmol/g CHO (sample-OC2) were obtained by the TEMPO oxidation process. Both samples showed a significant increase in sorption characteristics compared to unmodified cellulose. A sample of OC2 with a higher content of COOH and CHO groups bound approximately the same amount of drug as a sample of OC1. When sorbing a drug from a solution of higher concentration, reactive centers are occupied and a significantly larger amount of drug cannot be bound compared to sorption of the drug from a solution of lower concentration. For this reason, both OC samples can be considered a satisfactory sorbent for the removal of diclofenac from water. The process of TEMPO oxidation of cellulose should be guided in the direction of the formation of higher content of carboxyl and carbonyl groups.

For this reason, both OC samples can be considered as a satisfactory sorbent for removing diclofenac from water.

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Original scientific article

DETERMINATION OF TOTAL AND WATER-LEACHABLE MAJOR ELEMENTS IN ASH FROM LUPM WOOD CHARCOAL

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Abstract

Charcoal is made from different lump wood (beech, cherry, ash, maple, poplar, willow, plum, etc.). It is used daily for home heating and food preparation. As a product of combustion, a significant amount of ash is produced, which contains important major nutrients, such as K, Na, Ca, Mg, P and Fe. N-P-K fertilizers are most often used as fertilizers, but ash can be a very good replacement. Also, due to the presence of alkali and alkaline earth metals, ash is used to regulate the pH of the soil. Using the inductively coupled plasma optical emission spectrometer (ICP-OES) nine ash samples were analyzed and the content of major elements was in the following order: CaO > K₂O > MgO > P_{tot} > S_{tot} > Fe₂O₃, Al₂O₃ > Na₂O > BaO. The water-leaching test showed that the concentration of Al, Ba and Fe was below LOQ. The pH value of the water-extract was high, with an average value of 10.61. Based on the obtained results for the total content and the water-leaching test of ash, the ash should be analyzed for leaching of major elements and in an acidic environment in order to get a more complete picture of the mobility of major elements.

Keywords: Charcoal ash, Major elements, ICP-OES, Nutrients mobilization.

Introduction

After wood conversion to charcoal at 250-500°C, charcoal is used as fuel for home heating in industry and food preparation (Rodrigues & Braghini Junior, 2019). After the charcoal combustion, remaines a small amounth of ash, which can be used in different ways. Ash is a solid product of biomass, coal, charcoal, waste and similar fuels combustion. Ashes are mostly mineral product, but usually still contain small amount of combustible organic or other oxidizable residues. Brighter colored ashes are product of complete combustion, but the darker the ash is, the higher are the content of remaining organic components. The color of ashes can be gray, brown, dark gray, yellowish and red (Jambhulkar et al., 2018). The best known types of ash are wood, biomass, coal bottom and fly ash, charcoal ash,

volcano and incinerator ash. As in any other ash, the chemical composition (in w/w %), of mineral substances, of next oxides is: alumina (Al₂O₃), hematite (Fe₂O₃), magnetite (Fe₃O₄), quartz (SiO₂), mullite (3Al₂O₃·SiO₂), magnesium oxide (MgO), rutile (TiO₂), lime (CaO), phosphorus pentoxide (P₂O₅), barium oxide (BaO), sodium oxide (Na₂O), potassium oxide (K₂O), strontium oxide (SrO), sulfur as sulphates (gypsum CaSO₄·H₂O), carbon as carbonates and chlorines (Kraszkiewicz et al., 2017). In ashes also, can be found high concent of calcite (CaCO3), anhydrite(CaSO₄), gehlenite (CaAl₂SiO₇) and sylvite (KCl) (Girón et al., 2013). Ashing the charcoal samples at high flame temperatures, macro elements were converted into oxides (CaO, MgO, Na₂O) and can form with present sulphur anhydrite or to generate sulphates (Li et al., 2016).

Ash is a complex material containing variouse minerals as muscovite (KAl₂AlSi₃O₁₀(OH, F)₂), albite (NaAlSi₃O₈), sepiolite (Mg₄Si₆O₁₅(OH)₂·6H₂O), serandite (Na (MnCa)₂Si₃O₈(OH)), feldspars (NaAlSi₃O₈–CaAl₂Si₂O₈, KAlSi₃O₈) and etc., (Vassilev et al., 2013). The average chemical composition of ash is high percentage of silica (60–65%), alumina (25–30%), magnetite Fe_2O_3 (6–15%), CaO (1-40%), MgO (0-10%), Na₂O (0-6%) and K₂O (0-45%) (Galloway et al., 2015). Ash also contains different essential elements, as Zn, Cu, Mn, B, and Mo, for plant growth (Kraszkiewicz et al., 2017). Since ashes contain high concentration of K and P, they are used as soil and plant fertilisers and as material for regulating the pH value of acidic soil and for neutralizing acidic wastewater, remove phosphate, fluoride. boron. pesticides and organic compounds from wastewater (Ahmaruzzaman, 2010). Also they are used as components for the production of various cements and concrete (Chowdhury et al., 2015; Olutoge & Adesina, 2019), soap production or feed supplement. Since ash is a waste material, scientist are researchig to converse ash into useful product as zeolite (Querol et al., 2002). Park et al. (2012) evaluate the use of wood pellete ash as nutrition source for rey grass and oats. They also concluded that the wood pellete ash increases the soil pH from 2.4 to 2.6 units. So wood ash is highly alkaline with pH of 9-13.5 (Etitgni & Campbell, 1991). Generally, Ca and Mg are more soluble in the pH range of 7 and 8, Na and K are high solubile at pH above 6.0, but especially above 7.5 (Pereira et al., 2012). Applying ash on soil changes the pH, the base cation composition and nutrient status of the soil in the top several cm of the soil layer (Hansen et al., 2017). By treating soil with ash, minerals are returned to the soil so that plants adopt them through the root system. Jagodzinski et al. (2018) study demonstrated the promotion of plant (Lemna minor) growth, as well as the toxic characteristics of wood ash and it's phytotoxicity due to the alkaline character and elemental composition of the ash. Ash have compositions which vary within used fuel materials. Plant species accept from soil all the essential macro elements needed for plant grows, so knowing the ash composition is crucial if the ash is used as fertilizer and as a material for adjustment and for the soil pH improvement. Nine charcharol ashes were investigated in this reasherch for the possibility of their

usage as soil and plant fertilizer. The composition of charcoal ash depends of the type of used wood, the location where it has been growing, age, air and wood chemical composition, way of charcoal production and temperature (Wittkuhn et al., 2017). Combusting the charcoal to the temperature of 750°C gradually for several houres, it has been producted ash, without remaning organic component.

The concentration level of nutrients in charcoal ashes are often determined using ICP-OES, atomic absorption/emission spectrometry (AAS/AES), X-ray fluorescence (XRF) and others. ICP-OES is an instrumental technique that enables fast and simultaneous determination of macro and micro elements in complex samples. It has a wide dynamic and working range, the technique is robust and very sensitive. It can be used to determine macro elements in the ash samples after digestion with strong acids. Although ICP-MS (inductively coupled plasma mass spectrometer) may have even lower detection limits, ICP-OES was used in this study. The ICP-OES showed good detection limits (LOD) and quantification limits (LOQ) (as shown inTable 2).

Materials and Methods

Ashing of lump wood charcoal materials

To produce ash samples, nine different charcoal samples were added in the furnace (sample lab code can be seen in Table 1.). The charcoal samples were put in the open oven, and gradually combusted to the temperature of 750°C and after cooling, stored in the exicator. The obtained ashes were analysed for Al, Ba, Ca, Na, K, Mg, P and S on ICP-OES spectrometer (Spectro Arcos).

Lump wood charcoal	Ash	Lump wood charcoal	Ash
Wild plum	A1	Ash tree	A6
White willow	A2	Beech	A7
Wild cherry	A3	Quercus cerris L.	A8
Wild apple	A4	Acer	A9
Black poplar	A5		

Table 1. The names of nine lump wood charcoal samples used to make the ash samples

Digestion of the ash samples

Ash samples $(0.1000 \pm 0.0001 \text{ g})$ were acid digested in teflon vessels to the ASTM D6357-11 method using hydrochloric acid (37%, Merck), nitric acid (65%, LabExpert), hydrofluoric (HF, Carlo Erba) acid and hydrogen peroxide (30%, Macron). Ultra-pure water (Type 1 Water Purification Systems, Thermo Fisher Scientific) was used throughout the work.

Water-leaching tests an pH measurement

Water-leaching experiments were conducted for all ash samples. In plastic cuvette was measured 0.2000 g of ash sample and added 25 mL of ultra-pure water. The content of the cuvette was shaked (Shaker AW-2 As One) for 4 hours at the room temperature (23°C). After shaking, the cuvette was centrifuged (Sigma 3-16L) at 3600 rpm for 30 minutes. The content of water-leachable major element and the pH value (WTW InoLab 1 pH meter) of water extract were measured from the supernatant.

Evaluation of method and ICP-OES measurment conditions

The evaluation of the method was done first by determining the limit of detection and the limit of quantification. The values for LOD, LOQ and correlation coefficients (R) can be seen from Table 2. The measurement conditions can be seen in the Table 3. The range of the calibration curve is 0.1 to 50 mg/L (single standards, 1000 mg/L, AccuStandard, USA).

Table 2. Received values for LOD, LOQ and correlation coefficient on ICP-OES for analyzed major elements.

K Na P S
766.4 589.59 177.4 180.7
91 2 95 31
0.049 0.0079 0.001 0.013
1 0.0079 1 5
0.343 0.133 0.247 1.665
1.000 1.0000 1.000 0.999
$\begin{array}{cccccccccccccccccccccccccccccccccccc$

Table 3. The measurement conditions on ICP-OES during analyzing ash samples.

Measurement conditions of	f ICP-OES
Optics range 129.230 – 77	1.210 nm
Sample flow 2.0 mL/min	
Rinse time 10.0 s	
Gas pressure main Argon	6.2 bar
Gas pressure nebulizer 2.1	bar

Quality control

While ashing the charcoal samples, blank sample was also prepared, in order to check the cleanliness of the oven. The blank sample was pure quartz sand. During the acid digestion, blank sample was prepared, in order to check the cleanliness of the vessels, the dissolution conditions and the purity of the chemicals themselves. Each sample was dissolved in duplicate. With the samples, reference materials

1633C (NIST) was dissolved and certified. While the samples were prepared for water-leaching test, the blank quartz sand sample was prepared, too. All blank samples were clean, with the concentration of analyzed major elements below LOQ.

Results and discussion

Major element contents in charcoal ashes

If we consider ash as a potential fertilizer, it should determine the total content of nutrients, as well as the content of easily accessible and slowly accessible components in the surrounding medium. Also the content of major nutrients should be more than 1%. The total content of the toxic elements must be minimal. The major element concentrations in all charcoal ashes are reported in Table 4. With respect to major elements, ashes are dominated by the presence of K and Ca with the concentration of 20.00%. Based on nine ash samples investigated in this study, the average content of major elements followed the decreasing order: K > Ca > Mg> P > S > Fe > Al > Na > Ba. Calculating the concentration of major elements on oxides, sample A7 had the highest concent of Al₂O₃ and A8 the lowest content of Al₂O₃. The lowest content of BaO had samples A1, A3 and A4 as 0.03%, and the highest A7 with 0.46%. Sample A6 had the highest content of CaO (39.02%) and A7 the lowest content of CaO (19.00%). The lowest content of Fe_2O_3 had samples A4, A8 and A2 (0.14, 0.15 and 0.18%), and the highest A5 (1.00%). The highest contenh of MgO had A9 (6.55%) and the lowest A1 (1.67%) sample. The highest content of K₂O had samples A2 (33.73%) and A4 (32.09), and the lowest A3 (14.16%). Sample A5 had the highest content of Na₂O (0.45%), and samples A4 and A8 the lowest content of Na_2O (0.07% and 0.09%). For the total conten of P, sample A7 had the highest content of P (1.78%) and sample A4 the lowest (0.30%). Samples A1 and A4 had the lowest content of total S (0.32%) and sample A2 the highest content of total S (1.47%). Bakisgan et al. (2009) analyzed wheat straw, hazelnut shells and olive bagasse ashes for major element. Our samples had similar level of K₂O (hazelnut shells and olive bagasse ashes had higher content), CaO, MgO, Al_2O_3 and P (calculated as P_2O_5). All of the ashes had Fe in highest concentration among the other trace elements (700 to 1100 mg/kg), compareing with our samples, charcoal ashes had higher content of Fe. Our samples had similar content of CaO, K₂O, P (calculate to P₂O₅) and S (calculated to SO₃) as Wang et al. (2020) biomass ash samples, but also we had lower content of Al₂O₃, Na₂O, MgO and Fe₂O₃. Maschowski et al. (2019) analyzed fly ash and bottom ash samples from six biomass power plants. Compared to wood chips ashes, we had generally lower content of Al₂O₃, Fe₂O₃ and Na₂O, similar content of CaO, MgO and P (as P₂O₅), but higher content of K₂O. If we compare our A5 with chemical composition of ashes from poplar clones (Rodrigues & Nunes, 2020), our sample had higher content of K₂O, similar content of Fe₂O₃, but lower content of CaO, BaO, MgO,

Na₂O, P₂O₅ and Al₂O₃. This also depend of the location where the poplar tree grows. Total contents of major nutrients in the ash from corn pellets burned at 700–800°C, showed lower content of Ca and K, similar content of Mg and P, but higher content of Al, Fe and S, than our ash samples (Zhang et al., 2018). The highes sum of all major elements had sample A8 (68.81), and the lowes A7 (49.14%). Based on qualitative interpretations of ash content, Ca and K are dominant metals in ash samples. Also, compared with the above studies, it can be concluded that charcoal ashes are rich in Ca, K, P and Mg, accordingly, ash samples can be used as a potential source of major nutrients.

concenti	_ concentrations of major elements was tess than 5%.								
Sample	Al_2O_3	BaO	CaO	Fe_2O_3	MgO	K ₂ O	Na ₂ O	Р	S
A1	0.25	0.03	25.19	0.20	1.67	25.49	0.11	0.38	0.32
A2	0.11	0.06	22.90	0.18	3.39	33.73	0.20	0.36	1.47
A3	0.27	0.03	34.98	0.23	4.62	14.16	0.13	1.01	0.66
A4	0.06	0.03	24.43	0.14	2.59	32.09	0.07	0.30	0.32
A5	0.58	0.05	33.87	1.00	5.69	20.95	0.45	0.61	0.84
A6	0.41	0.07	39.02	0.32	3.42	20.08	0.08	1.64	0.42
A7	1.01	0.46	19.00	0.56	5.16	20.51	0.15	1.78	0.51
A8	0.06	0.06	36.43	0.15	4.80	25.78	0.09	0.94	0.50
A9	0.20	0.08	24.10	0.24	6.55	25.75	0.17	1.42	0.55

Table 4. Major elements (%) in charcoal ash. The uncertainty in measurement of concentrations of major elements was less than 5%.

Water-leaching test an pH value

In order to get some information on charcoal ash for its fertilizer application, water- leaching test was adopte for its measurement to embody its nutrition characteristics, as a simulaton if the ash was applied on an open filed and a rain would fall down. It was proposed to describe the mobility of nutrients in the ash. In literature (Fan et al., 2018; Sun et al., 2019), deionized water is often used as solvent for ash analysis. The water-leached content of major elements is given in Tables 5a and 5b.

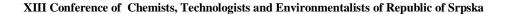
Sample	Al	Ba	Fe
A1	< 0.19	< 0.12	< 0.47
A2	< 0.19	< 0.12	< 0.47
A3	< 0.19	< 0.12	< 0.47
A4	< 0.19	< 0.12	< 0.47
A5	< 0.19	< 0.12	< 0.47
A6	< 0.19	< 0.12	< 0.47
A7	< 0.19	0.12 ± 0.00	< 0.47
A8	< 0.19	< 0.12	< 0.47
A9	< 0.19	< 0.12	< 0.47

Table 5a. Concentration of analyzed major water-extractable elements measured in n = 3 replicates (mg/L) \pm standard deviation.

replicates $(mg/L) \pm standard deviation.$							
Sample	Ca	Mg	K	Na	Р	S	
A1	1.22 ± 0.04	11.31 ± 018	1788.87 ± 6.57	3.01 ± 0.03	$\begin{array}{c} 2.57 \pm \\ 0.05 \end{array}$	41.42 ± 0.16	
A2	3.16 ± 0.02	91.76 ± 0.15	2009.06 ± 14.56	7.99 ± 0.02	1.89 ± 0.03	$\begin{array}{c} 219.72 \pm \\ 0.08 \end{array}$	
A3	9.49 ± 0.07	106.24 ± 0.07	925.25 ± 6.15	4.62 ± 0.01	$\begin{array}{c} 0.27 \pm \\ 0.02 \end{array}$	$\begin{array}{c} 102.60 \pm \\ 0.54 \end{array}$	
A4	1.68 ± 0.03	$41.05{\pm}0.00$	1989.99 ± 218.21	1.42 ± 0.00	1.74 ± 0.00	35.11 ± 0.20	
A5	5.27 ± 0.01	$\begin{array}{c} 88.49 \pm \\ 0.23 \end{array}$	1220.96 ± 4.36	$\begin{array}{c} 22.08 \pm \\ 0.23 \end{array}$	$\begin{array}{c} 0.51 \pm \\ 0.00 \end{array}$	$\begin{array}{c} 115.78 \pm \\ 0.34 \end{array}$	
A6	5.45 ± 0.08	$24.36\pm\!\!0.23$	1115.80 ± 22.39	0.82 ± 0.01	1.18 ± 0.02	47.21 ± 0.86	
A7	7.50 ± 0.20	$\begin{array}{c} 71.07 \pm \\ 0.07 \end{array}$	1897.48 ± 26.35	5.33 ± 0.01	5.71 ±0.11	70.65 ± 0.51	
A8	2.53 ± 0.09	$\begin{array}{c} 16.55 \pm \\ 0.10 \end{array}$	860.79 ± 0.28	3.31 ± 0.03	< 0.25	41.49 ± 0.51	
A9	3.01 ± 0.03	$\begin{array}{c} 30.09 \pm \\ 0.13 \end{array}$	1232.71 ± 13.72	2.02 ± 0.01	$\begin{array}{c} 0.64 \pm \\ 0.01 \end{array}$	59.88 ± 0.84	

Table 5b. Concentration of analyzed major water-extractable elements measured in n = 3 replicates (mg/L) \pm standard deviation.

It can be seen, that from water-leaching, K is the most extractable element. Concentrations of Al, Ba (except for sample A7) and Fe were below LOQ. Al mainly exist as the insoluble aluminosilicate, and his leaching ability is extremely low. Sample A3 had the highest concentration of Ca and Mg, sample A2 the highest concentration of K and S. Samples A8 and A3 had the lowest concentration of P. Wang et al. (2020) had higher amounts of Na, K and Ca in water-leaching samples from biomass ashes, but we had similar result for leached Mg. The leaching rates of alkali metals Na and K is much higher than those of alkaline earth metals as Mg and Ca. Ca and Mg can be in the for of insoluble carbonates. In addition, pH values were measured from water-extraction solution, too. The pH value of each ash sample is given in Chart 1.



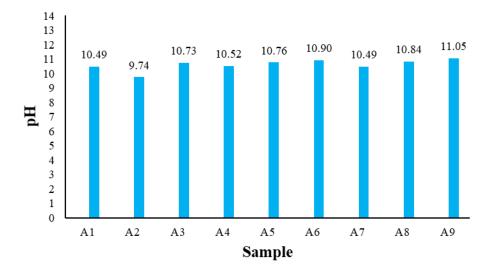


Chart 1. The pH value of water extract for nine ash samples.

From Chart 1 it can be seen that the all water extract had high pH values. The highest value had A6 and the lowest A2. Since the A6 had the highest content of Ca, it was expected that sample A6 will have the highest pH. Sample A2 had highest content of K, so it was unexpected to have the lowest pH, but it also had the highest content of S, who can be in form of acidic SO_4^{2-1} ion. Comparing to the Saqib and Bäckström (2016) waste incineration bottom ash samples, we had similar concentration level of S, and they determined the leached concentration of sulphates, dissolved with water. Limit values of sulphates from waste ash is 1000 mg/kg. If we calculate the leached S to sulphates, the highest concentration of $SO_4^{2^\circ}$ would be 658.23 mg/kg $S/SO_4^{2^\circ}$, which means that the leached S enters the the regulatory limit. Wang et al. (2020) got that ash samples from biomass power had pH 9.2 which will inhibit the leaching for various elements. The lower the pH is, the higher leached amount of toxic components is (pH < 2). Sun et al. (2019) reported the leaching of Ca and Mg from cement concrete and incinerator ashes is high in extreme acidic condition and decreases as the pH increases. Based on high pH, and present OH⁻ ion, applying charcoal ashes could stop the leaching and mobility of toxic element in soil, if the soil is acidic, by increasing the pH value of the soil. Hytönen (2016) showed that adding the wood ash to soil increased concentrations of extractable Ca, K, P and Mg in the soil, and this was associated with growth stimulation of trees (biomass production in willows and birches). Also Jagodzinski et al. (2018) in their study showed the substantially increas growth for L. minor in medium supplemented with wood ash. Since our ash samples show a similar level of leaching of major elements as Jagodzinski et al. (2018), most likely our ash samples would have a stimulating effect of plants growth.

Conclusion

The sum of all major component in charcoal ash is A8 > A6 > A5 > A2 > A4 > A9 > A3 > A1 > A7. The White willow ash sample contains the highest content of K₂O and P, and the Wild cherry ash sample the lowest content. Ash sample A2 is the most suitable source of K and P and to be used as fertilizer. All ash samples can be used to increase soil pH. During the water-leaching a certain amount of major nutrients, K, Mg, Ca, Na i P is released, and will be absorbed by the surrounding medium or plants. Regarding the current used charcoal ashes, an extension for the near future is the use of the same ashes for more accurate results on the acid-leaching of the nine ashes as the simulation of acid rain and the behavior and relising of major nutrients in an acidic environment.

ACKNOWLEDGMENTS

- Ministry of Education, Science and Technological Development Republic of Serbia: agreement on the realization and financing of scientific research work of scientific research organization Mining and Metallurgy Institute Bor, in 2020, Registration number: 451-03-68 / 2020-14 / 200052.
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ODREĐIVANJE SADRŽAJA UKUPNIH I VODENO-EKSTRAKTIBILNIH MAKRO ELEMENTA U PEPELU ĆUMURA

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Sažetak

Ćumur se proizvodi od različite vrste drveta (bukva, trešnja, jasen, javor, topola, vrba, šljiva itd.). Svakodnevno se koristi za grejanje domova i pripremu hrane. Kao proizvod sagorevanja nastaje značajna količina pepela koji sadrži važne, makro, korisne komponente, poput K, Na, Ca, Mg, P i Fe. N-P-K dubriva se najčešće koriste kao đubriva, ali pepeo može biti vrlo dobra zamena istih. Takođe, zbog prisustva alkalnih i zemno alkalnih metala, pepeo se koristi za regulaciju pH Korišćenjem induktivno spregnute plazme optičkog emisionog zemljišta. spektrometra (ICP-OES) analizirano je devet uzoraka pepela i sadržaj makro elemenata. Sadržaj makro elemenata bio je sledećeg reda: $CaO > K_2O > MgO > P_{tot}$ $> S_{tot} > Fe_2O_3$, $Al_2O_3 > Na_2O > BaO$. Test ispiranja vodom pokazao je da je koncentracija Al, Ba i Fe ispod LOQ, dok se vodom iz pepela najviše izlužio K, S i Mg. Slabo izluženje Al i Fe ukazuje da se ova dva metala nalaze u formi nerastvornih silikata. Alkalni zemno alkalni metali su dobro rastvorni u vodi, pa je i povišen sadržaj K i Mg u vodenom ekstraktu razumljiv. Vrednost pH vodenog ekstrakta pepela bila je visoka, sa prosečnom vrednošću od 10,61. Shodno tome, pepeo predstavlja pogodan materijal za regulaciju pH kiselih zemljišta i stimulaciju rasta biljnih vrsta. Na osnovu dobijenih rezultata za ukupan sadržaj i testa ispiranja pepela vodom, zaključuje se da je pepeo ćumura bogat hranljivim makro nutrijentima. Za neka buduća istraživanja, pepeo treba analizirati na ispiranje makro elemenata i u kiseloj sredini kako bi se dobila još potpunija slika o mobilnosti makro elemenata. Pre bilo kakve dalje aplikacije pepela, trebalo bi isti ispitati i na sadržaj mikro metal(oid)a.

Ključne riječi: pepeo, makro elementi, ICP-OES, Mobilnost makro nutrijenata.

Original scientific article

THE ROLE OF SODIUM DODECYL SULFATE IN REMOVAL OF PB(II) IONS THROUGH BULK LIQUID MEMBRANE SYSTEMS

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Abstract

In previously published papers, interactions between different metal ions and surfactants were observed, mostly through different membrane transport techniques. Due to their amphiphilic properties and the possibility of micellar aggregation, surfactants are widely used in various analytical procedures. In this paper, the influence of the anionic surfactant: sodium dodecyl sulfate (SDS), on the efficiency removing Pb(II) ions, trough bulk liquid membrane system, were investigated. Macrocyclic ligands: 18-crown-6. dibenzo-18-crown-6. dicyclohexano-18-crown-6 and benzo-18-crown-6 dissolved in organic solvents (dichloromethane, and chloroform) were used as carriers for Pb(II) ions. Metal ions concentration in aqueous phases was monitored by flame atomic absorption spectrophotometry, after 3 hours of membrane transport. The presence of an anionic surfactant SDS increases transport efficiency to about 50% comparing with the system without surfactant. From the aspect of the macrocycle used, the addition of an anionic surfactant in the receiving phase also reflected in an increased amount of removed Pb(II) ions from the source phase, following the order: DCH18C6>18C6>B18C6>DB18C6.

Keywords: Sodium dodecyl sulfate, Pb (II) removal, bulk liquid membrane

Introduction

Removal of heavy metal ions from aqueous solution is important in environmental concern, because heavy metals can induce serious problems to human health through the water resources. Therefore, so many projects focus on the removal of heavy metals ions to protect water resources (Khobragade & Pal, 2016). A variety of separation methods such as chemical precipitation, ion-exchange, adsorption, membrane filtration, solvent extraction, and liquid membrane transport have been utilized to remove toxic heavy metal ions from the environmental and biological systems (Fu & Wang, 2011). The name of the liquid membrane often implies some

of the types of membranes, such as fully liquid membranes (BLM-Bulk Liquid Membranes), membranes supported by appropriate polymers (SLM-Supported Liquid Membranes) or emulsion membranes (EM). Most of these methods are based on the principle of extraction as an essential separation process. Polyether ligands are among the most suitable host molecules for many metal ions, due to the presence of oxygen atoms as electron donors in their structure, which enables the formation of a coordination-covalent bond. Crown ethers have the specific macrocyclic structure of their molecules, consists of the polyether chain-forming "the crown" with hydrophilic cavity and hydrophobic surface. The macrocyclic structure of these ligands provides high stability of formed complexes with metal ions due to the "macrocyclic effect" (Geary et al., 2005). Surfactant systems have been recognized as very useful alternatives for improving analytical methodologies and the development of new concepts in analytical chemistry.

Coexistence of hydrophilic and lipophilic part in the same surfactant molecule (polar "head" and non-polar "tail") enables their aggregation in formations known as micelles (Flores et al., 2011). At concentrations higher than "critical micellar concentration" (CMC) surfactants can provide a certain level of solubilization for hydrophobic organic compounds (Ying, 2004). Sodium dodecyl sulfate (SDS) is a synthetic organic compound (salt) of an amphiphilic structure composed of an anionic organosulfate (tail – chain consists of 12–atoms of carbons) attached to a sulfate group with the chemical formula $CH_3(CH_2)_{11}SO_4Na$. The chemical structure of SDS is presented in Figure 1. SDS is extensively used for industrial applications as well as for fundamental studies due to its chemical, physicochemical, and utility properties.

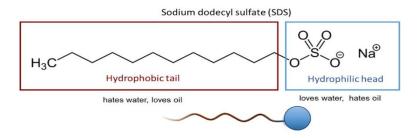


Figure 1. Chemical structure of SDS

The amphiphilic nature of surfactants is expressed in terms of the balance between the hydrophobic and hydrophilic portions of the molecule. This is estimated by the HLB values (Attwood & Florence, 1983). The lower the HLB value, the more lipophilic is the compound and vice versa. HLB values for many compounds are between 1 and 40. Lower HLB means higher lipophilicity. Classification of tensides is based also on this parameter: very lipophilic (1 to 9), amphiphilic (10 to 15) and hydrophilic (> 15). Anionic surfactant; sodium dodecyl sulfate, we used in this paper have the best solubilization properties among other tensides; SDS (HLB = 40) (Table 1).

Surfactants	Molar Weight (g mol ⁻¹)	Charge Type	Hydrophilic- lipophilic balance (HLB)	Critical micelle concentration CMC (mM)
SDS	288	Anionic	40	8.10
Igepal CA-720	75	Anionic	14.6	0.23
Tween 80	1310	Neionic	15	0.01
Triton X-100	628	Neionic	13.5	0.31
Lecitin	773	Zwitterion	3-4	610 mg/L

Table 1. The critical micellar concentration (CMC) and hydrophilic-lipophilic balance number (HLB) of some tensides

In this work, we examined the effect of an anionic surfactant SDS in the receiving phase on the efficiency removing Pb(II) ions, trough bulk liquid membrane system. It has been shown that, in the course of the carrier-mediated transport of a metal ion, the use of an anionic surfactant laying at the MP/RP interface can successfully catalyze the exchange process of the metal ion and measurably facilitate its transport (Rouhollahi et al., 2007). The addition of these surfactants to the receiving phase leads to a better transport efficiency.

Materials and Methods

Preparations of two aqueous solutions and one nonaqueous organic solution (membrane), were performed for every transport experiment, using following material.

Reagents:

Source Phase preparation:

- Standard Pb (II) solution (1000 mg/L), (Pb(NO₃)₂ in 0,5M HNO₃), Merck
- $C_6H_3N_3O_7$ (picric acid); 99%, Kemika
- Acetate buffer solution (pH = 5), prepared from CH_3COOH (purris. p.a., Fluka) and NaOH (g.r., Merck)

Membrane Phase preparation:

- Organic solvent: CH₂Cl₂, dichloromethane; CHCl₃ chloroform p.a. Kemika
- Macrocyclic ligands: 18-crown-6 (18C6); benzo-18-crown-6 (B18C6); dibenzo-18-crown-6 (DB18C6); dicyclohexano-18-crown-6 (DCH18C6); (>99%, ACROS ORGANICS)

Receiving Phase preparation:

- Acetate buffer solution (pH = 5), prepared from CH₃COOH (purris. p.a., Fluka) and NaOH (g.r., Merck)
- Na₂S₂O₃, sodium thiosulphate; purrum.p.a. Sigma-Aldrich
- Anionic surfactant: sodium dodecyl sulphate (SDS) p.a. Sigma-Aldrich

Procedure:

Transport experiments involved the application of a cylindrical glass vessel, "transport cell" (Figure 2.), with an inner diameter of 5 cm, containing a glass tube (2 cm in diameter) in a central position. The central tube represents a physical barrier between the two aqueous phases. The source phase (SP) contained 10 mL of a mixture of tested metal ion $(1 \cdot 10^{-3} \text{ mol/L})$ and the counter ion, picrate $(1 \cdot 10^{-3} \text{ mol/L})$. The receiving phase (RP), which is outside the central tube, contained a stripping agent (sodium thiosulphate) and anionic surfactant SDS. The membrane phase (MP) contained 50 mL of a suitable ligand $(1 \cdot 10^{-3} \text{ mol/L})$ dissolved in an organic solvent; the membrane layer lies beneath the aqueous phases and connects them. The membrane phase is mixed with a magnetic stirrer so that under these conditions the contact surfaces between the aqueous phases are straight and precisely defined. Both aqueous phases were analyzed by atomic absorption spectrometry after 3 hours, and the concentration of metal ions transported through the membrane was measured.

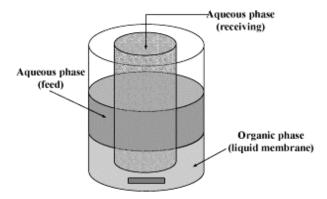


Figure 2. "*Transport cell*" used for the experiment: SP-source phase; RP-receiving phase; MP-membrane phase; A-magnetic stirrer

Instruments

pH measurements of aqueous solutions were performed using the pH meter (GLP31 Crison Instruments). Quantification of metal ions removed during the transport experiments was obtained by Flame Atomic Absorption Spectrometry technique, using the instrument Perkin Elmer AAnalyst 200.

Results and discussion

Since in our previous investigations of BLM systems (Suljkanović et al., 2020). higher dielectric constant and lower viscosity for dichloromethane and chloroform as a liquid membrane contributed to higher removal rate, this gave an advantage for preparing the same liquid membranes in this experiment. Significant interactions between metal cations and nonionic surfactants inside the membrane phase of transport systems in our previous results lead to certain removal of cations (up to 62% of Pb(II) with Brij 58 in chloroform) from the source phase into the membrane, enabling possible application of some nonionic surfactants as carriers for cations (Suljkanovic 2017). In this paper, transport experiments followed by Pb(II) complexation with different macrocyclic ligands (18C6; DB18C6; B18C6 and DCH18C6) within dichloromethane and chloroform as a liquid membrane, including anionic surfactant; sodium dodecyl sulfate (SDS), in receiving phase was investigated. Previous research has shown, that the addition of anionic surfactants to the final phase of the transport system increases the transport efficiency of metal cations according to the principle of electrostatic attraction of positive cations and negative molecules of anionic surfactants (Rouhollahi et al., 2007). In Figure 3. the influence of the anionic surfactant SDS on the efficiency transported Pb(II) ions into the receiving phase was investigated. The effect of anionic surfactant was ultimately examined in two concentration ranges: above and below the critical micellar concentration. It is evident that addition of SDS to the final phase of the transport system increases the transport efficiency of Pb(II) ions. SDS added to the receiving phase, probbably according to the principle of electrostatic attraction, may sobbed Pb²⁺ via ion exchange, whereby dissociating sodium dodecyl sulfate (SDS) in aqueous solution, the formed Na (I) ions may replace some exchangeable Pb^{2+} cation located on the water-organic phase surface. In the same time, dodecyl sulfate anions (DS⁻) has negative hydrophilic head that attract Pb (II) cations to the final phase and thus increases the efficiency of transport. It is evident that the surfactant achieves greater efficiency in the micellar region, which is explained by the mechanism of cation incorporation within the formed anionic surfactant micelle, rather than by interactions with individual surfactant monomers (below CMC). The addition of surfactant increases transport efficiency to about 50%. comparing with the system without surfactant in the receiving phase. Regarding the efficiency of macrocycles as a ligand in the membrane, in these systems with an anionic surfactant, all 18C6 derivatives are very close to each other, which indicates a positive effect in complexation with Pb(II) ions.

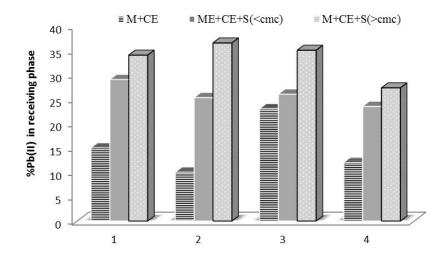


Figure 3. Influence of the anionic surfactant SDS on the efficiency transported Pb(II) ions into receiving phase 1-18C6; 2-DB18C6; 3-B18C6; 4-DCH18C6

The results of the measured content of Pb(II) ions in the original and final phase, and calculated for the membrane phase, were analyzed for the investigated systems that had SDS (above CMC) in the final phase (Table 2.). In this way, the percentage distribution of Pb(II) ions after the end of transport can be observed. It has long been known that the extraction of Pb(II) ions from the original (SP) into the MP phase is relatively easier compared to the re-extraction from MP to RP. From the results showed in Table 2. the uptake from the SP is evident for all used macrocycle. Different structures of macrocyclic ligands are related to different transport rates: DCH18C6>18C6>B18C6>DB18C6. The presence of two cyclohexyl groups causes an increase in the basicity of the oxygen atoms in comparison with DB18C6 which leads to the ability of the DC18C6 complex to adapt to different conformations as required for greater stability of the complex.

Table 2. Measured content of Pb (II) ions in aqueous phases of BLM system after 3h of transport for different crown ethers and anionic surfactant (SDS) in receiving phase

	% Pb(II)				
Type of macrocycle in DCM membrane	SP	MP	RP	REMOVAL	
18C6	14,30	51,70	34,00	85,7	
DB18C6	47,10	16,40	36,50	52,90	
B18C6	36,00	29,00	35,00	64	
DCH18C6	8,25	64,39	27,36	91,75	

Conclusions

According to the principle of electrostatic attraction, dissociating sodium dodecyl sulfate (SDS) in aqueous solution, the formed Na (I) ions may replace some exchangeable Pb(II) ions located on the water-organic phase surface and increases transport efficiency. Introducing SDS in the receiving phase to a systems with different macrocycle crown ethers, showed increased transport efficiency to about 50% for all used ligands comparing with systems without surfactant. Dicyclohexano-18-crown-6 (DC18C6) due to its very lipophilic character and its corresponding cavity size for selective complexation with Pb (II) ion compared to other ligands proved to be a selective and efficient carrier for Pb (II) transport via BLM, removing 91,75% transported Pb (II) ions from source phase after 3 hours of transport experiment.

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ULOGA NATRIJUM-DODECIL SULFATA PRI UKLANJANJU Pb (II) IONA SISTEMOM TEČNE MEMBRANE

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Sažetak

Uklanjanje iona teških metala iz vodenih rastvora je važno za okoliš, obzirom da teški metali mogu stvoriti ozbiljne probleme ljudskom zdravlju kroz vodene resurse. Stoga se mnogo projekata fokusira na uklanjanje iona teških metala radi zaštite vodnih resursa. Za uklanjanje toksičnih iona teških metala iz okruženja i bioloških sistema koriste se razne metode kao što su: hemijsko taloženje, izmjena jona, adsorpcija, membranska fitracija kao i transport kroz tečnih membrane. U ranije objavljenim radovima zabilježene su interakcije između različitih iona metala i surfaktanata uglavnom pomoću različitih tehnika transporta membrane. Zbog svojih amfifilnih svojstava i mogućnosti micelarne agregacije, površinski aktivne tvari široko se koriste u raznim analitičkim postupcima. Dosadašnja istraživanja pokazala su da dodavanje anionskih surfaktanata u krajnju fazu transportnog sistema povećava transportnu efikasnost metalnih kationa prema principu elektrostatičkog privlačenja pozitivnih kationa i negativnih molekula anionskih surfaktanata. U ovom radu istražena je uloga anionskog surfaktanta: natrijum dodecil sulfata (SDS), pri uklanjanju Pb(II) jona, kroz sistem tečnih membrana. Makrociklički ligandi: 18-kruna-6. dibenzo-18-kruna-6, dicikloheksano-18-kruna-6 i benzo-18-kruna-6 rastvoreni organskim u rastvaračima (dihlormetan i hloroform), su korišteni kao ligandi za Pb(II) jone. Koncentracija metalnih iona u vodenim fazama svih analiziranih sistema, praćena je atomskom apsorpcionom spektrofotometrijom, nakon 3 sata transporta. Prisutnost anionskog surfaktanta SDS u krajnjoj fazi povećava transportnu

efikasnost za oko 50% u poređenju sa sistemom bez surfaktanta. Sa aspekta korištenog makrocikla, dodavanje anionskog surfaktanta u krajnju fazu utiče na povećanu količinu uklonjenih Pb(II) iona iz izvorne faze, slijedećim redoslijedom: DCH18C6> 18C6> B18C6> DB18C6. Dicikloheksano-18-kruna-6 (DC18C6) u poređenju sa ostalim ligandima se može izdvojiti kao najefikasniji za transport Pb(II) jona putem sistema tečnih membrana, uklanjajući 91,75% Pb (II) iona iz izvorne faze nakon 3 sata transportnog eksperimenta.

Original scientific article

CONDUCTOMETRIC STUDY OF TRITON X-100 INFLUENCE ON THE PB(II) COMPLEXATION WITH 18C6 IN DICHLOROMETHANE

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Abstract

The complexation of Pb(II) with 18-crown-6 in aqueous solutions has been widely studied and stoichiometry of the resulted complex was well defined using conductometry and UV/VIS spectrophotometry. In this paper, the influence of nonionic surfactant Triton X-100 on the complexation of Pb(II) ions was investigated using conductance measurements in aqueous and nonaqueous (dichloromethane) solutions. The results show that the addition of a nonionic surfactant TX-100 lead to a better-defined stoichiometry of the Pb(II) complex in dichloromethane, significantly contributed to its stability and the absolute conductivity values increased. The effect of TX-100 on the complexation of Pb(II) ions in the aqueous medium is opposite and lower conductivity values were measured. Both effects confirm the existence of significant interactions between surfactant micellar structures and formed Pb(II) complexes.

Keywords: Conductometry, Triton X-100, 18-crown-6, Pb (II)

Introduction

Complexation reactions of metal ions with different ligands have been widely studied, especially in the case of macrocyclic ligands crown ethers. Since the first synthesis of crown ethers by Pedersen in 1967., these investigations spread widely within the research community, due to their wide applications in chemistry, such as microanalysis, sensing, and separation of metal ions (Aragoni et al., 2002). Polyether ligands are among the most suitable host molecules for many metal ions, due to the presence of oxygen atoms as electron donors in their structure, which enables the formation of a coordination-covalent bond. Crown ethers have the specific macrocyclic structure of their molecules, consists of the polyether chainforming "the crown" with hydrophilic cavity and hydrophobic surface. The macrocyclic structure of these ligands provides high stability of formed complexes with metal ions due to the "macrocyclic effect" (Geary et al., 2005). One of the

most important factors influencing complex formation is the compatibility between "the host" molecule (ligand) and "the guest" (metal ion). In the case of complexation of macrocyclic ligands, there are many factors which can make significant contributions to the stability of their metal ion complexes: the cation size, the ionic solvation of the charged species involved, conformations of the free and complexed crown ethers, the electronic structure of metal ion and the binding strengths of solvent-ion and crown-ion. It seems that solvent properties such as donor number, dielectric constant, and their dipole moments influence upon the enthalpy and entropy. Crown ethers have a strong affinity for alkali and alkaline earth metal ions. The main factor governing the binding strength and selectivity is the size compatibility between the cation radius and the ligand cavity. The cations fitting the cavity best are located in its center and optimize the interactions with the oxygen heteroatoms. Table 1. gives the ionic radius of the alkali, alkaline earth, and heavy metals cations as well as the radius of the cavities of the crown ethers determined by CPK (Corey-Pauling-Koltun) molecular models (Vögtle, 1995). Specifically, the highest selectivities are expected in cases where the ratios of cation radius and cavity radius of the ligand are closest to 1.

Table 1. Overview of ion radius of alkali, alkaline earth, and heavy metals cations as well as some crown ethers (Vögtle, 1995)

Cations	Ionic radius/pm	Cations	Ionic radius/pm	Cations	Ionic radius/pm
Li^+	74	Mg^{2+}	72	Ag^+	115
Na^+	102	Ca^{2+}	100	\mathbf{Tl}^+	150
\mathbf{K}^+	138	Sr^{2+}	116	Pb^{2+}	120
Rb^+	149	Ba^{2+}	136	Cd^{2+}	109
Cs^+	179				

Ligand cavity radius/pm				
Crown ether	Ionic radius /pm			
12C4	60-75			
15C5	85-110			
18C6	134-143			
B18C6	134-155			
DB18C6	260-320			

In this paper effect of the nonionic surfactant Triton X-100 on the Pb(II) ion complexation with 18C6 has been investigated. Surfactants have also been found, to influence the complexation reactions of cyclic polyethers with metal cations. The main reason for this being either the complexation of surfactant counter ions with the crown ethers themselves or the localization of the ligand or complex or both in the surfactant micelles (Vaidya et al., 1997). Nonionic surfactants have a definite advantage over the ionic in that they are compatible with all other types of surfactants and their properties are little affected by changes in pH of the solution,

also by virtue of their low CMC's they are effective in much lower concentrations. Previous studies of crown ether complexation in various solvents (Solov'ev et al., 1996) showed that the metal complexes are more stable in organic (nonaqueous), compared to aqueous solutions. This enhancement of stability is primarily an enthalpic effect. The amphiphilic nature of nonionic surfactants is expressed in terms of the balance between the hydrophobic and hydrophilic portions of the molecule. This is estimated by the HLB values (Attwood & Florence, 1983). The lower the HLB value, the more lipophilic is the compound and vice versa. TX-100 (HLB ~18) is found to be the least lipophilic among the surfactants. Conductometric titrations with crown ethers have proved to be very useful in determining the stability constants, selectivity, and also the thermodynamic parameters of the crown ether complexes with various cations in nonaqueous and aqueous/nonaqueous media.

Materials and Methods

Conductometry is an electroanalytical method that measures the electrical conductivity, as a consequence of the existence of free mobile charge carriers (ions) in solution. Ions move freely in solutions under the influence of an electric field and contribute to the overall conductivity of the solution, depending on their concentration and mobility. The electrical conductivity (κ) is directly related to the concentration (C), through the value of molar conductivity (Λ).

Reagents:

The macrocyclic ligand: 18-crown-6, 18C6, (99%, ACROS ORGANICS) The nonionic surfactants: Triton X-100, (p.a. Sigma-Aldrich)

Organic solvent : dichloromethane (DCM), (p.a. Kemika)

All measurements were carried out at 25° C with a GLP31 Crison Instruments digital conductometer, which was calibrated regularly with the Mettler Toledo standard solutions. All molar conductivities were calculated after correcting for the solvent conductivity. The uncertainty in the measurement of conductivities was ±0.1 µS.

Procedure:

The GLP31 Crison Instruments digital conductometer, presented in Figure 1. was used for the measurements. Measurements were performed at room temperature. The change in the electrical conductivity of the solution depending on the change in the ligand concentration was monitored. Namely, the titration of the metal ion solution $(1 \cdot 10^{-3} \text{ mol/L})$ with ligand solution was performed until the molar ratio of ligand: metal = 3: 1 was reached. The results presented by the diagram of the dependence of electrical conductivity on the molar ratio of ligand / metal made it possible to define the stoichiometry complex. The Pb(II) nitrate $(1.10^{-3} \text{ mol/L})$

dissolved in surfactant TX-100 $(4 \cdot 10^{-3} \text{ mol/L})$ was placed in the cell and the conductivity was measured. The crown ether solution (~0.02 mol/L) was added to the cell in small increments until the total concentration of the crown ether was approximately 2 to 3 times as large as that of the metal nitrate. The conductivity was measured after each addition as above.



Figure 1. GLP31 Crison Instruments digital conductometer

Results and discussion

The electrical conductivities of the 3-component system (metal ion-macrocyclic ligand-nonionic surfactant) in an organic solvent (DCM) were measured. In earlier investigations of surfactant interactions with cations (Suljkanović et al., 2016) during their complexation with macrocyclic ligands, the influence of surfactants was evident, but not well defined in terms of exact surfactant role in it. The presence of a nonionic surfactant TX-100 influenced the transport rate of Cd(II) and Pb(II) ions through the organic liquid membrane by slowing it, probably due to additional interactions between surfactant micelles and cations/complexes within the membrane (Suljkanović et al., 2017). In this paper, the influence of TX-100 on the stability and stoichiometry of the Pb(II) complex formed in dichloromethane was investigated. In Figure 2, the dependence curves of the electrical conductivities were compared for 2-component and 3-component systems: Pb2+-18C6 and Pb2+-18C6-TX-100 in dichloromethane, respectively. The influence of TX-100 is evident from the shape of the curves: better-defined stoichiometry of Pb(II) complex in the presence of TX-100 (sharper curve fracture at the same position). Also, higher absolute values of conductance in 3-component systems were

measured. A possible explanation could be an aggregation of nonionic surfactant TX-100 molecules in organic solvents and the formation of "reverse" micellar

structures, which allow the dissolution of polar compounds in a non-polar medium. It is obvious that these structures contributed to greater stability of the complex: by increasing the ligand/metal molar ratio, the conductivity in dichloromethane decreases, which is possible due to the formation of metal-ligand complex and probably its incorporation into micellar structures which stabilize the complex. Addition of surfactant did not affect the stoichiometry.

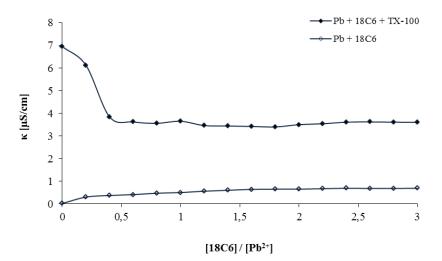


Figure 2. Influence of the surfactant TX-100 on a conductivity of 2-component system Pb(II) + 18C6 in dichloromethane solution

The same study of TX-100 influence on the stability and stoichiometry of the Pb(II) complex formed in aqueous solutions was conducted. In Figure 3., the dependence curves of the electrical conductivities were compared for aqueous 2-component and 3-component systems: Pb2+-18C6 and Pb2+-18C6-TX-100, respectively. Results showed sharper curve fracture (better-defined stoichiometry) for 2-component systems in aqueous solutions. Explanation of surfactant effect is similar compared to the nonpolar medium: in aqueous solution, aggregation of TX-100 molecules leads to the formation of "normal" micellar structures that enable solubilization of nonpolar compounds in polar medium. We can assume that formed metal-ligand complexes can be incorporated into these micellar structures (aqueous pseudo phase), which stabilizes formed complexes (approximately constant conductivity values after 1:1 molar ratio). Incorporation of formed complexes into micellar structures and the existence of hydrophobic interactions,

leaving less room for the movement of free ions so that the conductivity of the solution is lower.

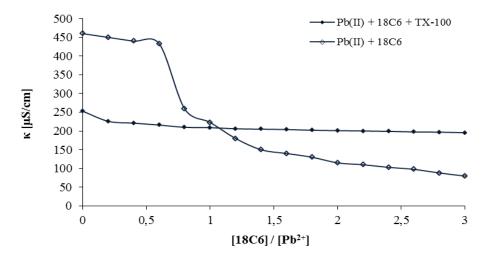


Figure 3. Influence of the surfactant TX-100 on a conductivity of 2-component system Pb(II) + 18C6 in aqueous solution

Conclusions

The addition of nonionic surfactant TX-100 caused opposite effects on Pb(II) complexation with 18C6 in an aqueous and non-aqueous medium. The presence of reverse micellar structures in dichloromethane increases absolute conductivity values and contributes to better definition of stoichiometry and stability of the formed complex. The presence of normal micellar structures in aqueous solution decreases absolute conductivity values and does not enhance the complex stability and definition of stoichiometry. Although the opposite, both effects confirm the existence of significant interactions between metal ions or formed complexes and surfactant micellar structures.

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KONDUKTOMETRIJSKA STUDIJA UTICAJA TRITON X-100 NA KOMPLEKSIRANJE Pb(II) IONA SA 18C6 U DIHLORMETANU

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Sažetak

Površinski aktivne tvari nalaze široku primjenu u različitim analitičkim postupcima zbog svojih amfifilnih svojstava i mogućnosti micelarne agregacije. Primjena površinski aktivnih tvari kao liganada za metalne katione te njihov uticaj na kompleksiranje između metalnih kationa i cikličnih polietera je predmet brojnih istraživanja. Objašnjenje tih interakcija se temelji na mehanizmu domaćin-gost prošireno mehanizmom micelarne solubilizacije metalnih iona ili njihovih kompleksa unutar agregata površinski aktivne tvari (micele). Kompleksiranje Pb(II) iona sa 18-kruna-6 u vodenom rastvoru je široko ispitivano dok je stehiometrija formiranog kompleksa izrazito definirana koristeći metode konduktometrije i UV/VIS spektrofotometrije. Konduktometrijske titracije s krunastim eterima pokazale su se vrlo korisnima u određivanju konstanti

stabilnosti, selektivnosti, kao i termodinamičkim parametrima kompleksa krunastih etera s različitim kationima u nevodenom i vodenom / nevodenom mediju. U ovom radu je istražen uticaj neionskog tenzida TX-100 na kompleksiranje Pb(II) iona koristeći konduktometrijska mjerenja u vodenom i nevodenom (dihlormetan) rastvoru. Rezultati pokazuju da je dodavanje nejonskog tenzida TX-100 izazvalo suprotan uticaj na Pb (II) kompleksiranje s 18C6 u različitm medijima. Dodavanje neionskog tenzida TX-100 dovodi do bolje definirane stehiometrije kompleksa Pb(II) u dihlormetanu što značajno doprinosi njegovoj stabilnosti i povećava vrijednosti apsolutne provodljivosti. Prisustvo "reverznih" micelarnih struktura doprinosi većoj stabilnosti kompleksa: povećanjem molarnog omjera ligand / metal, provodljivost u dihlormetanu opada, što se objašnjava stvaranjem kompleksa metal-ligand i vjerojatno njegove ugradnje u micelarne strukture koje stabiliziraju kompleks. Dodavanje tenzida nije uticalo na stehiometriju. Uticaj neionskog tenzida TX-100 na kompleksiranje Pb(II) iona u vodenom rastvoru je suprotan te su izmjerene niže vrijednosti provodljivosti. Oba efekta potvrđuju postojanje značajne interakcije između površinski aktivnih micelarnih struktura i formiranih Pb(II) kompleksa.

Ključne riječi: konduktometrija, Triton X-100, 18-kruna-6, Pb (II)

XIII Conference of Chemists, Technologists and Environmentalists of Republic of Srpska

CHEMICAL ENGINEERING

Original scientific article

STRUCTURE INVESTIGATION OF THE AL-CU ALLOYS USING EDS AND X-RAY POWDER DIFFRACTION ANALYSIS

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Abstract

Al–Cu alloys are widely used in aerospace, automobile, and other fields, due to their high strength-to-weight ratio. Among all compounds in the Al–Cu system, the Al₂Cu phase has been extensively investigated due its significant effect on the properties of Al–Cu alloys. The formation of Al₂Cu compound is monitored by the application of X-ray powder diffraction method. The X-ray diffraction analysis was performed on the Al-Cu alloys and on pure aluminium and pure copper, using a wide range of angles (2 θ) from 5 to 100° with a step size of 0,02° and a holding time of 0,40 sec. at each step. The following microstructural parameters have been calculated: the average sub-grain size, the microvoltage and the dislocation density. Al₂Cu phase were identified in all samples in view of the XRD and EDS analyses.

Keywords: aluminium - copper alloys, EDS analysis, X-ray powder diffraction method

Introduction

In Al–Cu alloys aluminium is the primary constituent and in the cast alloys the basic structure consists of cored dendrites of aluminium solid solution, with a variety of constituents at the grain boundaries or interdendritic spaces forming a brittle, more or less continuous network of eutectics. Copper has been the most common alloying element almost since the beginning of the aluminium industry, and a variety of alloys in which copper is the major addition, were developed. Cast Al-Cu alloys contain soluble phase Al₂Cu which appear in various amounts and at various locations in the microstructure. The formation of compound Al₂Cu in Al-Cu alloys is monitored by the application of X-ray powder diffraction method and electron microscopy. It was reported that Al₂Cu adopts a tetragonal structure with a = b = 4.28 Å. and c = 2.40 Å, as determined by Owen et al. through powder X-ray diffraction patterns (hereafter named the Owen phase). Then, Jette et al. suggested a larger tetragonal unit cell (a = b = 6.052 Å and c = 4.878 Å) should be used to describe the θ -Al₂Cu phase. Finally, Friauf confirmed Jette's results and provided

the exact atomic positions of θ -Al₂Cu. During the next ninety years, it was again confirmed to have a tetragonal space group (a = b = 6.067 Å and c = 4.877 Å), which was generally accepted by the community (Grin et al., 2005).

Materials and Methods

Alloys containing Al-5.09wt.%Cu were cast from high-purity elements, from 99.5% pure aluminium and 99.9 % pure copper at 700°C. In the binary aluminium-copper system, the aluminium-rich terminal solid solution is in equilibrium with the intermetallic phase θ with the approximate composition Al₂Cu, since some solid solubility exists. Characterization of Al-Cu alloys having a copper content 5 wt.%, was performed with X-ray powder diffraction and electron microscopy. The X-ray diffraction analysis was performed on the AlCu5 alloys using a wide range of angles (2 θ) from 5 to 100° with a step size of 0,02° and a holding time of 0,40 sec. at each step. A diffractometer with a graphite monochromator and a constant divergence slit (D) of 1mm was used. The current and the voltage of the X-ray tube during the analysis were 30mA and 40kV, respectively. The width of the receiving slit (R) was of 0,1mm, corresponding to fine focussed X-ray tubes. The radiation was Cu K α_1/α_2 , doublet ($\lambda \alpha_1 = 1,54060$ Å and $\lambda \alpha_2 = 1,54438$ Å). Also, microstructure was investigated by the SEM and EDS. X-ray analysis showed the presence of eutectic gray phase, while copper is found in the eutectic bright phase.

Results and discussion

X-ray diffraction line profile analysis was performed to calculate sub-grain size, microvoltage and dislocation density. From the X-ray diffractograms the following microstructural parameters have been calculated: the average sub-grain size is 641 Å, the microvoltage is 0.1920 Å and the dislocation density is $7.3 \times 10^{10} \text{ cm}^{-2}$.

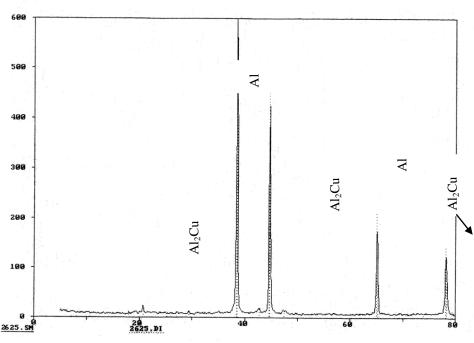


Figure 1. X-Ray diffraction spectrum of Al-Cu alloy

The sub-grain size is the area of the lattice of the crystal grain from which the Xrays are coherently diffracted. The sub-grains are separated with dislocation walls and have a space orientation which is different by several angle minutes. Using Xray diffraction of polycrystals, the sub-grain is defined as a range of quantitative values, starting from the average length in a definite crystallographic direction, through the average volume, to their dimensional distributions. Microvoltages are the most-often used parameter of crystal-lattice deficiency and represent the deviations in the distance d between two crystal planes having identical {hkl} indices in a determined crystallographic direction. This kind of a crystal-lattice deficiency is the result of the distribution of dislocations or differences in the chemical composition of the alloy. The dislocation density is also a parameter of the lattice defectiveness. It is most often defined as the minimum density of dislocation-free areas compared to the number of dislocations on the sub-grain boundaries. The X-ray examination of the aluminium-copper alloys showed very high microvoltage values, which were expected because of the way the alloys were manufactured and the method used for their investigation (Zlaticanin et al., 2004). Using X-ray diffraction, we established that the tetragonal intermetallic compound Al₂Cu are formed. The lattice parameters determined for the tetragonal intermetallic compound Al₂Cu are: for AlCu5 alloy a = 6,085 Å, c = 4,863 Å and V = 180,1 $Å^3$. The lattice parameters determined for the tetragonal intermetallic

compound Al₂Cu agree with published data from literature. In the JCPDS card 25 0012 the parameters for Al₂Cu are a = 6,065 Å, c = 4,873 Å and V = 179,28 Å³.

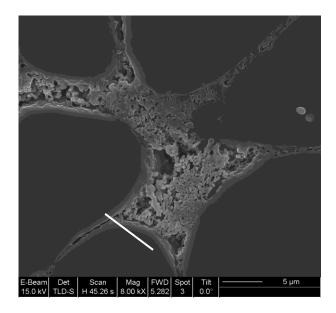
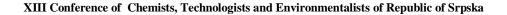


Figure 2. Microstructure of Al-Cu5wt% alloy - SEM

In this investigation mean attention was paid to mechanism of solidification and microstructure. By careful analysis of experimental images (fig. 2-3), we saw that they presents a eutectic structure containing Al and Cu. Eutectic Al₂Cu phases can cause localized melting at temperatures that are lower than in similar alloys which do not contain the Al₂Cu, which can limit high temperature thermo-mechanical treatments (Zlaticanin et al., 2003). Figure 2 shows typical Scanning Electron Micrographs (SEM) of binary Al-Cu alloy. Chemical composition of Al₂Cu phase was confirmed by EDS analysis (Figure 3).



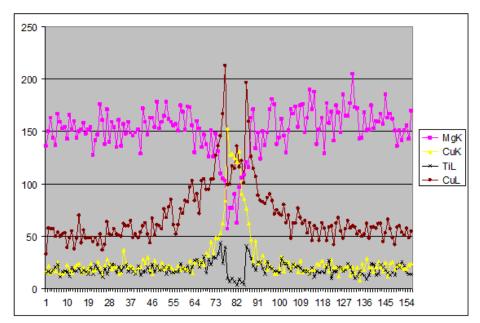


Figure 3. EDS analysis of the most common phase Al₂Cu found in the Al-Cu5wt% alloy (for line on figure 2)

Conclusion

From the obtained data the following conclusions can be drawn: The microstructure of binary Al-Cu alloys was analyzed, and two different types of phases are confirmed in this alloy, these are the primary Al phase and the Al₂Cu phase. Generally, Al-Cu system shows a combination of eutectic morphologies Al₂Cu phase into a α - Al rich matrix. Al₂Cu particles located mainly on the α -Al grain boundaries are different in size, with a morphology resembling continuous or isolated sectored plates.

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Original scientific article

INFLUENCE OF COOLING RATE ON THE STRUCTURE AND MECHANICAL PROPERTIES OF ALUMINIUM AND ALUMINIUM COPPER ALLOYS

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Abstract

The effect of cooling rate on the structure and properties of pure aluminium and on the structure and properties of Al-Cu alloys is investigated using two types of mould. The results show that the rate of cooling is faster the specimen obtained has the highest value of strength and hardness. Also, the results show that the secondary dendrite arm spacing (DAS) are better refined by using this technology with rate of cooling is faster. It was observed that as the cooling rate increased the secondary dendrite arm spacing of the alloys decreased but their hardness and strength increased. Phase-transformation temperatures and enthalpy of solidification of these alloys have been measured using differential scanning calorimetry.

Keywords: aluminium - copper alloys, cooling rate, thermal analysis, microstructure

Introduction

Interest in the system Al-Cu alloys during the last decades was due to the wide use of these alloys in the industry and transportation. According to the diagram of the Al-Cu system, eutectic α -Al + Al₂Cu are formed at a copper content of 33% (mass.) and aluminium 67 % (mass.) Depending on the casting conditions and alloy composition, microstructure, properties and characteristics of the aluminium alloys will be different. The cooling rate affects the structure of as-cast alloys in a wellestablished manner, i.e., the grain size, the dendrite arm spacing (DAS) and the size of structure constituents (both primary and eutectic) decrease with increasing the cooling rate (Eskin et al., 2005). Many techniques are available to investigate the solidification of metals and alloys. Some of them were standardized such as DTA and DSC.

Materials and Methods

Binary Al–Cu5 alloy with the compositions given in Table 1. was prepared in an electrical resistance furnace from 99.5% pure aluminium and 99.9 % pure copper. To study the variations in the mechanical properties with respect to cooling rate, the alloy was cast by conventional air-cooled and water-cooled methods. Special attention was given to an assessment of the different structural parameters by modern quantitative microstructure analysis, using an automatic device for quantitative picture analysis and linear measuring method, which was considered as more reliable, accurate and faster than conventional manual methods of microstructure analysis. Properties of the materials have been investigated, eg.: hardness and determination of compression strength. Hardness has been measured by use of the Brinell method. Compression strength of the samples have been tested on an electronic tensile testing machine of 10t. DSC analyses have been performed in a differential scanning calorimeter type Shimadzu DSC-50 under protective argon atmosphere, at a scanning rate of 10°C/min, to the maximum temperature of 725°C. This method has produced DSC - curve on which basis the transition enthalpy (the activation energies of the transformations responsible for the thermal effects) was calculated.

TYPE OF S	SAMPLE	% Al	%Ti	%Fe	%Si	%Cu	%Zn	%Cr	%Mn
	0% Ti	99.67	0.000	0.18	0.08	0.012	0.047	0.002	0.009
	0.02% Ti	99.69	0.023	0.15	0.07	0.006	0.052	0.001	0.007
Al	0.08% Ti	99.62	0.077	0.16	0.07	0.003	0.054	0.002	0.008
	0.15% Ti	99.56	0.133	0.17	0.07	0.003	0.052	0.002	0.008
	0.25% Ti	99.42	0.343	0.11	0.05	0.010	0.058	0.002	0.009
Al-Cu5	0% Ti	93.86	0.000	0.11	0.07	5.90	0.054	0.002	0.009

Table 1. Chemical composition of the investigated Al and Al-Cu alloys (in mass%).

Results and discussion

This paper analyzes the influence of cooling rate on the structure and properties of pure aluminium and on the structure and properties of Al-Cu alloys. In Figure 1 there are represented the obtained significant structures for solidified samples at different cooling rates. When a liquid alloy solidifies in a mold, there can be up to three distinct zones in the microstructure (Figures 1 and 2).



Figure 1. Macrostructure of samples 99.5% Al with different cooling rates, the top surface: a) air-cooled, b) water cooled

In contact with the wall, the chill zone is formed, in which the grains are fine, equiaxed and have a largely random crystallographic orientation. The nucleation of grains in this zone may be on the wall itself or on heterogeneities in the melt, and is driven by the chilling that occurs when the liquid first makes contact with the cold wall. The zone can be eliminated by heating the mold. As solidification continues towards the center of the casting, the grains become elongated, giving the columnar zone. For pure metals, the columnar zone continues to the center of the casting, but for impure metals and alloys there is often an equiaxed zone in the final stages of solidification (Figures 1 and 2), in which a random crystallographic orientation is restored. The casting temperature for both cooling rates were at 760°C, 735°C, 715°C and 680°C, respectively (Zlaticanin et al., 2004). In casting alloys, nonuniform microstructures (mixed columnar and equiaxed) are undesirable, and mostly an entirely equiaxed microstructure is strongly preferred. Fully equiaxed structures can be obtained by adding nucleant particles to the melt.

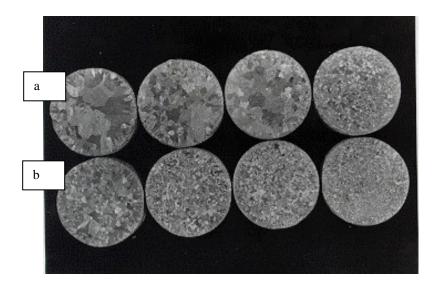


Figure 2. Macrostructure of solidified samples 99.5% Al with different cooling rates, the bottom surface: a) air-cooled, b) water cooled

Figure 3. shows the microstructure results obtained from a higher cooling rate, and that higher cooling rate produced finer grain size. The two important phases in the microstructure are the primary phase that solidifies first and the secondary phase that solidifies second. Figure 3a, show the dendritic microstructure of the Al-5 wt.% Cu at higher cooling rate. The microstructure configurations consisted of dendrites and the interdendrite Al₂Cu eutectic. The eutectic structure of this allow with higher magnification is presented in Fig. 3b. The microstructure configurations for other alloys were similar. For all alloys, in both cooling rates, non-equilibrium eutectic is formed during solidification. It is found that the volume fraction of eutectic increases with increasing cooling rate (Table 2). Phasetransformation temperatures and enthalpy of solidification of these alloys have been measured using differential scanning calorimetry. For the studied alloys, it has been found that with increasing cooling rate, liquidus temperature increases slightly, whereas solidus temperature decreases from 524.5°C to 508.3°C (Zlaticanin et al., 2003). Enthalpy of solidification increases with increasing cooling rate. Besides, with increasing cooling rate, the secondary dendritic arm spacing decreases from 37.80 µm to 30.19 µm. Fast cooling rate condition produced smallest grain size.

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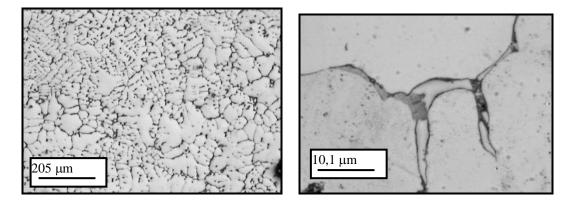


Figure 3. Microstructure of Al-5wt. %Cu

Table 2: Effect of cooling rate and composition on the amount of non-equilibruim eutectic

TYPE OF SAMPLE	non-equilibruim eutectic (wt/%)	
	air- cooled	water cooled
Al - Cu5 (0%Ti)	6.4	8.64

Table 3: Hardness and compression strength of the Al and aluminium-copper alloysobtained during the experiment

TYPE OF SAMPLE	HBaverage		$\sigma_{0,2p}$ (N/mm ²)		σ_{mp} (N/mm ²)	
	air- cooled	water cooled	air- cooled	water cooled	air- cooled	water cooled
Al (0%Ti)	24.15	25.02	38.22	43.31	119.74	127.39
Al (0,02%Ti)	24.87	25.50	45.86	45.86	137.58	150.32
Al (0,08%Ti)	25.45	27.00	49.94	50.96	141.66	157.96
Al (0,15%Ti)	26.27	28.57	50.96	63.64	145.22	167.2
Al (0,25%Ti)	26.90	29.65	58.60	63.70	146.24	168.15
Al - Cu5 (0%Ti)	47.30	55.55	84.08	88.98	315.92	382.16

In this study the mechanical properties like compressive strength and hardness of both air-cooled and water cooled cast specimens were tested and the results were compared. Increases in hardness and compressive strengths of the water cooled cast specimen have been encountered from the present work. This result reveals that increase in cooling rate leads to enhancement of the mechanical properties.

Conclusion

The effect of different cooling rates during the solidification of the Al and aluminium - copper alloy was examined. The following conclusions can be made: The microstructure and mechanical properties of cast products are greatly influenced by the cooling rate during their solidification. It is evident that the increase in cooling rate improves the mechanical properties of the cast alloy. The DAS decreases with increasing cooling rate, and the hardness and strength increase correspondingly. In addition, higher cooling rates produced a finer primary α -phase particle.

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CHEMICAL TECHNOLOGY

Original scientific article

AIR QUALITY IMPROVEMENT IN ROOMS WITH INCREASED BENZENE CONCETRATION

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Abstract

Pollutants that are present in closed spaces are increasingly becoming a problem for people's health. One of the most present pollutants in developed urban and industrial areas is benzene. This paper shows the adsorption characteristics of ZSM zeolites (ZeoFlair 100 and ZeoFlair 110), silica gel (silica gel 60/0-40µm) and 50:50 silica gel and ZEOflair 100 compound (ZEOflair 100 + silica gel 60/0-40µm (50:50)). Adsorption isotherms of the benzene on the examined adsorbents are generated by simulating the adsorption process in the closed room conditions (with atmosphere pressure, 26°C temperature and 60% chamber humidity at the beginning of adsorption), using free diffusion mechanism. High coefficients of determination were obtained by using the nonlinear models (Langmuir and Freundlich). For ZEOflair 110, ZEOflair 100 + silica gel 60 /0-40 µm samples and silica gel 60/0-40µm, determination coefficients obtained by using nonlinear Langmuir model (0,9495; 0,9711 and 0,9829 respectively) were bigger than those obtained by using Freundlich nonlinear model. Low value of the Langmuir constant (K_L) for examined samples shows high affinity between examined adsorbents and benzene. The maximum adsorption capacity values Q^0_{m} , were obtained by experiments and models with silica gel (248,74mg/g), and the lowest for ZEOflair 100 (38,13mg/g).

Key words: benzene, adsorption isotherms, maximum adsorption capacity, zeolite, silica gel

Introduction

The research in the previous years have shown high presence of various pollutants in closed spaces like carbon-monoxide (CO), volatile organic compounds (VOC), particles (PM), aerosol, biological pollutants etc. (Arenes et al., 2006; Chan et al., 2003; Edwards et al., 2001; Tran et al., 2020; Yu et al., 1998). Conditions in closed spaces are affecting the overall human health significantly considering that most people spend around 90% of their time in closed spaces, mostly at home or at work (Zhang et al., 2002). The most significant pollutants are volatile organic compounds (VOC), which include toluene, acetaldehyde, methanol, ethanol, benzene, formaldehyde etc. They can enter closed spaces from close surroundings, or from materials that are present in the room (Marć et al., 2015; Zhang et al., 2002; Won et al., 2001). The quantity of the volatile organic compounds is influenced by pollutant concentration, temperature conditions in the room (temperature, airflow, relative humidity), light and noise. Benzene is one of the most common, easily volatile organic compounds in developed urban and industrial areas and it is considered to be anthropogenic pollutant (ATSDR, 2007; WHO, 1993). It is a good dissolvent of

rubber, resin, all kinds of fats, caoutchouc and other similar substances and it's used in pharmaceutical products, in producing colors, explosives, rubber and rubber products, artificial leather, linoleum, celluloids, varnishes, glues etc. The fact that 61 million tons of benzene were produced during year 2017. alone, confirms the vast usage of benzene (Garside, 2020). The basic physical and chemical characteristics of benzene are shown in table 1.

Features	Value
Molar mass [g·mol ⁻¹]	78,11
Melting point [°C]	5,558
Boiling point [°C]	80,08
Density at 20° C [g·mL ⁻¹]	0,8756
Water solubility at 25° C [mg·L ⁻¹]	1790
Vapor voltage at 25°C [mm Hg]	94,8
Henry's constant at 25 °C [mol·atm ⁻¹]	0,21
Ionization potential [eV]	9,24
Van-der Waals surface [Å ²]	88
Standard molar enthalpy of dissolution [kJ·mol ⁻¹]	30,3

Table 1. The basic physical and chemical characteristics of benzene (Chan et al., 2003)

According to the classification made by International Agency for Research on Cancer (IARC), which is the part of World Health Organization (WHO), the Benzene belongs to the group 1 of carcinogenic substances (ATSDR, 2007; WHO, 1993).

Adsorbents are used in reduction of volatile organic compounds. The choice of right adsorbent is influenced by many factors like: temperature, pressure, adsorbent amount, affinity towards adsorbent etc. The choice of the correct adsorbent is not easy and it is defined by conditions in which it is used and characteristics of adsorbent itself (adsorption capacity, constancy, hydrophilicity, hydrophobicity etc.). Most used adsorbents are: active coal, natural and synthetic zeolites, silica gel, activated alumina etc.

Zeolites are very good as organic compounds adsorbents. Advantages of zeolite are: great stability, low temperature regeneration, their hydrophilic and hydrophobic character, ease of use etc. Assessment of the adsorption characteristics is done based on obtained adsorption isotherms. Research performed up to now were aimed at obtaining adsorption isotherms of gaseous organic compounds (light hydrocarbons), CO_2 etc., mainly from the gaseous phase, where only those components are present (Bao et al., 2011; Brosillon et al., 2010; Cheng, 2007; Lee et al., 2004; Osmari et al., 2013). It is known that the air in closed rooms is multicomponent system, thus, we can expect that the presence of additional gaseous components can hinder or increase the adsorption capacity of the adsorbent. Some researchers have shown that for VOC, the presence of water vapor in some cases increases and, in some cases, decreases adsorption capacity (Sochard et al., 2010; Huang et al., 2006).

Materials and Methods

In this paper, highly silicate ZSM zeolites by company Zeochem (ZEOflair 100, ZEOflair 110), silica gel (silica gel 60/0-40 μ m) and 50:50 silica gel and ZEOflair 100 compound (ZEOflair 100 + silica gel 60/0-40 μ m (50:50)) are used as adsorbents (Table 2.).

Parameter	ZEOflair 100	ZEOflair 110	Silica gel 60 / 0-40 μm
Loss of annealing, w %	2.5	3.1	-
d(10), μm	1.3	-	-
d(50), μm	2.5	< 10	15-35
Molar ratio SiO ₂ /Al ₂ O ₃	384	926	-
Na content, w %	1.2	1.32	-
BET, m^2/g	355	434	450 - 550
Water residue, w %	-	-	< 10
pH (5%)	-	-	6-8
Pore size, nm	-	-	4.7 - 8

Table 2. Physical and chemical characteristics of ZEOflair 100, ZEOflair 110 and Silica gel 60/0-40µm

Closed room conditions were simulated in order to obtain adsorption isotherms. Benzene adsorption is performed using free diffusion mechanism. Benzene adsorption is performed in adsorption chambers with 2,5 dm³ volume and examined samples of approximately 0.5g each. All the experiments are performed on atmosphere pressure, 26° C temperature and 60% chamber humidity at the beginning of adsorption. Different amounts of benzene are injected into the chambers (10-250µl). Adsorption process lasted for 3h. Gaseous phase in the chambers was analyzed before and after the adsorption, during which the total organic carbon was determined using the Shimadzu TOC highly sensitive device. Based on the concentration of organic carbon, andbenzene, the adsorbed quantity of benzene is determined using the expression (1).

$$q_e = \frac{(\mathcal{L}_0 - \mathcal{L}_e)V}{m} \tag{1}$$

Where:

 q_e – adsorbed benzene quantity per gram of zeolita (mmol/g) C_0 -benzene concetration at the beggining of adsorption(mol/m³) C_e – benzene concentration equilibrium benzena (mol/m³) V- chamber volume (m³) m- adsorbent mass (g)

Percentage of removed benzene (%) =
$$\frac{C_o - C}{C_o} \cdot 100$$
 (2)

To determine the constants for Langmuir isotherms in nonlinear form we use expression (3).

$$\begin{array}{l}
Q^0 \\
q_e = \frac{max}{1+K_L \cdot C_e}
\end{array}$$
(3)

To determine the constants for Freundlich isotherms in nonlinear form we use expression (4).

$$q_e = K_f \cdot C_e^n \tag{4}$$

To calculate the parameters of adsorption isotherms using nonlinear method, the tool called "Solver" was used in the program "Microsoft Excel". To describe the error of the regression analysis, the nonlinear chi-square test (χ^2) was used according to the equation (5).

$$\chi^2 = \sum_{i=n}^{n} \frac{(q_{e,exp} - q_{e,izra\check{c}.})^2}{q_{e,izra\check{c}.}}$$
(5)

Results and discussion

ZEOflair 100, ZEOflair 110 are highly silicate zeolites with hydrophobic character unlike silica gel which is hydrophilic adsorbent.ZEOflair 110 is a zeolite who by his chemical composition has greater molar ratio SiO_2/Al_2O_3 (926) and specific area $(434m^2/g)$, BET method) than ZEOflair 100 whose molar ratio $SiO_2/Al_2O_3 = 384$ and specific area $355 \text{ m}^2/g$. Out of examined adsorbents, silica gel is adsorbent with greatest specific area $(450-550 \text{ m}^2/g)$. Benzene adsorption was done out of the atmosphere with humidity level 60% with different initial benzene concentrations. Based on experimental results, adsorption isotherms were obtained for every adsorbent as well as for the compound 50:50 ZEOflair 100 and silica gel $60/0-40\mu m$ (figures 1-4.).

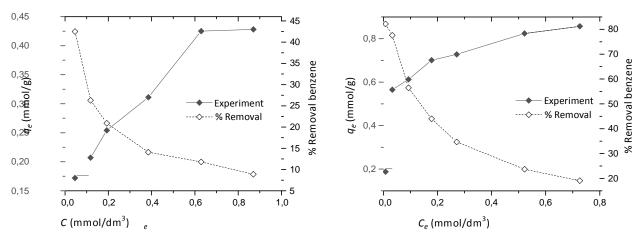


Figure 1. Benzene adsorption isotherm with ZEOflair 100 removal efficiency

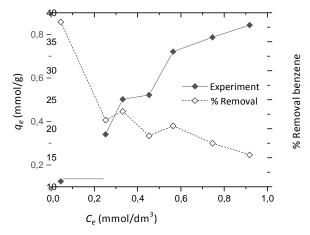


Figure 3. Benzene adsorption isotherm with ZEOflair 100 +silicagel 60/0-40 μ m (50:50) removal efficiency

Figure 2. Benzene adsorption isotherm with ZEOflair 110 removal efficiency

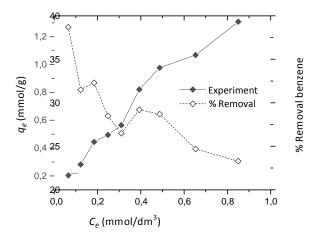


Figure 4. Benzene adsorption isotherm with Silica gel 60/0-40 µm removal efficiency

It is visible for all samples that, the increase of the initial benzene concentration in adsorption experiments, caused also the adsorption increase. At the same time, the increase of the initial

benzene concentration and the adsorption capacity cause the reduction of removal efficiency. For Zeoflair 100 sample, the removal percentage is reduced from 42.5% to 8.9% while the Zeoflair 110 had removal percentage decline from 82.2% to 19.1%. Slightly smaller reduction in removal percentage was noticed for samples with Zeoflair 100+silica gel 60 (from 38,4% to 15,5%) and silica gel 60 (from 38.7% to 23.3%). The reason for this kind of a behavior could be explained by increase of the concentration gradient that is increasing with initial benzene concentration and also increases with the decrease of available adsorption spots. The values of the determination coefficients for adsorption isotherms Langmuir and Freundlich for examined adsorbents are shown in the Table 2.

			Parameter values for adsorbents			
Model	Parameter	ZEOflair 100	ZEOflair 110	ZEOflair 100 + Silica gel 60 (0-40 μm)	Silica gel 60 (0-40µm)	
Langmuir	K_L (dm ³ /mg)	0,086	0,560	0,015	0,010	
Ū.	$Q^0(mg/g)$	38,13	64,96	127,96	248,74	
	\mathbb{R}^2	0,8905	0,9495	0,9711	0,9829	
Parameter values for adsorbents	$R_{ m L}$	0,99 - 0,92	0,98-0,67	1,00 - 0,98	1,00 - 0,99	
	χ^2	2,893	2,102	1,4112	1,955	
	n	0,353	0,217	0,631	0,742	
Freundlich	$K_F(mg/g)/(mg/dm^3)^n$	7,750	29,24	4,642	4,628	
Parameter valuesfor	R ²	0,9670	0,8733	0,9682	0,9801	
adsorbents	χ^2	0,471	7,623	1,793	2,514	

Table 2. Adsorption constants of the isotherms for examined samples using nonlinear models (Zeolite concentration = 0.2 g/dm^3 , T = 26 °C, adsorption time = 3h)

From the Table 2. we can see that the determination coefficients obtained with nonlinear Langmuir model for samples ZEOflair 110, ZEOflair 100 + silica gel 60 /0-40 µm) and silica gel 60/0-40µm, very high (0,9495; 0,9711 and 0,9829 respectively). The coefficients obtained with Freundlich nonlinear model are lower than those obtained by Langmuir model and their values are 0,8733 for ZEOflair 110 sample; 0,9682 for ZEOflair 100 + silica gel 60 /0-40 µm, and 0,9801 for silica gel 60/0-40µm sample. Obtained results show that this is a monolayer adsorption. Small values of Langmuir constant (K_L)for examined samples indicates that there is a high affinity between examined adsorbents and benzene. Dimensionless parameter R_L is approaching 1 for samples ZEOflair 100 + silica gel 60 /0-40µm, which is an indication for linear adsorption. This is especially pronounced with silica gel 60/0-40µm sample which is also visible on the figure 5. Even though the values of the maximum adsorption capacity Q^0 are much higher than those obtained by experiment, small values of χ^2 test are in line

with the claims mentioned above.

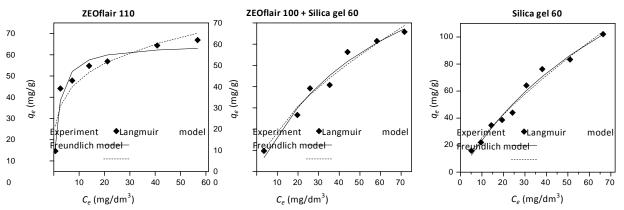


Figure 5. Application of the nonlinear Langmuir and Freundclihmodels onexperimental dataof the equilibrium concentration of adsorbed benzene with adsorbents ZEOflair 110, ZEOflair 100 +silica gel 60 /0-40 µm) i silica gel 60/0-40µm

Unline the mentioned samples, ZEOflair 100 sample shows better performance with Freundlich model, with determination coefficient of 0.967 which goes in favor to the multilayer adsorption shown in figure 6.

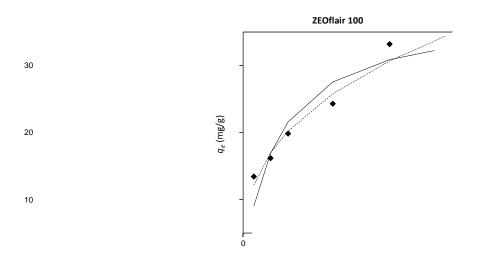


Figure 6. Application of the nonlinear Langmuir and Freundclih models on experimental data of the equilibrium concentration of adsorbed benzene with adsorbents ZEOflair 100

Conclusion

Benzene adsorption isotherms on the examined adsorbents are obtained by simulating the adsorption process in the conditions of a closed space (atmospheric pressure, temperature 26° C and 60% humidity in the chambers at the beginning of adsorption) using free diffusion mechanism. By applying nonlinear models (Langmuir and Freundclih) high determination coefficients are obtained. Determination coefficients obtained with nonlinear Langmuir model for samples ZEOflair 110, ZEOflair 100 + Silica gel 60 /0-40 µm) and silica gel 60/0-40µm (0,9495; 0,9711 and 0,9829 respectively) were higher than with Freundlich model. For zeolite

sample Zeoflair 100, determination coefficient obtained with Freundlich model was higher than the determination coefficient with Langmuir. Small values of Langmuir constant (K_L) for examined samples, shows high affinity between examined adsorbents and benzene. The values of the maximum adsorption capacity Q^{0}_{m} , obtained both by modeling and experiments are highest with silica gel (248,74mg/g), and smallest for ZEOflair 100 (38,13 mg/g). Even though the absorption was performed with initial humidity of 60% and silica gel has hydrophilic character, the presence of the water vapour didn't hinder the benzene adsorption.

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POBOLJŠANJE KVALITETA VAZDUHA U PROSTORIJAMA SA POVEĆANOM KONCENTRACIJOM BENZENA

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Sažetak

Polutanati prisutni u zatvorenom prostoru danas predstavljaju značajan problem po zdravlje ljudi. Jedan od najčešće prisutnih polutanata u urbanim i industrijski razvijenim sredinama je benzen. U radu su ispitivane adsorpcione karakteristike ZSM zeolita (ZeoFlair 100 i ZeoFlair 110), silika

gela (slilikagel 60/0-40 μ m) i smješa 50:50 silika gela i ZEOflair 100 (ZEOflair 100 + Silika gel 60/0-40 μ m (50:50)). Adsorpcione izoterme benzena na ispitivanim adsorbensima su dobijene simuliranjem adsorpcije u uslovima zatvorene prostorije (pri atmosferskom pritisku, temperaturi

26°C i pri vlažnosti u komorama na početku adsorpcije od 60%), mehanizmom slobodne difuzije. Primjenom nelinearnih modela (Langmira i Frojndliha) dobijeni su visoki koeficijenti determinacije. Za uzorke ZEOflair 110, ZEOflair 100 + Silikagel 60 /0-40 μ m) i Silika gel 60/0-40 μ m, koeficijenti determinacije, dobijeni nelinearnim Lengmirovim modelom (0,9495; 0,9711 i 0,9829 redom) su bili veći od koeficijenata determinacije dobijenih Frojndlihovim modelom. Male vrijednosti Lengmirove konstante (*KL*) za ispitivane uzorke ukazuju na visok afinitetizmeđu ispitivanih adsorbenasa i benzena. Vrijednosti maksimalnog kapaciteta adsorpcije Q^0m , dobijene eksperimentalno i modelovanjem, najveće su za silika gel (248,74mg/g), a najmanje za ZEOflair 100 (38,13 mg/g).

Ključne riječi: benzen, adsorpcione izoterme, maksimalni kapacitet adsorpcije, zeolit, silika gel

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BIOTECHNOLOGY

Original scientific article

INFLUENCE OF APPLE JUICE ADDITION ON CHARACTERISTICS OF MINT AND NETTLE KOMBUCHA BEVERAGES

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Abstract

Kombucha tea is slightly sweet and acidic refreshing beverage consumed worldwide, tasting like sparkling apple cider and mostly produced by fermentation of black or green tea and white sugar using a tea fungus. In addition to black and green tea, some herbal teas can also be used, so the aim of this work is to produce kombucha beverages by fermentation of mint and nettle herbal teas and honey with the addition of different concentrations of apple juice (2.5; 5 and 10% v/v). For the purposes of this study, the following parameters were measured: pH value, acidity, dry matter and residual sugar content. For the determination of antioxidative capacity, the content of total phenolics was measured and two tests were performed: DPPH and FRAP. The fermentations lasted for 10 days, and with regard to the results of measuring the pH value, acidity, dry matter and residual sugar content, there was no excessive difference among the obtained kombucha beverages. Mint kombucha beverages showed better antioxidant activity, and in most cases the best effect was shown in samples in which the smallest amount of apple juice was added (2.5% v / v). Mint and nettle herbal teas proved to be adequate substrates for obtaining kombucha beverages, and the addition of apple juice had a positive effect on the characteristics of the product.

Keywords: Mint and nettle herbal teas, Kombucha, apple juice

Introduction

Kombucha tea is slightly sweet, acidic refreshing beverage, mostly produced during a 7–21 days fermentation of black or green tea and white sugar using a tea fungus, a symbiotic culture of bacteria and yeast - SCOBY (Lee, 1996; Dufresne & Farnworth, 2000) and associated with remarkable health benefits (Dickmann et al., 2017). The word Kombucha is a combination of Japanese words "seaweed" (Kombu) and "tea" (cha) (Ernst, 2003). Kombucha frequently called "tea fungus", although there is actually no fungus involved in the fermentation (Sreeramulu et al., 2000). Various health benefits are related to its antioxidant and antibacterial

activities and attributed to the presence of polyphenols and certain organic acids (acetic, gluconic etc) produced during Kombucha fermentation (Dufresne & Farnworth, 2000; Bhattacharya et al., 2011). In addition to black and green tea, some herbal teas can also be used (Cvetković, 2008; Velićanski, 2012; Gramza-Michałowska et al. 2016; Rahmani et al. 2019). All of these herbal teas possess many bioactive compounds, provide the desired antioxidant status and might prevent diseases that occur as a result of oxidative stress (Cetković et al., 2007; Velićanski et al., 2014). Mint (Mentha piperita) is a perennial herbaceous plant that grows in many countries around the world, characterized by a pleasant smell of menthol, and is one of the most important medicinal plants for the production of essential oil. It has a refreshing and soothing effect, and alleviates breathing problems. A leaf or stem with leaves and a flower is used as a medicine (Tucakov, Balkan countries, stinging 1997). In the nettle leaves are used in the form of an herbal infusion for the treatment of various medical problems (Tucakov, 1997). Different part of stinging nettle contains chlorophyll, vitamins, tannins, essential oil, proteins, minerals (Fe, Cu, Mn and Ni), acethylcholin, histamine and flavonoids (Stanković, 1995; Tucakov, 1997; Chaturvedi, 2001; Akbay et al., 2003). To enhance the character and complexity of beverages, a variety of fruits, vegetables, herbs, or spices may be added. Fruits and their pulps have been highly recommended because of their richness in carbohydrates, fibers, minerals, vitamin C, carotenoids, phenolic and sulfuric substances. Also, their antioxidant action can help to maintain a balance between production and elimination of reactive oxygen species and other related compounds, thereby attenuating free radical-induced damage to cells (Amorim-Souza et al., 2018). Apple has been identified as a potential source of carbohydrates, minerals, fiber and phenolic antioxidant (Wolfe & Liu, 2003; Alberto et al., 2006). Some studies show that the consumption of apples and apple juice can provide antiproliferative, anticarcinogenic and anti-inflammatory health benefits and is strongly associated with a lower incidence of lung cancer, viral diseases and cardiovascular disorders (Leontowicz et al. 2003; Boyer & Liu, 2004; Alberto et al., 2006). Taking all the above into account, the aim of this work is to produce Kombucha beverages by fermentation of mint and nettle herbal teas and honey with the addition of different amounts of apple juice.

Materials and Methods

Two types of herbal tea were chosen - mint (M) (*Mentha piperita*) and nettle (N) (*Urtica dioica*). Samples of selected plant species originate from the village of Krstače, municipality of Bileća, Republic of Srpska (material collected in the summer of 2018). Meadow honey from the mountain Ljubić, municipality of Prnjavor, Republic of Srpska was used as a source of carbohydrates. In addition, different concentrations of freshly squeezed apple juice (2.5; 5 and 10% v/v) were

added to the fermentation broth. The substrate for tea fungus cultivation was prepared by adding 100 g of honey in 1 L of boiled tap water. Then 5 g/L of mint (M) or nettle (N) herbal tea was added and allowed to infuse for 15 minutes. The medium was filtered into a sterilized glass jar and after cooling to room temperature inoculated with tea fungus (SCOBY) and 10 vol% of the fermentation broth from the previous fermentation. Sterilized glass jars were covered with cheesecloth, and the fermentation at 28 ± 1 °C was monitored for 10 days. Control sample (MK or NK) was kombucha prepared as described above without the addition of apple juice.

Sample	M1	M2	M3	MK	N1	N2	N3	NK
The amount of added apple juice (%)	10	5	2.5	-	10	5	2.5	-

Chemical analysis

During and at the end of fermentations dry matter content, pH, total acidity was determined according to standard methods (OIV, 2015) and reducing sugars by 3,5-dinitrosalicylic acid method (Miller, 1959). All the chemicals and reagents used were of analytical grade.

Antioxidant activity determination

The total phenolic content was determined using the modified method of Folin-Ciocalteu (Wolfe et al., 2003). The testing of antioxidant activity using the Ferric reducing/Antioxidant power (FRAP) assay was carried out in accordance with Banzie & Strain (1996) and the 2,2-diphenyl-1-picryl-hydrazyl (DPPH) assay using the method of Brand-Williams et al. (1995). All the chemicals and reagents used were of analytical grade.

Statistical analysis

The data were evaluated by analysis of variance (ANOVA). The means were compared by Tukey's test, with a significance level of 95% (p<0.05) using IBM SPSS Statistics 23.0 statistical software.

Results and discussion

The changes of the basic parameters of fermentation broths during kombucha fermentations were presented in Tables 2-4. The decrease of pH values (Table 2) follows the increase in acidity (Table 3) as a result of metabolic activity of tea fungus yeasts and acetic acid bacteria which metabolized sucrose into organic

acids. Yeasts from tea fungus ferment glucose and fructose to ethanol, which is then oxidized by acetic acid bacteria to acetic acid. This is the main metabolic path of kombucha fermentation, with acetic acid, ethanol and gluconic acid as the main tea fungus products (Cvetković, 2008) but other components are also present: different sugars, ethyl gluconate, oxalic, saccharic, lactic, 5-ketogluconic acid, 2,5ketogluconic acid, water soluble vitamins, tea components and hydrolytic enzymes (Bauer-Petrovska & Petrushevska-Tozi, 2000). In first four days of fermentation the pH decreased by about 0.4-0.6 units and in next five days decreasing was less than 0.1 units. Changes in pH during tea fungus fermentation were similar for M and N mediums (Table 2). The total acidity of both mediums increased constantly from the beginning until the end of the fermentation process (Table 3). Our data were in line with Goh et al. (2012) and Velićanski et al. (2014). They noticed that kombucha pH dropped gradually as the fermentation proceeded. Sreeramulu et al. (2000) and Belloso-Morales & Hernandez-Sanchez (2003) used similar cultivation conditions and observed the same trend for the changes of pH and total acidity. The incompatible changes in the pH and total acidity could be explained by the buffer capacity of the fermentation broth (Cvetković et al., 2008). Therefore, total acidity should be considered as a critical parameter, which determines the end of kombucha fermentation instead of the pH, and to obtain a pleasantly sour beverage the fermentation should be terminated when the titratable acidity reaches 4-4.5 g/L (Cvetković, 2008; Velićanski et al., 2014).

Sample	M1	M2	M3	MK	N1	N2	N3	NK
fermentation day								
1	3.16 ^{a*}	3.35 ^b	3.37 ^b	3.74 ^c	3.26 ^d	3.19 ^e	3.20 ^e	3.72 ^c
4	2.82 ^a	2.90 ^b	2.89 ^{b, c}	3.35 ^d	2.73 ^e	2.84 ^{a, c}	2.85 ^{a, c}	3.38 ^d
8	2.78 ^{a, b}	2.90 ^c	2.84 ^d	3.08 ^e	2.76 ^a	2.81 ^f	$2.8^{b, f}$	2.97 ^h
10	2.76 ^a	2.8 ^b	2.77 ^{a, c}	2.86 ^d	2.76 ^a	2.81 ^b	2.79 ^{b, c}	2.84 ^d

Table 2. pH values

*a-h values in the same row with different superscripts are significantly different (p < 0.05)

Sample								
fermentation day	M1	M2	M3	MK	N1	N2	N3	NK
1	0.36 ^{a*}	0.32 ^b	0.29 ^c	0.18 ^d	0.31 ^b	0.29 ^c	0.27 ^c	0.2 ^d
4	1.01 ^a	0.77 ^b	0.83 ^c	1.17 ^d	1.23 ^e	0.90^{f}	0.89 ^{f, g}	0.85 ^g
8	1.53 ^a	1.43 ^b	1.49 ^c	1.64 ^d	2.23 ^e	1.44 ^b	1.54 ^a	1.45 ^b
10	2.21 ^a	2.46 ^b	1.78 ^c	2.41 ^d	2.81 ^e	1.83 ^f	2.27 ^g	2.04 ^h

Table 3. Total acidity content (%)

*a-h values in the same row with different superscripts are significantly different (p < 0.05)

Sample	M1	M2	M3	МК	N1	N2	N3	NK
fermentation day	IVII	1412	WI3	IVIIX	111	142	113	INIX
1	8.60 ^{a, c*}	8.40 ^a	8.10 ^b	8.10 ^b	8.70 ^c	8.70 ^c	8.50 ^{a, c}	8.10 ^b
4	8.40 ^a	8.40 ^a	8.00 ^b	8.20 ^b	8.90 ^b	8.90 ^c	8.90 ^c	8.00 ^c
8	8.30 ^{a, b}	7.20 ^c	8.10 ^a	7.60 ^d	7.50 ^d	8.40 ^b	8.20 ^{a, b}	7.30 ^c
10	7.50 ^a	6.90 ^b	7.70 ^a	7.10 ^b	7.70 ^a	7.70 ^a	7.10 ^b	6.50 ^c

Table 4.Dry matter content (%)

*a–d values in the same row with different superscripts are significantly different (p < 0.05)

The dry matter content in the samples, as can be seen from Table 4, decreased with each new measurement during fermentation. Initially, the highest dry matter content was found in the sample containing the higher concentration of apple juice.

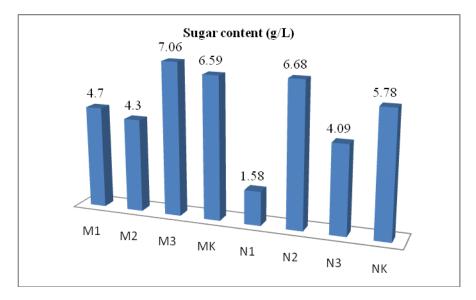


Figure 1. Sugar content

Regarding the content of reducing sugars in the tested samples, based on the data from Fig. 1, it can be seen that sample N1 had the smallest amount of sugar and the largest sample M3.

Sample	M1	M2	M3	MK	N1	N2	N3	NK
Total phenolic content (µgGAE/ml)	369.28	322.88	354.88	152.48	207.28	215.68	166.88	107.28
DPPH IC50 (ml/ml)	45.02	61.3	64.09	61.95	57.56	41.51	34.75	39.11
FRAP (mmolFe ²⁺ /ml)	7.81	7.15	7.71	3.6	2.61	2.2	2.11	2.96

Table 5. Results of total phenolics content and antioxidant activity

The total phenolic content and the antioxidant activity of kombucha beverages were examined and the results are shown in Table 5. It can be seen that the phenolic content in beverages with added apple juice was higher than in the control beverages, especially for beverages with mint tea. This indicated that the addition of juice had a positive effect on the phenolic content in the beverages, which are considered to be responsible for the antioxidant properties. All mint beverages to which apple juice was added (M1-M3) had a stronger antioxidant effect measured by the FRAP method compared to control beverage (MK) and the activity generally increased with increasing amount of added juice. Also, they showed a much stronger effect compared to nettle beverages. Besides that, the addition of apple juice to nettle tea reduced antioxidant effect of obtained beverages measured by FRAP method. However, when it comes to the DPPH test, the situation is significantly different. Nettle beverages in most cases showed a much better effect on the DPPH radical, which indicates that the choice of the type of tea used has a significant effect on the ability to quench the DPPH radical, and not just the number of phenolic compounds. The differences in the antioxidant potential measured by FRAP and DPPH methods are due to different mechanisms of both methods. In the latter method, the DPPH radical uses the free electron transfer reaction, and the FRAP method utilizes metal ions for oxidation. Additionally, the DPPH method does not allow the determination of hydrophilic antioxidant activity. Rania et al. (2020) and Amarasinghe et al. (2018) shown that antioxidant activity of different kombucha types were increased with fermentation time. Lobo et al. (2017) found that the metabolic conversion of tea constituents during fermentation by microbial enzymes may contribute towards the increase in antioxidant activity of kombucha when compared to tea. Furthermore, many health beneficial effects of kombucha such as the alleviation of inflammation and arthritis, cancer prevention and immunity enhancement may be associated to its antioxidant activities, and these effects are attributed to the presence of polyphenols and certain organic acids which are produced during fermentation (Vijayaraghavan et al., 2000). The study about antioxidant activity of Kombucha beverages made from Echinacea herb and root (Echinacea purpurea L.) and winter savory (Satureja montana L.) infusions showed higher activity against DPPH and OH radicals compared to the tradiional beverage (Cvetković et al., 2008). This indicates that with the use of medicinal herbs for kombucha production, beverages with higher biological activity are produced. According to Kruawan and Kangsadalampai (2006) phenolic compounds were suggested as the responsible factor for herbal antioxidant. This action refers to the hydroxyl group in phenolic compound which donate hydrogen proton and classified as a reducing agent (Shahidi and Wanasundara, 1992; Pietta, 2000). At the end of the fermentation process, an organoleptic evaluation of the kombucha beverages was performed. The beverages were filtered and color, taste and smell were evaluated. The addition of apple juice did not affect the color of the beverages. All beverages had an acceptable smell characteristic, with small variations among them (beverages M1 and K1 had more pronounced sour smell). The biggest difference among the beverages occured in terms of taste and M3 and K2 had the most pleasant taste.

Conclusion

Mint (Mentha piperita) and nettle (Urtica dioica) infusions can be used as the medium for kombucha fermentation. The fermentations lasted for 10 days, and with regard to the results of measuring the pH value, acidity, dry matter and residual sugar content, there was no excessive difference among the obtained kombucha beverages. The phenolic content in beverages with apple juice was higher than in control beverages. Addition of apple juice improved antioxidant effect of mint beverages measured by the FRAP method and the activity generally increased with increasing amount of added juice, with much stronger effect compared to nettle beverages. Nettle beverages in most cases showed better effect on the DPPH radical, indicating that the choice of the type of tea used had a significant effect on the ability to quench the DPPH radical, and not just the number of phenolic compounds. Organoleptic evaluation determined that the addition of apple juice did not affect the color of the drink, but that higher amounts of juice concentration could affect the smell and taste (samples with the highest concentration of juice had a pronounced taste and sour smell).

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Original scientific article

THE INFLUENCE OF THE ADDITION OF VARIOUS TEAS ON THE PRODUCTION OF METHELGIN

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Abstract

Mead is a traditional alcoholic beverage containing between 8 and 18 vol% alcohol produced by fermentation of diluted honey under the influence of yeast. By adding various spices or herbs, a drink called methelgin is obtained. The aim of this paper is production of mead with the addition of three types of tea (green, linden and elderberry) in three different concentrations and testing their antioxidant activity. The pH value and dry matter content of methelgins were measured before and after fermentation and the changes in the weight of the bottles were monitored daily. For the determination of antioxidative capacity the content of total phenolics was measured and two tests were performed: DPPH and FRAP. Fermentation activity was slightly improved only by the addition of green tea. The obtained results showed differences in antioxidant properties of mead with the addition of different tea types and the strongest antioxidant effect was shown by the samples to which green tea was added. Also, with the increase in the amount of added tea, the antioxidant properties of the beverages were more pronounced.

Keywords: Mead, Methelgin, tea, antioxidant activity

Introduction

Honey is the natural sweet substance produced from the nectar of blossoms, or from the secretion of living parts of plants, which honey bees collect, transform, and combine with specific substances of their own, and then store and leave in the honey comb to ripen and mature (Estevinho et al., 2011). Honey is a highly concentrated solution of a complex mixture of sugars and small amounts of minerals, proteins, vitamins, organic acids, flavonoids, phenolic acids, enzymes and other phytochemicals. The components in honey responsible for antioxidative effects are flavonoids, phenolic acids, ascorbic acid, catalase, peroxidase and carotenoids (Srimeena et al., 2014).

Mead is an alcoholic drink known since ancient times, produced by yeast fermentation of diluted honey (Pereira et al., 2014). The quality of mead is affected

by many factors including the quality of the raw materials used for production (honey, herbs, juices, spices, fruits) as well as the water (Czabaj et al., 2017). Mead to which spices and herbs are added is called methelgin (Rodrigues et al., 2015).

The controlled fermentation process of honey is performed by free yeast cells of the *Saccharomyces cerevisiae*, typically at temperatures between 15 and 22°C. Low fermentation temperature helps to achieve a steady fermentation and a better transformation of the aromatic and taste qualities of the ingredients into the final product (Šmorgovičová et al., 2012).

The phenolic content and antioxidant activity of mead greatly depend on the quality and type of honey used for mead production. Thermal processing has a strong impact not only on sensory quality and production process, but it can also alter the total phenolic content and antioxidant activity (Czabaj et al., 2017).

Phenolic compounds are plant secondary metabolites closely responsible for the sensory properties of food. They are believed to be the dominant antioxidants in most plants by acting as reducing agents as well as hydrogen donors (Wissam et al., 2017). The antioxidant activity of teas depends on the type and quality of the ingredients used in the process of tea production, location of the crops, and manner of the raw material processing (Zieniewska et al., 2020). Qualitatively important components in green tea are free amino acids, caffeine and polyphenols. Especially, catechins, the main component of polyphenols, are well known for their antioxidant properties, which have led to their evaluation in many diseases radicals, including cancer, cardiovascular free associated with and neurodegenerative diseases (Lee et al., 2014). Plants of Tilia cordata (linden) contain a number of derivatives such as hydrocarbons, esters, terpenoids, quercetin, kampferol, phenolic compounds, condensed tannins and scopoletin. Linden flowers have been used to treat several illnesses like bacterial infections as well as their effects in reducing tension (Wissam et al., 2017). Infusions of elderberry flowers are known to have diaphoretic, anti-catarrhal, expectorant, diuretic, and antiinflammatory actions. Results from various sources have shown that both elderberry fruit and flower are rich in polyphenols (Cejpek et al., 2009). The aim of this work is production of mead with the addition of three types of tea (green, linden and elderberry) in three different concentrations and testing their antioxidant activity.

Materials and methods

Meadow honey, diluted with water in a ratio of 1:3, was used to obtain meads. Teas in the amount of 1, 2.5 and 5 % were added and the solutions were pasteurized (heated to a temperature of 65° C for 10 min). Three types of tea were used: green, linden and elderberry, produced by Mladegs Pak (Bosnia and Herzegovina). As control sample (C) was used pasteurized honey solution (honey: water in a ratio 1:3) without added tea. The solutions were cooled, poured into bottles, baker's

yeast in the amount of 600 mg/L was added and fermentation started. The bottles were weighted and the change in bottle weight during fermentation, which lasted for 14 days, was monitored.

Table 1. F	Prepared samples
Sample name	Addition of tea
С	-
G1	Green tea, 1 %
G2	Green tea, 2.5 %
G3	Green tea, 5 %
L1	Linden tea, 1 %
L2	Linden tea, 2.5 %
L3	Linden tea, 5 %
E1	Elderberry tea, 1 %
E2	Elderberry tea, 2.5 %
E3	Elderberry tea, 5 %

- II

Chemical analyses

Analyses of the solution were performed before and after fermentation. The dry matter content and pH value were determined according to standard methods (OIV, 2015).

Antioxidant activity determination

The total phenolic content was determined using the modified method of Folin-Ciocalteu (Wolfe et al., 2003). 0.2 mL of aqueous honey solutions was mixed with 1.5 mL 7.5 % NaHCO3 and 1.5 mL Folin-Ciocalteu reagens. The mixture was left to stand 30 min in the dark and absorbance was read spectrophotometrically at 765 nm. The results were expressed as mg of gallic acid equivalent (GAE)/L mead. The testing of antioxidant activity using the Ferric reducing/Antioxidant power (FRAP) assay was carried out in accordance with Banzie and Strain (1996). 0.4 mL of aqueous honey solutions was mixed with 3.6 mL solutions of FRAP reagens. The mixture was left to stand 10 min on the 30 °C and abrosbance read spectrophotometrically at 593 nm. The results were expressed as mmol Fe^{2+}/L . The 2,2- diphenyl-1-picryl-hydrazyl (DPPH) assay using the method of Brand-Williams et al. (1995) with some modification. A 0.1 mM solution of DPPH (1,1-diphenyl-2picrylhydrazyl) in methanol was prepared. 1 mL of aqueous honey solution was mixed with 1 mL of DPPH solution. The mixture was left to stand for 20 min in the dark and absorbance was read spectrophotometrically at 517 nm. The results were expressed as µg of gallic acid equivalent (GAE)/mL mead. All the chemicals and reagents used were of analytical grade.

Statistical analysis

All tests were performed in duplicate and the results were expressed as means \pm standard deviation. Variance analysis (ANOVA) was applied to test significant differences among samples. Tukey's test was used to identify differences between mean values obtained in samples (p \leq 0.05).

Results and Discussion

Sample	pH v	value	dry matter o	
	before	after	Before	after
	fermentation	fermentation	fermentation	fermentation
C	3.96 [°]	3.33 ^ª	14.8 ^ª	6.8 ^{ab}
G1	4.40 ^b	3.67 ^b	15.8 ^{abc}	6.2 ^{bc}
G2	4.70 ^c	3.90 ^c	16.3 ^{bcd}	6.3 ^{bc}
G3	4.93 ^d	4.11 ^d	17.5 ^d	6.8 ^{ab}
L1	4.66 ^{cf}	3.64 ^b	15.1 ^{ab}	6.2 ^{bc}
L2	4.89 ^d	3.94 ^{ce}	16.2 ^{bcd}	6.2 ^{bc}
L3	5.10 ^e	4.14 ^d	16.5 ^{cd}	6.6 ^{abc}
E1	4.63 [†]	3.96 ^e	16.0 ^{abc}	6.0 ^c
E2	5.11 ^e	4.53 ^f	16.3 ^{bcd}	6.3 ^{bc}
E3	5.24 ^g	4.64 ^g	16.8 ^{cd}	7.1 ^b

Table 2. Results of physicochemical analyses of samples before and after fermentation

* Mean values with different superscript letters in the same column have statistically significant difference by Tukey test ($p \le 0.05$)

The results of the physicochemical analyses are shown in Table 2. Based on the obtained results, it can be noticed statistical difference among samples before and after fermentation. The lowest pH value before fermentation was measured in control sample and the highest pH value in sample E3 (with added 5 % of Elderberry tea). Also, by increasing the amount of added tea, the pH value increades. After fermentation lower pH values of samples, compared to samples before fermentation were noticed. pH value was higher in samples with added larger amounts of tea, and the lowest pH was measured in sample L1 (with added 1 % of Linden tea). Decreased pH values after completion of fermentation can be explained by the fact that volatile acids are formed during alcohol fermentation and the majority of them form acetic acid (Gupta and Sharma, 2009; Pereira et al. 2014; Akalin et al., 2016; Sroka and Satora, 2017). Acidity plays a significant role in alcohol beverages as it has a direct impact on their taste and stability (Akalin et al., 2016). In addition, excessive decrease in the pH value may contribute to reduced fermentation performance yield of a yeast strain (Pereira et al., 2014). Before fermentation, the dry matter content in control sample was 14.8%, but after addition of teas dry matter content increased due to extraction of tea components

into the solution. After the fermentation, the dry matter content was much lower compared to the initial solutions and ranged from 6.0 to 7.1. The dry matter comes from substances such as disaccharides (saccharose, maltose, isomaltose), trisaccharides, tetrasaccharides (Pereira et al. 2015), glycerol, etc.

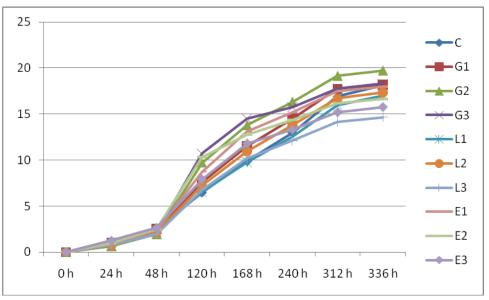
Table 3. Results of antioxidant activity (total phenolic content, DPPH and FRAP test) of the samples before and after fermentation

Sampl	FRAP (mmol Fe ²⁺ /mL)		DPPH (µg	gGAE/mL)	Total phenolic content (mg	
е					GA	E/L)
	before	after	before	after	before	after
	fermentatio	fermentatio	fermentatio	fermentatio	fermentatio	fermentatio
	n	n	n	n	n	n
С	0.30 ^a	0.37 ^a	1.46 ^ª	1.21 ^ª	118.56 ^ª	124.16 ^ª
G1	11.61 ^b	11.86 ^b	856.72 ^b	849.34 ^b	1364.8 ^{bc}	1448.8 ^b
G2	27.38 ^c	23.52 ^c	1522.74 ^c	1403.36 ^c	2864.8 ^d	2588.8 ^c
G3	31.64 ^d	30.89 ^d	2314.89 ^d	2467.70 ^d	4544.8 ^e	4224.8 ^d
L1	3.77 ^e	3.46 ^e	193.36 ^e	102.93 ^e	620.8 ^f	588.8 ^e
L2	7.60 ^f	8.27 ^f	532.96 ^f	266.23 [†]	1240.8 ^b	1116.8 ^f
L3	9.51 ^g	10.13 ^g	1085.59 ^g	652.59 ^g	1481.76 ^c	1348.8 ^g
E1	4.13 ^e	4.73 ^h	189.66 ^e	132.46 ^h	720.8 [†]	728.8 ^h
E2	8.22 [†]	9.04 ^f	313.92 ^h	287.85 ⁱ	1164.8 ^g	1232.8 ⁱ
E3	13.94 ^h	12.71 ^b	615.40 ⁱ	518.85 ^j	2024.8 ^h	1968.8 ^j

*Mean values with different superscript letters in the same column have statistically significant difference by Tukey test ($p \le 0.05$)

The results of antioxidant activity are shown in Table 3. Total phenolic content in control sample, before fermentation, was 118.56 mg GAE/L. After the addition of teas, a significant increase in these values was observed. The largest changes in total phenolic content are noticed in samples with green tea (from 1364.8 to 4544.8 mg GAE/L). After fermentation, in most samples a decrease in the total phenolic content was observed, probably due to interaction and coagulation of some phenolic compounds with honey. Švecová et al. (2014) observed that content of phenolic compounds in meads highly depends on the type of mead. Natural meads, composed only of honey and water, had a small content of these compounds. But, the meads with an added herbal extract were rich on these compounds, which is in line with results of this study. The obtained value for the FRAP assay in the initial C sample was 0,30 mmol Fe^{2+}/mL . The addition of teas resulted in a significant increase in these values. It can be seen that the biggest changes were noticed after the addition of green tea, where the values for the samples before fermentation ranged from 11.61 to 31.64 mmol Fe^{2+}/mL . Within the same type of tea, increasing the amount of added tea resulted in a steady increase in FRAP values. After

fermentation, insignificant decreases or increased changes in FRAP values compared to initial solutions were visible. The DPPH value for sample C was 1.46 μ g GAE/mL. With the addition of teas, there was again a significant increase in these values. The biggest changes can be seen in the samples to which green teas was added. The obtained results could be described by the fact that increasing the amount of added tea leads to the extraction of a larger amount of total phenolics and compounds that affect the antioxidant properties of the solution.



Graphic 1. Monitoring the fermentation flow

In Graphic 1 was shown the fermentation flow for all samples. Monitoring of the change in the weight of the bottles was performed by weighing the bottles at a certain time. Based on the results presented in Graphic 1 it could be noticed that the fermentation had a similar flow in all samples, which means that the addition of teas did not interfere with the growth and development of yeast. Changes in bottle weight between individual samples were not negligible. The best fermentation activity was observed in sample G2 (with added 2.5 % of Green tea). Kawa-Rygielska et al. (2019) observed that fruit additives in the mead making process have a significant effect on their fermentation process.

Conclusion

Herbals and teas can be used as raw materials for preparing meads. After fermentation, the pH value and dry matter content decreased. Addition of teas increased the values of FRAP and DPPH tests indicating that the greater the amount of added tea the higher the values were obtained. Herbal meads are richer in phenolic compounds than mead without additive, and also have stronger antioxidant activity than classic mead. The fermentation had a similar flow in all samples, which means that the addition of teas did not interfere with the growth and development of yeast, but changes in bottle weight between individual samples were not negligible.

Acknowledgments

This study is a result of the research conducted within the Project (19/6-020/961-68/18) financially supported by the Ministry for Scientific and Technological Development, Higher Education and Information Society of the Republic of Srpska.

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"XIII CONFERENCE OF CHEMISTS, TECHNOLOGISTS AND ENVIRONMENTALISTS OF REPUBLIC OF SRPSKA"

FOOD TECHNOLOGY

Original scientific article

APPLICATION OF 2-D NMR TECHNIQUE FOR CHARACTERISATION OF POLYPHENOLS FROM PLANT MATERIALS

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Abstract

Nuclear magnetic resonance spectroscopy (NMR) is wide spread method for investigation of organic compounds structure including polyphenols. For the identification of polyphenols, the most common NMR technique include one - dimensional NMR techniques such as ¹H and ¹³C. However, to overcome problems of spectral overlap two-dimensional nuclear magnetic resonance spectroscopy (2D NMR) is used. 2D NMR is a set of NMR methods that gives data plotted in a space defined by two frequency axes rather than one. The most popular two-dimension NMR experiments are the homonuclear correlation spectroscopy (COSY) sequence, heteronuclear single-quantum correlation spectroscopy (HSQC) and heteronuclear two-bond or multiple-bond correlation spectroscopy (H2BC, HMBC, respectively). In this study, results of eight different polyphenol compounds structure determined by advanced 2D-NMR technique (COSY, HSQC, H2BC, and HMBC) are shown.

Keywords: NMR, COSY, HSQC, H2BC, HMBC

Introduction

Nuclear magnetic resonance (NMR) spectroscopy was discovered in 1945 independently in two research groups led by F. Bloch and E.M. Purcella (Fossen and Andersen, 2006). The first NMR spectrometer was made and used in 1951, in the laboratory of the University of Leipzig. Since its discovery, NMR spectroscopy has undergone continuous technical development motivated by the wide range of problems its studies, from physics (material research), chemistry and biology (structure determination) to medicine (diagnostics). Nuclear magnetic resonances spectroscopy is based on the interaction of a sample with electromagnetic radiation in the frequency range from 100 MHz to 1 GHz, or wavelengths from 300 cm to 30 cm, which corresponds to the radio wavelength range of the spectrum. Nuclear magnetic resonance spectroscopy is currently one of the most powerful techniques for determining the structure of organic and inorganic compounds (Elipe, 2012).

The advantage of this technique is that it is feasible with very small amounts of a sample without damaging the studied sample. Nuclear magnetic resonance spectroscopy can be used to analyse different nuclei (¹H, ¹³C, ¹⁵N, ¹⁹F, and ³¹P) since the spin of named nuclei is nonzero and radio wave absorption occurs. In other words. NMR can be applied to nuclei that have a magnetic moment, and these are usually nuclei with an odd atomic number or an odd mass number. NMR spectroscopy is a very powerful analytical technique for determining the structure of flavonoids, although due to poor sensitivity, permeability, and difficulties in analysing more complex mixtures, there are some limitations. However, the progress made in the development of NMR spectroscopy, today allow us a complete assignment of all protons and carbon atoms of flavonoids, isolated in the low milligram range. The assignment is based on the chemical shift (d) and coupling constants (J) of ¹H and ¹³C nuclei in the one-dimensional NMR spectrum or in combination with diagonal or cross signals in homo- or heteronuclear correlations of two-dimensional NMR spectroscopy (Fossen and Andersen, 2006). Other nuclei such as ¹⁷O are rarely used to study the structure of flavonoids. However, the use of ¹⁷O NMR spectroscopy has been reported to study the effects of sugar on anthocyanin degradation and water mobility in roselle anthocyanin model solutions. The most common solvents used in NMR analysis of flavonoids are deuterated dimethyl sulfoxide (DMSO-d6) and tetradeuterated methanol (CD₃OD) (Andersen et al. 2003 Alcantara et al. 2004). For the analysis of relatively nonpolar flavonoids, solvents such as hexadeuterated acetone (acetonedeuterated chloroform (CDCl₃), carbon tetrachloride (CCl4) d6). and pentadeuterizedpyridine. Most flavonoids dissolve very easily in DMSO-d6. A solvent peak of 39.6 ppm and a residual solvent signal (2.49 ppm) are used as secondary references for ¹³C and ¹H spectroscopy, respectively. However, due to the relatively high melting point, analyzes with DMSO at lower temperatures are impossible. In these cases, a CD₃OD having a melting point of -98 °C and a low boiling point (65 ° C) can be used, which allows easy recovery of dissolved flavonoids by evaporation of the solvent. The solubility of flavonoids is more limited in CD₃OD than in DMSO, however, a mixture of CD₃OD and deuterated trifluoroacetic acid in various ratios (2 to 20%) is currently the most commonly used solvent for anthocyanin analysis. The use of acidified NMR solvents can cause proton exchange such as methylene protons of the malonyl residue and anthocyanin H-6 and H-8 with deuterium thereby also preventing the correlation of ¹³C signals in heteronuclear correlation analyzes. When using acidic solvents, dicarboxylic acid acylated anthocyanins can be esterified, and hydrolysis of flavonoid glycosides can also occur (Andersen et al. 2003 Alcantara et al. 2004). Polyphenolic substances form one of the most numerous and widespread groups of compounds in plants, to which more than 9000 different compounds belong. The most important and largest group of polyphenols are flavonoids (Martens and Mithöfer, 2005). The most common flavonoids in plants are flavonols, flavanols

and anthocyanins. In addition to flavonoids, we can often find phenolic acids in plants. Certain polyphenols are characteristic of certain types of fruits and vegetables, such as dihydrochalcones, which are characteristic polyphenolic compounds in apples and apple products (juice, fruit wine, porridge, bread, etc.). Analysis and monitoring of these compounds in apples have been proposed to identify counterfeit products (McRae et al., 1990; Amiot et al., 1992; Burda et al., 1998). The aim of this paper is to determine the structure of the most common subgroups of flavonoids and phenolic acids, or their representatives; (+) catechin, (-) epicatechin, rutin, quercetin, phloretin, phloridzin, chlorogenic acid and caffeic acid using ¹H and ¹³C NMR spectroscopy.

Materials and Methods

Materials

Polyphenol standards phloretin, phloridzin, (+) catechin, (-) epicatechin, ruthin, quercetin, chlorogenic acid, caffeic acid, CD₃OD were purchased from Sigma Chemical Co. St. Louis, USA. Figure 1 shows the structures of the determined polyphenols.

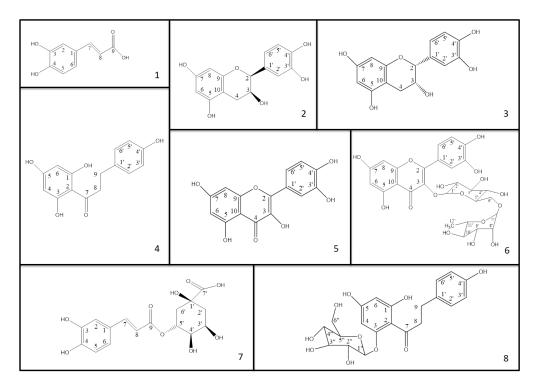


Figure 1. Structures of determined polyphenols: 1 - caffeic acid; 2 - catechin; 3 - epicatechin; 4 - phloretin; 5 - quercetin; 6 - ruthin; 7 - chlorogenic acid; 8 – phloridzin

Sample preparation and measurement

The weighed standard (5 mg) was dissolved in as little solvent as possible (methanol-d4) and the solution thus prepared was transferred to NMR tubes. The structure of the polyphenols was determined on an NMR Varian 400 MHz device (Varian, Palo Alto, California, USA). Two-dimensional (2D) NMR spectra obtained by mononuclear and heteronuclear analyzes were used to determine the structure at ¹H and ¹³C. Homonuclear ¹H – ¹H correlation NMR spectroscopy, COSY, and heteronuclear HSQC, H2BC, and HMBC were used in the experiment. The results were processed on the program MestreNova 10 (Mestrelab Research, Santiago de Compostela - Spain).

Results and discussion

The purpose of standard ¹H-NMR spectroscopy is to record chemical shifts, spinspin coupling constants, and data integration thus providing information on the relative number of hydrogen atoms. If the above analysis is applied to flavonoids, the information that can be obtained can help us to identify aglycones, acyl groups, the number of monosaccharides and the anomeric configuration of monosaccharides. Analysis of ¹H alone is not sufficient in determining the structure of flavonoids. Therefore, ¹³CNMR analysis is performed in combination with 2D NMR spectroscopy, especially techniques that use gradient pulses, which increases the sensitivity allowing the assignment of all ¹H and ¹³C NMR signals (Fossen and Andersen, 2006).

In this work, the structure of flavanol ((+) catechin and (-) epicatechin) was determined; flavonols (rutin and quercetin); dihydrochalcone (phloretin and phloridzin) and phenolic acids (chlorogenic acid and caffeic acid).

Example ¹H and ¹³C and COSY, HSQC, H2BC, HMBC NMR spectra are shown in Figure 2 on the example of caffeic acid. The ¹H NMR and ¹³C NMR spectroscopy detected signals of chemically non-equivalent protons and carbon atoms in the analyzed compounds (Figure 2a, b). The number of protons and carbon atoms was estimated based on the ratio of the integral of the surfaces under the individual signals. The COSY (correlation spectroscopy) technique was used to obtain information about the connection of protons via a scalar coupling through two or three chemical bonds (Figure 2c). The obtained scalar coupling of 15.6 and 15.7 Hz between protons with a chemical shift of 7.51 and 6.21 ppm indicates the existence of *trans*- isomers as possible at positions 7 and 8 of the caffeic acid molecule. To determine the connection between hydrogen atoms and carbon atoms through a single bond, HSQC (hetero nuclear single quantum coherence) was used through two H2BC bonds (hetero nuclear 2 bond correlation) and two or more HMBC bonds (hetero nuclear multiple bond correlation technique). HSQC is a technique that correlates ¹³C nuclei with ¹H nuclei in molecules through a single bond

coupling between them. In HSQC ¹H magnetization is directly detected while ¹³C is indirectly detected, unlike the HETCOR technique in which ¹H magnetization is indirectly detected and translates to 13 C magnetization which is then directly detected. There are several advantages in the way magnetization is detected in the HSQC experiment, including increased sensitivity (<1.0 mg flavonoid sample required for analysis) and the ability to see interactions between distant ${}^{13}C$ and ${}^{1}H$ nuclei using the HMBC variant. The technique is adapted for 3JCH and 2JCH coupling, however, the intensity of the diagonal peaks obtained by this experiment may be unexpected; some 1JCH couplings may appear as an asymmetric doublet, while in rare cases diagonal signals caused by, n > 3JCH coupling can be observed. In the aromatic region of the spectrum, some 2JCH couplings may be too small to be detected as diagonal signals. The main application of the HMBC technique in the characterization of flavonoids involves the assignment of resonance of unprotonated carbon nuclei of aglycones and potential acyl groups (Davis et al., 1996; Ngameni et al., 2004). After the assignment of proton signals by the ${}^{1}\text{H} - {}^{1}\text{H}$ COSY technique, the correlation of the ${}^{1}\text{H} - {}^{13}\text{C}$ single bond observed in the HSQC, H2BC and HMBC spectrum gives us the possibility of assignment of the corresponding ¹³C signals. Figure 2 d shows the HSQC spectrum of caffeic acid by which we linked δ (C) 113.61ppm; 115.06ppm; 121.46ppm; 145.61ppm; 114.13ppm with δ (H) 7.02ppm; 6.77ppm; 6.93ppm; 7.51ppm and 6.21ppm. The H2BC spectrum of caffeic acid shown in Figure 2 e allowed us to associate δ (C) 113.61 ppm and 115.06 ppm with δ (H) 6.93 ppm; δ (C) 121.46 ppm with δ (H) 7.02 ppm and 6.77 ppm; δ (C) 145.61 ppm with δ (H) 6.21; δ (C) 114.13 ppm with δ (H) 7.51 ppm. The last spectrum is shown in Figure 2 fallowed us to associate δ (H) 7.02 ppm with δ (C) 121.46 ppm, 145.61 ppm, and 148.02 ppm; δ (H) 6.77 ppm with δ (C) 126.37 ppm, 145.36 ppm and 148.02 ppm; δ (H) 6.93 ppm with δ (C) 113.61 ppm, 145.61 ppm and 148.02; δ (H) 7.51 ppm with δ (C) 113.61 ppm, 121.46 ppm and 169.61 ppm; δ (H) 6.21 ppm with δ (C) 126.37 ppm and 169.61 ppm. These techniques have allowed us to connect individual spin systems. The results obtained by 2D techniques allowed us to assign all the atoms in the molecule. ¹H and ¹³C NMR result for CD₃OD (400 MHz) for caffeic acid: H2 7.02; H5 6.77; H6 6.93; H7 7.51; H8 6.21. C1 126.37; C2 113.61; C3 145.36; C4 148.2; C5 115.06; C6 121.46; C7 145.61; C8 114.13; C9 169.61. The same procedures were used to determine the structures and other polyphenols tested. The ¹H and ¹³C NMR results in CD₃OD (400 MHz) for (+) catechin: H2 4.55; H3 3.96; H4 α2.84, β2.50; H6 5.92; H8 5.85; H2' 6.83; H5' 6.75; H6' 6.71. C2 81.48; C3 67.39; C4 27.02; C5 156.49; C6 94.85; C7 156.15; C8 94.02; C9 155.49; C10 93.99; C1' 130.77; C2' 113.83; C3' 145.70; C4' 145.73; C5' 114.62; C6' 118.71. The ¹H and ¹³C NMR results in CD₃OD (400 MHz) for (-) epicatechin: H2 4.81; H3 4.17; H4 α2.73, β2.86; H6 5.93; H8 5.91; H2' 6.97; H5' 6.75; H6' 6.79. C2 78.45; C3 66.07; C4 27.80; C5 156.58; C6 94.94; C7 156.25; C8 94.43; C9 155.94; C10 98.62; C1' 130.85; C2' 113.88; C3' 144.52; C4' 144.36; C5' 114.62; C6 117,71. The ¹H and ¹³ C NMR for CD₃OD (400 MHz) for quercetin: H6 6.17; H8 6.38; H2' 7.73; H5' 6.87; H6' 7.63. C2 147.32; C3 138.38; C4 175.87; C5 161.06; C6 97.80; C7

164.23; C8 92.97; C9 156.78; C10 103.08; C1' 122.70; C2' 114.52; C3' 144.78; C4' 146.54; C5' 114.70; C6 H 120.21. The ¹H and ¹³C NMR results in CD₃OD (400 MHz) for chlorogenic acid: H2 7.04; H5 6.26; H6 7.55; H7 6.95; H8 6.77; H9 5.32; H2' 3.72; H3' 4.16. C1 145.37; C2 113.73; C3 148.34; C4 167.24; C5 113.83; C6 145.62; C7 121.53; C8 115.02; C9 70.55; C1' 74.71; C2' 72.04; C3' 69.87; C4' 36.80; C5' 126.36; C6' 37.36; C7' 175.62. The ¹H and ¹³C NMR results in CD₃OD (400 MHz) for phloretin: H4 5.8; H6 5.8; H8 3.26; H9 2.84; H2' 7.03; H3' 6.68; H5' 6.68; H6' 7.03. C1 164.29; C2 103.86; C3 164.29; C4 94.32; C5 164.8; C6 94.32; C7 204.83; C8 45.88; C9 30.09; C1' 132.55; C2' 128.87; C3' 114.67; C4' 155.05; C5' 114.67; C6' 128.87. The ¹H and ¹³C NMR results in CD₃OD (400 MHz) for phloridzin: H4 6.17; H6 5.95; H8 a3.43, β3.43; H9 a2.87, β2.87; H2' 7.06; H3' 6.68; H5' 6.68; H6' 7.06; H1" 5.02; H2" 3.46; H3" 3.38; H4" 3.45; H5" 3.35, α3.70; H6" β3.90, C1 159.31; C2 105.33; C3 160.87; C4 94.03; C5 164.82; C6 96.93; C7 205.07; C8 45.54; C9 29.43; C1' 132.44; C2' 128.94; C3' 114.64; C4' 154.98; C5' 114.64; C6' 128.94; C1" 100.62; C2" 73.28; C3" 69.68; C4" 77.08; C5" 48.05; C6" 61.00. The ¹H and ¹³C NMR results in CD₃OD (400 MHz) for rutin: H6 6.22; H8 6.41; H2' 7.68; H5' 6.87; H6' 7.64; H1" 5.11; H2" 3.48; H3" 3.3; H4" 3.27; H5" α3.42, β3.84; H6" 3.38; H7" 4.53; H8" 3.64; H9" 3.54; H10" 3.28; H11" 3.45; H12" 1.13. C2 157.89; C3 134.54; C4 179.40; C5 161.54; C6 98.51; C7 164.64; C8 93.43; C9 157.08; C10 104.17; C1' 121.68; C2' 116.27; C3' 144.37; C4' 148.58; C5' 114.58; C6' 122.09; C1-103.28; C2" 74.30; C3" 75.79; C4" 69.97; C5" 76.77; C6" 67.12; C7" 100.99; C8" 70.68; C9" 70.81; C10" 72.51; C11" 68.28; C12" 16.46.

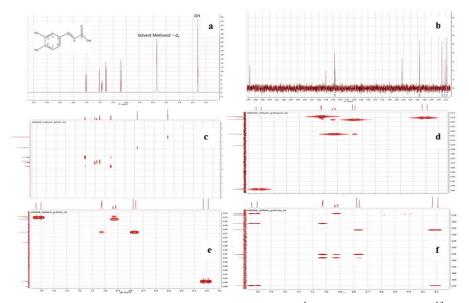


Figure 2. Example of NMR spectra of caffeic acids. a) ¹H NMR spectrum; b) ¹³C NMR spectrum; c) COSY spectrum; d) HSQC spectrum; e) H2BC spectrum; f) HMBC spectrum

Conclusion

The paper provides an insight into the possibility of using NMR techniques to determine the structure of polyphenols. It can be seen from the results of the work using only standard ¹H and ¹³C NMR analyses is not enough to determine the structure of polyphenols. However, using two-dimensional NMR spectra obtained by homonuclear and heteronuclear analyzes, we were able to determine the position of all atoms in the observed polyphenol molecules.

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PRIMJENA 2-D NMR SPEKTROSKOPIJE U KARAKTERIZACIJI POLIFENOLNIH SPOJEVA IZ BILJNIH MATERIJALA

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Sažetak

Spektroskopija nuklearne magnetske rezonancije najmoćnija je spektroskopska metoda za određivanje strukture organskih spojeva. Omogućuje, između ostaloga, detekciju jezgri vodikovih (¹H) i ugljikovih (¹³C) atoma te je od velike koristi u istraživanju polifenola. Polifenoli su spojevi koji u svojoj strukturi imaju jednu ili više -OH skupina koje su vezane direktno na benzenski prsten. Polifenolni spojevi imaju važnu ulogu u prevenciji različitih bolesti (engl. "health-promoting" compounds). Mnoga istraživanja su pokazala da polifenoli u voću i povrću imaju antikancerogeno, protuupalno, antihepatoksično, antibakterijsko, antivirusno te antialergijsko djelovanje. U ovom su radu prikazani rezultati 2-D NMR-analize (COSY, HSQC, H2BC, and HMBC) osam različitih polifenolnih spojeva.

Ključne riječi: NMR, COSY, HSQC, H2BC, HMBC

Original scientific article

ADSORPTION OF INDIVIDUAL POLYPHENOL GROUPS FROM APPLES ONTO *B*-GLUCAN

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Abstract

The aim of this work was to obtain information about interactions between individual groups of polyphenols from apples and β -glucan. Polyphenols were extracted from peel and flesh of apple Idared with ultrasonic assisted extraction. Different groups of polyphenols from apple were separated by using the gel chromatographic method in a glass column with Sephadex LH-20 gel. Polyphenols characterized reversed-phase high-performance were by using liquid chromatography. In the apple flesh flavan-3-ols were present in the first fraction, then phenolic acids in the second and the flavonols in the third. In the apple peel flavan-3-ols were presented in the first fraction, then anthocyanins in the second and flavonols in the third. Interactions between polyphenols from apples and β glucan were studied through adsorption process. The adsorption was conducted at 25 °C and pH 5.5 for 16 h. Adsorbed polyphenols were determined with reversedphase high-performance liquid chromatography. In order to obtain information about adsorption process different models were applied. The experimental data (amount of adsorbed (q_e) and un-adsorbed (c_e) polyphenols) were modelled with non-linear regression using adsorption isotherm equations like Langmuir, Freundlich and Dubinin-Radushkevich. Apple polyphenols interacted with β glucan. Polyphenols from peel showed slightly higher adsorption capacity than polyphenols from flesh. It was shown that adsorption was concentration depended process. It can be suggested that bonds between individual groups of polyphenols and β -glucan were H bonds and Van der Waals forces.

Keywords: adsorption, interactions, polyphenols, β -glucan.

Introduction

Polyphenols are secondary plant metabolites that can be found in fruits and vegetables. Apples are important source of polyphenols because they are present all year around. It was shown that polyphenols can interact with dietary fiber like β -glucan, but these interactions are not completely investigated (Jakobek, 2015). It

was shown that dietary fiber can carry out polyphenols to the lower parts of the digestive tract where they can show positive effects in their intact form (Gorelik et al., 2008; Kanner et al., 2012). That is why interaction of polyphenols and dietary fiber are investigated in the present study.

Dietary fibers can be found in cereals, mushrooms, seaweed and yeast (Laroche and Michaud 2007). β -glucan is dietary fiber that can be found in cereals and early studies showed that he can interact with polyphenols (Gao et al., 2012; Simonsen et al., 2009; Veverka et al., 2014; Wang et al., 2013).

Adsorption process can be used for studying the interaction between polyphenols and dietary fiber. In the adsorption process molecules from the solution (adsorbate) adsorb onto the surface of the adsorbent (Soto et al., 2011). During the adsorption adsorbate is transporting in the solution to the adsorbent surface, then adsorbate is diffusing across adsorbent liquid film, then intra-particle diffusion is occurring and the adsorption and desorption from the surface of the adsorbent (Plazinski et al., 2009). After adsorption process equations called adsorption isotherms can be applied (Foo and Hameed, 2010; Soto et al., 2011) like Langmuir, Freundlich and Dubinin-Radushkevich.

The aim of these work was conduct adsorption between individual groups of apple polyphenols with β -glucan. Polyphenols were extracted from peel and flesh of apple Idared with ultrasonic assisted extraction and separated by using the gel chromatographic method in a glass column with Sephadex LH-20 gel. Reversed-phase high-performance liquid chromatography was used for determination of polyphenols before and after the adsorption process. After the adsorption process Langmuir, Freundlich and Dubinin-Radushkevich were applied in order to obtain more information about interaction.

Materials and Methods

Chemicals

The chemicals were purchased from Kemika (Zagreb, Croatia): sodium hydrogen phosphate dodecahydrate and sodium dihydrogen phosphate dehydrate, then from Fluka (Buchs, Switzerland): orto-phosphoric acid (85 % HPLC-grade), J.T. Baker (Poland): methanol (HPLC grade). Polyphenol standards were purchased from Extrasynthese (Genay, France) (cyanidin-3-galactoside chloride, procyanidin B1, procyanidin B2, quercetin-3-O-rhamnoside, quercetin-3-O-galactoside, phloretin-2'-O-glucoside, phloretin) and from Sigma-Aldrich (St. Louis, MO, USA) (*p*-coumaric acid, chlorogenic acid, (-)-epicatechin, (+)-catechin hydrate, quercetin dihydrate and quercetin-3-glucoside). Standard of β -D-glucan from barley was obtained from Sigma-Aldrich (St. Louis, MO, USA).

Extraction of apple polyphenols

The peel and flesh of around 1 kg of apple Idared were separated. Apple peel was ground in a coffee grinder. The flesh was cut, seeds were removed and homogenized with a stick blender. Samples were stored at -18 ° C. Ten sample of peel were weight (around 0.5 g) in the plastic cuvettes. Furthermore, 1 mL of 80 % methanol in water was added to each cuvette. The samples were vortexed (Grant Bio, UK) and extraction was carried out by using an ultrasonic bath (RK 100, Berlin, Germany) for 15 min. Samples were centrifuged (Eppendorf, Hamburg, Germany) for 10 min at 10.000 rpm and extracts of all 10 samples were combined. The same procedure was done for preparing the extract of apple flesh.

Separation of individual groups of polyphenols

Different groups of polyphenols in apples were separated from the prepared extracts of apple peel and flesh. Separation was carried out by using the gel chromatographic method in a glass column with sephadex LH-20 gel. Sephadex LH-20 gel was prepared in the glass column by adding 30 ml of 80 % methanol and 5 g of Sephadex overnight. The column was rinsed with 10 ml of 60 % methanol and 20 ml of 80 % methanol. Ten millilitres of flesh extract were added to the column. The column was rinsed with 5 ml of 10 % methanol, 5 ml of 40 % methanol, 10 ml of 60 % methanol, 20 ml of 80 % methanol, 20 ml of 80 % methanol and 5 ml of 100 % methanol and 5 ml of 60 % methanol and 5 ml of 60 % methanol, 20 ml of 80 % methanol, 20 ml of 100 % methanol, 10 ml of 60 % methanol, 20 ml of 80 % methanol, 20 ml of 100 % methanol and 5 mL 80 % methanol (fraction 2), 15 mL 100 % methanol (fraction 3).

Then column was rinsed with 80 % methanol and ten millilitres of peel extract was added. The eluate of apple peel after adding 10 mL of 60 % methanol was collected (fraction a), then 20 mL of 80 % methanol (fraction b), 20 mL 100 % methanol (fraction c). Fractions of apple peel and flesh were evaporated and 1 mL of 100 % methanol was added. Fractions were filtered through a 0.45 μ m PTFE syringe filter and analysed with RP-HPLC to determine the initial number of polyphenols.

Adsorption process

Reaction solution (0.5 ml) consisted of polyphenol extract (20, 40, 50, 60 μ l), β -glucan (5 mg/L) and the rest was phosphate buffer (pH 5.5). Reaction solutions were mixed in a laboratory shaker (IKA KS 130, Werke, Germany) for 16 h at 25 °C. Then solutions were centrifuged (Minispin, Eppendorf, Hamburg, Germany) at 10.000 rpm for 10 minutes through polyethersulfon membrane (Vivaspin 500, Sartorius, Goettingen, Germany). Solutions were filtered through a 0.45 μ m PTFE syringe filter and analysed with RP-HPLC in order to determine the equilibrium

concentration (c_e). Adsorption capacity (q_e) (mol of polyphenols adsorbed onto g of β -glucan) was calculated:

$$q_{\rm e} = \frac{c_{\rm adsorbed} \cdot V_{\rm m}}{\gamma_{\rm a} \cdot V_{\rm a}} \tag{1}$$

where $V_{\rm m}$ is the total volume of a model solution (L), $\gamma_{\rm a}$ is the β -glucan initial concentration (g/L) and $V_{\rm a}$ is the volume of model solution (L).

RP-HPLC method

Apple extracts before and after the adsorption process were analysed using an HPLC system 1260 Infinity II (Agilent technology, Santa Clara, CA, USA) with quaternary pump, PDA detector and vialsampler, Poroshell 120 EC C-18 column, 4.6 x 100 mm, 2.7 μ m and a Poroshell 120 EC-C18 4.6 mm guard-column. Mobile phases were 0.1 % H3PO4 (mobile phase A) and 100 % methanol (mobile phase B). The flow rate was 0.8 mL/min, and the injection volume 10 μ L. The gradient was: 0 ml 5% B, 5 min 25 % B, 14 min 34 % B, 25 min 37 % B, 30 min 40 % B, 34 min 49 % B, 35 min 50 % B, 58 min 51 % B, 60 min 55 % B, 62 min 80 % B, 65 min 80 % B, 67 min 5 % B, 72 min 5 % B. For the standard identification, the retention times and the spectrum of peaks were compared to spectrum of authentic standards.

Adsorption isotherms

The values q_e and c_e were modelled using non-linear models like Langmuir (eq. 2), Freundlich (eq. 3) and Dubinin-Radushkevich (eq. 3-7) (Foo and Hameed, 2010; Marsal *et al.*, 2012; Soto *et al.*, 2011):

Langmuir
$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e}$$
 (2)

Freundlich
$$q_e = K_F c_e^{1/n}$$
 (3)

Dubinin-Radushkevich
$$q_e = q_s exp(-\beta \varepsilon^2)$$
 (4)

$$\varepsilon = RT ln\left(\frac{c_{\rm S}}{c_{\rm s}}\right) \tag{5}$$

$$E = \frac{1}{\sqrt{2\beta}} \tag{6}$$

Dubinin-Radushkevich becomes
$$q_e = q_s exp\left(-\beta R^2 T^2 \left(ln \frac{c_s}{c_e}\right)^2\right)$$
 (7)

where q_e is the amount of polyphenols adsorbed per gram of β -glucan at equilibrium (mol/g), K_F is constant of relative adsorption capacity ((mol/g) (L/mol)^{1/n}), 1/n is constant od adsorption intensity, c_e is the polyphenol concentration in the solution at equilibrium (mol/L), K_L is the Langmuir constant (L/mol) or apparent affinity constant, q_m is the theoretical maximum adsorption capacity of β -glucan (mol/g), q_s is the theoretical isotherm saturation capacity (mol/g), β is a constant related to the adsorption capacity (mol²/J²), ε is the Polanyi potential (J/mol), R is the gas constant (8.314 J/mol K), T is the temperature (K), E is the adsorption mean free energy (J/mol), c_s is the theoretical saturation concentration or solubility (mol/L).

Statistical analysis

Adsorption experiment was conducted one times for each concentration level and polyphenols were measured once. The q_e and c_e were modeled using adsorption isotherm equations with non-linear regression and the standard error (*se*) was calculated:

$$se = \sqrt{\frac{\left(\sum_{i=1}^{n} \left(q_{e,meas} - q_{e,model}\right)^{2}\right)}{(n-a)}}$$
(8)

where $q_{e, meas}$ and $q_{e, model}$ is the measured q_e and the q_e calculated by the model, n is the total number of data points and a is the number of parameters of the model.

Results and discussion

In this paper adsorption process between polyphenols from apple peel and flesh was carried out. Apples are great source of polyphenols and they are available all year. Polyphenols were first fractionated from peel and flesh in order to obtain the individual groups of polyphenols. The most abundant polyphenols groups in the apple flesh were flavan-3-ols and phenolic acids in fraction 1, then phenolic acids in fraction 2, and flavonols in fraction 3 (Figure 1). On the other hand, the most abundant polyphenols groups in apple peel were flavan-3-ols in fraction a, then flavan-3-ols and antocyanins in fraction b, and flavonols in fraction b (Figure 1). Also, the number of polyphenols were higher in the peel then in the flesh which is in accordance with literature (Escarpa and González, 1998).

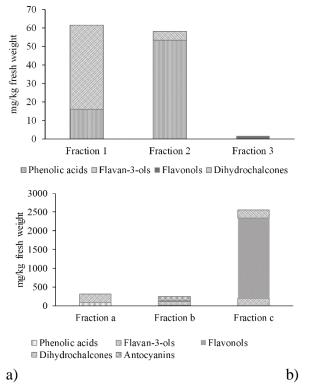


Figure 1. Distribution of individual polyphenols in apple before adsorption in mg/kg fresh weight. a) flesh; b) peel

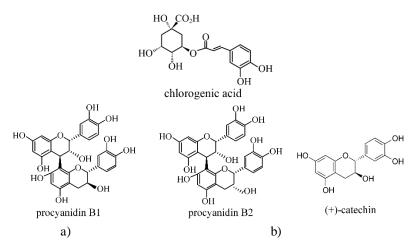
Adsorption was carried out between polyphenols from fractions of peel and flesh. The reaction solution contained polyphenols from fractions and dietary fiber (β glucan) at a constant temperature. Adsorption of polyphenols from apple flesh was monitored with flavan-3-ols (procyanidin B1and (+)-catechin) from fraction 1, then with phenolic acids (chlorogenic acid) from fraction2. The adsorption was not monitored with fraction 3 because of very low amount of flavonols in the fraction. From the polyphenols of apple flesh, adsorption was monitored with flavan-3-ols (procyanidin B1, procyanidin B2 and (+)-catechin) from fraction a, then anthocyanin (cyanidin-3-galactoside) from fraction b, and with flavonols (quercetin-3-glucoside, quercetin-3-galactoside, quercetin-3-rhamnoside) from fraction c. During the adsorption process polyphenols adsorbed onto β -glucan. After the adsorption process adsorption capacities of β -glucan were calculated (Table 1). In the apple flesh, phenolic acid (chlorogenic acid) showed higher adsorption capacity then flavan-3-ols. In the group of flavan-3-ols, (+)-catechin showed higher capacity then procyanidin B1. In the apple peel, flavonols shoed the highest adsorption capacity followed by phenolic acid, anthocyanin, and flavan-3ols. In the flavan-3-ols group the procyanidin B1 showed the highest capacity followed by (+)-catechin and procyanidin B2. In flavonols group the adsorption capacity order was: quercetin-3-rhamnoside, quercetin-3-galactoside and quercetin-3-glucoside.

	Adsorptic	on capacity*
	mr	nol/g
Polyphenols	Flesh	Peel
Phenolic acids		
chlorogenic acid	0.79	0.60
Flavan-3-ols		
procyanidin B1	0.019	0.57
(+)-catechin	0.34	0.11
procyanidin B2		0.068
Flavonols		
quercetin-3-galactoside		9.26
quercetin-3-glucoside		1.18
quercetin-3-rhamnoside		20.25
Anthocyanins		
cyanidin-3-galactoside		0.60

Table 1. Adsorption capacities of β *-glucan for polyphenols from peel and flesh of apples*

*adsorption capacities from the experiment in which a 60 µl of peel or flesh extract was added to the reaction solution

The order of adsorption capacity can be connected with the initial number of polyphenols in the extract. Polyphenols with higher initial amount in the extract (Figure 1) showed higher adsorption capacity (Table 1). The chemical structures of polyphenols are shown in Figure 2. In the flavan-3-ols group the chemical structure of procyanidin B1 was more favorable then for (+)-catechin and procyanidin B2. It seems that spatial arrangement of OH groups on the molecules of procyanidin B1 and procyanidin B2 influenced the adsorption capacity. In the flavonols group the structure of quercetin-3-rhamnoside was more favorable then for quercetin-3-galactoside and quercetin-3-glucoside (Table 1). It seems that molecule of rhamnose is more favorable than molecule of galactose and glucose.



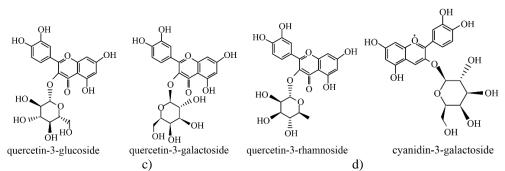


Figure 2. Chemical structures of polyphenols. a) phenolic acids; b) flavan-3-ols; c) flavonols; d) anthocyanins

After adsorption process various equations like Langmuir, Freundlich and Dubinin-Radushkevich can be applied to experimental data (c_e vs q_e) (Babaeivelni et al., 2013; Foo and Hameed, 2010; Gao et al., 2012; Marsal et al., 2012; Soto et al., 2011; Wu et al., 2011). From the parameters of adsorption isotherms data about the adsorption process between polyphenols and dietary fiber can be obtained (Table 1 and Table 2). The Freundlich model describes a multilayer adsorption where a molecule can bind to the surface of adsorbent without any saturation (Wu et al., 2011; Marsal et al., 2012). The Langmuir model describes a monolayer adsorption at the surface of the adsorbent (Wu et al., 2011; Marsal et al., 2012; Limousin et al., 2007). From Dubinin-Radushkevich model, the theoretical saturation capacity and the type of bonding can be determined (Foo and Hameed, 2010; Marsal et al., 2012; Soto et al., 2012).

Table 2 presents the parameters of Langmuir, Freundlich and Dubinin-Radushkevich isotherm for the adsorption of polyphenols from apple flesh. From the parameters $q_{\rm m}$, and $q_{\rm s}$ which are the theoretical adsorption capacity and saturation it can be seen that phenolic acid showed higher capacity then flavan-3-ols. Adsorption was favorable for all polyphenols (1/n was lower than 1). The parameter E which presents the mean free energy of adsorption, indicates the physical adsorption between polyphenols and β -glucan like H bonds and Van der Waals forces (Marsal et. al., 2012).

	Freundlich			Dubinin-			
	Langi	nuir			Radushkevich		
	$q_{ m m}$	KL	1/n	$K_{ m F}$	$q_{\rm s}$	Ε	
		L/mol		(mol/g)	mmol/g	J/mol	
Polyphenols	mmol/g			$(L/mol)^{1/n}$	-		
Phenolic acids							
chlorogenic acid	8.10	45193	0.85	2.48	9.00	5807	
Flavan-3-ols							
procyanidin B1	0.045	23737	0.98	4.47	0.046	5219	
(+)-catechin	0.53	105179	0.78	4.48	0.56	6104	

Table 2. Parameters of Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherms of polyphenols from apple flesh

Table 3 presents the parameters of Langmuir, Freundlich and Dubinin-Radushkevich isotherm for the adsorption of polyphenols from apple peel. From the parameters $q_{\rm m}$, and $q_{\rm s}$ it can be seen that flavonols showed higher capacity followed by anthocyanin, flavan-3-ols and phenolic acid. Adsorption was favorable for all polyphenols (1/*n* was lower than 1). The parameter *E* indicate the physical adsorption between polyphenols and β -glucan like H bonds and Van der Waals forces (Marsal et. al., 2012).

Table 3. Parameters of Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherms of polyphenols from apple peel

			Fı	reundlich	Duł	oinin-		
	Lang	muir				Radu		
	$q_{ m m}$	KL	1/n	$K_{\rm F}$	$q_{\rm s}$	Ε		
		L/mol		(mol/g)	mmol/g	J/mol		
Polyphenols	mmol/g			$(L/mol)^{1/n}$	C			
Phenolic acids								
chlorogenic acid	0.45	460889	0.77	1.55	0.59	4392		
Flavan-3-ols								
procyanidin B1	0.65	38624	0.97	17.40	0.68	6120		
procyanidin B2	0.17	254699	0.78	2.65	0.18	6221		
(+)-catechin	0.26	70467	0.78	0.98	0.26	6060		
Flavonols								
quercetin-3-galactoside	10.00	254090	0.77	15.48	11.00	5383		
quercetin-3-glucoside	1.12	86189	0.88	9.48	1.13	6634		
quercetin-3-rhamnoside	17.20	253071	0.23	0.15	17.60	4997		
Anthocyanins								
cyanidin-3-galactoside	0.70	275909	0.25	0.0087	0.68	6589		

Polyphenols from apple peel and flesh adsorbed on β -glucan. Adsorption capacities were in in accordance with earlier studies (Gao et al., 2012; Le Bourvellec et al., 2004; Le Bourvellec and Renard, 2005; Liu et al., 2016; Phan et al., 2017; Zhang et al., 2017). Polyphenols from peel showed higher adsorption capacity than polyphenols from flesh. It was shown that adsorption was concentration depended

process. Polyphenols with higher amount in extract showed higher adsorption capacity. In apple flesh the amount of chlorogenic acid was the highest and it showed the highest adsorption capacity compared to other present polyphenols. In apple peel the amount of flavonols was the highest and they showed the higher capacity of all other polyphenols. It seems polyphenols bonded onto β -glucan with H bonds and Van der Waals forces. In the literature, polyphenols also bonded onto β -glucan with hydrogen bonds (Gao et al., 2012; Wu et al., 2011), or H bonds and maybe hydrophobic interactions (Le Bourvellec et al., 2004; Renard et al., 2001).

Conclusion

The number of polyphenols extracted from apple peel were higher than the number of polyphenols in apple flesh. Adsorption was conducted with individual groups of polyphenols from apple peel and flesh with β -glucan. During the adsorption process polyphenols from apple adsorbed onto the surface of β -glucan. Polyphenols concentration before and after the adsorption process was monitored by using reversed-phase high-performance liquid chromatography. Adsorption models like Langmuir, Freundlich and Dubinin-Radushkevich were used to get more information about the adsorption process. Polyphenols from peel showed higher adsorption capacity than polyphenols from flesh. It was shown that adsorption was concentration depended process. Polyphenols with higher amount in extract showed higher adsorption capacity. It can be suggested that bonds between individual groups of polyphenols and β -glucan were H bonds and Van der Waals forces.

Acknowledgments: This work has been fully supported by the Croatian Science Foundation under project number HRZZ-IP-2016-06-6777.

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Original scientific article

EFFECT OF PARTIAL REPLACEMENT OF SODIUM CHLORIDE WITH POTASSIUM CHLORIDE ON THE PROPERTIES OF ACID-COAGULATED CHEESES

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Abstract

Excessive sodium intake is considered to be the cause of certain health problems in humans, such as hypertension and cardiovascular disease. The aim of this paper is to investigate the effect of partial replacement of sodium chloride (NaCl) with potassium chloride (KCl) on chemical composition, water activity, pH value, acidity, colour, textural properties and sensory properties of acid-coagulated cheeses. A control sample with sodium chloride (100% NaCl) was produced as well as samples in which a certain amount of sodium chloride was replaced by potassium chloride (25%, 50% and 75%). Based on the obtained results, it was determined that the replacement of sodium chloride with potassium chloride affects (p<0.05) the examined physico-chemical and sensory properties of the produced cheeses. Cheeses with reduced sodium content had statistically significant (p<0.05) higher water content and a lower fat and protein content, and therefore a lower dry matter content. It was also found that cheeses with a higher amount of KCl had statistically significant (p<0.05) lower hardness and higher values of lightness (L*) and higher values of yellow colour (b*) compared to samples produced with 100% sodium content. Complete replacement of sodium chloride with potassium chloride in the production of acid-coagulated cheeses gives an unacceptably bitter product. The obtained results showed that, in the production of these types of cheese, up to 50% of sodium chloride can be replaced by potassium chloride without negatively affecting the sensory properties, while a higher level of substitution negatively affects the quality of the produced cheese.

Keywords: cheese, sodium replacement, potassium chloride.

Introduction

Cheese is the crown of dairy production – the oldest and safest form of concentrating and preserving the nutritional value of milk. Cheese is not only a valuable basic foodstuff but has recently become a favourite food to enjoy, especially in countries with a high standard of living, where the consumption of

cheese is also growing (Popović-Vranješ, 2015). There are many different types of cheese on the market today. Acid and acid-heat coagulated cheeses are cheese varieties produced by the coagulation of milk, cream, or whey or blends thereof via direct chemical acidification, culture acidification, or a combination of chemical acidification and high heat treatment (Chinprahast et al., 2015; Farkye, 2017).

An important ingredient in cheese is sodium chloride, which reduces the amount of water in the cheese, affects the formation of the crust, promotes protein swelling, helps shape the plasticity of the curd, acts selectively on the microflora, affects the sensory properties of cheese and improves cheese durability (Tratnik, 1998). Although sodium participates in a number of essential metabolic functions in the human body and plays an important role in maintaining water balance within cells, excessive sodium intake is associated with certain health problems in humans, such as high blood pressure and other chronic diseases (Felicio et al., 2013).

Nowadays, there is plentiful evidence that food consumption is related to health. All nutritional trends are moving towards a reduction of fat, sugar and salt in food. Increased sodium intake can be crucial for the incidence of hypertension, a phenomenon observed in modern societies, especially in the elderly. Sodium intake far exceeds nutritional recommendations, especially in modern and industrialized countries. The main source of sodium in food products is derived from sodium chloride i.e. table salt (Lilić et al., 2014).

Dairy products, including cheese, are suitable material for developing products with dietary and functional properties that can have a positive effect on maintaining and improving human health. The modern concept of nutrition implies the growing popularity of products with the content of milk fat and table salt, which can have negative effects on human health, reduced to a minimum. In this regard, current research includes studies of the possibility of producing cheeses with reduced fat and salt content (Costa et al., 2019; Gomes et al., 2011; Gore et al., 2019; Puđa & Miočinović, 2009).

One of the basic roles of table salt in human nutrition is to provide the necessary amounts of sodium necessary for the smooth functioning of metabolism. Reducing the salt content, given its great importance for quality, usually requires a modern scientific and technological approach in cheese production (Puda & Miočinović, 2009). The development of food products that can contribute to reducing risks to human health is a challenge for the dairy processing industry. Due to the negative effects of salt on consumers' health, such as increased blood pressure and reduced calcium absorption, high intake of salt from food is a significant problem of modern society. Given that the consumption of cheese in the world is increasing, it is important to pay attention to reducing the amount of salt as a carrier of sodium in cheese. To this end, the possibilities are being investigated of producing food products with partial or complete substitution of NaCl with other salts such as KCl, MgCl₂ and CaCl₂ (Charlton et al., 2007; Cruz et al., 2011; Fieira et al., 2015; Fosberg & Joyner, 2018; Gomes et al., 2011). Due to its similar structure and salty

taste, KCl can be used as a partial substitute for NaCl, which can have a positive effect on lowering blood pressure, low risk of heart disease and stroke (Lu & McMahon, 2015). The aim of this paper was to examine the effect of partial replacement of sodium chloride with potassium chloride on the physicochemical and sensory properties of cheese produced by heat-acid coagulation of milk.

Material and methods

For this work, four samples were produced of pasteurized 3.2% fat cow's milk cheese (Pađeni Dairy, Bileća). A control sample was produced with 100% NaCl and 3 samples were produced in which a certain amount of NaCl was replaced with KCl (25%, 50% and 75% KCl) (Table 1). Fresh pasteurized milk was heated to a temperature of 95°C, 0.3% citric acid was added to the milk and the milk was stirred for 5 minutes to coagulate i.e. form curd. After coagulation, the cheese curd was strained through cheesecloth to separate whey (2-3 min). Salting was done using 2% of salt in relation to the weight of the cheese curd (Table 1.). After that, moulding and pressing (2 kg/1 kg of cheese) were performed for 1 hour. Until the analysis, the samples were stored in polyethene bags at $+4^{\circ}C$.

The moisture content and the total solids content of the cheese samples was determined by drying at $103\pm2^{\circ}$ C to constant weight (BAS EN ISO 5534:2006). The total content of ash was also determined gravimetrically after heating of sample in a muffle furnace (Micronal) at 550°C (Carić et al., 2000). The content of proteins was calculated by determination of total nitrogen by Kjeldahl method, and it was converted to total crude protein using a nitrogen conversion factor of 6.38 for milk proteins (BAS EN ISO 8968-1:2015). Determining the content of fat in cheeses was performed by acid-butyrometric method (BAS ISO 11870:2012). The chloride content was determined by potentiometric titration (BAS EN ISO 5943:2015). Water activity (a_w) was measured by direct readings in AW Meter (Novasina LabMaster-AW 1119971). The acidity of the cheese was determined by the Soxhlet Henkel method (Carić et al., 2000). Measuring the pH value in cheese was performed in a cheese solution prepared by mixing equal amounts of cheese and water (Carić et al., 2000) using a pH meter (Hanna instruments, HI 2211). Sensory evaluation of selected quality indicators of tested cheese samples was performed by a team of five trained evaluators. A 5-point hedonic scale (1=very considerable deviation from the expected quality to 5=no deviation from the expected quality) was used to evaluate appearance, colour, consistency, odour and flavour (BAS ISO 22935-2:2011; BAS ISO 22935-3:2011).

All analyses were performed with three repetitions except for instrumental colour and texture measurement, as well as sensory analysis of the cheese. Instrumental measurement of colour and texture was performed with 10 and sensory analysis of cheese with five repetitions. The results of this study are presented as mean values \pm standard deviations. One factor analysis of variance (ANOVA) and Tukey's post

hoc test were performed using the IBM SPSS Statistics for Windows, version 22.0 (Armonk, NY, United States). Significance was established at $\alpha < 0.05$.

1	· · · · · · · · · · · · · · · · · · ·	
Sample	NaCl (%)	KCl (%)
1	100	-
2	75	25
3	50	50
4	25	75

Table 1. The composition of the salt mixture for salting of cheese

Instrumental colour measurement was performed using a spectrophotometer CM-2600d (Konica Minolta Sensing Inc., Japan), with 8 mm port size, illuminant D65 and a 10° standard observer, and after standardisation of the instrument with respect to the white calibration plate. Colour parameters, expressed as CIE L*, a* and b* values, were determined as indicators of lightness, redness and yellowness, respectively. The measurements were performed on the outside surface and on the cut surface immediately after cutting the cheeses.

The cheeses hardness was determined mechanically by the Texture Analyzer TA.XT plus (Stable Micro Systems), which measures the shear force needed to cut the sample. Warner-Blatzler shear force was used with the HDP/BSK knife cutting blade. The load cell was 25 kg, the speed was 4.00 mm s⁻¹, and the distance was 20.00 mm. The test samples were prepared by cutting rectangular forms from the cheese (1×1 cm, length 5 cm) on which the measurement was performed. The instrument measures the force (kg) needed to move the knife cell a certain distance (mm) into the cheese.

Results and discussion

Table 2. shows the values for the physico-chemical properties of the analysed cheeses. After the performed analyses, a statistically significant influence (p<0.05) was determined of sodium chloride concentration on the basic chemical composition of acid-coagulated cheeses. The results showed that by reducing the content of sodium chloride in cheeses, the fat and protein content, and thus the total dry matter, decreased significantly (p<0.05), while the water content increased. Sodium chloride in cheese promotes the separation of whey from cheese, which is confirmed by the obtained results. Sample 1 (produced with 100% NaCl) had the lowest water content (50.27%) and the highest fat content (24.50%), the protein content being 20.54%. Sample 4 (produced with 25% NaCl and 75% KCl) had the highest water content (52.17%) and the lowest fat content (22.00%), the protein content being 18.67%.

The decrease in NaCl concentration in cheeses affected the pH value and acidity of the cheeses while the a_w value did not change significantly. Sample 3 (produced with 50% NaCl and 50% KCl) had the highest pH value (5.55), while the control sample had the highest acidity (46.80 °SH). The lowest acidity (44.00 °SH) and pH value (5.44) were found in sample 2 (produced with 75% NaCl and 25% KCl).

Parameter	Sample 1	Sample 2	Sample 3	Sample 4
Water (%)	50.27±0.38 ^a	50.85±0.47 ^a	52.13±0.36 ^b	52.17±0.23 ^b
Dry matter (%)	49.73±0.38 ^a	49.15±0.47 ^a	47.87±0.36 ^b	47.83±0.23 ^b
Water in the fat-free substance of cheese (%)	66.59±0.94	66.46±0.66	67.71±1.01	66.89±0.17
Fat (%)	24.50±0.50 ^c	23.50±0.17 ^{bc}	23.00±0.71 ^{ab}	$22.00{\pm}0.50^{a}$
Fat in dry matter (%)	49.27±1.38 ^b	47.81±0.62 ^{ab}	48.05±0.76 ^{ab}	46.00±0.84 ^a
Proteins (%)	20.54±0.38 ^c	20.26±0.18 ^c	19.51±0.26 ^b	18.67 ± 0.15^{a}
Chlorides (%)	1.98±0.03 ^b	1.87 ± 0.02^{a}	2.05±0.03 ^c	$2.28{\pm}0.02^{d}$
Ash (%)	2.65 ± 0.02^{a}	2.67±0.03 ^a	3.09 ± 0.08^{b}	3.06±0.03 ^b
a _w	0.948±0.001	0.949 ± 0.001	0.943±0.001	0.947 ± 0.001
pH value	$5.54 \pm 0.02^{\circ}$	5.44 ± 0.01^{a}	$5.55 \pm 0.02^{\circ}$	$5.49{\pm}0.01^{b}$
Acidity (°SH)	46.80±0.10 ^c	44.00±0.26 ^a	45.40±0.20 ^b	44.40 ± 0.40^{a}

Table 2. Physico-chemical properties of the analysed cheeses

^{a-d} mean values with different letters in the same column differ statically significantly with 95% probability (p <0.05)</p>

According to the Rulebook on the quality of dairy products (Official Gazette of BiH, 21/11), cheeses that have a percentage of water in fat-free substance from 69 to 85% belong to fresh cheeses, and those with a percentage of water in the fat-free substance of 54-69% belong to semi-hard cheeses. The tested cheeses contained 66.47% - 67.70% of the water in the fat-free substance of the cheese and, according to the water content in the fat-free substance, they belong to semi-hard unripened cheeses. According to the same rulebook, the analysed cheeses belong to full-fat cheeses because the share of milk fat in the dry matter of cheese ranged from 46.00% to 49.27%.

Table 3. shows the values of the instrumentally measured colour parameters of the tested cheese samples. From the results obtained for the colour of the analysed cheeses, changes can be observed that occurred as a result of replacing sodium chloride with certain amounts of potassium chloride. On the surface of sample 1

(produced with 100% NaCl), the average measured L* value was 83.69, while sample 3 (produced with 50% NaCl and 50% KCl) and sample 4 (produced with 25% NaCl and 75% KCl) had significantly higher values (p<0.05) for lightness (85.48 and 85.92 respectively).

Statistical analysis of the obtained results did not show a significant difference of the proportion of red colour (a*) on the surface of the tested cheeses (p>0.05), while a higher proportion of yellow colour (p<0.05) was found in samples with 50% and 75% sodium chloride replaced with potassium chloride (26.49 and 27.01, respectively) relative to sample 1 (produced with 100% NaCl) (b*=24.96) and sample 2 (produced with 75% NaCl and 25% KCl) (b*=25.06).

The lighter surface of the cheese samples can be related to the higher water content in the samples, and the higher proportion of yellow colour to the higher fat content in the samples.

Analysis of the obtained results for hardness showed that samples with a higher amount of potassium chloride (samples 3 and 4) had statistically significantly lower instrumentally measured values for hardness (p<0.05) compared to other samples (Table 3.), which can be connected to the water content in the tested samples.

Parameter	Sample 1	Sample 2	Sample 3	Sample 4
L* value	83.69±0.59 ^a	83.87±0.41 ^a	85.48±0.64 ^b	85.92±0.54 ^b
a* value	0.32±0.07	0.36±0.07	0.37±0.06	0.31±0.04
b* value	24.96±0.49 ^a	25.06±0.51 ^a	26.49±0.45 ^b	27.01±0.43 ^b
Hardness (kg)	0.3297±0.01 ^b	0.3223±0.02 ^b	0.2640±0.02 ^a	0.2558 ± 0.02^{a}

Table 3. Instrumentally measured parameters of color and texture of tested cheese samples

 $^{a-b}$ mean values with different letters in the same column differ statically significantly with 95% probability (p <0.05)

Figure 1. shows the mean values of the scores for the observed sensory properties of the tested cheeses. Sensory analysis of the cheeses showed a statistically significant effect (p<0.05) of partial replacement of sodium chloride with potassium chloride on the taste of produced cheeses, while a statistically significant effect of the said replacement on other sensory properties was not determined (p>0.05). The external appearance of samples 2, 3 and 4 was rated slightly lower (Figure 1.) due to the uneven surface and visible cracks on the surface of the cheese. The colour of all tested cheese samples was white with a yellowish tinge. The smell of all tested samples was pleasant and distinctive, without the presence of external odours. Samples with reduced sodium chloride content were given lower scores for taste because sample 3 (produced with 50% NaCl and 50% KCl) was less salty than the control sample, while sample 4, in which sodium chloride

was replaced with 75% of potassium chloride, had a bland, bitter, metallic, unpleasant taste. The consistency of all analysed cheeses was homogeneous, moderately hard and without whey separation.

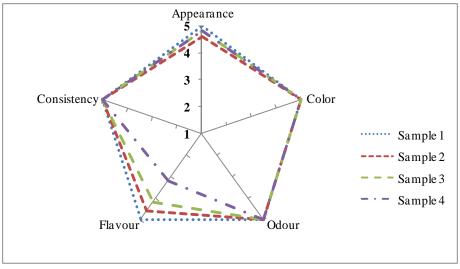


Figure 1. Graphic presentation of the results of sensory analysis of tested cheeses

Moatsou et al. (2019) also reported that the substitution of sodium (NaCl) with potassium (KCl) resulted in lower scores for the sensory properties of semi-hard sheep's milk cheese due to the metallic or bitter taste coming from KCl.

Gore et al. (2019) proposed a new method for reducing the sodium content in blue mould cheese (blue cheese) by partially replacing sodium chloride with alkaline organic calcium salts. Cheeses made by applying 75% NaCl substitution with calcium lactate contained about 33% less sodium compared to salted cheese produced with NaCl alone. Sensory analysis showed that 75% of the amount of NaCl in cheese could be replaced by calcium lactate or calcium citrate without affecting the perception of the salty and bitter taste of the produced cheese. Costa et al. (2019) reported that the partial substitution of 25% of sodium chloride with potassium chloride in Minas Padrao cheese was well accepted by consumers, demonstrating that it is possible to use KCl for partial sodium reduction in the manufacture of Minas Padrao cheese.

Conclusion

Based on the obtained results, it can be concluded that substitution of salt in the production of acid-coagulated cheeses changed the physicochemical and sensory properties. The obtained results showed that replacing the proportion of sodium chloride with potassium chloride increased the proportion of water and reduced the proportion of fat and protein in the cheese. The texture and colour also changed

significantly. The sensory analysis showed that the replacement of salt did not negatively affect the colour, odour and consistency. Cheese with a reduced content of sodium chloride had a less salty taste, and adding a larger amount of potassium chloride (50% and 75%) gave a metallic, bitter taste. The results of this study have shown that a maximum of 50% sodium chloride in the production of this type of cheese can be replaced by potassium chloride without negatively affecting sensory properties. A higher proportion of potassium chloride negatively affects sensory properties, giving the product an unacceptable, bitter taste. Replacing sodium chloride salt with potassium chloride up to 50% can be used as one of the ways to reduce the proportion of salt in the production of this type of cheese.

Acknowledgements

This paper is a part of the research project titled 'Examination of the quality of cheeses obtained by various procedures of heat-acid coagulation of milk' cofinanced by the Ministry of Scientific and Technological Development, Higher Education and Information Society of Republic of Srpska.

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UTICAJ DIJELIMIČNE ZAMJENE NATRIJUM HLORIDA KALIJUM HLORIDOM NA SVOJSTVA KISELO-KOAGULIŠUĆIH SIREVA

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Sažetak

Prekomjeran unos natrijuma smatra se uzrokom određenih zdravstvenih problema kod ljudi, kao što su hipertenzija i kardiovaskularne bolesti. Cilj ovog rada je istražiti uticaj djelimične zamjene natrijum hlorida kalijum hloridom na hemijski sastav, aktivitet vode, pH vrijednost, kiselost, boju, teksturalna svojstva i senzorna svojstava kiselo-koagulišućih sireva. Proizveden je kontrolni uzorak sa natrijum hloridom (100% NaCl) i uzorci u kojima je određena količina natrijum hlorida zamjenjena kalijum hloridom (75% NaCl i 25% KCl, 50% NaCl i 50% KCl i 25% NaCl i 75% KCl). Na osnovu dobijenih rezultata utvrđeno je da zamjena natrijum hlorida sa kalijum hloridom utiče (p<0,05) na ispitivana fizičko-hemijska i senzorna svojstva proizvedenih sireva. Sirevi sa smanjenim udjelom natrijuma su imali veći sadržaj vode i manji sadržaj masti i proteina, a time i manji sadržaj suve materije. Takođe je uočeno da su sirevi sa većom količinom KCl imali manju tvrdoću (p<0,05) i veće vrijednosti za svjetlioću (L*) i veće vrijednosti za udio žute boje (b*) u poređenju sa uzorcima koji su proizvedeni sa 100%-tnim udjelom natrijuma. Potpuna zamjena natrijum hlorida sa kalijum hloridom u proizvodnji kiselo-koagulišućih sireva daje neprihvatljiv proizvod, gorkog okusa. Dobijeni rezultati su pokazali da se, u proizvodnji ovih vrsta sireva do 50% natrijum hlorida može zamijeniti kalijum hloridom bez negativnog uticaja na senzorna svojstva, dok veći udio zamjene negativno utiče na kvalitet proizvedenog sira.

Ključne riječi: sir, zamjena natrijuma, kalijum hlorid.

"XIII CONFERENCE OF CHEMISTS, TECHNOLOGISTS AND ENVIRONMENTALISTS OF REPUBLIC OF SRPSKA"

QUALITY CONTROL AND FOOD SAFETY

Original scientific article

QUALITY ASSESSMENT OF SAUSAGES WITH REGARD TO PROTEIN CONTENT AND COLLAGEN CONTENT FROM THE REPUBLIC OF SRPSKA MARKET

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Abstract

The Regulation on chopped meat, semi-finished products and meat products ("Official Gazette of the Republic of Srpska", No. 46/15) prescribes quality requirements for meat products. In addition to the content of meat proteins or total proteins, one of the prescribed quality requirements for sausages is the relative content of connective tissue proteins in meat proteins or total proteins, respectively collagen content.

The aim of this research is to examine the protein content and collagen content in different types of sausages from the Republic of Srpska market and to determine the quality of the product based on the test results. As part of the official control and self-control, in the period from April 2018 to April 2019, the mentioned tests were conducted by reference accredited methods.

A total of 136 samples were analyzed, of which 29 samples of fermented dry sausages, 97 samples of heat-treated sausages and ten samples of cooked sausages. Lower protein content was found in 11 products (8.09%), of which in one sample of dry sausage, nine samples of heat-treated sausages and one sample of cooked sausage. The higher content of the collagen was determined in eight products (5.88%), of which in two samples of dry sausages, five samples of heat-treated sausages and one sample of cooked sausage.

The obtained results indicate the need for constant control and improvement of the quality of basic ingredients, as well as determination and improvement of certain phases of the technological production process, which affect the quality of the final product, all in order to achieve uniform and required quality of sausages placed on the market of Republic of Srpska. and the required quality of sausages.

Keywords: sausages, quality requirements, protein content, collagen content.

Introduction

The quality requirements that meat products must meet in production and placing on the market relate to names, definitions and general requirements, composition and sensory properties, type and quantity of raw materials and other substances used in production and processing, technological procedures applied in production and processing and additional labeling requirements.

Sausages are products made of different types and quantities of meat, mechanically separated meat, offal, blood, fatty and connective tissue, different degrees of fineness and other additional ingredients, which after various types of processing, processing and filling into natural or artificial casings or other packaging are preserved procedures. According to the Ordinance on minced meat, semi-finished products and meat products ("Official Gazette of the Republic of Srpska", No. 46/15) (hereinafter referred to as the Ordinance), based on the composition, technological process of production and method of canning, sausages can be produced and placed on the market such as: fermented sausages, heat-treated sausages, cooked sausages and fresh sausages. For the largest number of sausages, according to the Ordinance on minced meat, semi-finished products and meat products ("Official Gazette of Republika Srpska", No. 46/15) (hereinafter the Ordinance), among others, prescribes requirements relating to the content of total or protein meat and connective tissue content, expressed as the relative connective tissue protein content in total or meat proteins (collagen content). The choice of basic ingredients, first of all meat, and then fat tissue, is the most important initial task that determines the further course of the technological process (Petrović et al., 2007).

Meat proteins are by definition nitrogenous compounds derived from the basic ingredients of the product. The quality of meat proteins and meat products depends on the amount of extracellular connective tissue proteins present in bone, heart and smooth muscle tissues (ie collagen, elastin, proteoglycans, etc.). The structure and quantity, ie the content of connective tissue in meat is extremely important because it affects its many properties, primarily those related to its softness (Kerth, 2013). Significant amounts of poor quality meat (from an economic and nutritional point of view), rich in connective tissue, can be determined by assessing the content of collagen or hydroxyproline (Messia et al., 2008). Hydroxyproline in collagen is unique and can be used analytically to distinguish collagen from other proteins (Asserin et al., 2015).

Collagen is the main protein component of connective tissue, it has little biological value. Due to the insufficient presence of essential amino acids in connective tissue, the biological value of this tissue is almost three times less than the biological value of muscle tissue (Rogowski, 1981). Contributes to changes in the tenderness and texture of the meat. It is found in three specific muscle areas and in different shapes and types. Collagen molecules are linked by molecular bonds that

help provide structure and strong bonds. Cross-links are initially reduced, but over time are replaced by mature, thermally stable, and less soluble cross-links (Weston, et al., 2002; Nishimura, 2010), resulting in the meat of older animals being less tender, rougher in texture, and harder than younger animals' meat. (Vuković, 1998; King et al., 2009; Kerth, 2013).

At lower collagen content in meat, meat is tenderer (Moon, 2006). Collagen toughness increased 3 to 4 times with increasing age of animals between 30 months and 11 years. This increase in toughness can be partially reduced by heat treatment at slightly lower pH values (Lepetit, 2009). The content of total or protein meat in sausages, depending on the type of sausage, can vary from 8 to 22%. According to the Ordinance, the lowest minimum protein content is prescribed in pates, hot dogs, boiled sausages and related products, and the highest for fermented dry rurable sausages, cured meat and smoked products. Also, according to the Ordinance, depending on the basic ingredients of the product used, the relative part of connective tissue proteins in total or meat proteins (collagen content), for different types of sausages, can be from 10% to 30%. The aim of this research is to determine the protein content and relative connective

The aim of this research is to determine the protein content and relative connective tissue protein content in total or meat proteins in different types of sausages (collagen content) from the market of Republika Srpska and to determine compliance with the Ordinance prescribed quality regulations for each type of product.

Materials and Methods

As part of official controls and self - monitoring, in the period from April 2018 to April 2019, tests for total protein, hydroxyproline and collagen content were carried out by accredited reference methods. Meat and meat products -Determination of nitrogen content (Reference method). 136 samples were analyzed, of which 29 samples of fermented dry sausages, 97 samples of heattreated sausages and ten samples of cooked sausages. The samples were homogenized using an analytical homogenizer (Moulinex), after which they were stored in glass dishes at +4 ° C until the moment of analysis (maximum 24 hours). The method for determining the hydroxyproline content of meat involves hydrolysis of the test portion of the sample with sulfuric acid at 105 °C. After filtration and dissolution of the hydrolyzate, and oxidation of hydroxyproline with chloramine-T, a red colored compound with p-dimethyl-aminobenzaldehyde is formed. Spectrophotometric determination was performed at 558 nm on a spectrophotometer (Cary 60 UV-VIS, Agilent Technologies). The connective tissue protein content (%) is obtained when the amount of hydroxyproline (%) is multiplied by a factor of 8. The total protein content was determined by the Kjeldahl method. The first determination phase is carried out in the destruction unit (DKL, Velp) and the second phase in the distillation unit (UDC 127, Velp). Determination of the relative content of connective tissue proteins in total or meat proteins is calculated from the ratio of connective tissue proteins (collagen) and the content of total proteins.

During the test, the requirements of both standards were met in the part related to the analytical purity of chemicals. Internal and external measures are periodically implemented to ensure the validity of test results using reference materials (Fapas, NIST) and participation in PT/ILC schemes.

Results and discussion

The paper presents the results of testing the content of total protein, hydroxyproline, connective tissue protein (collagen) and relative connective tissue protein content in total or meat proteins in 136 samples of meat products, of which 29 samples of durable sausages, 97 samples of heat-treated sausages and ten samples of cooked sausages. Tables 1 to 4 show the quality requirements of the Ordinance relating to the minimum content of total or meat proteins (%) and the maximum relative content of connective tissue proteins in total or meat proteins (%) (collagen content). The share of connective tissue protein content in total or meat proteins is the value obtained by calculation, from the ratio of collagen (%) and the content of total proteins (%), expressed in %.

 Table 1. Requirements of the Ordinance regarding the meat protein content and relative connective tissue protein content in meat proteins (collagen content) for fermented dry durable sausages

	un uste sunsuges	
Fermented dry permanent	Protein content (%)	Collagen content (%)
sausages		
Kulen	\geq 22 meat proteins	≤ 15
Winter sausage	\geq 22 meat proteins	≤ 15
Srem sausage	\geq 16 meat proteins	≤ 20
Sudzhuk	\geq 16 meat proteins	≤ 20
Tea sausage	\geq 16 meat proteins	≤ 20
Related products	\geq 16 meat proteins	\leq 20 / \leq 10 of poultry meat

 Table 2. Requirements of the Ordinance regarding protein content and relative connective tissue protein content in total or meat proteins (collagen content) for finely and coarsely chopped boiled sausages

enopped conten subsuges			
	finely chopped boiled sausages		
Pro	tein content (%)	Collagen content (%)	
Paris and Special	\geq 10 meat proteins	$\leq 20^*/\leq 10$ of poultry meat*	
Hot dog	\geq 10 meat proteins	$\leq 20^* / \leq 10$ of poultry meat *	
Related products	\geq 10 meat proteins	$\leq 25^* \leq 10$ of poultry meat **	
coarsely chopped boiled sausages			
Pro	tein content (%)	Collagen content (%)	

Tyrolean sausage	\geq 10 meat proteins	$\leq 20*$
The ham	\geq 12 meat proteins	≤ 15 *
Carniolan	≥ 10 meat proteins	$\leq 20*$
sausage		
Mortadella	\geq 12 meat proteins	$\leq 30^{**}$
Related products	≥12 ***	$\leq 20^* / \leq 10$ of poultry meat *

* relative connective tissue protein content in meat proteins

** relative connective tissue protein content in total proteins

*** total or meat protein content

Table 3. Requirements of the Ordinance regarding the protein content and relative connective tissue protein content in meat proteins (collagen content) for cooked sausages

Cooked sausages	Protein content (%)	Collagen content (%)**
COOKed sausages	Trotein content (70)	Conagen content (70)
Liver and meat pate	≥ 8 meat protein	$\leq 25^{*} \leq 15^{*}$ of poultry meat

Table 4. Requirements of the Ordinance regarding the protein content and relative connective tissue protein content in total or meat proteins (collagen content) for pieces of meat sausages

 medi sausages		
Meat sausages in pieces	Protein content (%)	Collagen content (%)
Ham in a wrapper	\geq 13 meat proteins	≤15 *

Tables 5. to 7. show the intervals of obtained values for the content of total proteins, hydroxyproline, collagen and the relative content of connective tissue proteins in total proteins, average values and standard deviation of results for each individual group of sausages. Charts 1. to 3. show the average values of total proteins, collagen content and connective tissue protein content.

Durable sausages	Interval (%)	x (%)	SD (%)
(29 samples)			
Total protein content	15.93-28.92	23.61	2.344
Hydroxyproline content	0.15-0.66	0.30	0.083
Collagen content	1.20 -5.28	2.40	0.659
Relative connective tissue protein	4.93-22,33	10.42	3.052
content in total proteins			

Table 5. Test results for fermented dry durable sausages

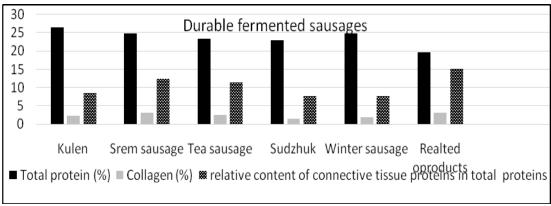


Chart 1. Mean values of protein content, collagen and relative connective tissue protein content in total proteins in durable sausages

Finely chopped boiled sausages (31 samples)	Interval (%)	x (%)	SD(%)
Total protein content	8.08-15.24	11.51	1.109
Hydroxyproline content	0.05-0.28	0.13	0.013
Collagen content	0.42-2.23	0.77	0.492
Relative connective tissue protein	4.25-15.53	8.84	0.497
content in total proteins			
Coarsely cho	pped boiled sausages (59 sa	mples)	
Total protein content	10.22-18.49	13.17	0.909
Hydroxyproline content	0.05-0.38	0.21	0.063
Collagen content	0.40-3.05	1.70	0.503
Relative connective tissue protein	3.33-23.14	12.81	3.442
content in total proteins			

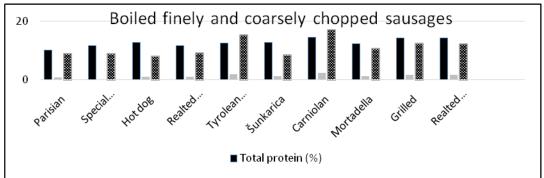


Chart 2. Mean values of protein, collagen and relative connective tissue protein content in total proteins of finely and chopped boiled sausages

Tuble 7. Test Testitis for wrapped hams and pute			
Ham in wrapper (7 samples)	Interval (%)	x (%)	SD(%)
Total protein content	11.79-15.04	13.72	1.110
Hydroxyproline content	0.08-0.14	0.11	0.019
Collagen content	0.65-1.14	0.91	0.672
Relative connective tissue protein	4.32-9.67	6.73	1.672
content in total proteins			
Pate (10 samples)			
Total protein content	7.44-12.21	9.89	1.818
Hydroxyproline content	0.07-0.22	0.13	0.057
Collagen content	0.56-1.76	1.02	0.457
Relative connective tissue protein	5.90-15.41	10.87	3.700
content in total proteins			

Table 7. Test results for wrapped hams and pate

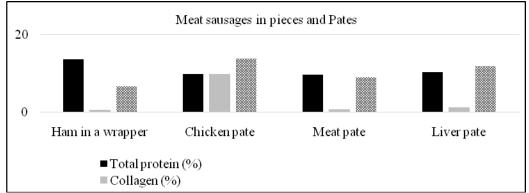


Chart 3. Mean values of protein, collagen content and relative connective tissue protein content in total proteins of meat sausages in pieces-ham in wrapper and cooked sausagespate

Proteins are the most valuable ingredients in meat products in terms of nutrition and technology. Therefore, the protein content is used as an objective criterion on the basis of which the quality of the product can be evaluated (Vuković, 2001). From the results obtained in this paper, it can be seen that durable sausages had the highest average total protein content (23.61 \pm 2.344%). The hydroxyproline average content was 0.30 \pm 0.083%, with the lowest values (0.15%) recorded in sudzuk, and the highest in related products from the mentioned group of sausages (0.66%). Based on the hydroxyproline content, the average collagen content of 2.40 \pm 0.659% was determined in durable sausages, which is in accordance with the results of Peinović (2018).

Of all examined durable sausages (29 samples), the highest of total proteins was found in kulen of 28.92%, with average content 26.38% and tea sausage of 28,66%, but, according to the average value of the protein content, winter salami had the highest value after kulen (24.88%). In kulen, an average hydroxyproline content of 0.28% was found, and the collagen content ranged from 1.36% to 2.88%

with an average content of 2.25%. For winter salami, the hydroxyproline content ranged from 0.20% to 0.26%, with an average content of 0.23%, and the collagen content from 1.60% to 2.11% with an average content of 1.86%. Karolyi (2011) obtained results by examining the protein content in kulen, which shows that due to prolonged drying or maturation (weight loss up to 50%) and a high proportion of lean meat used in the preparation of stuffing, the protein content in mature kulen increases by the end of production process (from 30 to 40%), indicating the high nutritional value of the finished product.

In samples of kulen and winter sausage, Peinović (2018) determined the hydroxyproline content ranging from 0.2193% to 0.4264%, with an average of 0.2928%, and the amount of collagen from 1.754% to 3.411% with an average of 2.487 %, which is close to our results for the specified types of sausages.

By comparing the results of testing the protein and relative content of connective tissue proteins in total proteins content (content of collagen) with the minimum requirements of the Ordinance for kulen and winter sausage, it was determined that the mentioned types of tested sausages agree according todinance. The lowest protein content from the group of durable fermented sausages was determined in the sample of tea sausage (15.93%), and the determined value is lower than the minimum required protein content of meat in the product ($\geq 16\%$), as shown in Tables 1. and 9. The average value of total protein content in tea sausages is 23.39%, which is slightly lower than the protein content cited by Mitrović (2016) (25.49%).

The average content of total proteins in sudzuk was 22.85% with variations from 21.20% to 24.50%, which is significantly lower compared to the obtained values obtained by Operta et al. (2012). They found a protein content of 27.78% to 33.40% in the sudzuk samples. Soyer et al. (2005) report a larger range in protein content in Turkish sudzuk, from 16.50 to 28.30%.

If we take into account all the results of testing the protein content in permanent fermented sausages, we can conclude that they are in agreement with the results stated by Peinović (2018) and Pećanac (2013), they are higher than the results obtained by Comi et al. (2005), and lower than the results reported by Kovačević et al. (2010), Pleadin et al. (2009), Pleadin et al. (2013) and Pleadin et al. (2014). The largest variations in protein content were found in sausages from the group of permanent fermented sausages (SD is 2.3445).

Based on the content of total proteins and collagen content, the average value of the relative content of connective tissue proteins in total proteins was determined $10.42 \pm 3.052\%$, and the highest proportion of connective tissue protein was determined in tea sausage (22.33%).

The connective tissue in boiled sausages is an important element of the structure. In the technology of incorporating connective tissue into the stuffing of cooked sausages, meat dough that contains a lot of protein is more thermostable than dough rich in fat and connective tissue. But if there is a lot of connective tissue in the stuffing, it is often difficult to achieve a solid structure after intense heating. If the meat dough contains 10% or more of connective tissue, problems arise due to the use of the skin. Skins that are processed raw or only poorly heat-treated swell strongly and as a result there is a risk of splashing the sausage casing. Due to the formation of gelatin from raw collagen, hot dogs are juicy, but also soft and weak in structure (Savić and Milosavljević, 1983).

The test results of finely chopped boiled sausages are shown in Table 6. and Chart 2. The test was performed in 31 sausage samples, and it was found that the total protein content ranged from 8.08% in Paris sausage to 15.24% in hot dogs with with an average content of $11.51 \pm 1.109\%$, which is in accordance with the results of Peinović (2018). Franjčec et al. (2011) in studies of finely chopped boiled sausages state an average total protein content of 11.51%.

The amount of hydroxyproline ranged from 0.05% to 0.28%, with an average content of $0.13 \pm 0.013\%$, and the amount of collagen ranged from 0.42% to 15.53%, with an average content of $0.77 \pm 0.492\%$, which is significantly lower than the results obtained by Peinović (2018). Jelka et al. (2009) found the most uniform protein content in hot dogs, Parisian and extra sausage and other products of boiled sausages from 11.87% to 13.43%. In the research of Franjčec et al. (2011) in boiled sausages (hot dogs) the average content of total proteins was 11.75% and hydroxyproline 0.24%. Sentandreu, M. and Sentandreu, M. (2014) conducted tests of protein and collagen content in several types of sausages, including bologna sausage, in which they found a protein content of 12.68% and a collagen content of 1.29%, which is slightly higher than the values obtained. Based on the content of total proteins and collagen content, the average value of the relative content of connective tissue proteins in total proteins was determined was $8.84 \pm 0.497\%$ and the highest proportion of connective tissue protein was determined in related products of this kind of sausage (15.53%). By comparing the results of testing the protein content with the minimum requirements of the Ordinance, the largest number of non-compliant samples in sausages from the group of finely chopped boiled sausages was determined (Table 8). Out of a total of five sausages, unsatisfactory results were found in three samples of chicken parizer sausage (9.88%, 9.89% and 8.08%), in one sample of chicken hot dog (9.85%) and one sausage from the group of related products (9.28%). Also, from this group of products, non-compliance with the provisions of the Ordinance was found in three sausages due to the increased relative content of connective tissue proteins in total proteins, which amounted to 11.17%, 11.68% and 11.63% (Table 10). Determining the collagen content in meat products is important both from the aspect of legislation and from the nutritional point of view (Andrășescu, 2014). Graph 2. shows the test results of coarsely chopped cooked sausages, conducted in 59 samples. The average value of total protein content, taking into account the test results for all sausages from the mentioned group, was $13.17 \pm 0.909\%$, with variations from 10.22% to 18.49%. The lowest and highest content of total proteins

was found in sausages from the group of related products of coarsely chopped sausages with an average value of total proteins of 14.20%. The content of hydroxyproline in the samples ranged from 0.05% in ham to 0.38% in related products, with an average of $0.21 \pm 0.063\%$. The collagen content ranged from 0.40% to 3.05%, and the average content value was $1.70 \pm 0.503\%$. Based on the content of total proteins and collagen content, the average value of the relative content of connective tissue proteins in total proteins was determined of $12.81 \pm 3.422\%$, and the highest proportion of connective tissue protein was determined in Tyrolean sausage. The average protein content of 13.53% was determined in Tyrolean and Carniolan sausage, which is in accordance with the results obtained from Peinović (2018). The average content of hydroxyproline and collagen determined in Carniolan and Tyrolean sausage is in accordance with the results obtained by Peinović (2018).

Based on the total protein content and collagen content, the average value of relative connective tissue protein content in total proteins in coarsely chopped cooked sausages was determined in the amount of $12.81 \pm 3.442\%$ (Table 6. and Chart 2.) and the largest share of connective tissue protein in Carniolan sausage (17.13%). The relative connective tissue protein content in the total proteins of Tyrolean sausage (23.14%) was higher than 20%, so that the Tyrolean sausage did not meet the requirements of the Ordinance (Table 10). Non-compliance with the provisions of the Ordinance (Table 10) was also found in Carniolan sausage, because the relative content of connective tissue proteins in total proteins was 22.44%, which is more than the upper limit prescribed by the Ordinance. Pleadin et al. (2009) found lower protein content in three ham samples than required for this type of product. In the research conducted in samples of semi-durable sausages, Peinović (2018) determined the content of total proteins from 10.09% to 15.34%, with an average content of 12.12%, which is lower than the average value determined in our research (13.14 \pm 0.909%). The average amounts of hydroxyproline of 0.3677% and collagen of 2.941, stated by Peinović (2018), are higher than the obtained values (hydroxyproline content of $0.21 \pm 0.063\%$; collagen content of $1.70 \pm 0.503\%$). The lowest average content of total proteins was found in mortadella and amounted to 12.33%, while the highest total protein of 14.24% was found in grilled sausages (Chart 3). From the group of meat sausages in pieces, tests of the mentioned quality parameters were performed in samples of ham in pieces. The average content of total proteins of $13.72 \pm 1.110\%$ varied from 11.79% to 15.04% and is in accordance with the statements of Peinović (2018), whose average content of total proteins is 14.16%. Also, according to the same author, consistency was also found in the average hydroxyproline and collagen content. In our paper, average values for hydroxyproline of $0.11 \pm 0.019\%$ and collagen of $0.91 \pm 0.672\%$ were determined, and according to Peinović (2018), average values for hydroxyproline of 0.1302% and for collagen of 1.042 were reported. %. In one of the seven tested samples of ham in the wrapper, a lower

share of total proteins (11.79%) than the minimum share (13%) prescribed by the Ordinance was determined. The paper examines cooked sausages, of which two chicken pates, five meat pates and three liver pates. The average content of total proteins was determined to be 9.89% with variations from 7.77% to 12.21%, which is not in accordance with the statements of Peinović (2018). The collagen content ranged from 0.56% to 1.76%, with an average value of 1.02%, which is consistent with an average value of 1.042% according to Peinović (2018). The result of testing one sample of meat pate in terms of protein content (7.44%) did not meet the provisions of the Ordinance, which prescribes a minimum meat protein content of 13% (Table 9). In the sample of chicken pate, the result of testing the relative content of connective tissue proteins in meat proteins (Table 10) is not in accordance with the maximum prescribed content in the Ordinance.

requirements from the groups of finely and coarsely chopped bolled sausages			
Groups / Type of	Total protein content	Quality requirement according to the	
sausage	determined in the sausage	Ordinance	
	sample (%)	Meat protein content (%)	
	Finely chopped boiled	sausages	
Chicken parizer	9.88	≥ 10	
	9.89	≥ 10	
	8.08	≥ 10	
Chicken sausage	9.85	≥ 10	
Related products	9.28	≥ 10	
	Chopped boiled sausages-semi	-durable sausages	
The ham	11.17	≥ 12	
Related product	10.22	≥ 12	
Related product	11.47	≥ 12	

Table 8. Overview of test results for protein content that did not meet the qualityrequirements from the groups of finely and coarsely chopped boiled sausages

Table 9. Overview of test results for protein content that did not meet the quality requirements from the groups of meat sausages in pieces, cooked sausages and permanent sausages

Groups / Type of	Total protein content	Quality requirement according to the						
sausage	determined in the sausage	Ordinance						
	sample (%)	Meat protein content (%)						
Meat sausages in pieces								
Ham in a wrapper	11.79	≥ 13						
Cooked sausages								
Meat pate	7.44	≥ 8						
Durable sausages								
Tea	15.93	≥16						

A kind of sausage	Content relative connective tissue	Quality requirement						
	protein content in total or meat	according to the Ordinance						
	proteins (%)	(%)						
Finely chopped boiled sausages								
Chicken parizer	11.17; 11.68	≤ 10						
Related products (chicken	15.53	≤ 10						
sausage)								
Chopped boiled sausage								
Tyrol sausage	23.14	≤ 20						
Carniolan koabsica	22.44	≤ 20						
Cooked sausages								
Chicken pate	15.28	≤ 15						
Durable sausages								
Tea sausage	$22.33 \leq 20$							
Related products	d products 21.47							

Table 10. Overview of test results of the relative connective tissue protein content in total proteins that did not meet the quality requirements by type of sausage

By comparing all the test results of sausages with the minimum requirements of the Ordinance, it was determined that one part of the product did not satisfy in terms of protein content. Lower protein content was found in 11 products (8.09%), of which in one sample of durable sausage, nine samples of heat-treated sausages and one sample of cooked sausage. Table 8. and Table 9. provide a detailed overview of the mismatched samples by type of sausage.

The higher content of the collagen was determined in eight products (5.88%), of which in two samples of dry sausages, five samples of heat-treated sausages and one sample of cooked sausage (Table 10).

Conclusion

Based on the established results obtained by conducting tests of selected sausage quality parameters, the following can be concluded:

1. The content of total proteins in the tested types of sausages is in the following intervals:

- for dry fermented sausages from 15.93 to 28.92%,
- for finely chopped boiled sausages from 8.08 to 15.24%,
- for coarsely chopped boiled sausages from 10.22 to 18.49%,
- for meat sausages in pieces from 11.79 to 15.04%,
- for cooked sausages from 7.44 to 12.21%.

2. Interval of hydroxyproline and collagen content by groups of sausages:

- for dry fermented sausages: hydroxyproline from 0.10 to 0.66%, collagen from 1.20 to 5.28%

- for finely chopped boiled sausages: hydroxyproline from 0.05 to 0.28%, collagen from 0.42 to 2.23%

- for coarsely chopped boiled sausages: hydroxyproline from 0.05 to 0.38%, collagen from 0.40 to 3.05%

- for meat sausages in pieces: hydroxyproline from 0.08 to 0.14%, collagen from 0.65 to 1.14%

- for cooked sausages: hydroxyproline from 0.07 to 0.22%, collagen from 0.56 to 1.76%.

3. In relation to the quality requirements regarding the minimum protein content, a lower protein content was found in 11 products (8.09%), of which in one sample of permanent sausage, nine samples of heat-treated sausages and one sample of cooked sausage. The lowest content of total proteins was found in sausages from the group of cooked sausages (7.44%), and the highest in sausages from the group of dry fermented sausages (28.92%).

4. Higher relative connective tissue protein content in meat proteins/total proteins was found in eight products (5.88%), of which in two samples of durable sausage, five samples of heat-treated sausages and one sample of cooked sausage.

5. The obtained results indicate the need for constant control of the basic ingredients of the product as well as identification and improvement of individual phases of the technological process of production that affect the quality of the final product, all with the aim of achieving uniform and necessary quality of sausages placed on the market.

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OCJENA KVALITETA KOBASICA SA TRŽIŠTA REPUBLIKE SRPSKE S OBZIROM NA SADRŽAJ PROTEINA I KOLAGENA

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Sažetak

Zahtjevi kvaliteta za proizvode od mesa propisani su Pravilnikom o usitnjenom mesu, poluproizvodima i proizvodima od mesa ("Službeni Glasnik Republike Srpske, br 46/15). Pored sadržaja proteina mesa ili ukupnih proteina, jedan od propisanih zahtjeva kvaliteta kobasica je relativan sadržaj proteina vezivnog tkiva u proteinima mesa ili ukupnim proteinima, odnosno sadržaj kolagena.

Cilj ovog istraživanja je da se u različitim vrstama kobasica sa tržišta Republike Srpske ispita sadržaj proteina i sadržaj kolagena i na osnovu rezultata ispitivanja utvrdi kvalitet proizvoda. Kao dio službene kontrole i samokontrole, u periodu od aprila 2018. do aprila 2019. godine, pomenuta ispitivanja su sprovedena referentnim akreditovanim metodama.

U radu je analizirano ukupno 136 uzoraka, od kojih 29 uzoraka fermentisanih suvih kobasica, 97 uzoraka toplotno obrađenih kobasica i deset uzoraka kuvanih kobasica. Niži sadržaj proteina utvrđen je u 11 proizvoda (8.09%), od kojih u jednom uzorku suve kobasice, devet uzoraka toplotno obrađenih kobasica i jednom uzorku kuvane kobasice. Viši sadržaj kolegana je utvrđen u osam proizvoda (5,88%) od kojih u dva uzorka suvih kobasica, pet uzorka toplotno obrađenih kobasica i jednom uzorku kuvane kobasice.

Dobijeni rezultati ukazuju na potrebu stalne kontrole i poboljšanja kvaliteta osnovnih sastojaka proizvoda, kao i utvrđivanje i unapređenje pojedinih faza

tehnološkog postupka proizvodnje, koje utiču na kvalitet konačnog proizvoda, a sve u cilju postizanja ujednačenog i zahtijevanog kvaliteta kobasica koje se stavljaju na tržište Rebublike Srpske.

Ključne riječi: kobasice, zahtjevi kvaliteta, sadržaj proteina, sadržaj kolagena.

XIII Conference of Chemists, Technologists and Environmentalists of Republic of Srpska

TEXTILE TECHNOLOGY

Original scientific article

THE EFFECT OF PLASMA ON THE STRUCTURE OF TEXTILE MATERIALS

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Abstract

In this paper, changes in the structure of textile materials due to plasma exposure were investigated. Textile materials of different raw material compositions: cotton, polyester and a mixture of cotton/polyester were used. Textile materials have been treated for 5 minutes in radiofrequency (RF) plasma with argon gas. A high voltage RF generator with a standard frequency of 13.56 MHz was used to obtain RF discharges in the plasma. By modifying the surface of the textile materials with plasma, certain groups in the fiber structure were activated. The presence of carboxyl and carbonyl groups in the structure of textile materials after plasma treatment increases the degree of coloration, as well as the color fastness. Structural changes in textile materials were examined by FTIR spectroscopy. FTIR analysis is a very powerful method for determining structural changes in materials. Small changes in the structure of the material change the intensity and position of the peaks on the FTIR spectrum. The structural changes of knitwear and fabrics are discussed, as well as the changes caused by the treatment of the material with plasma.

Keywords: plasma, structure of textile, cotton, polyester, FTIR.

Introduction

Plasma treatments are highly recommended and environmentally friendly treatments for altering the surface properties of textile materials without detriment to their bulk properties. Unlike chemical processes which penetrate deep into the textile materials, plasma produced no more than a surface reaction. Plasma reacts with the surface of textile materials and a new functional group, such as -OH, -C=O, -COOH, are created, which leads to and also significantly increases the intensity of dyeing due to increased wetting ability and increased materials

swelling. (Grujić et al, 2015; Jocić, 2013; Ercegović-Ražić & Čunko, 2009; Shishoo, 2007). To activate the surface of textile materials, in order to achieve the best possible binding of plant extracts to the surface of the material, specific physical technologies can be used, such as low-temperature plasma treatment (Gorjanc et al, 2016).

In order to achieve the desired effects and appropriate modifications of the properties of the textile material during plasma processing it is very important to know the process parameters of plasma in which the material is processed. These parameters are: processing time, operating frequency, type of gas, gas flow, pressure (if it is a low-pressure plasma, then it is regulated by a vacuum pump), the number of electrodes, and the distance between the electrode and the substrate surface.

Plasma is considered a unique and efficient technology for surface treatment of materials because (Shishoo, 2007): enables obtaining the desired surface properties, operates at low temperatures that ensure the preservation of samples, opens new areas of research, is environmentally friendly.

Plasma processing has proven to be effective in the preparation of woolen fabrics and knitwear for printing because after a short action of plasma (air, oxygen, argon, corona) on the material significantly increases the intensity of dyeing due to increased wetting ability and increased swelling of fibers. Dyeing time can be shortened, because an increase in the rate of depletion has been observed in wool, which is very significant from the economic point of view (Radetić & Petrović, 2004).

The wettability and dyeing speed of silk is significantly increased by nitrogen plasma treatment. The study of the influence of plasma on the modification of cellulose fibers is mainly focused on cotton, although there are also studies dealing with flax and hemp. In the paper Radetić et al., A positive plasma treatment was found to increase the degree of staining in hemp (Radetić et al, 2007). In the field of modification of synthetic fibers, the application potential of plasma is based on functionalization, modification of morphological and electrokinetic properties of the surface. Therefore, the effects that can be achieved primarily depend on the type of fiber and the applied gas. Increasing the wetting ability and shortening the dyeing time is provided by treating PET, PA6 and PAN fibers with argon or reactive plasmas (Gorjanc et al, 2010).

In this paper influence of the argon plasma treatment on cotton, polyester and a mixture of cotton/polyester were examined by FTIR spectroscopy.

Materials and Methods

The following textile materials, cotton, polyester and cotton/polyester blend, were used to investigate the effect of plasma treatment on the surface structure of the material. The basic characteristics of these materials are shown in *Table 1* and microscopic photographs of cotton fabric and knitwear, untreated and treated by plasma, are shown at Fig.1.

The sign	Type of	Type	Surface	Densi	ty (cm ⁻¹)	Raw material
of	materials	of	mass	Warp/	Weft/	composition
materials		weaves	(g/m^2)	Verticale	Horizontale	composition
CO-F	fabric	plain	184.44	21.3	19.0	100 % cotton
PES-F	fabric	plain	163.50	21.4	18.4	100 % polyester
CO/PES-	fabric	plain	171.01	21.2	17.9	50 % cotton/50 %
F		_	1/1.01			polyester
CO-K	knitwear	singl	119.89	17.0	17.0	100 % cotton
PES-K	knitwear	singl	114.12	12.0	20.0	100 % polyester
CO/PES-	knitwear	singl	128.50	24.0	20.0	50 % cotton/50 %
Κ						polyester

Table 1. Basic characteristics of the materials

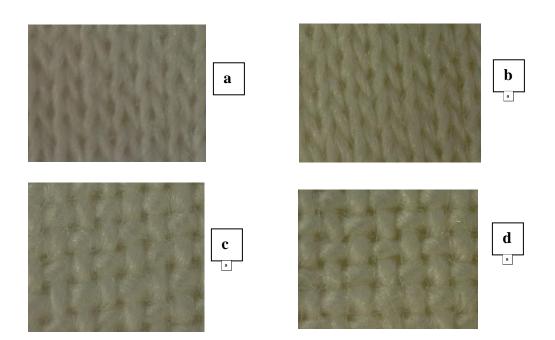


Figure 1. Microscopic photographs of a) untreated Cotton knitwear, b) treated Cotton knitwear with plasma, c) untreated Cotton fabric and d) treated Cotton fabric with plasma.

Modification of textile surface with radiofrequency plasma with argon gas

Bleached H_2O_2 textiles were treated in radiofrequency (RF) plasma with argon gas. A standard power supply of 13.56 MHz in the range of 40 to 100 W was used to power the electrode. Radiofrequency plasma was obtained in a capacitively coupled reactor with argon gas. The plasma reactor is placed in a cylindrical chamber 400 mm long and 100 mm in diameter made of 304 steel. A copper electrode 6 mm in diameter is placed in the center of the cylinder. A vacuum system with gas mass flow controllers was used to control the amount of gas. A high voltage RF generator with a standard frequency of 13.56 MHz was used to obtain RF discharges in plasma. The RF generator is connected to the central electrode, while the ground is connected to the outside of the chamber. Argon gas was introduced through gas mass flow controllers at a flow rate of 2 sccm. The pressure of pure argon gas in the chamber is 1 Torr (133.322 Pa) and the maximum voltage is 1200 V. The applied value of power during plasma discharge is 100 W. Samples of material are introduced into the plasma through a specially designed opening and treated for 5 or 10 minutes. On one side of the chamber, there is a quartz window that is used for optical measurements.

Scheme of RF capacitively coupled plasma reactor with power supply voltage frequency of 13.56 MHz and optical emission spectroscope (OES), at the Faculty of Physics, University of Belgrade, used for treatment of textile samples during the estimated optimal period of 5 minutes, presented is in Figure 2. The setup and the method of textile material modifications are described in more detail in (Pavlović, 2019 and Pavlović et al, 2019).

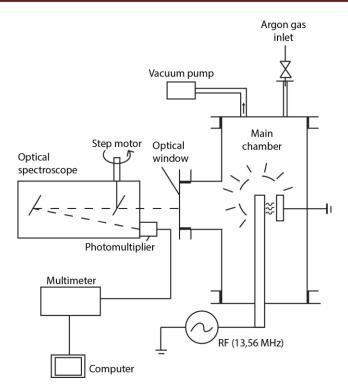


Figure 2. RF capacitively coupled plasma reactor and optical emission spectroscope (OES)

FTIR analysis of textile materials

Fourier transform infrared spectroscopy technique was used for the study of structural changes caused by treatment textile materials with plasma. This is an important research technique for the investigation of physical and chemical properties of textile materials. Changes in the increase or decrease of peak relative intensity are related to the creation or breaking of specific functional groups present in polymers. The transmission spectra were obtained using Shimadzu IRAffinity-1 (FTIR) spectrophotometer equipped with attenuated total reflectance accessory (FTIR–ATR) in the wavenumber range of 4000–500 cm⁻¹.

Results and discussion

The infrared spectra of the untreated polyester fabric and the plasma-treated polyester are shown in Fig. 3. The bands in the range 2900-3100 cm⁻¹ correspond to streching vibrations C-H groups. Two bands are clearly seen in this area, at 2908 and 2965 cm⁻¹. These two bands for the polyester knitwear are obtained at 2911 and 2969 cm⁻¹, see Fig.4. It is noticed that the streching vibrations of C-H groups have almost the same absorption bands for polyester fabric and polyester

knitwear sample. The C–H bending in the polyester appear at 723 cm^{-1} and 722 cm⁻¹ for fabric and knitwear sample, respectively. A very intensive band observed at 1713 cm⁻¹ corresponds ester C=O vibration. There are some changes in peak position for polyester fabric and knitwear samples before plasma treatment, see Fig. 3 and 4. The bands located at 1409 and 1340 cm^{-1} (1339 cm^{-1} for polyester knitwear) can be due to asymmetric and symmetric deformation band of methyl groups. The strong band at 1243 cm⁻¹ which appears in the spectrum of polyester is due to twisting vibration of CH₂ groups. The band at 971 cm⁻¹ is of C=C streching, 872 cm⁻¹ band shows C-H vibration. After plasma treatment polyester fabric there are no significant changes at the band position, but can be seen that after plasma treatment the intensity of the band at 1713 cm⁻¹ decreased. This band indicated the presence of C=O vibration, also the intensity of the bands at 723 and 872 cm⁻¹ decreased (Cecen et al. 2008). These changes in the intensity of the bands indicated that, due to the treatment of textile materials, certain changes in the structure of the molecules occurred. One can assume that partial breaking of specific bonds between atoms in the molecule took place, but more generally, energy deposition during treatment can lead to different processes in materials: breaking of long chains, networking, oxidation and amorphization (Maletić et al, 2019; Singh et al, 2006).

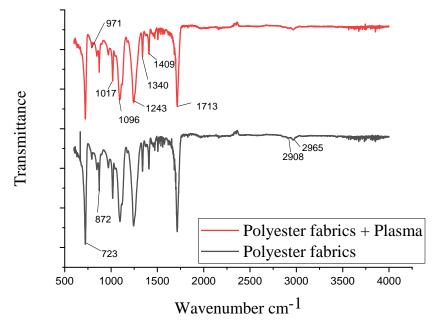


Figure 3. FTIR transmission spectra of polyester PES fabric due to plasma treatment: a) untreated (black line) and b) treated sample (red line).

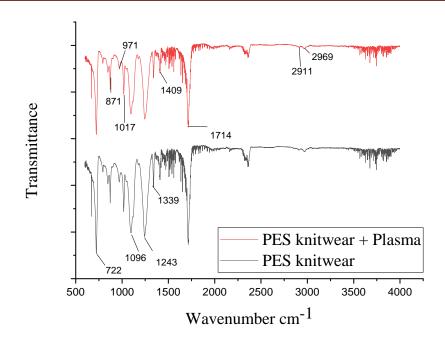


Figure 4. FTIR transmission spectra of polyester PES knitwear due to plasma treatment: a) untreated (black line) and b) treated sample (red line).

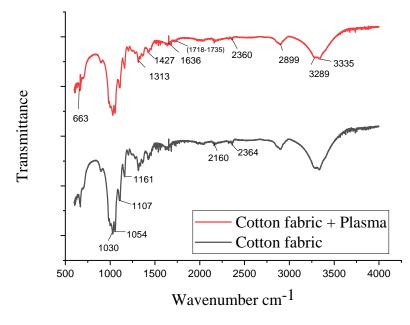


Figure 5. FTIR transmission spectra of Cotton fabrics due to plasma treatment: a) untreated (black line) and b) treated sample (red line).

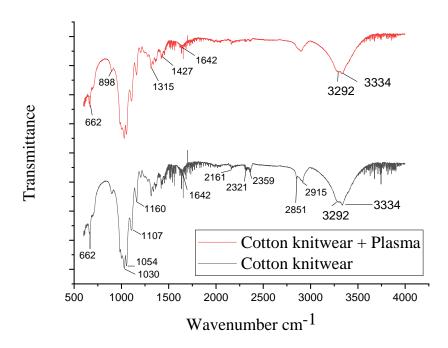


Figure 6. FTIR transmission spectra of Cotton knitwear due to plasma treatment: a) untreated (black line) and b) treated sample (red line).

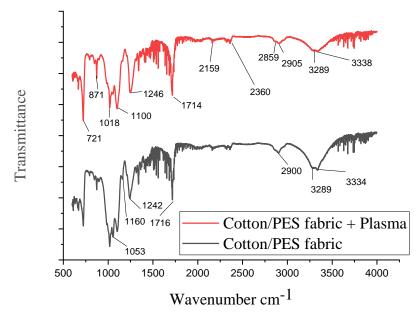


Figure 7. FTIR transmission spectra of Cotton/PES fabrics due to plasma treatment: a) untreated (black line) and b) treated sample (red line).

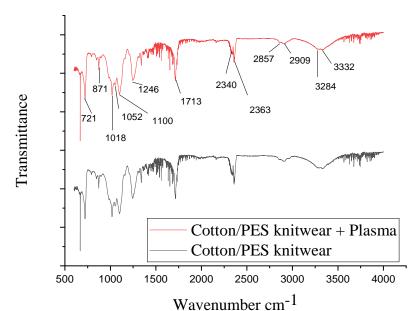


Figure 8. FTIR transmission spectra of Cotton/PES fabrics due to plasma treatment: a) untreated (black line) and b) treated sample (red line).

The infrared spectra of the untreated cotton fabric and the plasma-treated cotton fabric are shown in Fig. 5 and for the untreated and the plasma-treated cotton knitwear sample in Fig 6. For the cotton fabric and cotton knitwear we observed a broad band around 3300 cm⁻¹ corresponding to O–H stretching (Chung et.al, 2004). One can see two peaks at 3289 cm⁻¹ and 3335 cm⁻¹ for the cotton fabric and two peaks 3292 cm⁻¹ and 3334 cm⁻¹ for the cotton knitwear. Also, broad band at 3000-2800 cm⁻¹ region for C– H stretching were observed. The vibration located at 1636 and 1642 cm⁻¹ are attributed to O-H bending of adsorbed water molecules for cotton fabric and cotton knitwear, respectively (Abidi et al, 2011). The vibration located at 898 cm⁻¹ and 662 cm⁻¹ are attributed to β -linkage and to CH₂ rocking vibration, respectively. There are no so many variations for these bands after plasma treatment. For the cotton fabric after plasma treatment, we observed slight increase in the range from 1718 to 1735 cm⁻¹ which corresponds to C=O stretching of plasma generated COOH groups (Caschera et. al, 2014). Finally, for the Cotton/PES fabric and Cotton/PES knitwear after plasma treatment there are significant changes only in the fingerprint region, Fig 7 and 8.

Conclusion

In this work influence of the argon plasma treatment on cotton, polyester and a mixture of cotton/polyester samples were examined by FTIR spectroscopy. The significant structural changes of knitwear and fabrics of the same textile materials

are not, but changes in materials caused by the treatment of the material with plasma are detected.

There are no significant changes at the band position of infra red spectra of polyester fabric sample after plasma treatment, but can be seen that the intensity of the band at 1713 cm⁻¹ decreased. This band indicated the presence of C=O vibration, also the intensity of the bands at 723 and 871 cm⁻¹ decreased. For the cotton fabric we observed a broad peak centered 3300 cm⁻¹ corresponding to O–H stretching. Also we observed broad peak at 3000–2800 cm⁻¹ region for C–H stretching. For the Cotton/PES fabric after plasma treatment there are significant changes in the fingerprint region.

Since the presence of carboxyl and carbonyl groups in the structure of textile materials after plasma treatment increases the degree of coloration, as well as the color fastness, we expected confirm their presence. However, C=O band due to plasma treatment was detected only for cotton fabric. It can be explained by presence the intensive ester C=O band in PES and Cotton/PES samples, which overlapped weak C=O band due to plasma treatment. On the other hand, irradiation penetration depth under FTIR analysis reaches few micrometers, while modification by plasma allows to transform only few nanometers. In view of all of the above, we suggest additional analysis of the samples by X-ray photoelectron spectroscopy.

Acknowledgments

This work is supported by the Ministry of Scientific and Technological Development, Higher Education and Information Society of the Republic of Srpska (19.032/961-113/19 and 19.032/961-112/19).

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UTICAJ PLAZME NA STRUKTURU TEKSTILNIH MATERIJALA

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Sažetak

U ovom radu istraživane su promjene strukture tekstilnih materijala uslijed tretiranja plazmom. Korišćeni su tekstilni materijali različitih sirovinskih sastava: pamuk, poliester i mješavina pamuk/poliester. Tekstilni materijali tretirani su 5 minuta u radiofrekventnoj plazmi (RF) sa gasom argona. Za dobijanje RF pražnjenja u plazmi korišten je visokonaponski RF generator sa standardnom frekvencijom od 13,56 MHz. Tretiranjem površine tekstilnih materijala plazmom aktiviraju se određene grupe u strukturi vlakana. Prisutnost karboksilnih i karbonilnih grupa u strukturi tekstilnih materijala nakon obrade plazmom povećava stepen obojenosti, kao i postojanost boje. Strukturne promjene u tekstilnim materijalima ispitane su FTIR spektroskopijom. FTIR analiza je vrlo moćna metoda za određivanje strukturnih promjena u materijalima. Male promjene u strukturi materijala mijenjaju intenzitet i položaj pikova na FTIR spektru. Razmatrane se strukturne promjene pletenina i tkanina, kao i promjene uzrokovane tretmanom tekstilnih materijala plazmom argona.

Ključne riječi: plazma, struktura tekstila, pamuk, poliester, FTIR.

Original scientific article

APPLICATION OF WASTE FLAX FIBRES AS SORBENT OF HEAVY METAL IONS FROM AQUEOUS SOLUTION

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Abstract

In this paper, waste flax fibres were used for the removal of heavy metals present as contaminants in industrial wastewater. Short, tangled flax fibers have no significant practical application and they are treated as waste. These natural, biodegradable materials are very interesting for new areas of application, including the field of water purification. Sorption of heavy metal ions was tested from single ion solutions, where initial concentrations of heavy metal ions in the solution were 10 mg/L and 25 mg/L. The degree of sorption of heavy metal ions from aqueous solution of concentration 10 mg/L was in order $Pb^{2+} > Zn^{2+} ~Ni^{2+} > Cu^{2+} > Cr^{3+}$, while in the case of sorption from a solution of concentration 25 mg/L was in order $Pb^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+} > Cr^{3+}$. The results show that flax fibers can be used as a cheap, environmentally friendly sorbent for sorption of heavy metal ions from aqueous solution, where the sorption capacity of the fibers depends on the type of heavy metal and the initial concentration of metal ions in the solution.

Keywords: flax fibres, sorption, heavy metals

Introduction

Upon the separation of fibres from textile flax stem, in addition to other fibres which are further used in textile industry, we also get short, tangled fibres which do not have a significant practical application and so far have been treated as waste. On the other hand, the pollution of water and soil by heavy metals represents a big ecological problem and direct danger for the health of people. Presence of highly toxic heavy metals in the environment, particularly in the water, is a result of the increased use of metals and chemicals in industrial processes and uncontrolled emission of toxic substances into the immediate environment (Chowdhury et al., 2016; Florea & Büsselberg, 2006; Milly et al., 2002; Raza et al., 2017; Schwarzenbach et al., 2010).

The methods for removal of heavy metals from the water, which have been used so far, have certain deficiencies, out of which primary ones are high price and problems related to biodegradability of sorbent after the completed sorption (Burakova et al., 2018; Igwe & Abia, 2006).

For this reason, unconventional methods started to be used, like the sorbents based on natural, biodegradable materials. In the previous research, lignocellulose materials proved to be an excellent raw material for making filters for purification of the water contaminated with heavy metal ions, and thus far most frequently used fibre lignocellulose sorbents were hemp, jute, kenaf and ramie fibres (Bailey et al., 1999; Conrad & Hansen, 2007; Crini, 2005; Lee & Rowell, 2004; Pejić et al., 2009; Tofan & Paduraru, 2008; Vukčević et al., 2014; B.Wang & K.Wang, 2013). Since flax fibres belong to the same group of materials, it was concluded that the short and tangled flax fibres, which represent textile industry waste material, could be used for making filters for purification of the water contaminated with heavy metal ions.

In accordance with that, the possibility was examined of sorption of heavy metal ions by short flax fibres from aqueous solutions of Cu^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} and Cr^{3+} ions, which are as contaminants present in the waste waters of different industries.

Materials and Methods

Domestic water-retted flax fibers were used in this investigation. The short flax fibers samples were obtained from the flax Venica variety (Czech Republic) grown at the experimental grounds in the vicinity of Banja Luka (the Republic of Srpska, Bosnia and Herzegovina).

Sorption of heavy metal ions $(Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+})$ was performed from aqueous solution. Experiment was carried out in batch process for 24 h, at room temperature with constant shaking.

Fixed dosage of flax fiber samples (0.5 g) were added in 200 mL of ion aqueous solution. Initial concentration of ions in aqueous solution was 10 and 25 mg/L. Optimal pH value of 5.5, where maximum capacity for ions sorption was obtained during preliminary experiments, was used for sorption experiments. The ion uptake (q, mg/g) was determined as the difference between the initial concentration of ions in solution (c_0 , mg/L) and the final concentration of ions in the solution (c_t , mg/L) after 3, 5, 10, 15, 30, 60, 120, 180 and 240 min. For the determination of ions concentration in the solution atomic absorption spectrometer Agilent AA Duo was used.

$$q = \frac{c_0 - c_t}{m} \cdot V \quad \left(\frac{mg}{g}\right) \tag{1}$$

In Eq. 1, V is volume of the solution (L) and m is the weight of sorbent material - flax fiber sample (g).

Results and discussion

Chemical composition of used flax fibers are: water solubles - 1.81%, fats and waxes - 1.73%, pectin - 6.97%, α -cellulose - 75.81%, hemicelluloses - 7.84% and lignin - 4.03%.

The sorption of heavy metal ions by short flax fibres was performed individually from the aqueous solutions of Cu^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} and Cr^{3+} ions, with the concentration of 10 mg/L and 25 mg/L.

Figure 1. and Figure 2. present dependency of the quantity of sorbed ions of heavy metals on the length of duration of the sorption process.

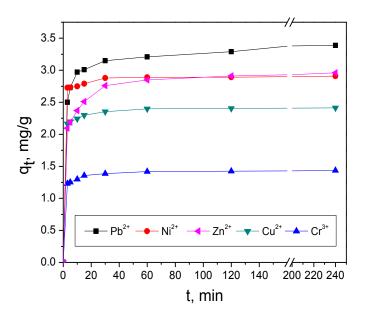


Figure 1. Dependency of the quantity of sorbed ions of heavy metals (q_t) on the length of duration of sorption (t) by the flax fibres from the solution of ions with the concentration of 10 mg/L

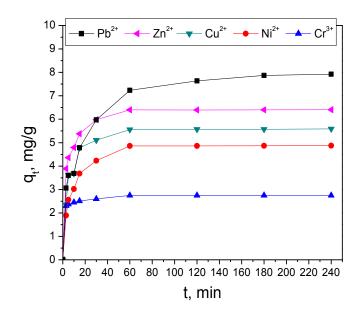


Figure 2. Dependency of the quantity of sorbed ions of heavy metals (q_t) on the length of duration of sorption (t) by the flax fibres from the solution of ions with the concentration of 25 mg/L

The biggest speed of adsorption, i.e. the biggest quantity of sorbed ions, was achieved in the first 3 minutes, during the sorption from the solution of the initial concentration of 10 mg/L. After ten minutes of sorption, changes were negligible, i.e. balanced sorption capacity was reached with all examined ions. Thus, for example, in the sorption of Pb^{2+} from the solution of the concentration of 10 mg/L, after 3 minutes of processing, 63% of ions were sorbed, which represents 90% of the total quantity of sorbed ions. On the other hand, during the sorption of different ions from the solution of the initial concentration of 25 mg/L, the balanced sorption capacity is reached 10 to 60 minutes later, depending on the type of ion.

After the sorption balance gets established, the quantity of sorbed ions from the aqueous solutions of Pb^{2+} , Cu^{2+} , Ni^{2+} , Zn^{2+} and Cr^{3+} ions with the concentration of 10 mg/L, was from 30% in the sorption of Cr^{3+} to 75% in the sorption of Pb^{2+} , and in the sorption from the aqueous solution of the mentioned ions with the concentration of 25 mg/L, from 30% in the sorption of Cr^{3+} to 80% in the sorption of Pb^{2+} .

The degree of sorption of heavy metal ions by the flax fibres from the solution with the concentration of 10 mg/L can be presented by the following sequence $Pb^{2+} > Zn^{2+} \sim Ni^{2+} > Cu^{2+} > Cr^{3+}$, and in the sorption from the solution with the concentration of 25 mg/L by the following sequence $Pb^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+} > Cr^{3+}$.

The reached balance sorption capacity for the examined metal ions depending on the initial concentration of ions for unmodified fibres and their mutual relation is presented in Figure 3.

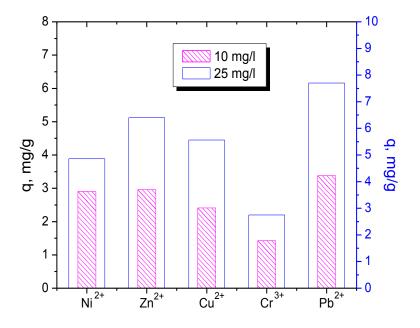


Figure 3. Dependency of balance sorption capacity (q) on the initial concentration of metal ions in the solution for the flax fibres

The lower sorption capacity of flax fibres was determined in the sorption of metal ions from the aqueous solutions with the concentration of 10 mg/L compared with the sorption capacity of flax fibres for the solution with the concentration of 25 mg/L, for all metals (Figure 3.).

It can be noticed that flax fibres sorbed the biggest quantity of lead ions, i.e. the biggest balance sorption capacity was reached in the sorption of Pb^{2+} for both concentrations. In the sorption from the solution of ions with the concentration of 10 mg/L, the balance sorption capacity amounted to 3.1 mg/g, while in the sorption from the solution of ion with the concentration of 25 mg/L, the balance sorption capacity amounted to 7.7 mg/g. The lowest sorption capacity in the solution with the concentration of 10 mg/L and the solution with the concentration of 25 mg/L, was recorded for the ions of chromium and amounted to 1.3 mg/g, i.e. 2.8 mg/g.

The interaction between the fibres of flax and metals depends on a great number of factors, both physical and chemical characteristics of metals, of chemical and morphological characteristics of fibres. Different percentage of sorption of metal ions from the solutions of equal concentrations, since the sorption was performed under the same conditions, primarily indicates the importance of dependency of sorption on physical and chemical characteristics of metals (Hube et al., 2011, Šćiban, 2013). Among other things, linear dependency was shown between the adsorption capacity and metal radius (Tobin et al., 1984). Lead has the smallest hydrated radius in comparison to the examined ions, which could explain the biggest sorption capacity of flax fibres for Pb²⁺ ions. Taking into account the structure of unmodified fibres, the surface of which is covered with various admixtures and impurities, which among other things prevent the breakthrough towards the fibre interior, the possibility of sorption is significantly limited by the size of sorbed ions.

Conclusion

The conducted experiments have proved that short flax fibres are good sorbents, which could be used in purification of the water contaminated with heavy metal ions $(Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} \text{ and } Cr^{3+})$, where a different sorption capacity of fibres was determined depending on the type of metal and initial concentration of the ions in solution.

Short flax fibres, as economical and ecologically acceptable materials, can be applied in the field of biosorption for making filters for purification of waste waters.

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PRIMJENA OTPADNIH VLAKANA LANA KAO SORBENTA JONA TEŠKIH METALA IZ VODENIH RASTVORA

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Sažetak

U ovom radu je ispitivana mogućnost korištenja vlakana lana za uklanjanje jona teških metala, koji su kao kontaminanti prisutni u otpadnim vodama različitih industrija. Kratka, zamršena vlakna lana nemaju značajnu praktičnu primjenu i tretiraju se kao otpad. Imajući u vidu, da se radi o prirodnim, biorazgradivim materijalima, mogućnost proširenja njihove upotrebe u novim, nekonvencionalnim područjima, uključujući i oblast prečišćavanja voda je od velikog značaja. Sorpcija jona teških metala vlaknima lana je vršena pojedinačno iz vodenih rastvora jona Cu²⁺, Ni²⁺, Pb²⁺, Zn²⁺ i Cr³⁺ koncentracije 10 mg/L i 25 mg/L. Stepen sorpcije jona teških metala iz rastvora koncentracije 10 mg/L može se prikazati sledećim nizom Pb²⁺ > Zn²⁺ ~Ni²⁺ > Cu²⁺ > Cr³⁺, a kod sorpcije iz rastvora koncentracije 25 mg/L, Pb²⁺ > Zn²⁺ > Cu²⁺ > Ni²⁺ > Cr³⁺. Rezultati ispitivanja pokazuju da se vlakna lana mogu koristiti kao jeftin, ekološki prihvatljiv sorbens za sorpciju jona teških metala iz vodenih rastvora, pri čemu sorpcioni kapacitet vlakana zavisi od vrste metala i početne koncentracije jona metala u rastvoru.

Ključne riječi: vlakna lana, sorpcija, teški metali

Original scientific article

UNCONVENTIONAL DYEING OF POLYAMIDE FABRIC WITH DIRECT DYE

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Abstract

The possibility of unconventional dyeing of polyamide fabric with direct dye was investigated in this paper. Dyeing of polyamide fabric with direct dye was realized in the laboratory with the tendency to apply it in industrial conditions. 100% raw polyamide 6.6 fabric was used. Polyamide belongs to the group of synthetic fibers. The fabric was dyed with a direct dye of a specific structure that has a predisposition to binding to the fiber. Direct dyes are sulfonated azo compounds derived from benzidine and its derivatives or amines of the diaminostilbene type, etc. and are commonly used to dye of cotton. The samples were dyed at a temperature of 95 °C. The dye used is C.I. Direct Green (Huntsman, USA). Samples of polyamide 6.6 fabric were dyed in a time period of 5, 10, 20, 30, 40, 50 and 60 minutes. The solution contained dye concentrations of 5, 10, 15, 20, 25 and 30 mg/dm³. Adsorption isotherms are of great importance for the investigation of the dyeing process, so several of them, Halsey, Jovanovic and Temkin, were used in this research. The Halsey model proved to be the most suitable for explaining polyamide dyeing with direct dye. The successful process of dyeing polyamide with direct dye has expanded the range of dyes that can be used for polyamide.

Keywords: direct dye, polyamide 6.6 fabric, *Halsey's* isotherm, *Jovanovic's* isotherm, *Temkin's* isotherm

Introduction

Polyamides (PA) or nylons were among the first synthetic polymers to be used for making fibers. Polyamide fibers are used for a different uses as textiles and carpets to rubber reinforcements. Polyamides are polymers where the repeating units are held together by an amide bond. PA can be classified into aromatic and aliphatic polyamides. Aliphatic PA consist only of aliphatic chains, while aromatic PA consist of aromatic rings in the main chain (Vasanthan, 2009).

Unlike polyethylene, polyamides have a high melting point and intermolecular hydrogen bonding. Hydrogen bonds play an important role in forming of PA fibers. Numerous attempts to produce high modular PA fibers have been made either by

different spinning methods or by coextrusion in solid state with various plasticizers (Jagur-Grodzinski, 1992).

Direct dyes can be valuable for wide use: textiles, clothing, but also for various types of technical textiles, such as draperies and upholstery fabrics, and even some car fabrics. Also, there are many uses for which some individual dyes have very suitable durability properties (Aspland, 1991).

Direct dyes are relatively cheap. They are available in a full range of shades, but not bright dyes. They show poor to moderate washing resistance. Therefore, they are used on materials where good durability is not crucial. Resistance to light of direct dyes can be improved by post-treatment with copper salts and resistance to wash can be improved by treatment with resins (Rattee and Breuer, 1974).

Benzidine is an organic chemical that belongs to the group of amines and it is used to obtain many dyes. Azo-dyes derived from benzidine are important because, unlike simpler types of azo-dyes, they become firmly fixed to cotton without mordant (Ishegbe et al., 2014).

This paper presents the unconventional dyeing of polyamide 6.6 fabric in laboratory conditions with a selected direct dye that has a high affinity for this fiber, in a slightly acidic bath without additives. The aim of the research is to develop a process for dyeing polyamide 6.6 with unconventional direct dye that is not used for dyeing this fiber, without the addition of any substances in aqueous dye solution in laboratory conditions with a tendency of being applied in industry.

Materials and methods

In the experimental part, 100% raw polyamide 6.6 fabric was used. One measurement was performed for each of the samples. Dyeing was performed in Erlenmeyer glass flasks in which a sample of raw polyamide 6.6 fabric was placed in a solution of acetic acid and direct dye.

The ratio of the spa was 20: 1. Processing time with continuous stirring was 5, 10, 20, 30, 40, 50 and 60 minutes. The used dye is C.I. Direct Green (Huntsman, USA). The solution contained a constant amount of dye concentrations of 5, 10, 15, 20, 25 and 30 mg/dm³. The samples were stained at a temperature of 95 °C. After staining, the samples were washed and dried. The absorbance at the maximum wavelength for the dye was measured, using a spectrophotometer (Cary 100 Conc UV-VIS, Varian). The absorption maximum for the dye used is 680 nm. The absorbance of the solution was measured to make a calibration curve and to determine an unknown concentration during staining.

The degree of dye exhaustion was calculated using the form (Tayebi et al., 2015):

The degree of exhaustion (%) =
$$\frac{C_0 - C_t}{C_0} \times 100$$
 (1)

where: C_0 and C_t (mg/dm³) are initial and dye concentration at time t.

The amount of absorbed dye per unit mass of the adsorbent (absorption capacity) was obtained using the equation (Tayebi et al., 2015):

$$q_t = \frac{C_0 - C_t}{w} \times V \quad \text{and} \quad q_e = \frac{C_0 - C_e}{w} \times V \tag{2}$$

where qt (mg/g), is mass of absorbed dye per unit mass at dye time t; qe (mg/g), is mass of absorbed dye per unit mass in equilibrium, $C_o \text{ (mg/dm}^3)$, is initial dye concentration; $C_t \text{ (mg/dm}^3)$, is dye concentration in solution at dye time t, $C_e \text{ (mg/dm}^3)$, is equilibrium dye concentration in solution; w (g), is mass of sample and $V \text{ (dm}^3)$, is volume of staining solution.

Temkin's isotherm is based on the following assumptions: the heat of adsorption of all molecules on the surface of the adsorbent decreases linearly with increasing degree of coverage, while adsorption is characterized by a uniform distribution of binding energy of dye molecules on the surface of the adsorbent. The *Temkin's* isotherm is represented by the following linear equation (Bagheri et al., 2018):

$$q_e = B_T \cdot \ln(K_T) + B_T \cdot \ln C_e \tag{3}$$

where $q_e - (\text{mg/g})$ is adsorbed mass of adsorbate per unit mass of adsorbent in equilibrium time, $C_e - (\text{mg/dm}^3)$ equilibrium concentration of adsorbate in solution, K_T (dm/mg³) and B_T - Temkin's constants, of which the first represents the adsorbate-adsorbent interaction, and the second is related to the adsorption heat B_T (J/mol) (Bagheri et al., 2018):

$$B_T = \frac{R \cdot T}{b_T} \,. \tag{4}$$

Jovanovic's linear model can be represented as following (Shahbeig et al., 2013):

$$\ln q_{\rm e} = \ln q_m + K_j \cdot C_{\rm e} \tag{5}$$

where: $q_e \text{ (mg/g)}$ is adsorbed amount of adsorbate per unit mass of adsorbent, $K_J \text{ (mg/dm}^3)$ –is isotherm parameter, $q_m \text{ (mg/g)}$ is maximum bound adsorbate or maximum adsorption capacity, C_e is equilibrium concentration of adsorbate (mg/dm³).

The linear *Halsey's* model is mathematically expressed through a logarithmic dependence as (Başar, 2006).

$$\ln q_e = \frac{1}{n_H} \cdot \ln K_H - \frac{1}{n_H} \cdot \ln \frac{1}{C_e}$$
(6)

where: n_H and K_H are Halsey's constants, which can be calculated from the slope and segment of the linear diagram based on the dependence $\ln(q_e)$: $\ln(1/C_e)$.

Results and discussion

The dyeing of polyamide with direct dye is organized in such a way that with the help of the adsorption model, the so-called isotherms clarify the way of dyeing and placement of dye molecules inside the fiber. Three models were used that can provide answers to the previous statement.

Jovanovic's model was derived for monolayer, nonlocalized adsorption on a homogeneous solid surface, without lateral interactions. The parameters in the *Jovanovic's* model have the same physical meaning as in the *Langmuir's* model. Figure 1 is a diagram of Jovanovic's linear isotherm for direct dye adsorption on a polyamide adsorbent (substrate). From the analytical expressions of this isotherm, constants were determined, and through them, the suitability of the *Jovanovic's* model for describing the process of adsorption of direct dye on the adsorbent was characterized.

According to the diagram in Figure 1, a greater scatter of experimental data ($R^2 = 0.811$, Table 1) is noticeable in relation to the fitting curve, so that this model in its linear form can be neglected for a specific case since preference is given to other linear models which are used.

Analyzing the result for Jovanovic's equilibrium model, it can be said that the possibility of certain mechanical contacts between adsorbed and desorbed molecules is partially missing, as well as that the occurrence of monolayer localized direct dye adsorption on polyamide without lateral interactions is questioned.

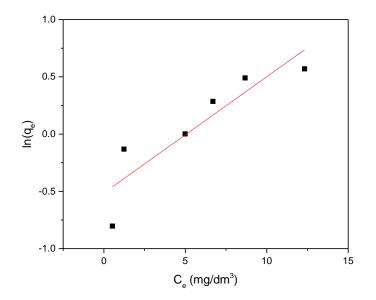


Figure 1. Linear regression model of Jovanovic for equilibrium dyeing of PA fabric with direct dye

The adsorption data, analysed according to the linear form of the *Temkin's* isotherm, are shown in the diagram in Figure 2. The appearance of the fitting curve of the experimental data confirms that the Temkin's isotherm is not the best choice for explanation of the adsorption of direct dye on the substrate surface. The coefficient of determination, R^2 , obtained from the *Temkin's* model (0.888) has ahigher value in compared to the Jovanovic's isotherm, which gives an advantage in the applicability of the *Temkin's* model, bun not absolute primacy and the best choice for describing adsorption of the direct dye on the surface of the PA fibers.

Heat of adsorption, b_T , determined from the *Temkin's* model, has a value of 8.08 kJ/mol. Given that the $b_T = \Delta H$, it is the change in enthalpy of -8.08 kJ/ mol, which assumes reeling exothermic process during dyeing. This energy adsorption is the sum of all the individual adsorption occurring in different places on the surface of the adsorbent. In addition, to the structure of the paint and the substrate, the value of the heat of adsorption (change in enthalpy), a large impact can have various additives (for example from the fabric), which directly affects the ability of the interaction and binding, by physical or chemical bonds.

Since the heat of adsorption is relatively low and the change in enthalpy ΔH is negative, it is presumed that interaction between PA and the color of the fibers mainly follows a reversible physical adsorption supported by weak electrostatic forces (dipole bonds, *van der Vaals's* forces or hydrogen bonds.

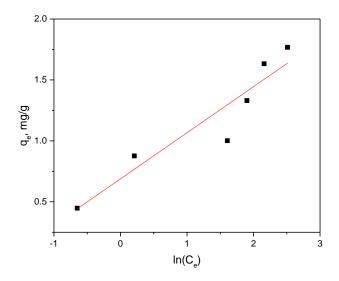


Figure 2 Temkin's linear regression model for equilibrium dyeing of PA fabric with direct dye

The *Halsey* isotherm explains the possibility of multilayer adsorption and heterogeneous distribution of dye molecule through the pore. According to this model, the typical multi-layer adsorption consists of three regions: an uncooperative adsorption on the very heterogeneous surface; cooperative adsorption on heterogeneous surfaces and cooperative multilayer adsorption caused by small *van der Vaals's* forces at a certain distance from the surface.

Thus, the *Halsey's* equation provides an expression for the condensation of multiple layers, so according to the layout of the diagram in Figure 3, it can be concluded that there is a good ability of this equilibrium isotherm to indicate multilayer direct color sorption on a polyamide substrate. The fitting curve covers the experimental points well, it goes to the nearest of those points as compared with the other models, as evidenced by and based on the values of the statistical parameters, the coefficient of determination, $R^2 = 0.917$. According to the good acceptability of this model, it can be said that it testifies to the relative heteroporous nature of the adsorbent.

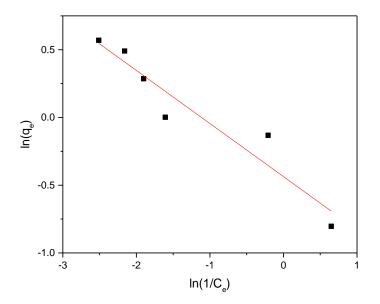


Figure 3 Halsay's linear regression model for equilibrium dyeing of PA fabric with direct dye

Table 1 Analytical expression of linear isotherms with coefficients for the direct dye-Pa	A
fiber system	

Modeli	Analitičke jednačine modela Parametri modela				
Jovanovic	$\ln q_{e} = -0.514 + 0.101 \cdot C_{e}$	q_m (mg/g)	0.598	0.811	
	$mq_e = -0.514 \pm 0.1010 C_e$	K_j (dm ³ /mg)	0.101		
Temkin	$q_e = 0.69 + 0.38 \ln C_e$	B_T	0.38	0.888	
		K_T (dm ³ /mg)	6.16		
Halsey	$\ln q_e = -0.44 - 0.39 \cdot \ln \frac{1}{C_e}$	K_H	0.33	0.917	
		n _H	2.55		

Conclusion

According to the results of experiments and statistical data, dyeing of PA 6.6 fabric can also be achieved in industrial conditions, which of course requires adapting the recipes to the new space and equipment. Modeling a dyeing process, it may be data that links the concentration of color, temperature, the presence of electrolytes and the efficiency achieved by dyeing the fabric or the amount of waste paint that remains in the bath after the dyeing.

Based on the obtained experimental results, it can be concluded: Dyeing PA 6.6 fabric with direct dye in laboratory conditions gives excellent results at a temperature of 95 °C. *Halsey's* linear isotherm is most effective in simulating the isothermal adsorption of direct dyes on PA 6.6 fabric. For even better results, it is

necessary to carefully select an adequate composition of the tub (appropriate acid, mineral-organic) and the method of dyeing, to elaborate dye phase in order to achieve better coloration of the fibers.

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NEKONVENCIONALNO BOJENJE POLIAMIDNE TKANINE DIREKTNOM BOJOM

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Sažetak

U ovom radu istražena je mogućnost nekonvencionalnog bojenja poliamidne tkanine direktnom bojom. Bojenje poliamidne tkanine direktnom bojom realizovano je u laboratoriji sa tendencijom da se koristi u industrijskim uslovima. Korištena je 100% sirova tkanina od poliamida 6.6. Poliamid pripada grupi sintetičkih vlakana. Tkanina je obojena direktnom bojom određene strukture koja ima predispoziciju za vezivanje na vlakno. Direktne boje su sulfonirana azo jedinjenja izvedena iz benzidina i njegovih derivata ili amina tipa diaminostilbene, itd. Obično se ove boje koriste za bojenje pamuka. Uzorci su obojeni na 95 °C, bojom C.I. Direct Green (Huntsman, SAD). Uzorci poliamidne tkanine bojeni su tokom perioda od 5, 10, 20, 30, 40, 50 i 60 minuta. Otopina je sadržavala koncentracije boje od 5, 10, 15, 20, 25 i 30 mg/dm³. Adsorpcione izoterme su od velike važnosti za istraživanje procesa bojenja, pa je nekoliko od njih, Halsey, Jovanovic i Temkin, korišteno u ovom istraživanju. Halsey model pokazao se najpogodnijim za objašnjenje bojenja poliamida direktnom bojom. Uspješan postupak bojenja poliamida direktnom bojom proširio je paletu boja koje se mogu koristiti za poliamid.

Ključne riječi: direktna boja, poliamid 6.6 tkanina, *Halsey* izoterma, *Jovanović* izoterma, *Temkin* izoterma.

Original scientific paper

OPTIMIZATION MODEL DEVELOPMENT FOR TEXTILE FIBRILIZED POLYPROPYLENE FOIL STRIPS

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Abstract

A scholar approach was used in performing an experiment done under process conditions during extrusion of polypropylene strip type 450 tex-2223 from pure and admixture granulate FY-6. Studied were the interaction factors during technological process using the theory of multiple and partial correlation. The dependence between the strip fineness, which was dependently variable, on the line operation time interval (h_i) and the temperature (t_i), regulated by warm air flow in the strip stretching chamber, was studied. The line speed was kept constant. Compared was the goodness degree of two strip products, one made from pure granulate and the other with an admixture of the secondary regenerate type FY-6 up to 8%, under the same production and technological conditions. It has been proven that the continuous line operation time with pure granulate compared to the granulate containing 8% of secondary impurities was 88/72 [h].

Keywords: extrusion, PP-strip, granulate FY-6.

Introduction

During polymer textile fibers extrusion technological process, the waste is generated (Ladany&So, 1994). To the extruding polypropylene (PP) granulate the generated waste can be added. The 8% secondary regenerate was added to the pure FY-6 granulate. The obtained product was type-320-tex-2818 and was described previously (Djapic, 2018). In this experiment, performed under the production conditions, the pure FY-6 granulate was used for the extrusion and the PP-strip obtained is marked: type-450-tex-2223. Its mechanical, physical and chemical properties are determined by standards and regulations. The strip is shown in Figure 1.



Figure 1. PP-foil type-450-tex-2223 made from pure FY-6 granulate using extrusion

The engineering experiment was conducted in order to investigate the strip, made from pure FY-6 granulate, its fineness interdependence during the operating time and the stabilization temperature. The strip fineness, [Nm] tex, was dependently variable, while the independent variables were the line operation time interval (h_i) and the hot air temperature supplied to the stretching chamber (t_i) . Other factors during the technological process were kept constant. The mathematical regularities, the theory of multiple and partial correlation, were used to study the phenomena and features during the technological process (Pantelić, 1976; Hadživuković, 1991). In order to have a complete insight into the technological process goodness degree, the factors influencing the technological process, were analyzed. Based on the experimental plan, the samples were taken, while tests were performed in the laboratory. The data analysis was done in order to find the PP-strip fineness. Results obtained permitted the regression curve construction that defined the production line technological process in the function of PP-strip fineness made from pure granulate for the purpose of comparison with the regression curve for a strip made with secondary (regenerated) granulate which was previously investigated (Djapic, 2018).

Theoretical Part

For the theoretical calculations used was the correlation theory, the multiple and partial correlation (Vukadinović, 1978; Hadživuković, 1991; Pantelić, 1976). The studied statistical elementar sets, occurrences and characteristics, vary under several factors influence. In this paper, one dependent variable and two independent variables, and their linear dependence were considered. The dependent variable is denoted by x_1 , the independent variables by x_2 and x_3 , while their relations are denoted by x_{1i} , x_{2i} and x_{3i} (i = 1, 2,3). The simplest regression equations, with the notations used in the textile industry, are $x_1 = N$, $x_2 = h$ and $x_3 = t$:

$$N_i = a + bh_i + ct_i \tag{1}$$

From the smallest square theory comes that the deviation square $S_{1.23}^2$ reaches minimum and then the system of normal equations is obtained: $\Sigma N_1 = na + b\Sigma h_1 + c\Sigma t$

$$\Sigma N_i h_i = a \Sigma h_i + b \Sigma h_i^2 + c \Sigma h_i t_i$$
(2)

$$\Sigma N_i t_i = a \Sigma t_i + b \Sigma h_i t_i + c \Sigma t_i^2$$

Variable standard deviation defined is by the equation:

$$s_{1} = \sqrt{\frac{1}{n} \Sigma N_{1i}^{2} - \left(\frac{1}{n} N_{1i}\right)^{2}}$$
³⁾

The square deviation sum is:

$$S_{1.23} = \sqrt{\frac{1}{n} \Sigma (N_{1i} - N_{r1i})^2}$$
(4)

The linear correlation coefficient is:

$$r_{12} = \frac{n\Sigma N_i h_i - (\Sigma N_i) (\Sigma h_i)}{\sqrt{\left[n\Sigma N_i^2 - (\Sigma N_i)^2\right]} \cdot \left[n\Sigma h_i^2 - (\Sigma h_i)^2\right]}$$
(5)

The same applies for r_{13} and r_{23} . N_{r1i} (i=1, 2, ..., n) where the value N_i is calculated from the equation (1).

The multiple correlation coefficient is:

$$R_{1.23} = \sqrt{1 - \frac{S_{1.23}^2}{s_1^2}} \tag{6}$$

The multiple determination coefficient is:

$$R_{1.23}^2$$

The partial correlation coefficient between N_i and t_i , taking into account that t_i is constant, is:

(7)

$$r_{12.3} = \frac{r_{12} - r_{13} \cdot r_{23}}{\sqrt{\left(1 - r_{13}^2\right)} \left(1 - r_{23}^2\right)} \tag{8}$$

The $r_{13.2}$ and $r_{23.1}$ are calculated in the same way.

Materials and Methods

The experiment was done in several steps, according to the planned plan. The experiment was done in the company ITES "Ivo Lola Ribar", Odžaci, Serbia. Monitored was the product, made according to the regular plan for the strip production, type-450-tex-2223 with PP pure granulate FY-6. The pure granulate

quality and properties were known: PP structure, density, melting point, softening point, elongation, surface properties, moisture content, reagent resistance, elasticity and were given by the manufacturer's certificate. Samples for testing were taken systematically in order to achieve generality under experimental conditions. The selected samples quality was controlled on measuring instruments, devices and tools.

The technological process was realized and included the following phases: granulate inflow for feeding extruder, extrusion, dosing, water cooling, foil formation, calendaring, strip cutting, stretching, fibrillation, stabilization, rolling, then rerolling, wrapping and packaging.

The ϕ 90 nm Covema GT90 Silver extruder was used for polymer processing. The foil strip was extruded. The liquid mass state during flow from the extruder was conditioned during the operation mode, the granulate type and the temperature along the extruder zones. The speed control device was synchronized with other line parts. At the cylinder outlet was a perforated plate for mass distribution on the filter. The purpose of the filter was to retain mechanical impurities. The filtered mass went to the extruder head system where a blown foil-balloon was formed. There was a cold air supply to the extruder head side participating in the balloon formation and maintenance. The rollers were compressed with air and maintained the balloon, influencing the volume, and then the balloon was pulled out. On the rollers the foil was cooled and the crystallization and drawing degree was regulated. Above the rollers were knives which cut the balloons into two equal parts, two foil strips with equal width and thickness. Further procedure was described previously (Djapic, 2018).

Results and discussion

The strip fineness investigation (tex) in the function of the extruder's working time, was done in four degrees, and the temperature in the chamber for stabilization, was done in three degrees. The measurements were done in triplicate for every degree combination. For the extruder's working time interval chosen, the temperature (t) was measured from one to three. After every change, measured was PP strip fineness. Results obtained are depicted in Table 1.

Split	Temperature		Time	interval		
Plots	t, ⁰C	24	32	40	48	Sum
		1.	2.	3.	4.	
	142 (1)	2364	2331	2248	2245	9188
1.	145 (2)	2342	2289	2233	2227	9091
	148 (3)	2398	2299	2284	2225	9206

Table 1. The temperature, extruder's working time interval and the PP strip fineness

2.	(1)	2393	2342	2278	2285	9298
	(2)	2393	2326	2299	2269	9287
	(3)	2345	2399	2280	2261	9285
3.	(1)	2372	2287	2275	2229	9163
	(2)	2364	2315	2279	2264	9222
	(3)	2340	2279	2282	2226	9127
Sum		21311	20867	20458	20331	82867

Working conditions have influenced the sample collection. The samples were taken from pots, randomly. Applied was the usual method for investigating the fineness, its longitudinal mass. It was determined on Uster-Autosorter 3 instrument. For data analysis used was the standard method ISO 2060 (1994). The product was PP strip tex 2223, used granulate was FY-6.

Data analysis was done by methods described in the theoretical part.

Regression analysis results were calculated from the equation (2) and obtained was the linear regression equation:

 $N_i = 2496, 27 - 5 h_i - 0, 1018 t_i$

where:

a=2496,27; b=-5; c=-0.1018

From the equation (9) calculated were values for N_{rmi} and are depicted in Table 2.

	N _m -tex	h_i	ti	N_{mi}^{2}	h_i^2	t_i^2	$N_{mi}h_i$	$N_{mi}t_i$	$h_i t_i$	N _{mri}
1.	2342	24	142	5484964	576	20164	56208	332564	3408	2361.8
2.	2393	24	142	5726449	576	20164	57742	339806	3408	2361.8
3.	2372	24	142	5626384	576	20164	56928	336824	3408	2361.8
4.	2342	24	145	5484964	576	21025	56208	339590	3480	2361.5
5.	2393	24	145	5726449	576	21025	57432	346985	3480	2361.5
6.	2364	24	145	5588496	576	21025	56736	342785	3480	2361.5
7.	2398	24	148	5750404	576	21904	57552	354904	3552	2361.2
8.	2345	24	148	5499025	576	21904	56280	347065	3552	2361.2
9.	2340	24	148	5475600	576	21904	56160	346325	3552	2361.2
10.	2331	32	142	5433561	1024	20164	74592	331002	4544	2321.8
to										
18.	2279	32	148	5193841	1024	21904	72928	337292	4736	2321.2
19.	2248	40	142	5053504	1600	20164	89920	319216	5680	2281.8
to										
27.	2282	40	148	5207524	1600	21904	73024	337736	5920	2281.2
28.	2245	48	142	5040025	2304	20164	107760	318790	6816	2241.8
to										
36.	2226	48	148	4955076	2304	21904	106848	329448	7104	2241.2
Σ	82854	1296	5220	190783840	49536	757116	2968358	12013808	187920	

Table 2. Regretion analysis results

Standard deviation was calculated from the equation $s_1=51.467$

(3):

(9)

Standard estimation error was calculated from the equation (4): $S_{1.23} = 21.908$ Linear correlation coefficient between N_i and h_i calculated was based on the equation (5): $r_{12} = -0.86808$ $r_{13} = -0.00048$ $r_{23} = 0$ (-) means that the factors are counteracting Linear multiple correlation coefficient N_i by h_i and t_i calculated was from the equation (6): $R_{1.23} = 0.8187$ Multiple determination coefficient was calculated from the equation (7): $R_{1\,23}^2 = 0.9048$ Linear partial coefficient was calculated from the equation (8): $r_{12.3} = 0.8681$ $r_{13,2} = 0.00042$ $r_{23,l} = -0.01707$

For the hipothesis proof, necessery was to do the comparison of the results obtained by the regression analysis method. Observed were the results obtained using the pure FY-6 granulate – etalon product. After, observed was the product with 8% secundary (regenerated) FY-6 granulate. Following the theory of linear dependance from the equation (2) obtained was the final equation (9) form. For the PP strip:

- 1. type-450-tex-2223
- 2. type-320-tex-2818

regression equation was:

- 1. $N_i = 2496.27 5 h_i 0.1018 t_i$
- 2. $N_i = 3453.93 7.15 h_i 2.365 t_i$

Multiple determination coefficients values determined by the equation (7) were:

1.
$$R_{1.23} = 0.818$$

2.
$$R_{1.23} = 0.763$$

Complete variation, determined by the regression equations, N_i to h_i and t_i was:

1. 82%

2. 76%

For the first product, the value for the linear partial correlation coefficient was $r_{12.3}$ = 0.8681, that was the etalon product. For the second product, the product that contained 8% regenerated PP FY-6 granulate was $r_{12.3}$ = 0.780 (Djapić, 2018). The factor that influenced the finesses mostly was the extruder working time. From the

 $r_{23.1}$ i $r_{13.2}$ observed was that changeable factors had small influence, in both cases. Mathematical interpretation by the regression curve analysis showed that the PP strip finesses, during the investigated products extrusion indicated that the same working factors influence the product quality. The factor that influenced, the most, was the extruder working time while the air temperature in the stabilization chamber had almost no influence at all. With the small approximation the curve can be reduced to the curve with one variable when the temperature is kept constant at 145°C (Figure 2.).

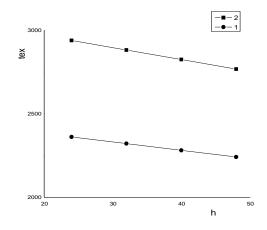


Figure 2. Curves for the PP strip finesses, pure granulate (1) and granulate with the 8% regenerated PP FY-6 granulate (2)

From the curve, geometrically and using interpolation, obtained can be the values for the strip thickness, the basis for the extruder working time calculation before and after general cleaning. The deviation moment for the first product (pure granulate) with the minimal strip thickness begins when the time is t = 88 h. For the product with the 8% regenerated PP FY-6 granulate the time value is t = 72 h. Achieved extruder working times, before general cleaning, allow the possibility to compare the technological process goodness degree and its optimization. The complete switch off time, cleaning time and switch on, was taken into account. Continuous production process is possible only in case when absolutely clean granulate is used, for both granulates investigated.

Conclusion

There are two key factors influencing the continuous line production length, the first is the granulate purity, while the second factor is the filter change without stopping the line which is technically impossible. The mathematical model permitted the insight into the technological working process and its optimization.

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OPTIMIZACIONI MODEL RAZVOJA TEHNOLOGIJE EKSTRUDIRANJA FOLIJSKIH TRAKA POLIPROPILENA

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U radu je prikazan školski pristup izvođenja eksperimenta koji je urađen u radnim uslovima pri ekstrudiranju polipropilen trake TIP-450 tex-2223 od čistog granulata FY-6 u cilju izučavanja interakcija faktora tehnološkog procesa. Korišćena je teorija višestruke i parcijalne korelacije u svrhu izučavanja zavisnosti između finoće folije pređe [Nm] tex, koja je bila zavisno promenljiva, od vremenskog intervala rada linije (h_i) i temperature (t_i) koja je dovođena toplim vazduhom u komoru za istezanje trake. Brzina linije je održavana konstantnom. Preko vrednosti faktora upoređen je stepen dobrote proizvoda vlakana izrađenih od čistog granulata i granulata sa 8% primesa sekundarnog regenerata tip FY-6 pod istim proizvodnim uslovima. Dokazano je da je vreme neprekidnog rada linije sa čistim granulatom u poređenju sa sekundarnim 88/72 [h].

Ključne riječi: ekstruzija, PP-trake, granulat FY-6.

Informative article

APPLICATION OF PLASMA FOR TEXTILE FINISHING

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Abstract

Textile finishing is applied to achieve the desired effects on the textile materials and produce textile products according to market demands. Finishing can modify the appearance and feel of the textile material and improve its performances. Traditional textile finishing wet processes, based on the application of chemicals, use large amounts of water and energy and generate large amounts of wastewater, which significantly increases the ecological footprint of textile. Growing concern for the environment and efforts to save energy have led to numerous studies aimed at replacing many wet finishing processes with low water consumption processes and dry finishing.

Plasma treatment is one of the specialized finishing procedures to achieve the desired functional properties of textiles, in which there are no harmful substances, no wet processes / wastewater and no mechanical damage to the textile material being treated.

The paper deals with plasma techniques application suitable for textile processing, functionalities achieved by this processing, as well as the advantages of plasma application as a unique efficient engineering tool for functionalization / improvement of surface properties of textile materials.

Keywords: textile materials, textile finishing, plasma technology.

Introduction

The textile industry is searching for innovative production techniques because of need to enhance the product quality and increasing requirements on the finishing of textile fabrics, increasing use of technical textiles with synthetic fibers, as well as the market and society demand for textiles that have been processed by environmentally sound methods (Atav, 2013).

Awareness about ecofriendliness in textiles is one of the important issues in recent years since textiles are used next to skin and called the second skin. Textile materials are used in a variety of applications where surface modification is of profound importance as it improves various properties, including functional properties (Praveen et al., 2019). Plasma technologies are an innovative environmentally friendly class of processes for the surface modification of materials, including textiles (Abidi 2009; Schönberger & Schäfer, 2003).

In the textile field, significant research work has been going on since the early 1980s in many laboratories across the world dealing with low-pressure plasma treatments of a variety of fibrous materials showing very promising results regarding the improvements in various functional properties in plasma-treated textiles. Appropriate choice of gas and control of plasma operation conditions provide a variety of effects on textiles. Surface modification via plasma treatment not only eliminates the need for wet processing, but also yields unique surface characteristics.

The reasons for the application of this technology in textiles are ecological, aesthetic and economic (Shishoo, 2007). Plasma technology, essentially a dry process, is an important alternative to wet treatments of textiles, because there is no water usage, treatment is carried out in gas phase, short treatment time is enough, it does not cause industrial waste, and it provides energy saving without any expenses on effluent treatment (Atav, 2013; Ahmed et al., 2019).

Plasma technology is applicable to most of textile materials for surface treatment – almost all kinds of fibre can be modified by plasmas – it is virtually limitless. It can be explored in various areas like pretreatment, dyeing, printing and finishing through different methodology to add functionality and modification of surface properties of textile materials. This technology can generate more novel products to satisfy customer's need and requirement (Turaga et al., 2015; Joshi et al., 2015).

Deffinition, generation, composition and characteristic parameters of plasma

Plasma is the 4th state of matter with a high, unstable energy level in which a gas is a partially ionized, composed of a dynamic mix of neutral particles, electrically charged particles and highly reactive radicals – electrons, ions, photons, free radicals, meta-stable excited species and molecular and polymeric fragments, produced by introducing energy into a gas and interaction of electromagnetic field with gas under appropriate pressure (Ahmed & El-Shishtawy, 2010; Shah & Shah, 2013, LEITAT, 2009). Generally, plasma can be easily generated by gas breakdown by (Chinta & Kumar, 2012; Joshi et al., 2015): electrical energy, nuclear energy, thermal energy, mechanical energy, radiant energy.

Characteristic parameters of plasma are (Shishoo, 2007; Mather, 2009): **primary** – gas type and residence time; and **secondary** – gas flow, frequency, power (ranges from 10 to 5000 W, pressure / low pressure (1-100 Pa), ambient temperature. Also, it should be mentioned: electron density; ion density; electron temperature; ion temperature; interactions (collisions) and plasma potential (LEITAT, 2009).

Plasma clasification

Plasma can be classified according to different parameters (Ahmed et al., 2019; Plasma classification, 2020; Peran & Ercegović Ražić, 2020; Souma, 2012; Kwong et al., 2014):

- according to gas/vapour used;
- according to temperature: *hot plasma* (thermal plasma $T_{electron} = T_{ion} = T_{gas}$) – in one which approaches a state of local thermodynamic equilibrium; *warm plasma* – is the state which lies between hot and cold plasma. It takes advantage of the fact that some dimensionless parameters occurring in the hot plasma models are << 1 in most cases; *cold plasma* (non-thermal plasma – $T_{electron} >>$ $T_{ion} = T_{gas}$) – is one in which the thermal motion of the ions can be ignored. This plasma technology is known as an excellent tool for surface engineering and a valid alternative for wet-chemistry-based surface engineering; *ultracold plasma* – is one which occurs at temperatures as low as 1K and may be formed by photoionizing laser-cooled atoms;
- according to a pressure in plasma chamber atmospheric pressure (APP) (high pressure) and low pressure plasma (LPP) (vacuum);
- according to discharge modes glow discharge; corona discharge; dielectric barrier discharge, arc discharge;
- according to the electron temperature versus electron density low-density, medium-density and high-density;
- according to a frequency of the power supply- direct current (DC) and alternating current (AC) plasma (low-frequency (LF, 40-450 kHz); radio-frequency (RF, 13.56 or 27.12 MHz); microwave (MW, 915 MHz or 2.45 GHz));
- according to presence or absence of magnetic field magnetized plazma and unmagnetized plasma;
- depending upon the electron affinity of the process gases used electropositive and electronegative gas plasma;
- according to complexity dusty plasmas (a plasma containing nanometer or micrometer-sized particles suspended in it) and grain plasmas (a plasma containing larger particles than dusty plasmas);
- according to ratios of ionized to neutral particles partially ionized plasma and fully ionized plasma;
- on the basis of crystalinity colloidal plasmas, liquid plasmas and plasma crystals;
- on the basis of activity of regions active plasmas and passive plasmas.

Important types of plasma

Low-pressure plasma process, called also vacuum plasma, is non-thermodynamic equilibrium process. Its equipment is generally more expensive than atmospheric-pressure equipment to install, but it tends to provide a better uniformity of treatment to a textile material. In addition, it uses far less gas, a factor that is particularly important for expensive gases such as fluorocarbons (Mather, 2009; Kwong et al., 2014). The success of these techniques is related to their ability to change the surface properties of a material by physical or chemical modification of its most external layers ($\leq 1 \mu m$), without modifying its bulk characteristics (Choudhary et al., 2018).

DC Glow discharge is the oldest type of plasma. It is produced at reduced pressure and assures the highest possible uniformly and flexibility of any plasma treatment. It is defined as a partially ionized gas containing equal volume concentrations of positively and negatively charged species with different concentrations of ground-state and excited species (Ahmed et al., 2019; Atav, 2013).

Atmospheric-pressure plasma (plasma at room temperature - cold plasma) is more appropriate for textile surface modification (Peran & Ercegović Ražić, 2020). To create a more economical, continuous, or high-speed process, a working pressure at or near 1 atm is a necessity (Ahmed et al., 2019). Cold gas plasma processes offer an efficient and reliable means to alter surface properties of all materials without affecting the bulk properties of the treated material. Challenges in atmospheric pressure plasma are: generation of glow plasma over a large surface area and in presence of liquid and gaseous precursors; carry out in-situ plasma reaction with textile substrates; achievement of durable functional finishes; carry out continuous plasma reaction. Cold plasmas can be used for various treatments such as: plasma polymerisation (gaseous monomers); grafting; deposition of polymers, chemicals and metal particles by suitable selection of gas and process parameters; plasma liquid deposition in vaporised form (Shishoo, 2007). Only cold plasmas are suitable for surface modifications of temperature sensitive textile materials. Atmospheric-pressure plasmas for textile treatment fall into several distinct categories (Mather, 2009). Traditional sources include transferred arcs, plasma torches, corona discharges, dielectric barrier discharges (DBD), atmospheric-pressure glow discharge (ATGD), and plasma jet. Recently, an atmospheric-pressure plasma jet has been developed, which exhibits many characteristics of a conventional, low-pressure glow discharge (Ahmed et al., 2019).

Other types of plasma are (Kwong et al., 2014; Shishoo, 2007; Mozetič et al., 2019; Peran & Ercegović Ražić, 2020; Gotoh et al., 2018): **plasma torch**; **corona discharge**; **dielectric barrier discharge** (DBD) or "silent discharge";

atmospheric-pressure glow discharge (APGD); plasma jet (atmospheric pressure plasma jet – APPJ).

Principle of plasma processing

An ideal plasma treatment for textile applications is a plasma system that can be introduced into the production line without major changes or system interruption, allowing for high speed and continuous processing (Chinta et al., 2012). The plasma process can be carried out in different manners (Joshi et al., 2015):

- The substrate can be treated directly in the plasma zone.
- The substrate can be positioned outside the plasma (remote process).
- The substrate can be activated in the plasma followed by a subsequent grafting.
- The substrate can be treated with a polymer solution or gas which will be fixed or polymerised by a subsequent plasma treatment.

In any textile processing application, the ionised gas will come into contact with a solid object. The atoms, molecules and radicals will arrive at the surface with a thermal distribution of energy. They react both with and on the surfaces. This principle is used for selective modification of material characteristics. Using appropriate device and power source, it is possible to generate cold or hot plasma. Hot plasmas are unsuitable for treating textiles. Cold plasmas are maintained at around room temprature, or slightly above it and it is the most commonly used physical method for a surface specific fiber modification, as it affects the surface both physically and chemically, and it can be successfully applied to textile materials (Mather, 2009; Atav, 2013).

Effects of plasma on the textile surfaces

As mentioned, the majority of successful plasma applications occurred using LPP and it is only recently that APP technologies have been developed which are considered to be more appropriate to continuous processing of textile fabrics.

Textile materials subjected to plasma treatments undergo major chemical and physical transformations including chemical changes in surface layers, changes in surface layer structure, and changes in physical properties of surface layers (Chinta et al., 2012; Kiron, 2012). The type of functionalisation imparted can be varied depending on plasma parameters. The depth of interaction and modification, however, is independent of gas type (Ahmed et al., 2019; Chinta et al., 2012). An important feature of plasma treatment is that it affects only the surface of a material subjected to treatment and a very thin near-surface layer whose thickness varies from 100 Å to several micrometers, according to different estimates. The bulk of the polymer remains intact under these conditions, retaining the mechanical, physicochemical, and electrophysical properties of the original material (Ahmed & El-Shishtawy, 2010).

Physical and chemical phenomena in plasma-assisted surface modifications are important:

- 1. Physical phenomena in plasma-assisted surface modifications are: *surface cleaning, ablation or etching / re-deposition* (Shishoo, 2007; Ahmed et al., 2019); *surface morphology and roughness changes* (Ahmed et al., 2019); *chain-scission* (Ahmed et al., 2019).
- 2. Chemical phenomena in plasma-assisted surface modifications are: modification of surface chemical structure / functionalization (Souma, 2012); radical formation (Ahmed & El-Shishtawy, 2010; Ahmed et al., 2019); grafting / surface activation (Chinta et al., 2012; Smith, 2019); oxidation; peroxide formation; polymerization / coating deposition (Sparavigna, 2008; Peran & Ercegović Ražić, 2020) (examples on textiles are: hydrophobic, hydrophilic, antibacterial, antistatic, filtration industry etc. (Chinta et al., 2012; Anand et al., 2019; Madhu, 2017)); cross-linking can result in improved mechanical properties, decreased solubility, elimination of the melting point, and increased resistance to corrosive attack, all of which are desirable.

Plasma treatment for apparel and industrial textiles

Plasma treatment can be performed on natural and man-made fibres. Plasma treatment for apparel and industrial textiles covers the following possible application fields (Höcke, 2002; Schönberger & Schäfer, 2003; Verschuren et al., 2007; LEITAT, 2009; Sun et al., 2017): pre-treatment, functionalizing, and design of surface properties of textile fibers. The potential use of plasma treatments of fibres, yarns and fabrics is for the following types of functionalisation:

enhanceing of mechanical properties (Sparavigna, 2008; Radetić et al., 2009); optical properties (Morent et al., 2008); wettability (Verscjiren, 2003; Wakida et al., 1993; Barz et al., 2019; Bai & Liu, 2010; Hala et al., 2017; Atav, 2013; Peršin et al., 2014; Ramakrishnan & Janani, 2018). hydrophobic / oleophobic finishing (Lam et al., 2012; Madhu, 2017; Zhou et al., 2019; Xu et al., 2019; Shah & Shah, 2013); adhesion; electrical properties / antistaticity (Shishoo, 2007; Shah & Shah, 2013; Sparavigna, 2008; Morshed, 2014); flame-retardant (Zhou et al., 2019; Shishoo, 2007; Madhu, 2017); anti-felting/shrink-resistance (Atav, 2013; Bhosale et al., 2013; Shah & Shah, 2013; Jhala, 2013; Madhu, 2017); wrinkle resistance / crease recovery finishing; softness (Peran & Ercegović Ražić, 2020); wear resistance (Sagbas, 2016; Mather, 2009); antimicrobial / antibacterial (Kolarova Raskova et al., 2018; Vaideki, 2016; Chinta et al., 2012; Shahidi & Ghoranneviss, 2016; Zhou et al., 2016; Vellingiri et al., 2014); other applications in biology and medicine / biocompatibility (Shishoo, 2007; Conway, 2016; Urbaniak-Domagala et al., 2016); applications in membrane and environmental technology (Morshed, 2014); sizing (Sun et al., 2013); desizing (Jhala, 2013; Shah & Shah, 2013; Lakshmanan &

Raghavendran, 2017; Kiron, 2012); *scouring* (Jhala, 2013; Chinta et al., 2012); *dyeing and printing* (Madhu, 2017; Atav, 2013; Zhang et al., 2015); *biostoning* (Chinta et al., 2012); *metal-coated organic polymers* (Tessier, 2013); *composites and laminates* (Morshed, 2014); *other properties* can be also achieved by different plasma treatments (Shah & Shah, 2013; Ramakrishnan & Janani, 2018); *product quality* (Shahidi & Ghoranneviss, 2016); *smart textile* (Sarma, 2018; Lee et al., 2015).

Advantages of plasma treatment

Although plasma treatment provides a unique opportunity for textile treatment, there are many advantages and disadvantages in comparison to the conventional wet processing of textiles (Sarmadi, 2013). Plasma technology is an environmentally friendly alternative to conventional technologies for functional finishing such as padding, the exhaustion method, printing, and coating. Plasma treatment of textiles has many advantages – environmental, economic, technical, in terms of product quality, functionality, etc. (Joshi et al., 2015; Schönberger & Schäfer, 2003; Shishoo, 2007; Sparavigna, 2008; Dowling et al., 2020; Madhu, 2017; Ahmed et al., 2019; Souma, 2012; Shah & Shah, 2013; Choudhary et al., 2018).

POTENTIAL FUTURE USES

One of the oldest and most frequent uses of plasma in the design of polymers and textiles is plasma functionalization of surfaces with the aim of improved bonding. Another application of plasma is precise functionalization for improved sensor performance for detection of hazardous molecules (gases, biomolecules, volatile organic compounds, etc.) to ensure safety in various working environments. Plasma micro- nanopatterning implies the use of plasma to produce nanostructures on a surface. A promising approach for the deposition of antibacterial coatings on industrial scale is plasma assisted polymerization (Turaga et al., 2015).

Many are predicting that plasma will be used in new ways in the near future. Typically, textiles for medical applications or uses in the sector of biotechnology are expected to increase in importance. Key future applications such as special selective filtrations, biocompatibility, and growing of biological tissues, would be interesting fields for plasma physics. One potential use is the destruction of toxic waste, including textile industry (Sparavigna, 2008). The plausible future development would be focused toward the design of integrating the plasma and antimicrobial finish treatment units to realize bulk production (Vaideki, 2016). The future grand challenges of plastic and textiles are (Cvelbar et al., 2019): developing enabling technology for plasma sources and processes; design of smart surfaces on polymers and textiles; design of complex surface coatings including those with

macromolecules and nanomaterials; design of new advanced materials and structures (to be constructed).

Conclusion

Textile industry is interested with processing technologies that save time, water, energy and chemicals, minimiz costs, that are more environmental friendly and not harmful to human health. Application of plasma technology can fulfill all the demands of the textile industry. Plasma is a dry, environmentally friendly alternative to various conventional solvent-based chemical surface treatment methods. This technology offers many attractive advantages and involves no hazardous chemicals, or effluents in its process. It is used to treat the fabric surface in order to provide functional abilities to the fabric. Its application can be widely used in medical textiles, protective clothing, building, geotextiles and other relevant industries.

The plasma application to textile improves fabric preparation, dyeing, printing and finishing of natural and synthetic fibre fabrics. It is a versatile technology to chemically and physically modify the surface of materials, allows modification in the nm - range. Plasma technology is used to achieve new or improved properties to textiles.

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PRIMENA PLAZME ZA DORADU TEKSTILA

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Sažetak

Dorada tekstila se primenjuje da bi se postigli željeni efekti na tekstilnim materijalima i proizveli tekstilni proizvodi prema zahtevima tržišta. Doradom se mogu modifikovati izgled i opip tekstilnog materijala i poboljšati njegove performanse. Tradicionalni procesi mokre obrade tekstila, zasnovani na primeni hemikalija, koriste velike količine vode i energije i generišu velike količine otpadnih voda, što značajno povećava ekološki otisak tekstila (*"footprint"*). Rastuća zabrinutost za okolinu i napori da se uštedi energija uslovili su brojna istraživanja u cilju zamene mnogih mokrih procesa dorade procesima sa malom potrošnjom vode i suvom doradom. Jedan od specijalizovanih postupaka dorade za postizanje željenih funkcionalnih svojstava tekstila, u kojima nema štetnih supstanci, mokrih procesa/otpadnih voda i mehaničkih štetnosti po tekstilni materijal koji se tretira, je i obrada plazmom.

U radu su obrađene tehnike primene plazme pogodne za obradu tekstila, funkcionalnosti koje se postižu ovom obradom, kao i prednosti primene plazme kao jedinstvenog efikasnog inženjerskog alata za funkcionalizaciju/poboljšanje površinskih svojstava tekstilnih materijala.

Ključne riječi: tekstilni materijali, dorada tekstila, tehnologija plazme.

Informative article

ULTRASOUND PROCESSING OF TEXTILE

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Abstract

There are many potential advantages of using ultrasound in wet processing of the textile. Ultrasound, with a frequency above the upper limit of human hearing, has been widely explored as a means of intensifying various wet processes for textile processing, including desizing, scouring, bleaching, dyeing, printing and finishing, as well as nanoprocesses (nanopretreatment, nanodyeing, nanoprinting and nanofinishing). Ultrasonic energy is used for development of diferent processes in the textile industry, which are environmentally friendly technologies with saving of energy, chemicals, water and time, including less generation of wastewater and solid waste, compared to classical processes. Also, introducing ultrasonic energy without affecting the properties of textile. All this increases the competitiveness of the textile industry.

In this paper are presented various possibilities of ultrasound application in the textiles area, especially recent developments in ultrasonic processing of textile.

Keywords: textile materials, textile finishing, ultrasound processing.

Introduction

Textiles, and their end products, constitute the world's second largest industry. Current wet textile processes suffer from two major drawbacks: large process time and low energy efficiency. Textile processes usually consume a lot of energy, water, and different chemicals. Despite over 100 years of process improvements, the pre-treatments, dyeing, and finishing of textiles continue to utilize large volumes of clean water and generate large amounts of wastewater (Vajnhandl & Le Marechal, 2005).

In recent years, the textile industry has been forced to develop new technologies to reduce energy and water consumption. The use of ultrasound in textile wet processing is one solution to this problem. The chemical and physical effects of ultrasound with a frequency above 16 kHz, higher than the audible frequency of the

human ear, have proven to be a useful tool for variety of systems ranging from the application of ultrasound in environmental remediation to the cooperation of ultrasound waves with chemical processing regarding as sonochemistry (Harifi & Montazer, 2015). As an alternative to the conventional methods, it accelerates mass transfer in textile materials and offers the potential for shorter reaction cycles (intensifying the reaction rate /reducing processing time; decreasing the processing steps), cheaper reagents, and less extreme physical conditions, leading to less expensive and smaller plants. Also, this advanced techniquecontributes to reducing water, energy and chemicals consumption, reducing environmental impact, improving the product quality and process enhancement in textile wet treatments (Parvinzadeh et al., 2010; Canoğlu & Yükseloğlu, 2017; Ranjbar-Mohammadi et al., 2013; Pan et al., 2019; Li et al., 2012).

The first step in introduction of acoustic cavitation was made in 1895 progressed with the advent of ultrasound as a means of reaction rate accelerator in 1927. It was then turned to degradation of synthetic polymers, free radical formation, ultrasonic cleaning, and ultrasonic physical aspects reaching to the foundation of sonochemistry group in 1987, facilitating the use of ultrasound in industry (Harifi & Montazer, 2015). During the last fifteen years the interest in ultrasonic processing has revived particularly in industrial sectors where the ultrasonic technology may represent a clean and efficient tool to improve classical existing processes or an innovation alternative for the development of new processes (Gallego-Juarez, 2010). In the last 100 years, ultrasound has had the potential for use in different textile areas including cleaning, desizing, degumming, bleaching, dyeing, printing, nanoparticles synthesis and waste water treatment. Textile sonoprocessing will contribute to the future of textile industry as a cleaner technology(Harifi & Montazer, 2015).

Power ultrasound potential

The potential of power ultrasound involves physical and chemical processes – power ultrasound can enhance a wide variety of chemical and physical processes. Physical processes are mainly ascribed to mechanical effects of the high-intensity waves in any medium while chemical processes refer to chemical effects induced by ultrasonic cavitation in liquids (sonochemistry). The general term for the whole area is sonoprocessing or ultrasonic processing (Gallego-Juarez, 2010). The chemical and biological effects of ultrasound were first reported by Loomis as early as 1927 (Vajnhandl & Le Marechal, 2005; Ahmed &EI-Shishtawy, 2010). Ultrasound, a cyclic sound pressure, spans the frequencies of roughly 18 kHz to500 MHz beyond human hearing, require a medium with elastic properties for propagationand not absorbed by molecules (Karaboğa et al., 2007; Li et al., 2012; Ranjbar-Mohammadi et al., 2013; Niaz et al., 2011; Harifi & Montazer, 2015; Burkinshawa & Jeong, 2012-I). When ultrasound passes through a liquid it

induces vibrational motions of the intermolecular bonds, and energy is thus transferred through the medium in the propagational direction (Vajnhandl & Le Marechal, 2005; Ahmed &El-Shishtawy, 2010). In liquid, these high-frequency waves produce microscopic bubbles or cavitations that result in heating of the liquid. With collapsing cavitational bubbles produced by ultrasound in the liquid, tiny but powerful shock waves are generated (Ranjbar-Mohammadi et al., 2013). The bubbles repeatedly expand and contract according to the pressure oscillation of an ultrasonic wave, but some bubbles collapse violently at the contraction phase of an ultrasonic wave. The dynamics of cavity growth and collapse depend on the local environment: properties of the solvent - type and purity of the liquid, properties of gases, external pressure, frequency of the sound wave (Vajnhandl & Le Marechal, 2005). The violent collapse of bubbles in less than a microsecond releases extreme heat, forming short-lived "hot spots", i.e., localized high temperature, high pressure, shock waves, microjets, and severe shear force capable of breaking chemical bonds (Ahmed &El-Shishtawy, 2010). Accelerating chemical reactions(also radical reactions), enhancing mass transfer, higher efficiency of the catalyst, generation of useful reactive species, shortening reaction cycles, improving reaction yield, altering reaction pathway, reduction of the reaction steps, increasing surface area between the reactants, accelerating dissolution, and improving the quality of the final product are some of the ultrasound effects (Harifi & Montazer, 2015; Karaboğa et al., 2007; Niaz et al., 2011; Gallego-Juarez, 2010; Vajnhandl & Le Marechal, 2005).

Microscopic cavitation bubbles cause a mechanical movement effective on the liquid/solid interface in the form of strong shock waves. The effect of cavitation in heterogeneous systems is hundreds of times more than homogeneous ones. The maximum effect of cavitation in water is seen at 49 °C. This temperature is also optimum for most of enzymatic processes. The most important point is that shock waves in ultrasound do not inactivate the enzyme. The diffusion of enzyme onto the fibre surface increases as long as it does not affect the activation (Karaboğa et al., 2007).

Areas of ultrasound application

Ultrasound waves are being successfully used in many industrial and medical fields and it is only natural that this form of energy may find application in the textile industry(Niaz et al., 2011). High-power ultrasound is a technology that offers several important possibilities to act as an efficient tool in processes for preventing or removing pollution. Applications in air cleaning, water purification, treatment of sludges, soil remediation and new sonochemical "green" processes, without hazardous substances, have strongly increased over the last few years (Gallego-Juarez, 2010).

Ultrasound application in textile

There are many reports from the 1950s and 1960s describing the beneficial effects of ultrasound in textile wet processes (Vajnhandl & Le Marechal, 2005). Use of ultrasound in the textile wet processing has been found to have some advantages as it alters the fibre structure to increase adsorption and also raises diffusion coefficient of the chemical molecules and the dye particles in the aqueous solutions (Niaz et al., 2011; Carr et al., 1995).

The role of ultrasound in the various textile applications is different classified into two categories: removing of materials/impurities from the surface of textiles (mostly in sonopreparation process) and diffusion and insertion of dye molecules/chemicals and nanoparticles into fibers (sonodyeing/sonoprinting and sonofinishing) (Harifi & Montazer, 2015).

As mentioned, ultrasound has been introduced to textile wet processing as a promising tool for reducing the operation time, energy and chemicals consumption and enhancing the quality of the products. It was followed by using the dispersing action of ultrasound for preparation of pre-treatment baths such as rapid preparation of starch sizing at low temperature, formation of long-time stable homogenous emulsions, dye dispersions and thickeners for print paste. The use of ultrasound for removing impurities from surface of the fibers and enhancing diffusion of dyes or chemicals into the fabrics was the next approach, whereas other investigations led to application of ultrasound in the textile wastewater remediation by the formation of oxidizing species. High intense ultrasound has been exploited for the synthesis of novel nanomaterials, ceramic and polymeric surfaces. Sonochemical technique has been also developed for the synthesis and deposition of nanoparticles on different textile substrates. Over the past years there has been an enormous effort on using sonochemistry for the synthesis of nanomaterials on various textile materials (Harifi & Montazer, 2015).

The ultrasonic energy has been adapted to textiles in wet finishing processes, almost the past twenty years (Canoğlu & Yükseloğlu, 2017). Recently, considerable efforts have been devoted on the application of ultrasonic waves in different textile wet processing, including desizing, scouring (especially enzymatic scouring) and bleaching of natural textiles, dyeing and printing of natural as well as synthetic fibers andfinishing and also nanoprocessing including nanopretreatment, nanodyeing, nanoprinting and nanofinishing, and dye effluent decolorization, since it increases the mass transfer effect. The efficiency of the wet finishing process is increased by raising the mass transfer towards to the inner parts of the textile material (Parvinzadeh et al., 2010; Karaboğa et al., 2007; Harifi & Montazer, 2015; Parvinzadeh, 2009). Better desizing and relatively higher absorbency and whiteness in scouring and bleaching are realised under the influence of ultrasound (Niaz et al., 2011).

The application of ultrasound has a special significance in the wet processesing of cotton and wool.Ultrasound allows for process acceleration and attainment of the same or better results than existing techniques under less extreme conditions, i.e., lower temperature and lower chemical concentrations. Textile wet processes assisted by ultrasound are of high interest for the textile industry for this reason. The intensification and acceleration of mass transport, particularly in the intrayarn pores, are the basis for the improvement of wet textile processes (Vajnhandl & Le Marechal, 2005).

Ultrasound pre-treatment – The effect of ultrasound on improving the transport of molecules by the local turbulence created under acoustic cavitation has been used for more efficient desizing with enzymes (Harifi & Montazer, 2015). Ultrasonic energy decreases processing times significantly too. The presence of ultrasound in the processing medium increases the effect of amylase enzyme by giving the enzymatic solution a mechanical movement and thus supporting mass (enzyme molecules) transfer into the fibre. When ultrasound is applied in desizing, realized with amylase enzyme or the scouring process performed with pectinase enzyme, the desizing degree and fabric wettability are distinctively higher than the processing without ultrasound and can be achieved in short processing times, with enzyme saving (Parvinzadeh et al., 2010; Karaboğa et al., 2007).

The interest in ultrasound micro-agitation as a cleaning technique helping the displacement of surface contaminants is back to 1954 (Harifi & Montazer, 2015). The new procedure was developed in which the textiles are exposed to the ultrasonic field in flat format and within a thin layer of liquid by applying specific plate transducers. Such process has been implemented at semi-industrial stage (Gallego-Juarez, 2010). Ultrasonic cleaning will be used in the overall cleaning of foreign matters on textile material and, combined with enzymes; ultrasound will remove the disadvantage of enzymes whose moving ability is low due to their large molecules and facilitate the realisation of the effect required from an enzyme (Karaboğa et al., 2007).

The cleaning process of laundry is synergistic actions between the mechanical, chemical, and thermal energy and time. The ultrasonic washing method has many compared conventional the washing advantages when to method. including:improved product quality /superior cleaning properties, reduction in process time, energy, water and chemicals consumption and less waste generation. Also, ultrasonic agitation produces less fiber migrations (Canoğlu & Yükseloğlu, 2017; Arikan et al., 2018; Harifi & Montazer, 2015). Ultrasonic energy generates millions of bubbles or cavities into the liquid with very high frequency which constantly strike at the target material surface and as a result, remove dirt off the fibers (Uzun, 2013; Choi et al., 2016; Gallego-Juarez et al., 2010; Karaboğa et al., 2007; Vajnhandl & Le Marechal, 2005).

For this reason, ultrasonic energy can be an alternative to conventional washing methods. For example, ultrasonic washing can present slightly higher mechanical properties than the conventional washing of the cotton yarns, and ultrasonically washed fabrics have better pilling values than the conventionally washed fabrics (Canoğlu & Yükseloğlu, 2017). Ultrasonic pretreatment can be applied in raw wool scouring and fabric scouring to achieve an efficient dye uptake (Pan et al., 2019). Wool scoured with ultrasonics has less fibre felting hence the subsequent top making process and product yield can be improved (Li et al., 2012). Ultrasound laundering was effective in stain removal from silk fabrics with less dimensional shrinkage, wrinkled appearance and tensile loss (Harifi & Montazer, 2015). The ultrasonically washed fabrics have higher thermal conductivities and considerably higher heat loss value than the conventionally washed fabrics (Uzun, 2013).

The treatment of fabrics with softeners in an ultrasound bath is more effective compared to conventional methods and that it enhances the physical properties of the cotton.Use of biocatalysts for desizing, scouring and bleaching of cotton by ultrasonic energy as a mechanical catalyst accelerates the mass transfer resulting in saveing water and energy consumption (Parvinzadeh, 2009; Parvinzadeh et al., 2010). The use of ultrasonic for accelerating the chemical and physical processes of wool has gained high importance (Ranjbar-Mohammadi et al., 2013). Ultrasonic agitation can be used as a method for chlorination and it reduces felting and area shrinkage during the laundering of wool fabric (Parvinzadeh, 2009).

The synergistic effect of biocatalyst and sonication intensifies the fabric whiteness comparing with conventional peroxide bleaching. More enzyme diffusion to the interior of the yarns and formation of reactive transient species as a result of cavitation regarded as the reasons for the superiority of laccase/ultrasound-aided bleaching system. Ecofriendly laccase–hydrogen peroxide/ultrasound-assisted bleaching of linen fabrics was also introduced as an alternative to conventional bleaching process causing less fiber damage and more uniform treatment. The main advantages of sonochemical cavitation reactors for laccase/hydrogen peroxide cotton bleaching were energy saving by lowering hydrogen peroxide, laccase, temperature and time accompanied with lower environmental impact (Harifi & Montazer, 2015). In some studies, the utility of ultrasonic methods has been considered in regards of the dyeability properties of bleached cotton yarns and woven fabrics (Canoğlu & Yükseloğlu, 2017). Ultrasound pre-treatment can increase the effectiveness of subsequent oxidative-reductive bleaching of wool (Li et al., 2012).

Dyeing/Printing – Improvements observed in ultrasound-assisted dyeing processes are generally attributed to cavitation phenomena and, as a consequence, other mechanical and chemical effects are produced, such as (Ahmed &El-Shishtawy, 2010; Karaboğa et al., 2007; Carr et al., 1995; Harifi & Montazer, 2015; Niaz et al., 2011; Parvinzadeh et al., 2010; Vajnhandl & Le Marechal, 2005):

- dispersion disintegration of aggregates of the dye particles into smaller units or in the molecular forms;
- degassing expulsion of dissolved or entrapped air from fiber capillaries;
- diffusion improvement in the movement of dye molecules to fibre surface andaccelerating the rate of diffusion of dye inside the fiber (coloration rate)/ increase in the diffusion coefficient of the dye molecules;
- increase in the fibre/dye partition coefficient.
- intense agitation of the liquid destruction of the diffusion layer at dye/fiber interfaces and increasing the area of the fiber–liquid interface which improves dyeing ability;
- generation of free radicals;
- dilation of polymeric amorphous regions (decreasing of crystallinity);
- increase in the swelling of fibres in water;
- decrease in the glass transition temperature of the fibre.

Therefore, the application of ultrasound in dyeing all types of fibers (cotton, silk, wool, synthetic fibers) with all classes of dyes shows significant advantages over conventional procedures (Vankar & Shanker, 2008; Burkinshawa & Jeong, 2012-I; Burkinshawa & Jeong, 2012-II; Ranjbar-Mohammadi et al., 2013; Adeel et al., 2017; Li et al., 2012; Canoğlu & Yükseloğlu, 2017; Yükseloğlu & Bolat, 2010; Pan et al., 2019):

- environmental benefits ecofriendly ultrasonic textile dyeing better dyeuptake and less auxiliary consumption resulting in less chemicals remaining in bath leading to less effluent to the environment; reduced energy consuption;
- efficiency; shorter processing time greatly reduced dyeing time; lower overall processing costs, thereby increasing industry competitiveness;
- decreases in activation energies;
- enhanced dye uptake, higher color strengthwithout harming the physical characteristics of fabric, enhanced exhaustion and dye fixation – enhanced effect after equilibrium coloration, increases in coloration rate;
- process enhancement by allowing real-time control of color shade;
- reduced concentration of dyes in the dyes-bath;
- reduced auxiliaries' consumption dyeing at lower salt levels, reduced alkali consumption, avoiding the use of auxiliary agents, etc.;
- reduced dyeing temperature;
- decrease in the glass transition temperature of fibers;
- improved the dyeing properties mproved wash-fastness and light-fastness; there was no apparent fibre damage caused by cavitation.

<u>Finishing</u> – There are many studies on the use of ultrasound in textile finishing processes. Introducing ultrasonic energy during enzymatic treatment of cotton fabric significantly improves enzyme efficiency without affecting the strength of

the fabric (Karaboğa et al., 2007). Ultrasound energy led to more efficient coating of the softener layer on the cotton fiber surface. Overall, the ultrasound-assisted reactions in textile finishing improve the finish add-on and accelerate the rates of textile finishing (Canoğlu & Yükseloğlu, 2017). The efficiency of wet finishing processes is increased by increasing the mass transfer toward the inner parts of the textile material. This ultrasonic technique offers fabrics with antibacterial properties (Ranjbar-Mohammadi et al., 2013). The softener treatment of fabrics with ultrasonic energy is more effective, and it enhances the physical properties of cotton. It uses less softener, improves the drapeability, crease resistance and softness of fabrics resulting to decrease the bending length and friction coefficient, and causes a decrease of moisture regain (Parvinzadeh, 2009).

Ultrasonic agitation can be used as a method for chlorination and it reduces felting and area shrinkage during the laundering of wool fabrics (Parvinzadeh et al., 2010). Ultrasound can remarkably speed up the scale-peeling process and greatly improve the shrinkage of wool fabrics. Moreover, the weight loss and strength reduction are within acceptable limits. Therefore, ultrasound became a beneficial means for wool anti-felting treatment in enzymatic process, for shorter time and at lower temperature (Liu et al., 2011). As a result of the ultrasonic treatment during defined time, wool protein chains in the macro fibrils are rearranged to a more regular and less flexible structure, with increased tenacity and reduced extensibility, less mass loss and a higher thermal degradation temperature. Also, the appropriate treatment can provide wool with increased water absorption (Li et al., 2012).

Using ultrasonic is a friendly environment method for grafting chitosan onto wool with enhanced dye ability and reduced shrinkage properties. Ultrasonic treatment decreases the molecular weight and enhances antibacterial activity of chitosan. Useful properties of this polysacharide such as nontoxicity, biodegradability, biocompatibility, chemical reactivity, antimicrobial activity, film-forming ability, and producing polycation in acidic water solution for binding with other polymers make it an acceptable substitute for synthetic polymers in textile finishing. Also, the chitosan pretreatment of wool reduces the damage caused by the subsequent enzymatic treatment with proteolytic enzymes (Ranjbar-Mohammadi et al., 2013).

Ultrasound is applied to finishing other fibers as well. The ultrasound/hydrogen peroxide surface-modified PGA (polyglycolic acid) monofilaments may have great potential for improving hydrophilicity and cytocompatibility. They may provide a good alternative for use as acupoint catgut embedding therapy material (Fu et al., 2019).

Different finishing processes ultrasound-assistedare applied.

<u>**Coating**</u> – Widely used an ultrasonic debubbling of liquid coating layers. High debubbling efficiency was obtained for all bubble sizes with the water based application while the effect was more selective for the solvent based application where a strong influence of the bubble size was observed (Gallego-Juarez, 2010).

<u>Nano sonofinishing</u> – Plenty works have been done on using high intensity ultrasound for the preparation or modification of a wide range of nanomaterials, especially for synthesis of different nanoparticles for imparting multi-functional properties on textiles including self-cleaning, water repellency, flame retardancy and antibacterial properties. Advantages of in situ sonosynthesis of nanoparticles on textiles are: reduced time, reduced temperature, smaller nanoparticies, high durability, low toxicity, and impact on other textile properties Physical attachment of nanoparticles occurs as a result of sonication that is independent of the nature of the textile material (Harifi & Montazer, 2015).

Other applications of ultrasound in textiles are also important:

- <u>Ultrasonic aided-extraction procedures</u> apply for constituent analysis of the substances or chemicals on textiles and are superior to conventional methods (Harifi & Montazer, 2015).
- <u>Pin sonic process</u> one of the early uses of ultrasonic bonding in textiles in manufacturing of mattress pads and bedspreads (Seram & Cabon, 2013).
- <u>Ultrasonic welding</u> is identified as an alternative method of joining waterproof, breathable synthetic materials only for straight seams in outdoor apparels, which offer many advantages over traditional sewing. It is an important tool for sealing, welding, bonding and cutting and slitting without heat, adhesive or consumabless. It eliminates needle punches and problems related to thread breakages and colour matching and thread un-raveling and no threat of thread deterioration over time. Fiber degradation is minimized because heat energy is generated within the fibers using ultrasonic energy at the point of the joint site. Moreover, the absence of heating elements, or the need for cooling and extremely low tooling costs make this process very cost effective when compared to other joining methods (Seram & Cabon, 2013; Gallego-Juarez, 2010). The main advantages are: short welding times, simple technique, and consistent performance when welding parameters are optimized, clean process, minimal thermal damage to fibers, no adhesive use, fabrics are not exposed to heat - safe process, no cooling phase is needed, and lower energy cost compared to the thermal bonding (Ahmed &El-Shishtawy, 2010). Some shortcomings of ultrasonic sewing were also observed (Jevšnik et al., 2015).
- Decolorization of textile effluents takes place using a combination of ultrasound and electro-oxidation methods (Parvinzadeh et al., 2010; Parvinzadeh, 2009). This process works on the principle of generating free radicals and their subsequent attack on the contaminant molecules with the aim of either, completely mineralizing the contaminants or converting it into less harmful or lower chain compounds which can then be treated biologically (Vajnhandl & Le Marechal, 2005; Harifi & Montazer, 2015). Ultrasonication has been effectively applied even on non-nanomaterials for dye adsorption process. The removal of dye is enhanced by ultrasonic radiation and high

temperature which increase the adsorption rate (Rajumon et al., 2019; Ibrahim et al., 2018; Jaafarzadeh et al., 2018).

Difficulties in the use of ultrasound in the textile industry

Ultrasound application in textile industry is limited. One of the main difficulties in the use of ultrasound in the textile industry is the development of scale-up strategies from laboratory to the industrial scale. The first steps in scaling up the process are burden with high operating costs. However, the processing cost may be off-set by the promising advantages of ultrasound that can bring to textile industry. The obstacle toward industrialization of ultrasound is the effect of acoustic cavitation on erosion damage. Ultrasound may cause potential degradation of softeners leading to more toxic compounds. This has to be taken into account in order to prevent a harmful environmental impact (Parvinzadeh et al., 2010; Parvinzadeh, 2009; Harifi & Montazer, 2015).

Conclusion

The textile industry must go towards developing of new technologies to reduce the energy, water and chemicals consumption, and wastewater generation. The use of ultrasound in textil wet processing is one way for this purpose. The importance of these environmentally-friendly techniques is increasing, as the industry tends to use ecological processes more and more because of the necessity to comply with certain compulsory measures and also to achieve environmental standards. Also, all wet textile processes ultrasound-assisted yielded more effective results than the classical methods, and it was found to be economical. Ultrasound can bring grate advantages to textile industry, such as acceleration in process rate, increase in productivity and the level of product quality while reducing pollution. Furthermore, process optimization possibly leads to a considerable saving in overall cost of the process and for any sonochemical process there is an optimum power for maximum effect. It is expected that the textile industry will benefit more from the ultrasonic energy on a commercial scale.

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OBRADA TEKSTILA ULTRAZVUKOM

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Sažetak

Postoje brojne potencijalne prednosti primene ultrazvuka u mokroj obradi tekstila. Ultrazvuk, sa frekvencijom iznad gornje granice ljudskog sluha, široko je istraživan kao sredstvo za intenziviranje različitih mokrih procesa obrade tekstila, uključujući uklanjanje šlihte, iskuvavanje, beljenje, bojenje, štampanje i doradu, kao i nanoprocese (nano prethodna obrada, nano bojenje, nano štampanje and nano dorada). Energija ultrazvuka koristi se za razvoj različitih procesa u tekstilnoj industriji, a to su ekološki prihvatljive tehnologije sa uštedom energije, hemikalija, vode i vremena, uključujući manje stvaranje otpadnih voda i čvrstog otpada, u poređenju sa klasičnim procesima. Takođe, uvođenje energije ultrazvuka tokom nekih tretmana tekstila značajno poboljšava efikasnost procesa bez uticaja na svojstva tekstila. Sve to povećava konkurentnost tekstilne industrije.

U ovom radu prikazane su različite mogućnosti primene ultrazvuka u oblasti tekstila, posebno najnovija dostignuća u ultrazvučnoj obradi tekstila.

Ključne riječi: tekstilni materijali, dorada tekstila, tehnologija plazme.

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GRAPHIC TECHNOLOGY AND DESIGN

Professional paper

TRENDS IN GRAVURE PRINTING

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Abstract

Printed products can be divided in three main categories: publication, commercial printing and packaging. Packaging group is growing consistently. Publication volumes and value are declining significantly, because there are alternative media versions of some traditional print products. For example, E-books, online, electronic and social media are direct replacements for print product. Commercial printing shows a decline to 2015 with volume static to 2020 and a small rise in value. One of the major processes in print market is gravure printing. Gravure printing is mainly used for high-volume publication and for packaging production. The aim of this paper is to present the current state of the market and predictions of gravure printing techniques future direction on major geographic market.

Keywords: gravure printing, trends

Introduction

Printed products can be divided in three main categories: publication, commercial printing and packaging (Kašiković, et al., 2016b). Publication group includes newspapers, magazines, books, directories and catalogues. Commercial printing includes photo products, advertising, business forms and ID, promotional, security, transactional and general commercial print products while Packaging group contains labels, cartons, corrugated, flexible, rigid plastics and metal printing.

Packaging group is growing consistently (Kašiković, et al., 2016a). Publication volumes and value are declining significantly, because there are alternative media versions of some traditional print products, with e-books, online, electronic and social media; some are direct replacements for print product. Commercial printing shows a decline to 2015 with volume static to 2020 and a small rise in value (Smith, 2017).

The major processes in print market are offset litho (sheetfed, heatset web and coldset web), flexography, gravure, screen, letterpress, electrophotography, ink jet and others (intaglio, indirect gravure (pad printing), dry offset, foiling).

The aim of this paper is to present the current state of the market and to present predictions of gravure printing techniques future direction on major geographic

market. Geographic market is divided on: Western Europe (France, Germany, Italy, the Netherlands, Spain, the UK and other West European countries), North America (USA and Canada), Latin America (Brazil, Mexico and other Latin American countries), Asia (China, India, Japan, South Korea and other Asian countries), Eastern Europe (the Czech Republic, Poland, Russia and other East European countries), Middle East (Turkey and other Middle Eastern nations), Africa and Australia (include all Oceania countries). All those markets are use in this research.

Gravure printing

Gravure printing is one of the oldest printing technologies; its beginning dates back to the early fifteenth century (Szentgyorgyvolgyi, 2016). It is used in highcirculation, high-quality printed products such as plastic films; metal foils; transparent films, carrier bags; security papers, stamps, bank notes (Kiphan, 2001). As run lengths fall, gravure is less widely used in high run publication rotogravure, despite developments to reduce the time and cost of print cylinder production, but it is still growing in packaging and label printing (Smith, 2017). Serrated or jagged edge on letters and lines, good image reproduction, with variable-depth gravure printing, square screen dots of the same size are present in all tone values are typical features of this printing techniques (Kiphan, 2001).

In table 1, we can see gravure printing output by geographic market 2012 - 2022 (\$ million, constant 2016 prices and exchange rates). It has increased by a small amount from \$64.3 billion in 2012 to \$64.4 billion in 2017 and it will rise to \$66.0 billion by 2022.

	2012	2016	2017	CAGR (%) 2012-17	2018	2022	CAGR (%) 2017-22
Western Europe	13314.20	11313.50	11064.20	-3.60	10879.80	10260.30	-1.50
North America	15735.20	14949.80	14491.40	-1.60	14074.90	12931.10	-2.30
Asia	28597.20	31416.40	32463.40	2.60	34207.10	36828.00	2.60
Latin America	3833.90	3527.30	3476.10	-1.90	3379.40	3150.50	-1.90
Eastern Europe	725.80	688.40	690.40	-1.00	701.50	748.30	1.60
Middle East	1116.80	1248.70	1253.20	2.30	1261.20	1262.80	0.20
Africa	254.10	252.80	252.20	-0.20	247.20	237.00	-1.20
Australia	797.70	748.90	729.30	-1.80	710.00	624.40	-3.10
Total	64374.90	64145.80	64420.20	0.00	65461.10	66042.50	0.50

Table 1. Gravure printing output by geographic market 2012 - 2022 (\$ million, constant 2016 prices and exchange rates) (Smith, 2017)

The best market for gravure printing is Asia. Asia was leader in 2012, 2017 and it will be the best market in 2022 with 56 % print values. The biggest CAGR (Compound annual growth rate) in 2012-2017 and 2017-2022 is in Asia (2.60 %). This is expected, because Asia has 4.5 billion inhabitants (as of June 2019) and constitutes roughly 60% of the world's population, more than all other continents combined. North America is second biggest market although we can see decrease in gravure printing value from 23 to 20% in period 2017-2022 (CAGR will be - 2,30 %). Western Europe in on third place, Latin America is fourth etc. The smallest market for gravure printing is Africa and Australia. Both of markets have negative CAGR. Positive CAGR value in period 2017-2022 have Eastern Europe (1,60 %) and Middle East (0,20%).

In Figure 2 we can see gravure printing output by six most important countries in period 2017-2022 (\$ million, constant 2016 prices and exchange rates). The biggest printing value in both cases are in Japan. In that country gravure printing dominates because quality-conscious Japanese packaging converters were not able to print the quality demanded using flexographic printing, particularly for kanji text characters before durable plates were introduced (Smith, 2017). United states of America are in second place, although both of these countries have decrease in printing value. Decrease in printing values are expected in Germany, while increase in printing value will happen in China, India as well as South Korea.

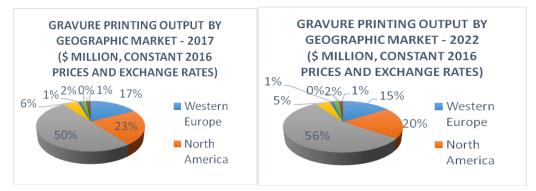


Figure 1. Gravure printing output by geographic market in 2017 – left side and in 2022 – right side (\$ million, constant 2016 prices and exchange rates)

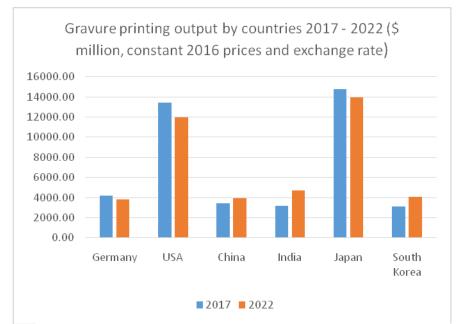


Figure 2. Gravure printing output by countries in 2017-2022 (\$ million, constant 2016 prices and exchange rates)

Over 2012-2022 period print volumes will grow from 3.8 trillion A4s to 4.2 trillion, largely through growth in packaging (Table 2). In 2017, 49 % gravure printing runs were printed in Asia. That percent will grow to 56% in 2022 with 4,30% CAGR. Positive CAGR will be in Latin America, Eastern Europe, Middle East and Africa. Western Europe will have decrease from 22% to 17% (-2.50 % CAGR). Decrease will be also in North America (17% to 14 %, -2.30 % CAGR) and in Australia (-1.40 % CAGR).

In Figure 4, we can see that the biggest gravure circulations are in China, while USA was in second place in 2017, with a declining tendency. In 2022, Japan will be in second place and Germany is today in fourth place where it will be also in 2022. If we compare, figure 2 and figure 4, we can conclude that price per runs is bigger in richer countries than in China or India.

Table 2. Gravure printing output by geographic market 2012 - 2022 (million A4 prints)(Smith, 2017)

	2012	2016	2017	CAGR (%) 2012- 17	2018	2022	CAGR (%) 2017-22
Western Europe	1119174.00	863105.00	832643.00	-5.70	811739.00	732452.00	-2.50
North America	741441.00	688047.00	665672.00	-2.10	649611.00	591794.00	-2.30

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Asia	1472815.00	1820654.00	1909066.00	5.30	2014938.00	2358585.00	4.30
Latin America	154222.00	156121.00	156035.00	0.20	159782.00	168222.00	1.50
Eastern Europe	82186.00	83697.00	85370.00	0.80	87981.00	98342.00	2.90
Middle East	118985.00	143604.00	150004.00	4.70	157378.00	184216.00	4.20
Africa	35199.00	39036.00	40230.00	2.70	41023.00	42120.00	0.90
Australia	49250.00	53606.00	53573.00	1.70	53362.00	50045.00	-1.40
Total	3773273.00	3847870.00	3892592.00	0.60	3975813.00	4225777.00	1.70

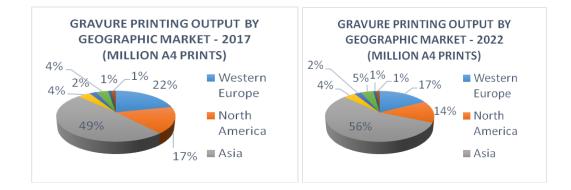


Figure 3. Gravure printing output by geographic market in 2017 – left side and in 2022 – right side (million A4 prints)

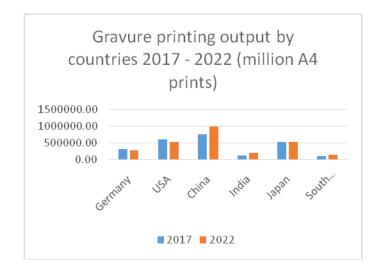


Figure 4. Gravure printing output by countries in 2017-2022 (million A4 prints)

The print market is segmented into 11 product sectors: books, magazines, newspapers, catalogues, directories, advertising print (inserts, direct mail, point-of-sale and posters), commercial print (leaflets, folders, business stationery, business forms, newsletters and manuals), security print (currency, cheques, tickets, passports, identity and plastic cards, licences), transactional print (mailed items expected by the recipient, bills, statements), labels (wet glue, tags, self-adhesives, in-mould, stretch and shrink sleeves) and packaging (including cartons, corrugated, flexible packaging, rigid plastics and metal packaging) (Smith, 2017).

It is interesting to see global gravure printing market by product type 2012 - 2022 (table 3 and table 4).

In table 3 it is shown printing value 2012 - 2022, while in table 4 you can number of prints.

	2012	2016	2017	CAGR (%) 2012-17	2018	2022	CAGR (%) 2017-22
Books	566.60	463.00	428.40	-5.40	394.00	254.50	-9.90
Magazines	12215.70	10633.90	10180.30	-3.60	9745.10	8213.10	-4.20
Newspapers	40.10	7.70	2.10	-44.70	1.80	0.80	-16.40
Advertising	4011.30	2979.60	2754.00	-7.20	2555.40	1941.10	-6.80
Catalogues	927.40	829.90	796.50	-3.00	790.90	704.80	-2.40
Commercial	1001.50	903.20	878.30	-2.60	870.90	761.80	-2.80
Directories	606.20	429.20	389.40	-8.50	356.00	261.20	-7.70
Security	908.00	659.40	607.90	-7.70	541.10	378.70	-9.00
Transactional print	0.00	0.00	0.00	n/a	0.00	0.00	n/a
Packaging	40358.60	42783.60	43765.70	1.60	45468.00	48038.00	1.90
Labels	3739.70	4456.40	4617.80	4.30	4737.90	5488.50	3.50
Total	64374.90	64145.80	64420.20	0.00	65461.10	66042.50	0.50

Table 3. Global gravure printing market by product type 2012 – 2022 (\$ million, constant 2016 prices and exchange rates) (Smith, 2017)



Figure 5. Global gravure printing market by product type in 2017 – left side and in 2022 – right side (\$ million, constant 2016 prices and exchange rates)

Gravure printing is still growing in packaging and label printing. In 2017 68% print values were in packaging, while in 2022 it will be 73 % (1.90 % CAGR). Label has 3.50 % CAGR in period 2017-2022. All others product has negative CAGR.

In Figure 6, we can see that packaging runs have positive CAGR 3.8 % and increase from 47% (2017) to 52% in 2022. Runs are growing also in labels and security products. 5.8 % is CAGR in period 2017 to 2022 in labels production, while in security production CAGR is also positive, but it is not so high (3.50 %).

Many magazines are still printed with gravure printing. In 2017, 33% prints in gravure printing were magazines runs (16 % values). That percent will be lower in 2022 (30 % runs, 13 % values). Newspapers are losing a huge market share. They had -56.70% CAGR in period 2012-2017, and same trend will be in period 2017-2022 (-15.70 % CAGR).

Table 4. Global gravure printing market by product type 2012 – 2022 (million A4 prints) (Smith, 2017)

	2012	2016	2017	CAGR (%) 2012- 17	2018	2022	CAGR (%) 2017-22
Books	81097.00	70733.00	69564.00	-3.00	68578.00	63293.00	-1.90
Magazines	1385543.00	1320905.00	1307171.00	-1.20	1318724.00	1257694.00	-0.80
Newspapers	17217.00	2969.00	261.00	-56.70	224.00	111.00	-15.70
Advertising	288609.00	224615.00	210602.00	-6.10	198361.00	160171.00	-5.30
Catalogues	110268.00	113468.00	113592.00	0.60	114639.00	116121.00	0.40
Commercial	74117.00	75923.00	76087.00	0.50	76684.00	78954.00	0.70
Directories	37445.00	27309.00	24983.00	-7.80	23035.00	17552.00	-6.80
Security	103076.00	122232.00	127397.00	4.30	131188.00	151323.00	3.50

Transactional print	0.00	0.00	0.00	n/a	0.00	0.00	n/a
Packaging	1560536.00	1749616.00	1815363.00	3.10	1889181.00	2184658.00	3.80
Labels	115367.00	140101.00	147573.00	5.00	155199.00	195901.00	5.80
Total	3773273.00	3847870.00	3892592.00	0.60	3975813.00	4225777.00	1.70



Figure 6. Global gravure printing market by product type in 2017 – left side and in 2022 – right side (million A4 prints)

High-speed publication rotogravure press manufacture has changed from bigger, faster machines to smaller, more agile models providing faster set-up and lower waste. Even these smaller machines are struggling to find a market. There are also packaging gravure presses, with wide web, narrow web and sheetfed models in flexible packaging, labels, cartons and corrugated (Smith, 2017). In Asian markets hybrid gravure/flexo presses, with gravure coating units are widely used, but generally sales of new gravure presses decrease. \$612 million press market in 2017, down from \$636.2 million in 2012, and the market will fall by an average CAGR of 2.6% in the five years to 2022 (Table 5) (Smith, 2017).

	2012	2010 pri 2016	2017	CAGR (%) 2012- 17	2018	2022	CAGR (%) 2017- 22
Western Europe	40.80	37.50	35.80	-2.60	34.70	30.90	-2.90
North America	30.50	26.60	25.80	-3.30	24.80	21.90	-3.20
Asia	385.10	357.70	353.90	-1.70	329.90	294.70	-3.60

Table 5. Sales of new gravure presses by geographic market, 2012–22 (\$ million, constant2016 prices and exchange rates) (Smith, 2017)

Latin America	20.80	21.80	21.40	0.60	20.70	19.50	-1.80
Eastern Europe	17.50	20.40	19.50	2.10	18.80	16.80	-2.80
Midle East	80.10	85.30	83.40	0.80	81.80	79.70	-0.90
Africa	59.40	69.40	70.30	3.40	68.50	72.00	0.50
Australia	2.00	2.10	2.10	1.20	2.10	2.20	0.70
Total	636.20	620.80	612.20	-0.80	581.30	537.80	-2.60

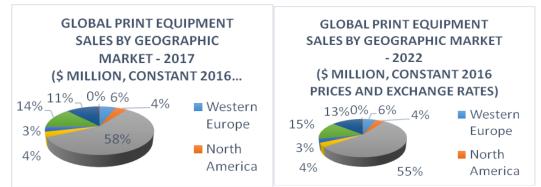


Figure 7. Sales of new gravure presses by geographic market in 2017 – left side and in 2022 – right side (\$ million, constant 2016 prices and exchange rates)

Almost all geographic markets show declining investments in new gravure presses. Positive CAGR in 2017-2022 will be in Africa and Australia (Figure 7). Sales of new gravure presses will increase in China and India, although Japan still invests the largest amount of money in new gravure printing press (Figure 8).

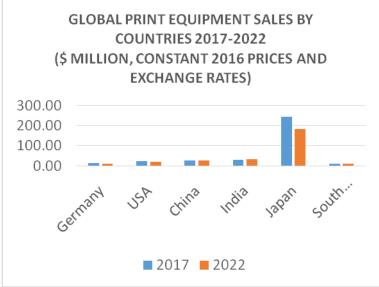


Figure 8. Sales of new gravure presses by countries in 2017-2022 (\$ million, constant 2016 prices and exchange rates)

Inks in gravure printing can be divided in three main categories: liquid, solvent and water-based ink. Liquid gravure inks used for a publication and they declining rapidly. Other type of inks (solvent and water-based inks) is holding up in packaging and labels and they are still in good position.

Gravure ink volume overall has been broadly stable at 550,000 tonnes from 2012 to 2017, with slight growth predicted to 2022, led by Asia, Middle East, Eastern Europe and Latin America. Volumes in Western Europe and North America will continue to decline (Table 6) (Smith, 2017).

	2012	2016	2017	CAGR (%) 2012- 17	2018	2022	CAGR (%) 2017-22
Western Europe	176041.00	132096.00	127033.00	-6.30	123427.00	109588.00	-2.90
North America	141385.00	130037.00	125204.00	-2.40	121681.00	108663.00	-2.80
Asia	178273.00	223963.00	234795.00	5.70	248325.00	289633.00	4.30
Latin America	18890.00	19420.00	19438.00	0.60	19991.00	21219.00	1.80
Eastern Europe	9866.00	9854.00	10002.00	0.30	10261.00	11203.00	2.30
Middle East	13378.00	15612.00	16198.00	3.90	16901.00	19470.00	3.70
Africa	3527.00	3988.00	4110.00	3.10	4186.00	4258.00	0.70

Table 6. Gravure printing ink consumption by geographic market, 2012-2022 (tonnes) (Smith, 2017)

Australia	7315.00	8116.00	8137.00	2.20	8129.00	7669.00	-1.20
Total	548675.00	543086.00	544916.00	-0.10	552900.00	571702.00	1.00

Asia is the main market for gravure printing and that is a reason why ink consumption is biggest. Ink consumption in Asia will have 4.30 % CAGR in period 2017-2022, and more than 50 % inks will be used for gravure printing in Asia (Figure 9). CAGR will be positive in Latin America (1.80 %), Eastern Europe (2.30 %), Middle East (3.70 %) and for Africa (0.7 %).

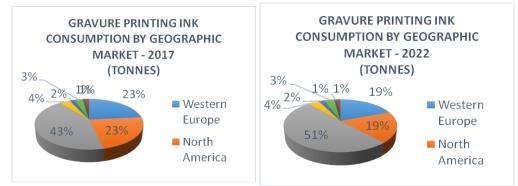


Figure 9. Gravure printing ink consumption by geographic market in 2017 – left side and in 2022 – right side (tonnes)

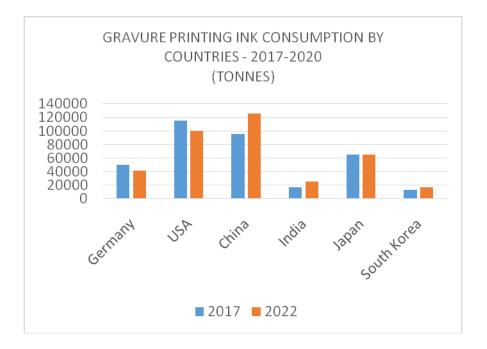


Figure 10. Gravure printing ink consumption by countries in 2017-2022 (tonnes)

As we saw in Figure 2, the biggest circulations are in China. That is correlated to ink consumption, so we can see from Figure 10 that the biggest ink consumption will be in China (2022). Increase in ink consumption in period 2017-2022 will be in Japan, India as well as South Korea.

Gravure ink printing value overall has been broadly stable at \$1925.5 million from 2012 to \$1986.2 million in 2017. The value will increase by an average CAGR of 1% in the five years to 2022 and it will be \$2092 million (Table 7) (Smith, 2017). Gravure ink printing value is predicted to increase from 2017 to 2022 in Asia (4.80 % CAGR), Latin America (1.70 % CAGR), Eastern Europe (2.80 % CAGR), Middle East (3.90 % CAGR) and for Africa (1.7 % CAGR). Western Europe and North America have negative CAGR (-3.50% and -2.7 %) and their percent in gravure printing ink volume will fall from 22 % to 18 % (Western Europe) and from 27 % to 22 % (North America).

	2012	2016	2017	CAGR (%) 2012-17	2018	2022	CAGR (%) 2017-22
Western Europe	588.90	456.80	439.10	-5.70	422.10	367.60	-3.50
North America	587.30	543.10	529.10	-2.10	516.10	462.30	-2.70
Asia	593.30	790.80	840.50	7.20	896.50	1064.30	4.80
Latin America	55.20	57.00	57.60	0.80	58.40	62.70	1.70
Eastern Europe	25.80	27.30	28.30	1.90	29.30	32.50	2.80
Middle East	41.50	48.50	50.60	4.10	53.10	61.30	3.90
Africa	10.40	12.30	12.90	4.30	13.50	14.00	1.70
Australia	23.00	27.70	28.10	4.00	28.40	27.20	-0.60
Total	1925.50	1963.70	1986.20	0.60	2017.40	2092.00	1.00

 Table 7. Gravure printing ink consumption by geographic market, 2012-2022

 (\$ million, constant 2016 prices and exchange rates) (Smith, 2017)

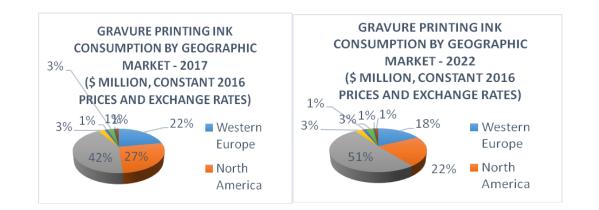


Figure 11. Gravure printing ink consumption by geographic market in 2017 – left side and in 2022 – right side (\$ million, constant 2016 prices and exchange rates)



Figure 12. Gravure printing ink consumption by countries in 2017 – left side and in 2022 – right side (\$ million, constant 2016 prices and exchange rates)

In 2022, the biggest gravure printing ink value will be in China. USA will be in second place. Except USA, fall in gravure printing ink value will be in Germany and very small in Japan.

Conclusion

Gravure printing value is expected to increase from 2012 to 2022 (\$ 1.7 billion). In that period, print volumes will grow 0.4 trillion A4s pages, largely through growth in packaging.

Asia is ideal geographic market for gravure printing, primarily because of the increasing consumer purchasing power in the area. The most developed countries have small fall in runs and in value. They are looking for other solutions for smaller runs, like flexo, offset, sometimes digital printing, but the biggest circulation will still be printed with gravure printing.

Only large printing groups are still able to afford the high initial investments and achieve an economic utilization of the installations, and that is a reason for small increase in the share of gravure printing.

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ANALIZA TRENDOVA RAZVOJA DUBOKE ŠTAMPE

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Sažetak

Grafički proizvodi mogu da se podele u tri glavne kategorije: izdavaštvo, komercijalna štampa i ambalaža. Područje ambalaže raste iz godine u godinu, bez obzira da li se gledaju tiraži ili novčana vrednost. Značajan pad u tiražima, kao i u

novčanoj vrednosti se beleži u grupi izdavaštvo, pre svega jer se sve više prelazi sa tradicionalnih štamparskih proizvoda kao što su knjige i novine na alternativne medije (e knjige, socijalni mediji, online mediji itd). U komercijalnoj štampi se beleži mali rast, kako u tiraži, tako i u novčanoj vrednosti.

Najvažnije tehnike štampe na tržištu su trenutno ofset štampa (tabačna, heatset rotaciona i coldset rotaciona), flekso štampa, duboka štampa, propusna štampa, letterpress, elektrofotografija, ink jet itd.

Duboka štampa se koristi za visokotiražne poslove sa visokim kvalitetom, pri čemu je glavno područje štampa ambalaže i etiketa. U ovom radu je predstavljena analiza duboke štampe, kao i trendovi u njenom razvoju, pri čemu se vodilo računa o tome da zastupljenost duboke štampe nije ujednačena u celom svetu. Zbog toga su u istraživanju prikazana posebno područja Zapadne Evrope (Francuska, Nemačka, Italija, Holandija, Španija, Velika Britanija i ostale zapadno evropske države), Severna Amerika (Sjedinjene američke države i Kanada), Latinska Amerika (Brazil, Meksiko i ostale Latino američke države), Azija (Kina, Indija, Japan, Južna Koreja i ostale azijske države), Istočna Evropa (Češka republika, Poljska, Rusija i ostale istočno evropske države), Bliski Istok (Turska i ostale blisko istočne države), Afrika i Australija (uključujući Okeaniju).

Istraživanje je pokazalo da su idealna tržišta u budućnosti za duboku štampu tržišta Azije, pre svega zbog toga što sve više raste kupovna moć stanovništva na tom području. Razvijene zemlje imaju mali pad, koji se objašnjava time da će se za sve manje tiraže u području pre svega ambalaže, tražiti alternativna rešenja, kao što su flekso, ofset, pa čak i digitalna štampa. Veći tiraži u razvijenijim zemljama će i dalje biti štampani tehnikom duboke štampe.

Ključne riječi: duboka štampa, trendovi

Original scientific article

INFLUENCE OF CYAN INK ON WATER VAPOUR RESISTANCE OF INKJET PRINTED TEXTILE SUBSTRATE

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Abstract

In the case of excessive body temperature, the human body activates the sweat mechanism, and heat evaporation leads to heat loss. Clothing, by its characteristics, largely determines the exchange of heat between the body and the environment. Today's clothing is often subjected to the printing process, in order to increase its aesthetic value. The printing process changes textile materials, and thus changes clothes made from these materials. This paper presents research on the influence of printing cyan ink on the thermo-physiological features of textile materials. The effects of ink on thermo-physiological characteristics of substrate materials were determined by measuring water vapour resistance. The obtained results show that cyan ink in combination with material characteristics have an impact on the water vapour resistance of textiles.

Keywords: Inkjet textile printing, Water vapour resistance.

Introduction

The human body constantly produces heat through metabolic processes. The amount of heat produced consists of basal heat, which is independent of physical activity, and the amount of heat produced during physical activity, which increases proportionally with increasing activity intensity (Gisolfi & Wenger, 1984; Umbach, 1978). The human body has developed a thermal regulation system that allows maintaining the temperature of the interior of the body at about 37 °C, while, in order to maintain thermal balance, balancing the produced and lost heat (Das & Alagirusamy, 2010). In the case of elevated body temperature, the veins in the skin dilate, which leads to an increase in blood flow and heart rate, and increases heat loss. If the body temperature continues to rise despite this, the sweat mechanism is activated, in order to increase heat loss by evaporating sweat. Otherwise, ie. when the body temperature is too low, there is a collection of veins in the skin, a decrease in blood flow and heart rate and an increase in metabolism by muscle stimulation, resulting in tremors (Li et al., 2006). The processes of heat exchange in dressed and

undressed people are qualitatively equal, while they quantitatively depend on the thermodynamic properties of clothing, which is the separating surface between the body and the environment (Grujić, 2010; Mecheels, 1991). A man without clothes can live in a very short range of ambient temperatures of 26 °C to 30 °C. With clothes, on the other hand, it is possible to live comfortably and perform various physical activities in a wide range of ambient temperatures, from -40 °C to +40 °C (Fanger, 1986). Thus, clothing provides thermal protection to the body by creating a comfortable microclimate between the body and the clothing, allowing the smooth flow of physiological functions at ambient temperatures that the human body alone cannot cope with (Das & Alagirusamy, 2010). About 90% of the surface of the human body is covered with clothing, which is practically worn 24 hours a day, at work, at rest and at night in bed. Based on that, it can be seen that the thermal properties of clothing are very important, because the human body reacts to the thermal conditions of the environment, precisely through clothing (Mecheels, 1991). When sweating, the sweat glands secrete water to the surface of the skin, which evaporates, thus removing excess heat (Grujić, 2010). Evaporation of sweat exclusively results in heat loss (Stoecker & Jones, 1982). Water vapor flow resistance of garments is the ability to transfer vaporized water vapor, i.e. sweat, from the body surface to the environment (Chidambaram et al., 2012; Oğlakcioğlu & Marmarali, 2007). The ability of garments to transmit water vapor depends on the type of fibers from which they are made, and on the structural characteristics, i.e. the degree of porosity of the material. The transmission of water vapor through a garment consists of the diffusion of water vapor through the pores between the fibers in the yarn, and the diffusion of water vapor through the fibers themselves. The diffusion rate through the textile material depends on the porosity of the material as well as on the diffusion coefficient of the fibers. The diffusion coefficient itself increases with the hygroscopicity of the material (Das et al., 2009). The speed of sweat evaporation largely depends on the clothes that represent a barrier to the evaporation process. In essence, clothing interferes with the evaporation of sweat from the surface of the skin, and this insufficient evaporation very often creates a feeling of discomfort when wearing clothing (Kim, 1999). The speed of evaporation itself affects the comfort felt when wearing clothes. The thermal resistance of textiles to the flow of water vapor is determined according to expression (1) (Kato Tech Co. Ltd., 1998):

$$R_{e} = \frac{(p_{s} - p_{d}) \cdot A}{H_{et}}$$
(1)
where:

•
$$R_e$$
 - water vapour resistance [Pa m²/W],

- H_{et} evaporated heat flux [W],
- A surface of BT plate $[m^2]$,
- p_s partial pressure on the surface of BT plate [Pa],
- p_a partial pressure of air in the wind column [Pa].

In other research (Stančić et al., 2017) the influence of the printing process on water vapour resistance was also investigated. It has been analysed water vapour flow characteristics of knitwear and fabrics made from cotton, polyester or a mixture of these two materials, and to which printing was applied with black ink. By measuring these values, it was determined that a higher number of printing passes as well as increase in tone value leads to a rise in water vapour resistance. The results indicated that water vapour resistance depend on the material composition of the printing substrate and the surface structure of the material as well as the printing parameters. However, Stančić et al. (2013) in earlier research came to a conclusion that certain process colors with their characteristics greatly affect the quality of printing. Given that, when considering the overall quality of prints, it is not enough to analyze the quality parameters printed in one color, which is the most common case.

Materials and methods

Textile materials intended for garment manufacture are used in two forms, i.e. knitwear and fabrics. At the same time, the most frequently used materials for garments production are cotton, polyester and the combination of these two materials. For this research, three types of knitwear were made, with different material composition and approximately the same basic weight, and surface structure. The fundamental characteristics of the used knitwear are shown in Table 1.

The printing process for the samples was done using digital printing technology with the inkjet printing system Polyprint TexJet and DuPont Artistri Pigment – P5100 cyan ink. Used ink is a pigmented water-based ink, designed for digital printing systems, and specially improved for digital printing of textiles. The samples were printed with three different passes types of the substrate material through the printing machine. Samples were printed using one, three or five passes of the material through the printing machine, i.e. using one, three or five ink layers, without an interdrying step. The printing process was conducted using a print resolution of 720x720 dpi. After the printing process, prints were subjected to drying and fixing of the printed inks. All the samples were dried using a thermal effect at 130 °C for 120 s. Measured tone values used in the experiment were 10%, 50% and 100% because these tone values represent the high, mid and dark tones.

Material	Type of	Type of weaves	Raw material composition (%)	Mass per unit weight (g/m ²)	Density (cm ⁻¹)	
label	materials				Vertical	Horizontal
СО	Knitwear	Single Cotton 100 %		111.89	17	17
PES	Knitwear	Pike	Polyester 100 %	114.12	12	20
CO/PES	Knitwear	Interlock	Cotton 50 % Polyester 50 %	128.5	14	20
Method	Method		ISO 1833	ISO 3801	ISO 7211-2	

Table 1: Basic characteristics of materials used in research

Measurement of resistance of textile materials to water vapor flow was performed in a wind tunnel using a larger BT measuring body, heated to a temperature of 35 °C, at a temperature of 20 °C \pm 2 °C and constant air movement at a speed of 1 ms⁻¹, which is in accordance with the standard ISO 11092: 2014 (ISO, 2014).

Results and discussion

The results of water vapor resistance testing of printed cotton knitwear are shown in Figure 1.The measured values of water vapour resistance of printed cotton knitwears are higher than the given values of the unprinted material. The values indicate that the values of water vapor resistance of printed cotton knitwears increase with increasing of tone value. The water vapour resistance value also increases with the increase in the number of ink applications. It can be noticed that by combining the tone value and the number of ink applications, it is possible to achieve similar values of water vapour flow resistance. Thus, approximately equal values of water vapour resistance were created by printing samples with 10% TV with five coats of ink and 50% TV with one coat, and in the case of printing samples with 50% TV with five coats and 100% TV with three coats.

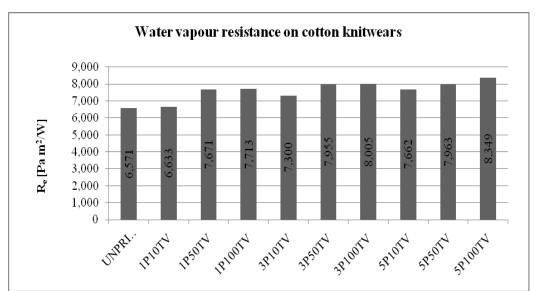


Figure 1. Water vapor resistance of printed cotton knitwears (Note: 1P, 3P and 5P mark indicates the print with 1, 3 and 5 passes, 10TV, 50TV and 100TV denote a print with 10%, 50% and 100% of tonal values)

The results of water vapor resistance of printed polyester knitwears are shown in Figure 2.

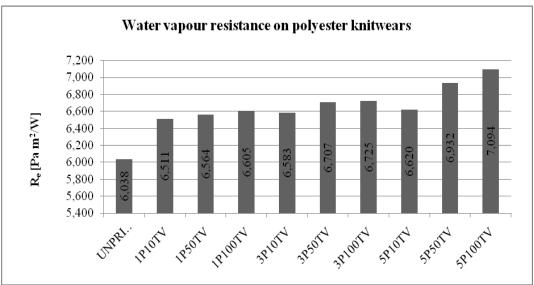


Figure 2. Water vapor resistance of printed polyester knitwears (Note: 1P, 3P and 5P mark indicates the print with 1, 3 and 5 passes, 10TV, 50TV and 100TV denote a print with 10%, 50% and 100% of tonal values)

The obtained results of water vapor resistance value of printed polyester knitwears show that increasing the tone value increases the value of water vapor flow resistance. At the same time, as the number of inks applications increases, the values of water vapor flow resistance increase, regardless of whether the samples were printed in one, with three or five ink applications. It can be noticed that the process of printing polyester knitwears obtained higher values of water vapour resistance in relation to the same values that occur with unprinted material. Obtained results also indicate that when printing samples, approximately equal values were obtained in the case of printing samples with 10% TV with three coats and 50% TV with one coat, and in the case of printing 10% TV with five coats and 100% TV in one go.

The results of the water vapour resistance of printed CO/PES knitwears are shown in Figure 3.

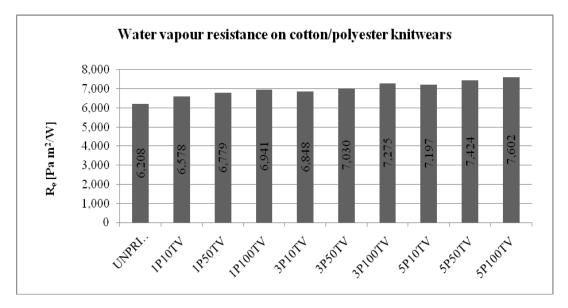


Figure 3. Water vapor resistance of printed cotton/polyester knitwears (Note: 1P, 3P and 5P mark indicates the print with 1, 3 and 5 passes, 10TV, 50TV and 100TV denote a print with 10%, 50% and 100% of tonal values)

By analyzing the water vapor resistance values of printed CO/PES knitwears, it can be noticed that increasing the tone value increases the value of the water vapour resistance. The values in Figure 3. also indicate that increasing the number of ink application also increases the water vapour resistance. In addition, the values of water vapor resistance of CO/PES knitwears before and after printing indicate that the given values are higher after exposing material to the printing process.

Conclusion

By increasing the number of inks in the print, as well as by increasing the tone value, there is a greater replacement of air with printing ink in the pores between the yarns as well as the pores between the fibers. In this way, a barrier is created for the unimpeded passage of water vapour from the body surface through the layers of clothing into the environment, and hence higher values of water vapour resistance with increasing the number of ink layers and increasing tone value.

In summary, printing process with cyan also changed the water vapour resistance values of investigated knitwear and confirmed the effect of this process on the properties of textile materials in same trend. But cyan colour had a slightly lower water vapour resistance values which can be due to ink density, this research should be done with yellow ink where it is assumed that the values of water vapour resistance should be the lowest.

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UTICAJ CIJAN ŠTAMPARSKE BOJE NA OTPOR PROTOKU VODENE PARE TEKSTILNIH MATERIJALA ŠTAMPANIH INKJET ŠTAMPOM

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Sažetak

U slučaju povišene temperature, ljudsko tijelo aktivira mehanizam znojenja, što dalje dovodi do gubitka toplote. Odjeća svojim karakteristikama u velikoj mjeri određuje razmjenu toplote između tijela i okoline. Današnja odjeća je često podvrgnuta postupku štampe kako bi se povećala njena estetska vrijednost. Postupak štampe mijenja tekstilne materijale, a samim tim i odjeću napravljenu od tih materijala. Ovaj rad predstavlja istraživanje o uticaju štampe cijan boje na termo-fiziološke karakteristike tekstilnih materijala. Uticaj štamparske boje na termo-fiziološke karakteristike materijala podloge je utvrđen mjerenjem otpora protoku vodene pare. Dobijeni rezultati pokazuju da cijan štamparska boja u kombinaciji s karakteristikama materijala utiče na otpor protoku vodene pare tekstila.

Ključne riječi: Inkjet štampa na tekstilu, Otpor protoku vodene

XIII Conference of Chemists, Technologists and Environmentalists of Republic of Srpska

ENGINEERING AND ENVIRONMENTAL PROTECTION

Original scientific paper

UTILIZING THE MAGNETITE-BIOCHAR PARTICLES AS A SUPPORT FOR COVALENT ENZYME IMMOBILIZATION

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Abstract

Metal-biochar composites are gaining increased attention for their potential to improve enzyme immobilization efficiency and their environmentally friendly nature. In this paper, the suitability of magnetite-biochar particles as a support for the horseradish peroxidase (HRP) was investigated. The change in enzymatic activity of the immobilized enzyme at different values of pH and temperature, as well as stability over time, was measured. The enzyme was bound to the support via glutaraldehyde as a crosslinker. The results showed that HRP can efficiently bind to magnetite-biochar particles by covalent bonding. The immobilized enzyme shows high activity at a wide range of pH and temperature. The highest activity of the immobilized enzyme was recorded at pH 7 and at temperatures of 40°C. Also, the immobilized enzyme retains 45% and 60% of its activity during storage at temperatures of 25 and 10°C after a period of 30 days, respectively. After first wash cycle, magnetite-biochar still retained 93% of HRP activity, however, further washing significantly reduced enzyme activity.

Keywords: carbon particles, magnetite-biochar, horseradish peroxidase, covalent enzyme immobilization, glutaraldehyde.

Introduction

Carbon particles, such as biochar, have proven to be good support for enzymes due to their specific characteristics. These supports have an inherently large surface area that leads to high enzyme loading and consequently high volumetric enzyme activity. However, recently in order to improve the performance of biochar, mixtures with metal/metal oxides such as magnetite are used. Magnetite-biochar is an attractive alternative material for enzyme immobilization due to its low cost and readily available starting materials. The porous nature of magnetite-biochar contributes to its loading capacity and attractiveness as a solid support material (Zhang & Hay, 2020). Furthermore, the heterogeneous iron and porous carbon nature contribute to the multifunctionality of magnetite-biochar (Cho et al., 2019).

Immobilization of enzymes on some solid support can increase their stability and reusability. There are several different methods for enzyme immobilization designed based on physical, covalent or affinity interactions. Binding of the enzyme onto the solid support by strong covalent bonding has a number of advantages, resulting in a stable enzyme that can be reused in a number of consecutive cycles. In order to bind the enzyme by covalent bonding, it is necessary to functionalize the biochar and/or to use one of the crosslinkers through which the enzyme would be adequately bound.

The aim of this work was to test magnetite-biochar utility as a support for horseradish peroxidase (HRP) covalent immobilization over glutaraldehyde as a crosslinker. The immobilized enzyme was tested for the effect of variations of pH and temperature on its activity, as well as for its stability over time.

Materials and Methods

Biochar was obtained from sawdust of a mixture of beech and oak wood by pyrolysis at 700°C (BASNA doo, Čačak, Serbia) and then functionalized in concentrated nitric acid in order to introduce oxygen functional groups on the surface of biochar. Magnetite-biochar was synthesized by precipitation method in basic conditions at 80°C. Functionalized biochar was mixed with aqueous Fe^{2+}/Fe^{3+} salt solutions upon NaOH treatment to pH value 10 (10 g biochar, 0.69 g FeSO₄ and 2.41 g NH₄Fe (SO₄) ^x12H₂O in 500 mL distilled water). Synthetized magnetite-biochar was treated by 5% glutaraldehyde and prepared for covalent enzyme immobilization.

Horseradish peroxidase was extracted from horseradish root according to the procedure given in Savić et al. (2014) and covalently bonded onto prepared magnetite-biochar particles. The activity of immobilized HRP (Units per gram of a solid support, U/g) was measured spectrophotometrically according to Worthington method (2011). The impact of temperature (10-80°C) and pH (4-8) variations on activity of immobilized HRP were investigated. The storage stability of immobilized HRP was evaluated by keeping the samples at 10 and 25°C for one month and measuring their peroxidase activity during one month period. The reusability of the immobilized enzyme was determined by measuring the retained activity of the immobilized enzyme after its washing with distilled water in a number of consecutive cycles.

Results and discussion

HRP was very efficiently covalently bound onto magnetite-biochar showing enzymatic activity of 16.72 U/g support at pH 7 at ambient temperature. The enzyme activity of immobilized HRP at different pH values and temperatures are

present in Figure 1 and Figure 2, respectively. It could be seen that the activity of investigated enzyme equally depends of both factors.

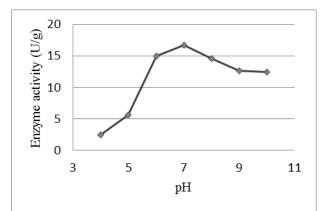


Figure 1. The activity of immobilized HRP at different pH values and 25°C.

Based on the results shown in Figure 1, it can be observed that the activity of the immobilized enzyme was low in an acidic medium and increases with increasing pH value. The optimal value was achieved at pH 7, which is consistent with the results of Chen et al. (2020), who tested the method of immobilizing HRP on nitrogen-doped carbon dots.

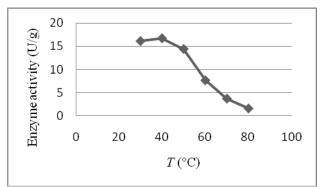


Figure 2. The activity of immobilized HRP at different temperatures and pH7.

The activity of HRP immobilized onto magnetite-biochar was the highest at 40°C, then decreased with increasing the temperature (Figure 2). The immobilized enzyme retains over 85% of its activity at temperature range 30-50°C. The decrease in the enzyme activity is a consequence of its denaturation at elevated temperatures.

The change in activity of immobilized HRP onto magnetite-biochar over a period of one month at 10° C and 25° C is shown in Figure 3. It could be seen that by storing the immobilized enzyme at temperatures of 10° C, as well as 25° C, can

preserve the stability of the enzyme almost equally well. By storing the enzyme at both temperatures in the first two weeks, the enzyme activity was maintained at 85%, while after a month, slightly better results are achieved at a lower temperature of 10°C (45% at 25°C and 60% at 10°C). Also, other researchers come to the same conclusion that the immobilized HRP exhibits high thermal, pH and storage stability (Vineh et al., 2018; Chen et al., 2020).

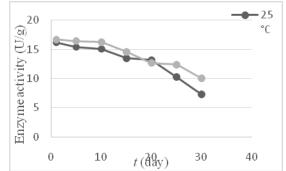


Figure 3. The stability of immobilized HRP during time.

The reusability of immobilized enzyme is an important factor in estimating the enzyme-support interactions. The change in activity of HRP immobilized onto magnetite-biochar particles after four washing cycles was shown in Figure 4.

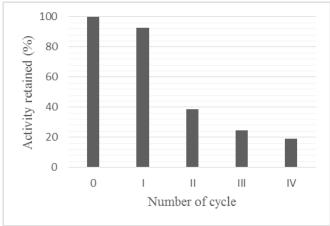


Figure 4. Reusability of immobilized HRP onto magnetite-biochar.

It could be seen that after one washing step immobilized HRP retains more than 90% of its activity. However, after the next wash, the enzyme activity was significantly reduced to 40%, while after the fourth wash cycle the activity was only 20%.

Conclusion

Magnetite-biochar particles have been shown to be a suitable support for HRP covalent immobilization *via* glutaraldehyde as a crosslinker. Immobilized HRP onto magnetite-biochar resulted in high enzyme activity and significant improvements to enzyme stability, but low reusability properties. It is necessary to optimize the preparation process of magnetite-biochar particles in order to provide more efficient covalent enzyme immobilization that will ensure reliable multiple reusability.

Acknowledgements

This study is conducted as a part of the project 451-03-68/2020-14/200134 funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia.

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PRIMENA MAGNETIT-BIOUGALJ ČESTICA KAO NOSAČA ZA KOVALENTNU IMOBILIZACIJU ENZIMA

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Sažetak

Kompozitni metal-biougalj materijali dobijaju sve veću pažnju zbog svog potencijala da poboljšaju efikasnost imobilizacije enzima i zbog svoje netoksične prirode po životnu sredinu. U ovom radu ispitivana je pogodnost magnetit-biougalj čestica kao nosača imobilisanog enzima peroksidaze iz rena (HRP). Praćena je promena enzimske aktivnosti imobilizovanog enzima pri različitim pH vrednostima i temperaturi, kao i stabilnost tokom vremena. Enzim je vezan za nosač preko glutaraldehida kao spone. Dobijeni rezultati su pokazali da se HRP može efikasno vezati za magnetit-biougalj čestice kovalentnom vezom. Imobilisani enzim pokazuje visoku aktivnost u širokom opsegu pH vrednosti i temperature. Najveća aktivnost imobilisanog enzima zabeležena je pri pH 7 i na temperaturi od 40°C. Takođe, imobilisani enzim zadržava 45% i 60% svoje aktivnosti tokom skladištenja na temperaturama od 25°C i 10°C nakon perioda od 30 dana, redom. Nakon prvog ciklusa ispiranja, magnetit-biougalj čestice su zadržale 93% aktivnosti enzima, međutim, dalje ispranje je značajno smanjilo aktivnost enzima.

Ključne riječi: ugljenični materijali, magnetit-biougalj, peroksidaza iz rena, kovalentna imobilizacija enzima, glutaraldehid.

Original scientific article

REMOVAL OF SODIUM LAURYL SULFATE FROM WASTEWATER BY ADSORPTION ON ACTIVATED CARBON

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Abstract

Sodium lauryl sulfate (SLS) is one of the main components present in detergents and personal hygiene products, therefore, it is the most common anionic surfactant substance in municipal wastewater, which during discharge endanger flora and fauna of the recipient.

During the present study, adsorption of sodium lauryl sulfate (SLS) was performed from the wastewater suspension model sample onto powdered activated carbon (PAC). The experiment was performed at room temperature $(20^{\circ}C)$ and the pH value range of the initial model samples from 6,40 to 7,51. The influence of adsorbent dose (PAC), the adsorbate concentration (SLS), and adsorption time on the removal efficiency of SLS from the model sample were monitored. The process was additionally controlled by measuring the pH value.

The use of powdered activated carbon gives satisfactory results in the removal of sodium lauryl sulfate from water, and the presented results of this research can serve as a foundation for further testing and implementation of this adsorption process for the removal of anionic surfactants from real wastewater samples.

Keywords: adsorption, sodium lauryl sulfate, powdered activated carbon, wastewater

Introduction

Surfactants (also called surface-active agents - SAA) are the large and diverse group of organic pollutants. Due to the specific molecule structure (hydrophobic and hydrophilic parts of the molecule), surfactants are used as parts of cleaning and hygiene products, emulsifiers, foaming agents, wetting agents, and certain medical preparations. Diverse and wide application leads to the presence of these substances in industrial and municipal wastewater.

At higher concentrations, SAA molecules tend to be grouped into larger aggregates of colloidal dimensions - micelles, and to achieve this, it is necessary to reach a critical micellar concentration (CMC) of the active substance. In micelles,

surfactants show the effect of solubilization. This leads to an increase in the solubility of otherwise insoluble or poorly soluble toxic organic compounds in water (Yuan et al, 2014). Anionic surfactants, since they represent the basic components of detergents and personal hygiene, are the most common SAAs found in wastewater.

There are several procedures for removing SAAs from water and aqueous solutions. Rios et al. (2017) achieved very good removal efficiencies, by an advanced oxidation process, using the H_2O_2/UV system. The coagulation and flocculation process, with the use of coagulants based on lime, aluminum and iron salts, gave different results in terms of the removal degree of anionic surfactants. The best coagulant was FeCl₃, which achieved 80% removal efficiency, expressed through COD (Mahvi et al, 2004; Aboulhassan et al, 2006). Adsorption is one of the physicochemical methods that also gives acceptable results in the removal of SAAs from water and wastewater. Natural zeolites can be used as adsorbents (Harutyunyan & Pirumyan, 2015). Natural zeolites are sorbents based on cheap natural and modified clays with different percentages of magnetite, especially suitable for removing low concentrations of anionic surfactants from wastewater (Makarchuk & Dontsova, 2016). Also, activated carbon, as a specially prepared *adsorbent, is used for adsorption*.

Sodium lauryl sulfate

Sodium lauryl sulfate (SLS) is one of the most commonly used anionic surfactants, so its potential for water pollution is extremely high. SLS is used as an ingredient of numerous pharmaceutical formulations, where, as a solubilizer, emulsifier, lubricant (in the manufacture of tablets and capsules), or as an agent for modified drug release, it exerts its effect. Due to its amphiphilic property, which is the result of the ester bonding of a chain of 12 carbon atoms to the sulfate group, SLS achieves strong surface activity (Bondi et al, 2015).

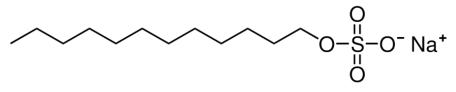


Figure 1. Chemical structure of SLS

Due to its bacteriostatic properties, foam forming, and cleaning ability, SLS is an indispensable ingredient in medical shampoos, washing, and cleaning products for skin and fabrics (Chaudhari et al, 2012). SLS concentration in these products depends on product type and varies between different manufacturers, but it is usually in the range of 0,01% to 50% in cosmetic products, and range of 1% to 30% in washing and cleaning products. The subject of this study was the removal

of sodium lauryl sulfate (SLS) from wastewater, using adsorption from aqueous suspension on powdered activated carbon (PAC). The experiment was performed on a model sample of wastewater containing SLS in different concentrations.

Materials and Methods

Wastewater model samples used in this experiment were prepared by dissolving Sodium Lauryl Sulfate in distilled water, in defined concentrations. SLS used in this experiment is analytical grade chemical, 25,5%, produced by Lach-Ner, s.r.o. The Czech Republic. Samples were treated with powdered activated carbon manufactured by Kemika, Zagreb. The experiment was performed in laboratory conditions on a Jar test apparatus with six samples. The doses of adsorbent (PAC) were: 10, 100, 200, 500, and 700 mg/L and the concentration of sodium lauryl sulfate was 10, 25, and 40 mg/L. The pH values of the initial water samples varied in the range of 6.40 to 7.51. The experiment was performed at room temperature (20°C), the adsorption time of 10 and 20 minutes, and with intensive mixing of the samples. After adsorption time, samples were left to precipitate for 60 minutes, and after precipitation, membrane filtration was performed. The obtained filtrate was analyzed for sodium lauryl sulfate content using the method for the determination of anionic surfactants (Ilišković, 2000).

Results and discussion

During the present study, adsorption of sodium lauryl sulfate (SLS) was performed from the wastewater suspension model sample onto powdered activated carbon (PAC). The influence of adsorbent dose (PAC), the adsorbate concentration (SLS), and adsorption time on the removal efficiency of SLS from the model sample were monitored. The process was additionally controlled by measuring the pH value. The removal efficiency of SLS from model water samples was calculated according to the relation:

Removed SLS (%) = $\frac{C_0 - C}{C_0} \cdot 100$

Where: c_0 is initial concentration of SLS in aqueous solution (mg/L);

c is final concentration of SLS in aqueous solution (mg/L).

The influence of adsorbent dose on adsorption efficiency depending on the initial sls concentration and the adsorption time.

The adsorption process of SLS onto the surface of powdered activated carbon takes place due to hydrophobic and electrostatic interactions (Bindes & Franko, 2010). During the SLS adsorbate monolayer formation, the charge of the activated carbon

surface changes, and its specific surface is saturated. When the adsorption capacity of activated carbon is reached, the removal efficiency of sodium lauryl sulfate decreases. Figures 2-6 show the percentage of removed SLS, depending on different initial concentrations, with adsorption time variations, for certain doses of PAC.

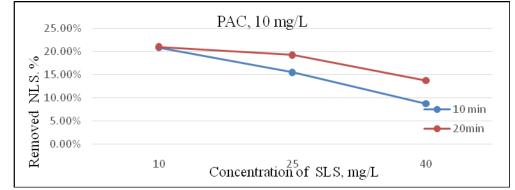
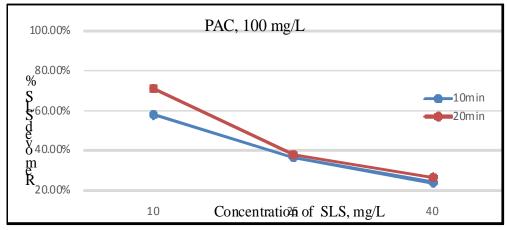


Figure 2. Percentage of SLS removed depending on SLS concentration at the amount of adsorbent dose of 10 mg/L and different adsorption time

The lowest dose of PAC (10 mg/L) insufficiently removes SLS from water samples, especially at higher concentrations of SLS, where the removal percentage is only 10-15% (Figure 2). The removal efficiency of the lowest SLS concentration is 20%, and it does not depend on the adsorption time. That is not the case with higher SLS concentrations, where the adsorption time correlates with the adsorption efficiency of SLS (higher SLS concentration requires longer adsorption



time to achieve a better removal percentage).

Figure 3. Percentage of SLS removed depending on SLS concentration at the amount of adsorbent dose of 100 mg / L and different adsorption time

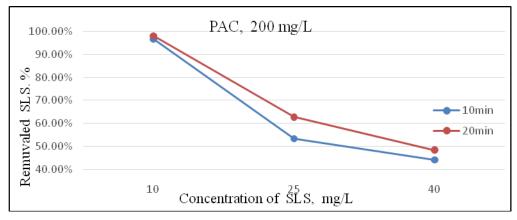


Figure 4. Percentage of SLS removed depending on SLS concentration at the amount of adsorbent dose of 200 mg / L and different adsorption time

Figures 3 and 4 show the removal efficiency of SLS at different doses of adsorbate, 100 and 200 mg/L. There is a significant difference in the removal efficiency of SLS by increasing the amount of PAC. Also, the time of adsorption correlates with the percentage of removed SLS. In both experiments, removal was more efficient at longer contact time between the adsorbent and the adsorbate.

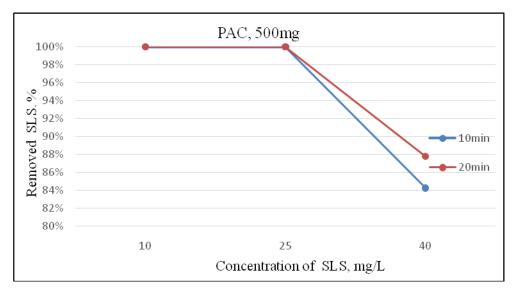


Figure 5. Percentage of SLS removed depending on SLS concentration at the amount of adsorbent dose of 500 mg / L and different adsorption time

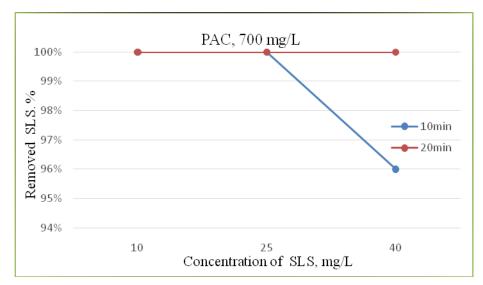


Figure 6. Percentage of SLS removed depending on SLS concentration at the amount of adsorbent dose of 700 mg /L and different adsorption time

Higher doses of PAC give very satisfactory results of adsorption of SLS from water (Figures 5 and 6). In both cases, the used dose of adsorbent completely removes SLS at lower concentrations (10 and 25 mg / L) after 20 minutes of adsorption time. With the adsorbent dose of 700 mg/L, even the higher SLS concentration is quantitatively removed.

The influence of the adsorbent dose on the adsorption efficiency is evident. In all samples, there is an increase in sodium lauryl sulfate removal with an increase in the amount of used powdered activated carbon (96-100%). The only question is the economy of this adsorption process due to the high consumptions of powdered activated carbon.

The influence of sodium lauryl sulfate concentration on the adsorption efficiency depending on the adsorbent dose and the adsorption time

The concentration of adsorbate also affects the adsorption process. As the adsorbate concentration increases, the adsorption efficiency will increase to a certain point, the saturation point of the adsorbent. Thereafter, a further increase in the adsorbate concentration does not affect the adsorption efficiency.

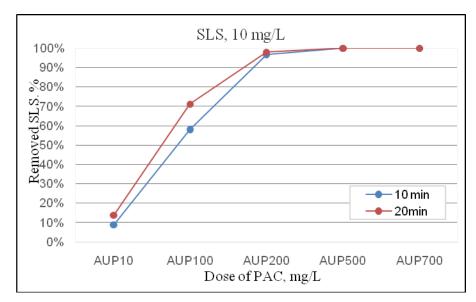


Figure 7. Percentage of SLS removed depending on PAC dose at SLS concentration of 10 mg/L and different adsorption time

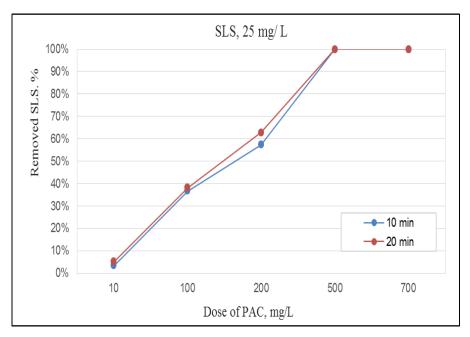


Figure 8. Percentage of SLS removed depending on PAC dose at SLS concentration of 25 mg/L and different adsorption time

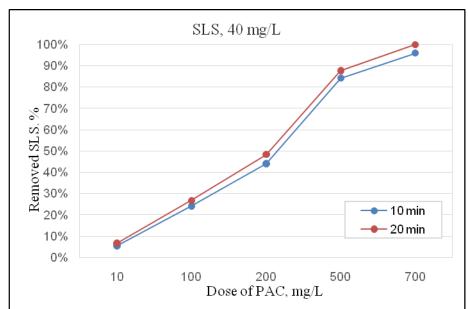


Figure 9. Percentage of SLS removed depending on PAC dose at SLS concentration of 40 mg/L and different adsorption time

Figures 7, 8, and 9 show the percentage of sodium lauryl sulfate removed at different doses of adsorbent and at different adsorption times, depending on the initial concentrations of sodium lauryl sulfate.

The adsorption efficiency, in all cases, varies with the dose of PAC. A higher initial SLS concentration requires a higher dose of PAC for removal to be satisfactory (90-100%). In all three cases, the adsorption time has a negligible effect on the efficiency of SLS removal.

Change in the pH value depending on the degree of SLS removed

The aqueous solution of sodium lauryl sulfate is neutral or slightly acidic, depending on concentration. The pH value of the aqueous solution of activated carbon is basic, ranges from 8 to 11, and originates from the dissolution of alkaline components from the coal itself.

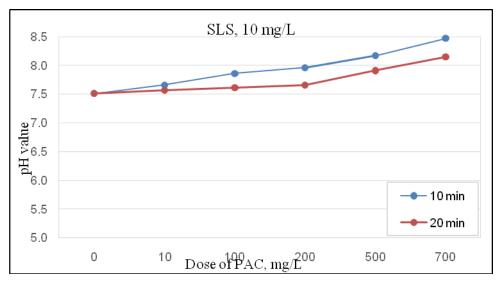


Figure 10. Change in the pH value of samples treated with different doses of PAC at different adsorption time and SLS concentration of 10 mg/L

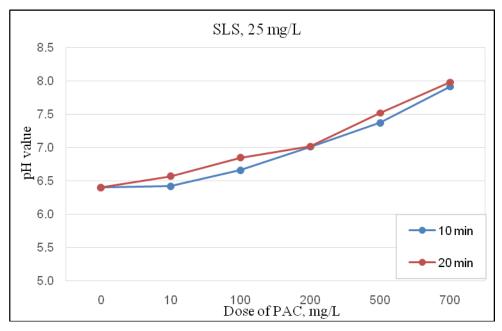


Figure 11. Change in the pH value of samples treated with different doses of PAC at different adsorption time and SLS concentration of 25 mg/L

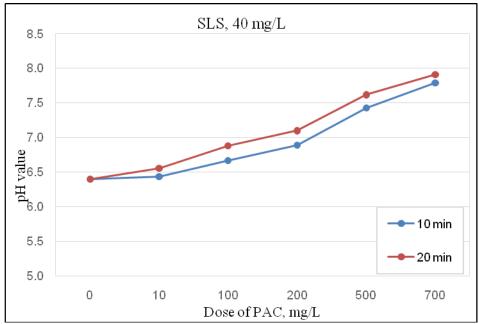


Figure 12. Change in the pH value of samples treated with different doses of PAC at different adsorption time and SLS concentration of 40 mg/L

The pH values after the adsorption in all water samples are compatible with the permitted values (6,5-9,0), according to the *Regulation on the conditions for discharging wastewaters into surface waters* (Sl. glasnik RS, 2001). The pH value of water samples increased with increasing the dose of PAC due to the dissolution of alkaline components in coal, and also because of the removed SLS, which led to decreasing its acidic effect on water. A slightly larger increase in the pH is visible in the case of adsorption time of 20 minutes. The exception is at the lowest SLS concentration, where the more intense increase in pH value is after adsorption time of 10 minutes.

Conclusion

Based on the conducted research on the removal of sodium lauryl sulfate (SLS) from the wastewater model samples by adsorption on powdered activated carbon (PAC), the following conclusions can be listed:

• The amount of adsorbent has a significant impact on the process of removing SLS from wastewater. By applying a higher dose of PAC, a better degree of adsorption is achieved, and the satisfactory percentage of SLS removal (95-100%) is achieved at PAC doses of 500 and 700 mg/L;

- Higher initial SLS concentration requires a higher dose of PAC for removal to be satisfactory (90-100%). The effect of time was more significant at higher concentrations of SLS;
- The pH values in the water samples after adsorption were within the allowed limits for wastewater discharge into surface streams (pH = 6.5 9.0) and depended on the used dose of PAC. By increasing the dose of PAC, the pH of water increases due to the intake of alkaline components from coal, as well as due to the removal of SLS from water, which led to decreasing its acidic effect on water.

The use of powdered activated carbon gives satisfactory results in the removal of sodium lauryl sulfate from water, and the presented results of this research can serve as a foundation for further testing and implementation of this adsorption process for the removal of anionic surfactants from water. Certainly, research should be continued on realistic wastewater samples.

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UKLANJANJE NATRIJUM LAURIL SULFATA IZ OTPADNE VODE PRIMJENOM ADSORPCIJE NA AKTIVNOM UGLJU

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Sažetak

Natrijum lauril sulfat (NLS), s obzirom da predstavlja osnovnu komponentu sredstava za pranje i održavanje lične higijene, jeste jedna od najčešće prisutnih površinski anjonaktivnih materija u komunalnim otpadnim vodama, koja prilikom ispuštanja ugrožava floru i faunu recipijenta. Tokom predmetnog istraživanja vršena je suspenziona adsorpcija natrijum lauril sulfata (NLS) iz model uzorka otpadne vode pomoću aktivnog uglja u prahu (AUP). Eksperiment je sprovođen na sobnoj temeparaturi (20°C), a pH početnih model uzoraka kretala se u intervalu od 6,40 do 7,51. Praćen je uticaj doze adsorbensa (AUP), koncentracije adsorbata (NLS) i vremena adsorpcije na stepen uklanjanja NLS iz model uzorka otpadne vode. Proces je dodatno kontrolisan mjerenjem pH vrijednosti.

Primjena aktivnog uglja u prahu daje zadovoljavajuće rezultate pri uklanjanju natrijum lauril sulfata iz vode, a prikazani rezultati mogu poslužiti kao osnova za dalja ispitivanja i implementaciju procesa adsorpcije za uklanjanje anjonaktivnih površinskih materija iz realnih uzoraka otpadne vode.

Ključne riječi: adsorpcija, natrijum lauril sulfat, aktivni ugalj u prahu, otpadna voda

Original scientific article

DEVELOPMENT AND ASSESMENT OF A MATHEMATICAL MODEL OF THE INFLUENCE OF ULTRASOUND ON BIOETHANOL PRODUCTION

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Abstract

This paper presents the development of a mathematical model of the influence of ultrasound duration and temperature on the initial sugar concentration in previously prepared substrates for subsequent fermentation, ie. bioethanol production. The effect of ultrasound duration was examined in the range of 2.17 - 7.82 min, and the effect of ultrasound temperature was examined in the range of 46 - 74°C. The selection of the experimental conditions and the corresponding development of the mathematical model were carried out by the Response Surface Methodology (RSM), specifically by the Central Composition Design (CCD) method. Statistical evaluation of the developed model and individual parameters of the model showed that the variation in durtiona and temperature of ultrasound in the selected range has no statistically significant effect on the final sugar concentration in all three tested substrates. Nevertheless, the presence of ultrasound itself affects the increase in sugar concentration in the starting substrates for bioethanol production. Ultrasound is used as one of the possible pretreatments for fermentation of various substrates for bioethanol production. Whole potatoes, peeled potatoes and the waste part of potatoes, i.e., their peel, were used as raw materials for obtaining the substrate.

Keywords: Bioethanol, mathematical modelling, ultrasound, CCD, waste, potatoes.

Introduction

Bioethanol is a renewable biofuel that is also oxygenated (35% oxygen), thus providing the potential to reduce automobile emissions. Compared to conventional gasoline however, the fuel has a low volumetric energy density which directly translates to vehicles requiring more bioethanol per kilometer (by as much as 50%) when compared to gasoline (Dahman, 2019). Bioethanol is a liquid biofuel that is produced from various renewable sources such as biomass, different agricultural feedstock and more recently microalgae. Potatoes are especially suitable substrates

since they contain sufficient quantities of starch, which can be hydrolysed to sugars with high yield and subsequently fermented to ethanol (Lin et al., 2010; Lantero & Shetty, 2010). Bioethanol production from starch involves 3 steps: hydrolysis, fermentation and distillation (Oliveira et al., 2008). To obtain high yields of ethanol it is very important to optimize pretreatments and fermentation conditions (Ferrari et al., 2013; Gurram et al., 2016; Gurram et al., 2015). Ultrasonic technology has attracted considerable interest in food science and technology due to its promising effects in food processing and preservation (Zenker et al., 2003) and has been confirmed to be applicable to many kinds of starches and polysaccharides (Lida et al., 2008). In starch-protein separation experiments, sonication recovered 97.3-99.5% of the total starch from degermed corn flour (Feng et al., 2008), so ultrasonic technology could provide a practical solution to improve bioethanol yield and cut down the production costs (Khanal, 2007). Also, ultrasonic exposure shows significant advantages due to higher selectivity, reduced use of chemicals and the treatment time, ease of the integration into the process stream, and serves as an environmentally friendly treatment (Ashokkumar et al., 2008; Naumenko et al., 2016; Bai et al., 2016).

Response surface methodology (RSM) is a collection of statistical and mathematical techniques used for the purpose of: (i) Setting up a series of experiments (design) for adequate predictions of a response, (ii) Fitting a hypothesized (empirical) model to data obtained under the chosen design, and (iii) Determining optimum conditions on the model's input (control) variables that lead to maximum or minimum response within a region of interest (Khuri, 2017). RSM was introduced by Box & Wilson in the 1950s, so it is also known as Box-Wilson methodology. More detailed information on the RSM methodology can be found in a series of review articles such as Myers & Montgomery (1995), Hill & Hunter (1996) and Mead & Pike (1975). Generally, RSM give different posibilites in surveying interaction effects of various parameters by following the path of steepest ascent and locating a stationary or central point (Humbrid & Fei, 2016). Also, it gives very valuble information for both process design and process optimisation. This has been successfully applied to optimize medium compositions and process control parameters in biofuel production (Humbrid & Fei, 2016), biodiesel production (Mutmaz et al., 2017), medicine (Jang et al., 2017) and in various other area of production, research and engineering (Ghelicha, et al.,2019; Şenaras, 2019; Miladinović et al., 2016; Guo et al., 2014; Oh et al. 1995).

A common way to optimize process conditions is to vary one of the parameters (independent variables) while keeping the other (one or more) parameters constant, what is called factorial experiments. This method of analysis leads to a large number of experiments, and at the same time can lead to less reliable conclusions (Oh et al.1995). In contrast, RSM with minimum numbers of experiments optimaze multiple variables, providing similar information. RSM develops models allowing plotting contours of depending (response) variables in one or two dimensions,

according to number of different factors used to describe it. Generally, the experiments in RSM are special cases of full factorial experiments that involve center points in the experimental space and face center points or edge center points. Such multilevel experimental points are used to fit the responses to different forms of polynomial equations, which can be generally written as:

$$y = f(x_1, x_2) + e$$
 (1)

y is response or dependent variable, x_1 and x_2 are independent design variables, while *e* is error or noise observed in response variable (experimental error) such as first. Since, the mathematical relationship between the response and the independent variables usually is unknown; the first step in RSM is to find a suitable approximation to the true relationship. The common relationships are low-order polynomials:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + e \tag{2}$$

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_1 x_{11}^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 + e$$
(3)

where equation (1), and (2), are first and second-order polynomials respectively. β is the regression coefficient.

Measuring the variability of the estimate of regression coefficients and thus the variability of the response estimate, one can conclude on quality of design of experiments. Generally, in order to evaluate the significance and reliability of mathematical models proposed by RSM, it is necessary to carry out analysis of variance (ANOVA) (Umbrid & Fei, 2016). One form of Umbrid the RSM is Central Composite design (CCD), which is more practical than the three-level factorial designs. The CCD is based on a two-level factorial design with the addition of 2k (k is the number of independent variables) points (star points) between the axes plus repeat points at the centroid (Wagner et al., 2014). Figure 1 shows the CCD for the case of 2 and the case of 3 independent variables.

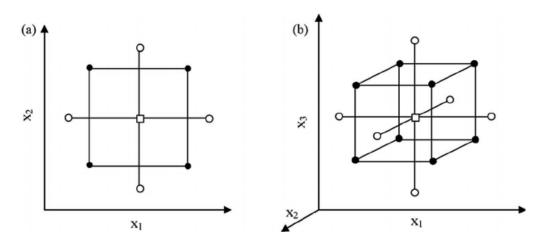


Figure 1. Graphical illustration of the CCD for: a) 2 independent variables at 2 levels, with 4-star (axial) points and one central; b) 3 independent variables at 2 levels, with 6 stare (axial) points and one central

Materials and Methods

Ultrasound pretreatment

Whole potato (WP), peeled potato (PP) and potato peel waste (PPW) were used as a raw material for obtaining the substrate for bioethanol production. One hundred and fifty grams of the prepared samples (100 g of WP, PP or PPW + 320 mL distillated water, respectively), was put in a beaker, closed with aluminium foil and put into an ultrasonic cleaning bath WUC-A03H (Witeg Labortechnik, Germany), which works at the frequency of 40kHz and the heating power of 172W. In order to examine the effect of ultrasound on the sugar content in the starting substrate for fermentation, i.e., obtaining bioethanol, a set of experiments were carried out in accordance with the requirements of CCD (5 min, 60 °C was selected as an optimal of ultrasound pretreatment). Reducing sugars were determined as glucose by using dinitro salicylic acid (DNS) reagent at optical density 575 nm, by the method described by Miller (1959).

The design of the experiments, analysis and processing of the obtained results was performed using the program Deign-Expert 11 (Stat-Ease, Inc.). For two independent variables (time – X_1 and temperature – X_2 of ultrasound) at two levels, low (coded value -1) and high (coded value +1), the total number of experiments was 13. Number of experiments was determined by the expression: 2^k ($2^2 = 4$: factor points) + 2k (2 x 2 = 4: axial points – coded value ±1,414) + 5 (center points: five replications – coded value 0), as shown in Tables 1.

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Table 1 The cod	led levels and actual values of the independent variables Coded levels						
	-1,414	-1	0	+1	+1,414		
Time (min.)	2,17	3	5	7	7,82		
Temperature (°C)	45,86	50	60	70	74,14		

The factors (variables) were coded according to the following equation:

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$$x_i = \frac{x_i - x_{i0}}{\Delta x_i} \tag{3}$$

where x_i is the coded value and X_i is the real value of the its independent variable, X_{iao} is the real value of the *its* independent variable at the center point, and Xu is the step change value.

A second-order polynomial model was developed by multiple regression technique for two factors by using mentioned software. The testing independent variables X_1 , X_2 and the mathematical relationship of the response Y on these variables are approximated by quadratic polynomial equation:

$$Y = b_0 + b_1 x_1 + b_2 x_2 + b_{11} x_1^2 + b_{22} x_2^2 + b_{12} x_1 x_2 + e$$
(4)

The statistical analysis of the developed mathematical models, i.e., the assessment of its significance, was performed using linear regression analysis and Fisher's statistical test in the analysis of variance (ANOVA).

Results and discussion

From the economic viewpoint it is recommended to keep sonication time low since ultrasound treatment consumes a large amount of energy, so 5 min and temperature 60 °C were selected as an optimal of ultrasound pretreatment. Relatively short duration and relatively low temperature of the ultrasound pretreatment were also selected by other investigators as appropriate for destroying the starch crystalline arrangement of various substrates and enhancing the glucose yield (Huang et al., 2007; Khanal et al., 2007; Shewale & Pandit, 2009; Nikolić et al., 2010; Nikolić et al., 2011).

The sugar content increased with ultrasonic treatment. Khanal et al. (2007) reported that glucose release from sonicated corn samples improved by 30% with respect to the control sample mainly due to reduction in particle size, better mixing due to the streaming effect, and release of additional lipid-bound starch. In the research of Nikolić et al. (2010) it was showed that ultrasound pretreatment (at a frequency of 40 kHz) effectively increased glucose concentration after liquefaction of corn meal

suspension compared with the untreated control sample, under determined optimal conditions of sonication (5 min, 60 °C). In the research conducted by Yaldagard et al. (2008) was investigated the influence of ultrasound treatment on barley α -amylase activity and their results indicated that ultrasound treatment increased α -amylase activity, which might be the explanation of α -amylase activity enhancement. Feng et al. (2008) and Nikolić et al (2010) showed that the application of ultrasound helps starch–protein separation and therefore enables the activation of amylolytic enzymes during mashing, which is in agreement with the results obtained in this study.

The surfaces in the presented figures (1,2,3) show changes in the sugar concentration in the analyzed samples and according to the obtained regression equations. Table 2 presents the obtained equations in the form of coded values. Each individual coefficient in the above equations was statistically evaluated by appropriate tests within the ANOVA analysis, as well as the obtained models (mathematical relations) as a whole, what is shown in the table 3, 4 and 5.

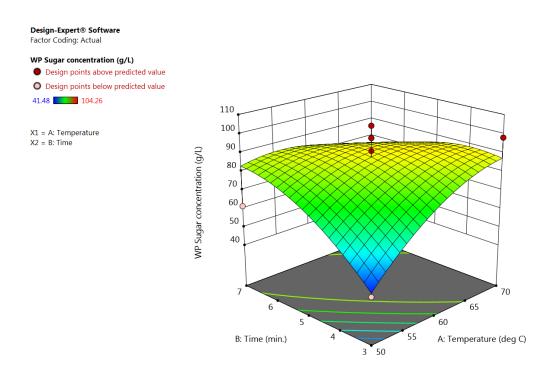


Figure 2. Sugar concentration of sample of whole potatoes (WP) as function of time and temperature of ultrasound

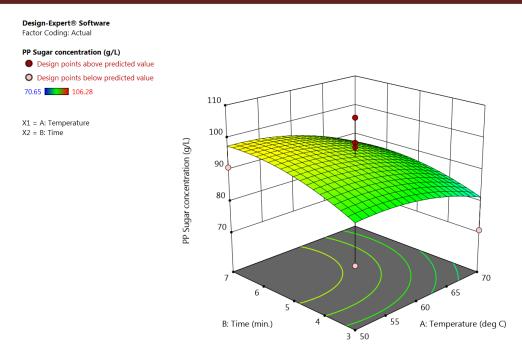


Figure 3. Sugar concentration of sample of peeled potatoes (WP) as function of time and temperature of ultrasound

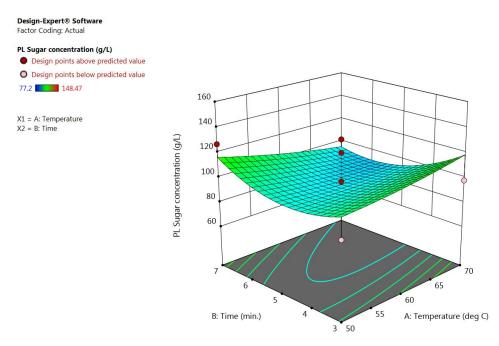


Figure 4. Sugar concentration of sample of waste part of potatoes (WP) in function of time and temperature of ultrasound

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
WP Potato						
Intercept	87.87	1	7.95	69.08	106.66	
A- Temperature	7.10	1	6.28	-7.76	21.95	1.0000
B-Time	5.02	1	6.28	-9.84	19.87	1.0000
AB	-14.79	1	8.88	-35.80	6.22	1.0000
A ²	-8.91	1	6.74	-24.84	7.02	1.02
B ²	-8.59	1	6.74	-24.52	7.34	1.02
PP Potato						
Intercept	94.16	1	5.47	81.23	107.09	
A- Temperature	-4.23	1	4.32	-14.46	5.99	1.0000
B-Time	3.80	1	4.32	-6.42	14.03	1.0000
AB	-0.8325	1	6.11	-15.29	13.62	1.0000
A ²	-2.72	1	4.64	-13.68	8.24	1.02
B ²	-2.78	1	4.64	-13.75	8.18	1.02
PL Potato						
Intercept	94.37	1	8.88	73.38	115.37	
A- Temperature	-2.09	1	7.02	-18.68	14.51	1.0000
B-Time	-3.12	1	7.02	-19.72	13.48	1.0000
AB	-8.54	1	9.93	-32.01	14.94	1.0000
A ²	1.83	1	7.53	-15.97	19.63	1.02
B ²	12.71	1	7.53	-5.09	30.51	1.02

Table 2. Coefficients of regression equation in terms of coded factors

The coefficient estimate represents the expected change in response per unit change in factor value when all remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the runs. The coefficients are adjustments around that average based on the factor settings. When the factors are orthogonal the VIFs are 1; VIFs greater than 1 indicate multi-colinearity, the higher the VIF the more severe the correlation of factors. As a rough rule, VIFs less than 10 are tolerable.

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	2422.02	5	484.40	1.53	0.2924
A-Temperature	402.73	1	402.73	1.28	0.2960
B-Time	201.38	1	201.38	0.6378	0.4508
AB	874.98	1	874.98	2.77	0.1399
A ²	552.39	1	552.39	1.75	0.2275
B ²	513.43	1	513.43	1.63	0.2429
Residual	2210.28	7	315.75		
Lack of Fit	1330.30	3	443.43	2.02	0.2542
Pure Error	879.98	4	219.99		
Cor Total	4632.30	12			

Table 3 ANOVA for quadratic model (Responce: WP Sugar concentration)

The Model F-value of 1.53 implies the model is not significant relative to the noise. There is a 29.24% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case there are no significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The Lack of Fit F-value of 2.02 implies the Lack of Fit is not significant relative to the pure error. There is a 25.42% chance that a Lack of Fit F-value this large could occur due to noise.

Table 4 ANOVA for quadratic model (Responce: PP Sugar concentration)

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	355.16	5	71.03	0.4751	0.7851
A-Temperature	143.39	1	143.39	0.9592	0.3600
B-Time	115.75	1	115.75	0.7743	0.4081
AB	2.77	1	2.77	0.0185	0.8955
A ²	51.45	1	51.45	0.3442	0.5759
B ²	53.94	1	53.94	0.3608	0.5670
Residual	1046.48	7	149.50		
Lack of Fit	679.86	3	226.62	2.47	0.2012
Pure Error	366.63	4	91.66		
Cor Total	1401.64	12			

The Model F-value of 0.48 implies the model is not significant relative to the noise. There is a 78.51% chance that an F-value this large could occur due to noise. In this case there are no significant model term, since there are no model terms with P-values less than 0.0500. The Lack of Fit F-value of 2.47 implies the Lack of Fit is not significant relative to the pure error. There is a 20.12% chance that a Lack of Fit F-value this large could occur due to noise.

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	1527.50	5	305.50	0.7751	0.5971
A-Temperature	34.78	1	34.78	0.0882	0.7751
B-Time	77.87	1	77.87	0.1975	0.6701
AB	291.56	1	291.56	0.7397	0.4182
A ²	23.20	1	23.20	0.0589	0.8153
B ²	1123.10	1	1123.10	2.85	0.1353
Residual	2759.13	7	394.16		
Lack of Fit	1709.82	3	569.94	2.17	0.2339
Pure Error	1049.31	4	262.33		
Cor Total	4286.64	12			

Table 5. ANOVA for quadratic model (Responce: PP Sugar concentration)

The Model F-value of 0.78 implies the model is not significant relative to the noise. There is a 59.71% chance that an F-value this large could occur due to noise. In this case there are no significant model terms (P-values values are greater than 0.1000). The Lack of Fit F-value of 2.17 implies the Lack of Fit is not significant relative to the pure error. There is a 23.39% chance that a Lack of Fit F-value this large could occur due to noise.

Conclusion

Based on the experimental data, the mathematical model of the influence of ultrasound duration and temperature on the initial sugar concentration in whole potatoes, peeled potatoes and the waste part of potatoes as substrate for bioethanol production was developed. According to statistical evaluation of the developed model and its individual parameters, one can conclude that the variation in duration and temperature of ultrasound in the selected range has no statistically significant effect on the final sugar concentration in all three tested substrates.

Acknowledgments This study is a result of the research conducted within the Project (19.032/961-111/19) financially supported by the Ministry for Scientific and Technological Development, Higher Education and Information Society of the Republic of Srpska.

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Original scientific article

SPATIAL AND TEMPORAL VARIABILITY OF PM_{2.5}/PM₁₀ RATIO IN REPUBLIC OF SRPSKA

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Abstract

Bosnia and Herzegovina is facing a wide range of challenges regarding air quality. The country's residents are exposed to the high levels of health-damaging particulate air pollution which are caused by a range of different emission sources and geographic circumstances.

The particulate matter (PM) value is usually used to indicate the degree of air pollution. In addition to that of $PM_{2.5}$ and PM_{10} , the use of the $PM_{2.5}$ / PM_{10} ratio as an indicator and assessor of air pollution has also become more widespread. This ratio reflects the air pollution conditions and pollution sources. However, the application of the ratio needs its varying pattern because PM concentrations change significantly at time and space. Hourly and daily $PM_{2.5}$ and PM_{10} observations at one monitoring site in the urban area, one urban-background site, and one urban-industrial site in the Republic of Srpska in 2017-2019 were collected to investigate both long-term, short-term temporal variation and spatial distribution of the ratio.

The results show that the annual average $PM_{2.5}/PM_{10}$ ratio is 0.45 at urban-site and 0.70 at the urban-background site and 0.57 at the urban-industrial site with apparent seasonal, monthly, and daily variations. Stable atmospheric conditions are prerequisite for maximum ratio in the winter season. There are apparent night-day differences of daily variation of the ratio and obvious spatial gradients of the ratio from urban, urban-background, and urban-industrial sites. This study provides further insights into the spatial and temporal variability of $PM_{2.5}/PM_{10}$ ratio that should be noticed in its applications.

Keywords: Air quality, particulate matter, PM, pollution sources.

Introduction

Suspended particles have a dominant impact on air quality in urban agglomerations and other parts of the Republic of Srpska. Suspended particles are a complex mixture of different organic and inorganic substances. They contain sulfates, nitrates, some crystalline species, sea salt, heavy metals, ions, and water. Suspended particles can be in a solid and liquid state, and can be found in various forms such as ash, smoke, soot, etc. The classification was made based on particle size, so suspended particles with an aerodynamic diameter of less than 2.5 μ m are called and marked as PM_{2.5} or fine particles, while suspended particles with an aerodynamic diameter of less than 10 μ m are called and marked as PM₁₀, and in addition to fine particles, also contain coarse particles in the range of 2.5 μ m-10 μ m. Sources of suspended particles are: central and local heating, traffic, dust from landfills and waste disposal sites, fires, industrial facilities (thermal power plants, cement plants, ore roasting plants), wind dust, dust from agricultural regions, dust from construction sites.

The PM_{2.5} fraction is formed mainly from the product of incomplete combustion, carrying with it sulfates and nitrates, elemental carbon, polyaromatic hydrocarbons, toxic and carcinogenic metals (*Chow et al., 1994*). Coarse particles are mainly formed from natural processes such as re-suspension of local soil, dust storms, as well as from anthropogenic sources like road dust and various industrial processes (Querol *et al., 2004*).

From the health risk point of view, fine particles are much more dangerous than coarse particles. PM_{10} has been linked to health problems such as asthma attacks, some respiratory and cardiovascular diseases (*Anderson et al., 2012; Brook et al., 2010*). $PM_{2.5}$ particle fractions can travel into the lungs, enter the circulatory system, and can cause much more serious problems than coarse particle fractions ($PM_{2.5-10}$) (*Owen et al., 1992*). A health study conducted in the US (*Dockery and Pope, 1994*) showed that an increase in PM_{10} concentration by 10 µg/m³, causes an increase in the daily mortality rate by approximately 1%. Another study also conducted in the US (*Schwartz et al., 1996*) shows a similar result for $PM_{2.5}$. Namely, an increase in $PM_{2.5}$ concentration by 10 µg/m³ leads to an increase in the daily mortality rate by approximately 1.5%.

The value of PM particles is usually used to indicate the degree of air pollution. In addition to the values of $PM_{2.5}$ and PM_{10} , the use of the ratio $PM_{2.5}/PM_{10}$ as indicators and estimators of air pollution has become more widespread. This ratio reflects the conditions of air pollution and sources of pollution. Since fine and coarse particles come from diverse sources and have different physic-chemical properties, the $PM_{2.5}/PM_{10}$ ratio can provide crucial information relating to the particle origin, its formation process, and its effects on human health (Blanco-Becerra *et al.*, 2015; Speranza *et al.*, 2014). Higher ratios of $PM_{2.5}/PM_{10}$ attribute particle pollution to anthropogenic sources and smaller ratios indicate considerable involvement of coarse particles, which might be related to natural sources, e.g. dust storm (Sugimoto *et al.*, 2016). Actually, the $PM_{2.5}/PM_{10}$ ratio is often used to characterize the underlying atmospheric processes within the local environment (Chu *et al.*, 2015; Yu and Wang, 2010).

PM concentration is influenced by various factors such as land use, population density, meteorology conditions (Xu *et al.*, 2016b), and there is obvious spatio-

temporal heterogenity of PM concentrations at urban or regional scales. Therefore, it is evident that the fraction of fine particles $(PM_{2.5})$ in PM_{10} also varies in time and space (Parkhurst *et al.*, 1999; Zhou *et al.*, 2016).

This study gives us an insight into the spatial-temporal variability of the $PM_{2.5}/PM_{10}$ ratio, it tells us about the contribution of $PM_{2.5}$ particles in PM_{10} . By using this ratio, as well as observing it's change trough different geographical areas at different time intervals, we can get useful information about the source of pollution, whether particles $PM_{2.5}$ are dominated by PM_{10} particles, which certainly indicates that the source of pollution is anthropogenic or the contribution is smaller which again indicates natural sources of pollution.

Materials and methods

Study Area

In this study, we have processed the data from three measuring areas in the Republic of Srpska: the urban-site city of Banja Luka, the urban-background site city of Prijedor, and the urban-industrial site municipality of Brod, for a period 2017-2019. The city of Banja Luka is the largest local government unit in the Republic of Srpska and the second in Bosnia and Herzegovina, with the First category of air quality, clean or slightly polluted air where the limit values of pollutants have not been exceeded, except in 2017, where we have the Third category of air quality-excessively polluted air. In the city of Prijedor and the municipality of Brod, we have the Third category of air pollution, excessively polluted air where the tolerance values for one and more pollutants are exceeded. The cities of Banja Luka and Prijedor, as well as the municipality of Brod, are faced with a problem in terms of increased concentration of $PM_{2.5}$ and PM_{10} , which are dominant during the winter.

PM Monitoring and Measurements

Continuous measurements and monitoring of air quality in the Republic of Srpska are performed in several cities and municipalities in the Republic of Srpska: Banja Luka, Prijedor, Bijeljina, Brod, Ugljevik, and Gacko. More detailed information on the measuring areas used in this paper can be found in Table 1.

The reference method for sampling and measuring the concentrations of suspended particles PM_{10} is described in the standard BAS EN 12341, air quality-determination of the fraction PM_{10} of the suspended particles-reference method, and field test procedure to demonstrate the equivalence of measurement methods.

The reference method for sampling and measuring the concentration of suspended particles $PM_{2.5}$ is described in the standard BAS EN 14907, ambient air quality-standard gravimetric

method for determining the mass fraction $PM_{2.5}$ of suspended particles.

No	Measuring point	Location	Measuring device	
1.	Banja Luka "CITY CENTER"	N 44.77; E 17.18	Bam 1020	
2.	Prijedor "METEOROLOGICAL STATION"	N 44.97; E 16.71	Grimm EDM 180+	
3.	Brod "BROD OIL REFINERY A.D"	N 45.13; E 17.98	Horiba APDA 371	

Table 1:	Measuring	sites used	in the paper
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Data Summarizing and Analysis

In this paper, hourly data were used for the city of Prijedor and the municipality of Brod, and daily data for the city of Banja Luka, in the period 2017-2019. Based on the data on concentrations obtained from the measuring stations for $PM_{2.5}$ and PM_{10} , the calculation of the ratio $PM_{2.5}/PM_{10}$ for hourly values was performed. The annual ratio average was obtained from the hourly ratios for the whole year.

The time period is divided into summer and winter, where the summer period includes months (April, May, June, July, August, and September), and the winter period includes the months (January, February, March, October, November, December), to get the change in the $PM_{2.5}/PM_{10}$ ratio depending on the seasonality, and thus reach a conclusion about the source of the pollution. We have also classified night and day regimes from summer and winter periods because increased or decreased concentrations of particles in the twenty-four-hour regime may indicate the influence of meteorological factors on pollutants.

On air quality stations, it is desirable to perform all meteorological observations necessary to determine the relationship between meteorological conditions and the state of air pollution and the spread of pollutants in the air. The basic meteorological parameters are monitored: wind direction, wind speed, relative humidity, air temperature, atmospheric pressure, precipitation, and insolation.

Results

Long-Term Variation of the Ratio

The long-term variation of the ratio in this paper is analyzed on an annual basis, but also seasonally, by dividing the year into two seasons, summer and winter. The processed measuring locations are: the urban-site city of Banja Luka, urban-background site city of Prijedor, and urban-industrial site municipality of Brod. The results show that the annual average of $PM_{2.5}/PM_{10}$ ratio is 0.45 at urban-site and 0.70 at the urban-background site and 0.57 at the urban-industrial site with apparent seasonal, monthly, and daily variations.

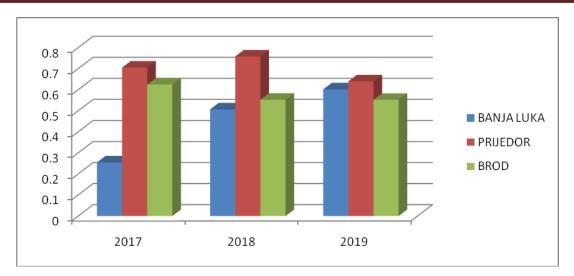


Figure 1. Change of ratio PM_{2.5}/PM₁₀, Banja Luka, Prijedor and Brod, 2017-2019.

If we observe the Figure 1. and the change in the $PM_{2.5}/PM_{10}$ ratio for Banja Luka, Prijedor, and Brod in the period 2017-2019, it is clear that ratios have been constantly increased in the urban-background site of Prijedor. The values of $PM_{2.5}/PM_{10}$ ratios in the city of Prijedor range from 0.64-0.75. Compared to the city of Prijedor, the values of ratios in the urban-industrial site municipality of Brod are lower and range from 0.55-0.62, and in the urban-site city of Banja Luka, the ratios show the lowest values in the range of 0.25-0.60.

Fine particles, as well as coarse particles, are emitted and produced due to human activities in the urban area, but fine particles can travel further than coarse particles before they are removed from the atmosphere, resulting in higher $PM_{2.5}/PM_{10}$ ratios in suburban (Parkhurst et al., 1999; Zhou et al., 2016). Parkhurst et al. (1999) demonstrated that the fractional contribution of PM_{2.5} to PM₁₀ appears greater at remote stations and lower at those stations which are more likely to be influenced by anthropogenic local sources. It should also not be overlooked that the concentration of suspended particles is affected by meteorological parameters. Meteorological parameters such as wind speed and direction, temperature and relative humidity, solar radiation, and atmospheric stability affect the dispersion of pollutants. At high relative humidity, the suspended particles absorb water, which leads to an increase in their volume and fogginess. There are significant natural mechanisms for removing suspended particles from the atmosphere, and these are strong current and precipitation. The amount of pollution is also affected by the proximity of mountains and rivers, the peripheral wind direction, and the amount of precipitation in an area. Wind speed and direction provide real-time information on regional transport of pollutants and are used to assess the ratio between sources and levels of air pollution. Taking into account all the above facts, the obtained increased ratios in the city of Prijedor in relation to the city of Banja Luka and the

municipality of Brod can be justified. Considering that in the city of Prijedor the prevailing wind direction is calm, the state without wind, the average wind speed is 0.9 m/s, the wind direction is 163.8-170°, the influence of meteorological parameters is obvious. The highest pollution occurs during the period of calm due to weak air diffusion, reduced wind speed. Weather conditions characterized by high air stability and low wind speed increase pollution levels due to reduced mixing between air layers. As a consequence of such weather conditions, the prescribed limit values of PM particle concentrations are exceeded more often. The average annual $PM_{2.5}/PM_{10}$ ratio of 0.70 in the city of Prijedor indicates the 70% contribution of PM_{2.5} in PM₁₀, which is a clear indicator of anthropogenic pollution. The annual average of $PM_{2.5}/PM_{10}$ ratio in the urban industrial area of the municipality of Brod is 0.57, with a 57% contribution of PM_{2.5} in PM₁₀, which is also an indicator of anthropogenic pollution. If we take into the consideration the fact that automatic monitoring station for air quality is located in the entrance of the Oil refinery Brod, in close proximity to river Sava, with predominant westsouthwest wind direction, average wind speed of 1-1.2 m/s, and wind direction 179-191°, where aeration is more pronounced in relation to the city of Prijedor, lower values of the contribution of PM_{2.5} particles are expected. The results from the urban measuring area of the city of Banja Luka indicate that the average annual ratio is 0.45, with a 45% contribution of $PM_{2.5}$ in PM_{10} . The data used for the city of Banja Luka are from the automatic monitoring station for air quality in the measuring area "city center", from which we can conclude that a large percentage of the pollution originates from the traffic, considering that the station is located in the city center where traffic is dominant.

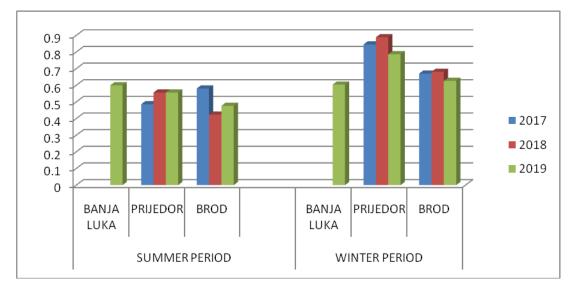


Figure 2: Changing ratios *PM*_{2.5}/*PM*₁₀ in winter and summer period.

On the Figure 2 we can monitor the variations of $PM_{2.5}/PM_{10}$ ratio during the winter and summer period. The maximum ratio in the winter period was recorded in the city of Prijedor with 0.88, while during the summer period the maximum ratio was reached in the city of Banja Luka, with 0.59, which is a clear indicator of seasonal variations. During the winter periods we are faced with an increased number of days with longterm fog, including the increased use of solid fuels in domestic heating, and at the same time with the lack of winds for dispersion of harmful particles, which certainly causes higher concentrations of particles within that period and higher values of seasonal variations. The secondary aerosol, one of the major sources of fine particles, is also accelerated due to the lower mixing height in winter are favourable for the dry deposition of coarse particles, but also favour the accumulation of fine particles in the air, resulting in the domination of fine particles in PM₁₀ in winter (Huang et.al., 2015).

Short-term variations

Short-term variations of $PM_{2.5}/PM_{10}$ ratios are presented through day and night variations in winter and summer period, for the urban background site-city of Prijedor and urban industrial site-municipality of Brod. The period of the day is from 7 AM to 5 PM in the winter period and from 6 AM to 8 PM in the summer period, while the period of the night is from 6 PM to 6 AM in the winter period and from 9 PM to 5 AM in the summer period.

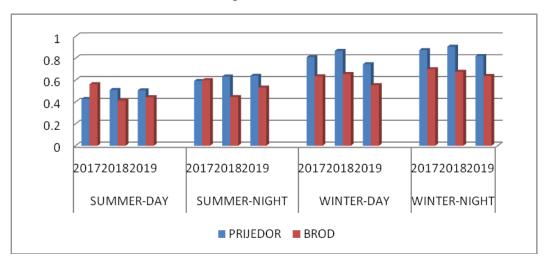


Figure 3: Day-night variations of the ratios $PM_{2.5}/PM_{10}$ between winter and summer, the city of Prijedor and municipality of Brod.

On the Figure 3, we can see daily-night variations of $PM_{2.5}/PM_{10}$ ratios for the city of Prijedor and the municipality of Brod. Due to technical difficulties, these data are not available for the city of Banja Luka.

On the following chart, we can see daily-night variations, where $PM_{2.5}/PM_{10}$ ratios are constantly higher during the night, independent of the seasonality. If we analyze the summer period for both locations, the values of ratios vary from 0.41 to 0.56 during the period of the day, while during the period of the night those values reach 0.64. That kind of variability trend is present also during the winter period, where during the day values vary from 0.55 to 0.86, and during the night reach up to 0.90.

The process of rapid cooling of the earth's surface to a temperature lower than the air temperature above the surface during the clear night, as a result of energy radiation, is called temperature inversion. Vertical air mixing is disabled due to temperature inversion, which causes an increase in the concentration of ozone and particle precursors. If the concentrations of precursors are higher, the chemical reactions in the production of secondary pollutants in the atmosphere are faster and more efficient. There are several different types of temperature inversion, but the most common one is the night inversion, and it occurs during the night when the ground surface cools faster than the air above it. The strongest inversions arise from long winter nights and clear night evenings. This kind of inversion enables the retention of emitted air pollution in the ground layer during the night. During the day the sun heats the ground surface that gradually starts the process of vertical air mixing, the night inversion is destroyed by noon and vertical dispersion of retained air pollution is enabled. If the cloud cover is present during the day or if the inversion is strong, the inversion can last longer and prevent vertical mixing of air pollution which causes higher concentrations of pollution.

The daily-night variations during the winter and summer period in the urban background site-city of Prijedor and urban industrial site-municipality of Brod, clearly show the increase of ratios during the night as a result of temperature inversion.

Spatial ratio distribution

In the observed period 2017-2019 in three measuring sites in Republic of Srpska, spatial disproportion of $PM_{2.5}/PM_{10}$ ratio is present. The values of three-year average of $PM_{2.5}/PM_{10}$ ratios are the following:

- urban measuring site-city of Banja Luka=0.45
- urban background site-city of Prijedor=0.70
- urban industrial site-municipality of Brod=0.57,

where we can see that the highest contribution of $PM_{2.5}$ particles in PM_{10} is present in the city of Prijedor, with 70%, followed by the municipality of Brod, with 57%, and the lowest contribution is present in the city of Banja Luka with 45%. Considering that it is has been proven that fine particles can travel further than coarse particles before being removed from the atmosphere, resulting in higher $PM_{2.5}/PM_{10}$ ratios in suburban areas, while also recognizing the impact of all meteorological parameters on the pollution, the highest three-year ratio in the urban background area of the city of Prijedor, with 70% can be explained. Somewhat lower contribution of PM_{2.5} particles in PM₁₀ has been calculated for the urban industrial area of the municipality of Brod, with 57%. The automatic measuring station for air quality in the municipality of Brod is located in the entrance of the Oil refinery Brod, in the proximity of river Sava, with predominant west-southwest wind direction, which surely contributes to the lower contribution of $PM_{2.5}$ particles in PM_{10} in relation to the city of Prijedor. The lowest percentage is calculated for the city of Banja Luka, with 45% of the contribution, where the station is located in the city center, which indicates that traffic is the major source of pollution. High values of PM_{2.5} particles in PM₁₀ on all three locations in the Republic of Srpska imply the pollution of anthropogenic origin and the most common sources are: central and local heating, traffic, road dust, fires, industrial facilities, dust from agricultural regions, construction dust, etc.

Discussion

In this study, spatio-temporal $PM_{2.5}/PM_{10}$ ratios have been analyzed for urban site, urban background, and urban industrial measuring site, by monitoring hourly and daily data for a period of three years.

The average annual ratio for three measuring areas in the Republic of Srpska is 0.57. It has been published that the ratio of 0.6 is considered to be a typical North American $PM_{2.5}/PM_{10}$ ratio (Dockery and Pope, 1994). In Asia the ratio is usually lower than 0.5 which indicates higher masses of coarse particles; but in urban locations in China, we have an average value of $PM_{2.5}/PM_{10}$ ratio higher than 0.5 (Hopke et al., 2008). Studies conducted in China, Wuhan, show that three year average of the highest ratio (0.66) has been discovered in the traditional industrial zone, which indicates a significant contribution of energy combustion and other industrial processes to fine particles. In the urban-industrial site of the municipality of Brod, a three-year ratio average is 0.57, which shows the lower contribution of industrial processes in the pollution. The three-year ratio average of 0.70, we can conclude that in both cases the high contribution of $PM_{2.5}$ shows a large contribution of anthropogenic pollution. The ratio values in urban locations in the

city of Wuhan vary from 0.58-0.66. The data from the urban measuring site of the city of Banja Luka show a value of 0.45, which is certainly lower compared to urban locations in Wuhan.

The spatial disproportion of ratios on three measuring areas varies in relation to the seasons but also to the periods of day and night. All three measuring sites in three years show the highest ratios during the winter period, while in the summer period the ratios are visibly decreasing, where the highest disproportion between three sites is present also in the winter period. If we consider all the facts, in practice, the $PM_{2.5}/PM_{10}$ ratio can provide useful information regarding the sources of the pollution, whether it is of anthropogenic or natural origin, however, in this paper we have been deprived of a diverse chemical composition of fine and coarse particles which is of great importance for the assessment of polluters.

Conclusions

In this study, the spatio-temporal variability of $PM_{2.5}/PM_{10}$ ratio has been analyzed. The contribution of fine $PM_{2.5}$ particles in PM_{10} varies in time and space, which has been shown in the example of two cities and one municipality in three years in the Republic of Srpska. During one day, ratios increase from day to night in all seasons, as a result of the temperature inversion, and if we pay attention to seasonality it is clear that during the winter period the content of fine particles in PM_{10} is higher compared to the summer period. We can see an apparent spatial gradient where $PM_{2.5}/PM_{10}$ ratio increases from urban measuring site-city of Banja Luka, urban industrial measuring site-municipality of Brod, to urban background measuring site-city of Prijedor, where the highest values have been confirmed. This study is of great importance because understanding the $PM_{2.5}/PM_{10}$ ratio can provide crucial information regarding the particle origin, generation process, and

provide crucial information regarding the particle origin, generation process, and its impact on human health, but also for better understanding of atmospheric processes.

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"XIII CONFERENCE OF CHEMISTS, TECHNOLOGISTS AND ENVIRONMENTALISTS OF REPUBLIC OF SRPSKA"

OTHERS

Preliminary report

DATA ABOUT CHENOPODIACEAE FAMILY ALLOCATION ON NEW HOLOCENE PERIOD IN ELBASAN CITY – ALBANIA

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Abstract

Paleopalynological data given in this scientific paper were taken from the deposit's samples of the last historical period of New Holocene in Elbasan city, one of the oldest cities positioned in Middle Albania. This study provides some palynological data on the distribution of the Chenopodiaceae family during New Holocene period.

The purpose for which this scientific research work has been undertaken is to present the connection that is created between the depth and the distribution of the Chenopodiaceae family over different time periods. All paleopalynological data on the Holocene presence of the Chenopodiaceae family in Elbasan city are given for the first time, having so far, no paleopalynological studies on this family.

In our judgment, based on the results obtained, the palynomorphs allocation of Chenopodiaceae family is clearly presented, where we can emphasize that: palynomorphs are present at all depths (in total 508 spores) also having at each depth level a constant distribution.

Keywords: Chenopodiaceae Family, Paleopalynological, Palynomorphs, New Holocene, Elbasan city.

Introduction

Based on the selection of plant pollen we are able to assess the evolution of primitive and specialized features of pollen exin (Paccini & Hesse, 2005). This paper belongs to the scientific discipline of Palinology, an Interdisciplinary Science that is closely related to both geology and biological sciences, as the object of study is pollen found in organic sediments including not only the study of current but also fossil paliniforms (Faegri & Iversen, 1989).

Due to the super resistance over the years of the outer wall of the pollen grains (or exine) pollen and spores are excellently preserved (Paccini & Franchi, 1978). Judging by the timely distribution of fossil pollen, we are able to realize the timely progress of the use and cultivation of plants by human hands, the way of its nutrition and in a way to determine the evolutionary paths of agriculture (Bryant & Holloway 1996).

This paper gives palynological data of New Holocene deposits in Elbasani town. Through this type of study, important results can be obtained for the reconstruction of prehistoric flora and climate as well as to determine the Holocene stratigraphy (Moore & Webb, 1978).

Regarding the Holocene deposits for this family, so far, no similar study has been conducted by local or foreign researchers for the Elbasan region (Jançe, 2015; Jançe et al. 2017). By studying the pollen Holocene deposits we can reach the determination of the transforming factors of the flora in Elbasan city, in the case of our study mainly for the evolution that the representatives of the Chenopodiaceae family have undergone (Forest, 1999; Jançe, 2015).

This scientific paper was started with the aim of presenting the ratio of pollen quantity and timely distribution to the Chenopodiaceae family.

Materials and Methods

Fossil pollen obtained from terrestrial sediments is analyzed qualitatively and quantitatively. Mainly for fossil pollen extraction all methods used focus on physico-chemical processing of 1 gram of sediment (Faegri & Iversen, 1989; Jançe, 2015).

Through detailed palynological study, concrete results are reached on the paleoecology and paleoclimate of the Quaternary and Holocene periods. (Huntley and Prentice, 1993; Allen et al. 2000). Also, through this record we are able to shed light on the human impact on the transformation of the natural environment (Miras et al. 2004).

During this research we have taken 16 soil samples, from 0.25 to 4 meters of depth with the distance between the sampling to 0.25 m.

Erdtman acetolysis method

The soil sampling is based on Erdtman method (Erdtman, 1960a; 1969b). In order to get better results first mix 1 cm^3 soil with 10ml KOH (10 %).

Erdtman acetolyze method consists on processing the material with an acetolyze mixture, acetic anhydride $(CH_3COO)_2$ and sulfuric acid (H_2SO_4) in a 9:1 ratio.

We cleaned with distillated water and mixed it with acetolyze solution, until a neutral environment is obtained. The emasculation process is followed by a centrifugal process for three minutes (3000 rotation/minute).

The acetolyze method is widely used in paleopalynology; because it gives better visibility over the spores and pollen compared with the other methods used during the microscopic observation process (Erdtman, 1960a; 1969b; Jançe, 2015; Jançe et al. 2017).

Fixture of prepared composites

The fixture of prepared composites was realized by using the method of gluepreparations through gel-glycerin, which was prepared based on the Kisser method (Kisser, 1935) by using 50 gram of gelatin, 175 ml of distillate water, 150-gram glycerin, 7-gram phenol (crystals). The composite was isolated to the edges of microscope slide with spray or paraffin and after 3 days it was ready to be used and stored.

Results and Discussion

Table 1 give the data about the spores' number for Chenopodiaceae family conform to the depth, also is presented the total spores number for this family. The maximum palynomorphs of Chenopodiaceae family (38 spores per sample) is taken in 0.25 m of depth (i.e., on the surface) while the minimum number, 26 spores, is taken in the deepest layer of 4m.

Sample	Depth (meters)	Number of spores (Chenopodiaceae Family)
1	4	26
2	3.75	28
3	3.5	28
4	3.25	30
5	3	32
6	2.75	29
7	2.5	31
8	2.25	33
9	2	35
10	1.75	29
11	1.5	31
12	1.25	34
13	1	36
14	0.75	33
15	0.5	35
16	0.25	38
Total r	number of spores	508

Table 1. Number of spores according to the depth

In figure 1 is shown almost the permanent palynomorphs presence of Chenopodiaceae family from the bottom near to the surface, with the exception of

the samples 9 where it is observed one decreasing tendency (exactly in 2 m of depth), as well the growing spore's number for this family is clearly seen during almost the entire passage from the depth to the surface.

The input shows the increase of the representative's presence of family Chenopodiaceae near to the surface should be associated with human impact on the cultivation of this family plant.

One other reason for this increase may be related to the fact that new forms of pollen are stored better than older ones to meet the depths samples.

Based on the record presented in table 1 the total palynomorphs number of Chenopodiaceae family is 508 spores. In sample 5, 9 and 13, the palynomorphs of Chenopodiaceae family undergoing an immediate decrease (Figure 2).

Climate is a very important factor that can cause changes in land use mainly affecting human societies that under the influence of climate change carry out fundamental changes in the environment (Mercuri et al. 2011).

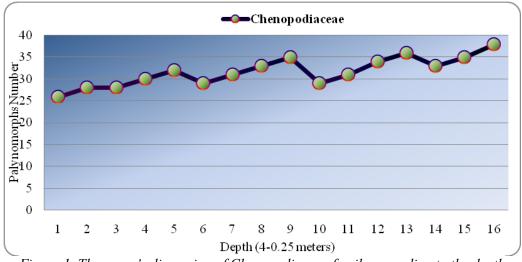


Figure 1. The spore's dispersion of Chenopodiaceae family according to the depth

The Chenopodiaceae are annual or perennial herbs, subshrubs, shrub or small trees (Kadereit et al. 2010). Chenopodiaceae are a subfamily of the flowering plant family Amaranthaceae.

The earliest fossil finds for Chenopodioideae are pollen grains found in the Maastrichtian sediments of the Edmonton Formation in Canada (Zhu, 1996).

Stable number of Chenopodiaceae palynomorphs in almost all samples probably indicates that the human factor has not had any effect on these plants or has had a constant relationship over time, focusing mainly on the use of the representatives of this family mainly as food.

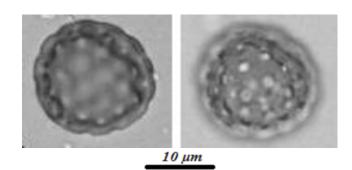


Figure 2. Chenopodiaceae family Pollen (Source: Jançe, 2019).

So, the cultivation of this family all the time in Elbasan city we think is the reason why these plants maintain the same presence over the years, experiencing a slight increase in the number of spores especially near the surface.

Many species are cultivated for their flowers fruit and above all for ornamental leaves. Food species comprise Spinach (*Spinacia oleracea*), Good King Henry (*Blitum bonus-henricus*), several Chenopodium species (*Quinoa, Kañiwa, Fat Hen*), Orache (*Atriplex spp.*), and Epazote (*Dysphania ambrosioides*) (Pan, 1993).

Elbasani town is covered with olive plantations, fruit trees and a rich vegetation grass cultivated. The influence of ecological but also human factors has an important role in the distribution of palynomorphs in time. Quantitative data presented for palynomorphs of Chenopodiaceae family show its evolutionary path.

Conclusion

- 1. Chenopodiaceae family palynomorphs are present in all depth samples.
- 2. The stable pollen number of Chenopodiaceae family but with a slight upward trend occurs with the passage of samples towards the ground surface.
- 3. Based on the fact that Elbasan city there were no important factors that have influenced on the vegetation change, we are mainly of the opinion that the changes presented over the years are mostly related to human impact on essential plants cultivation.

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Professional paper

PISTACIA TYPE PALYNOMORPHS DISTRIBUTION IN ELBASAN, ALBANIA

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Abstract

This paper presents paleopalynological data about the New Holocene period for Pistacia type palynomorphs (Anacardiaceae family). The results achieved on fossil pollen were obtained from land deposits of the last 20th centuries (New Holocene or Last Quaternary period) in Elbasani town.

All paleopalynological data are given for the first time without any study on Pistacia type palynomorphs. This scientific work was carried out with the aim of presenting the distribution of Pistacia type palynomorphs during the New Holocene periods.

Based on the data and the achieved results we can say that: Pistacia type palynomorphs (in total 476 palinomorphs) are absolutely present in all processed samples, also from the depth to the soil surface there is a stable presence of these palynomorphs. The change of vegetation over the years, in our opinion, has to do with the influence of human impact.

Keywords: Palynomorphs, Paleopalynological, Pistacia type, New Holocene, Elbasani town.

Introduction

This paper provides palynological data of New Holocene deposits in Elbasani town. This scientific paper belongs to the discipline of Palinology which is the Science that is related to both biological and geological sciences, it itself studies fossil palynoforms, chitinozoans, acritars and scolekodonts (Faegri and Iversen, 1989). Fossil pollen has a very important property that can be preserved over the years; this property is dedicated to the outer wall (exine) of grains which is extremely resistant (Paccini and Franchi, 1978). Through the study of the fossil pollen plant, we are given the opportunity to assess the evolution of the primitive and specialized features of the outer wall (exine) of grains. (Paccini and Hesse, 2005).

The study conducted in the New Holocene deposits provides important data regarding the impact of factors that affect the transformation of vegetation for one studied area (Moore and Webb, 1978; Kapidani, 1996; Forest, 1999; Jançe, 2015; Jançe et al. 2017).

Pistacia type microfossil plants have not been studied so far for Elbasan city and there is no study by local and foreign researchers for palynomorphs of Anacardiaceae family in the Holocene sediments for Elbasan area (Jançe, 2015; Jançe et al. 2017).

These types of works provide important information regarding the construction of the Paleoflora, Paleoclimate and Holocene stratigraphy. (Faegri and Iversen, 1989). Paleopalynological results make an important contribution to the description of the history of plant use and cultivation, the evolution of agriculture and the way of human nutrition. (Bryant and Holloway 1996).

The ponderable data of genus *Pistacia* part of Anacardiaceae Family, filed under the ground shows their evolutionary direction. The counting and the photo of the palynomorphs were carried out using a light microscope at 1500x magnification.

Materials and Methods

Paleopalynological observation of all samples showed that they all contained a large amount of organic matter that seemed suitable for pollen analysis. Basically all the ways of fossil pollen extracting are unified towards the principle of physicochemical processing of 1 gram of sediment (Faegri and Iversen, 1989). For this study we have taken 16 soil samples, starting from 4 to 0.25 m of depth with 25 cm distance between the sampling.

Erdtman acetolysis method

The soil sampling is based on Erdtman method (Erdtman, 1960; 1969). The acetolyze method is used in many cases in palynology because it gives clear visibility over the pollens and spores compared with the other methods used during the process of microscopic observation (Erdtman, 1960; 1969; Moore and Webb, 1978; Jançe, 2015).

Erdtman acetolyze method deals on treatment of the material with an acetolyze mixture, acetic anhydride $(CH_3COO)_2$ and sulfuric acid (H_2SO_4) in a 9:1 report. Deliberately to get better results first treat 1 cm^3 soil with 10 ml KOH (10 %). Then we cleaned it with distillated water, and then we mixed it with acetolyze ingredients, until a neutral environment is created.

Fixture of prepared samples

The fixture of samples was realized with method of glue-preparations by gelglycerin. The gel-glycerin was prepared in the Kisser method (Kisser, 1935) by using 50 gram of gelatin, 175 ml of distillate water, 150 gram glycerin, 7 gram phenol (crystals). The final ingredient was insulated to the edges of microscope slide with paraffin and after approximately 3 days it was ready to be stored and for its use.

Results and Discussion

Table 1 show the record about the palynomorphs presence of *Pistacia* type, representative of Anacardiaceae family by to the deepness and the total pollen number for this type. The minimum palynomorphs number (25 spores per sample) is taken exactly in 0.75 m of depth while the maximum number of spores for *Pistacia* Type (36 spores) is taken in 2 m deepness.

Sample	Depth (meters)	Palynomorphs number
		(Pistacia Type - Anacardiaceae)
1	4	29
2	3.75	30
3	3.5	33
4	3.25	32
5	3	27
6	2.75	29
7	2.5	31
8	2.25	30
9	2	36
10	1.75	30
11	1.5	26
12	1.25	30
13	1	32
14	0.75	25
15	0.5	27
16	0.25	29
Total number of spores		476

Table 1. Palynomorphs number according to the deepness

On figure 1 is clearly presented an increasing for the *Pistacia* Type palynomorphs, representative of Anacardiaceae family from the 4 m towards the 2 m of deepness. Taking cue from the data presented in table 1 the total palynomorphs number of *Pistacia* Type is 476 (Figure 2).

From the results presented in Table 1 for all stations it is noticed that, the *Pistacia* type palinomorphs are present at all depths and for this phenomenon we are of the

opinion that it is related to the human influence in the cultivation of *Pistacia* type plants. We also add that as shown in Figure 1, more or less from a depth to the surface is a consistency of palynomorphs presence. But it should be noted that in this type of storage and reservation of the palynomorphs presence may have influenced both ecological and human factors.

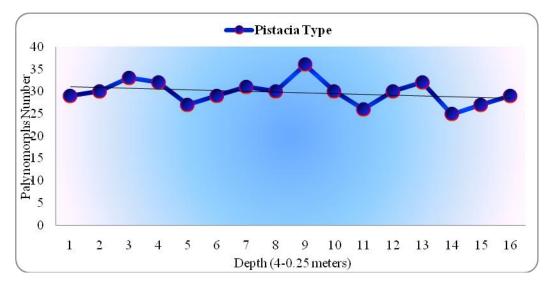


Figure 1. The palynomorphs distribution of Anacardiaceae family according to the depth

The Anacardiaceae, commonly known as the cashew family or sumac family, are a family of flowering plants, including about 83 genera with about 860 known species. Members of this family produce cashew and pistachio nuts, and mango and marula fruits. The genus *Pistacia* (which includes the pistachio and mastic tree) is now included, but was previously placed in its own family, the Pistaciaceae (Yi et al. 2008).



Figure 2. Pistacia type pollen (1500x) (Source : Jançe, 2014).

Pistacia plants are shrubs and small trees growing to 5–15 m tall. The genus is estimated to be about 80 million years old (Parfitt and Maria, 1997).

Pistacia terebinthus (terebinth), present in both Iran and the Mediterranean, has been used for turpentine. Since terebinths have the ability to kill certain bacteria, terebinth resin was widely used as a preservative in ancient wine. Archaeologists have unearthed terebinth resin deposits from 5400-5000 BC in jars that also contained grape juice residues (Al-Saghir, 2009).

In the end we are given the right to say that the human impact caused over the years with human lifestyle is exactly the main cause of vegetation transformations for Elbasan area.

Currently the vegetation of Elbasani town is represented by fruit trees and very rich vegetation. *Pistacia*-type palynomorphs show the evolutionary direction of this species over time.

Conclusion

- 1. The Anacardiaceae family palynomorphs are present to all deepness.
- 2. *Pistacia* type palynomorphs mainly present a constant presence with small fluctuations, where we distinguish the immediate decrease of their presence at 2 meters of depth.
- 3. Given to the palynomorphs presence of *Pistacia* type in all examined specimens corresponding to the whole time span, we are of the opinion that this is due to the inalienable human impact on the cultivation of vegetation and trees necessary for it.

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Professional paper

SOIL CONTAMINATION BASED ON CHEMICAL, PHYSICAL AND MICROBIOLOGICAL FACTORS IN ELBASAN AREA, ALBANIA

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Abstract

This paper provides chemical, physical and bacteriological data obtained in Elbasan area, located in Central Albania. This study enabled us to provide sufficient data on physico-chemical and bacteriological parameters and to judge on soil pollution for the Elbasan city in order to present a current assessment of soil pollution as a factor of particular importance affecting citizens' health, based mainly on the cultivation of agricultural crops.

For this purpose, many soil samples were taken during 2020, mainly in the area where the heavy industries of Elbasani town develop their activity. Physicochemical and bacterial data on soil pollution in Elbasan area also for the analyzed period are provided for the first time.

We emphasize the indisputable fact that Elbasan has always been valued over the years as one of the most polluted Albanian cities, where among the main causes are light and heavy industries that operate without applying the rules of environmental protection. Soil pollution is mainly due to pollution caused by human hands in agriculture mainly in the indiscriminate use of pesticides and chemical fertilizers and above all from industrial activity.

Keywords: Physico-chemical, Bacterial, Soil contamination, Agricultural crops, Elbasan.

Introduction

This work was performed in order to determine the physico-chemical, bacteriological parameters and the composition of heavy metals in the soil. The study of soil pollution mainly from heavy metals that comes as a result of the presence and activity of industrial facilities and mines has always been the study object of research and scientific papers by academic institutions. Microorganisms are found everywhere in nature, spreading through the air, water or soil, and being primarily responsible for food contamination or the transmission of various diseases (Madigan et al. 2006; Mali, 2007; Bogoev et al. 2010).

We mention, for example, the spread through the air of diseases such as tuberculosis, influenza and some diseases of plant and animal fungi (Jay et al. 2006). Also, the deposition in the soil and the presence above the allowed norms of heavy metals pose a significant risk for the pollution of the plant world as well as the drinking water, thus presenting a permanent risk for human health. Vegetation damage, productive inactivity of heavy industries, erosion as well as mismanagement and indiscriminate use of land have continuously destroyed natural resources mainly in areas adjacent to industrial sites (Mantovi et al. 2003; Bogoev et al. 2010; Jançe, 2015).

Heavy metals are generally considered essential for plants, but when they are above the recommended norms, they cause metabolic disorders and growth retardation for most plant species. Heavy metals affect the catalytic functions of enzymes, damage the cell membrane, inhibit the development of roots and shoots, reduce the assimilation of carbon dioxide, etc. (Wolfenden and Lewin, 1977; Censi et al. 2006).

Heavy metals are all those chemical elements with a specific gravity at least 5 times higher than the specific gravity of water. The specific weight of water is 1 at 4° C (39°F). (Elliot et al. 1986; McBride, 1994). All metals present in the soil have a specific pH value below which their solubility increases significantly. Heavy metals exist in the form of colloidal, ionic shapes and dissolved phase. Metals have high affinity for wet acids, clays and oxides (Elliot et al. 1986).

In this undertaken scientific work, we have tried to provide sufficient data on soil pollution in Elbasan area during 2020, and also to present the impact on human life. In order to realize as accurately as possible, the analysis of soil pollution for Elbasani town, we have conducted three types of analyzes: toxicological, physico-chemical and microbiological.

For the taken and analyzed samples in Elbasan city, we try to provide the right information on the factors that affect soil pollution.

Materials and Methods

Nine soil samples were taken for analysis at a depth of 20 to 50 cm during 2020 in Elbasan city. For the speciation analysis, determinations in water soil extracts were carried out by applying the colorimetric method diphenylcarbazide (Darrie, 2001). In this way 2.5 g soil samples were shaken with 25 ml of demineralized water for 2.5 hours. After centrifugation for 10 min at 3500 rpm, the water was filtered through a $0.45 \ \mu m$ Millipore filters (Armienta et al. 1996).

Instantly after extraction, the sample was acidified with a drop of concentrated ultrapure HNO_3 to bring the pH < 2. Afterward the sample was kept in a

refrigerator until analysis. To minimize valence changes, analysis was carried out within less than 24 h after extraction. Sober soil pH (after standard calibration at pH 4-7) in a suspension of 10 g of soil in 25 ml demineralized water, after magnetic stirring for 30 min, followed by 5 min sediment settling.

The analysis of the grain size performed on 10 g of sample were treated first with 1 M HCl to remove the calcareous material, then oxalic acid for Fe release and H_2O_2 for organic release.

Results and Discussion

From the achieved results we conclude that all samples taken and analyzed for Elbasani town show that this city has soil pollution above the recommended norms.

No.	Microbiological index	Recommended content (CFU/100ml)	Content found (CFU/100ml)	
1	Coliform bacteria	0 - 100	785	
2	Escherichia coli (E.	0 - 100	0	
	Coli)			
3	Enterococci	0 - 100	665	

Table 1. Microbiological analysis on soil samples

No.	Parameter	Recommended content (mg/l)	Content found (mg/l)	
1	pН	6.5 - 8.35	8.05	
2	Magnesium (Mg)	10	2.8	
3	Calcium (Ca)	20	18	
4	Pottasium	10	6.2	
5	Aluminum	40	25.5	
6	Nitrites (NO_2)	0.5	0.31	
7	Nitrates (NO ₃ ⁻)	3	3.3	
8	Phosphates (P ₂ O ₅)	1	0.82	
9	Carbonates (CO_3^{2-})	30	22.9	
10	Ammonium (NH_4^+)	0.1	0.82	
11	Chlorides (Cl ⁻)	25	12.4	
12	Sulphates (SO_4^{2-})	40	31	

Table 2. Physico-chemical analysis on soil samples

No.	Chemical elements	Recommended content (µg/l)	Content found (µg/l)
1	Lead (Pb)	3200	322.5
2	Zinc (Zn)	3200	132.8
3	Chromium (Cr)	2100	2928
4	Copper (Cu)	1500	330
5	Nickel (Ni)	800	1080
6	Cobalt (Co)	820	311
7	Arsenic (As)	350	112.4
8	Cadmium (Cd)	40	0.15

The results obtained for the entire analyzed period are grouped together to better perceive soil pollution as well as comparing the results achieved with the allowed values. Table 1 shows the microbiological contamination in soil samples. With the exception of *Escherichia coli*, the other two types of pathogenic bacteria, namely *Enterococci* and *Coliforms* are above the recommended rates. Mainly from the soil analysis micro biotic world in polluted areas has always been observed a significant presence of aerobic bacteria, fungi, actinomycetes and nitrogen-fixing microorganisms (Madigan et al. 2006; Bogoev et al. 2010; Jance, 2015).

In Table 2, constructed to show the physico-chemical parameters of soil samples we find that *Nitrates* (NO_3^-), and *Ammonium* (NH_4^+) are the only parameters that exceed the recommended norms, while the rest of the physico-chemical parameters are at the right levels. Whereas for Table 3, which presents the presence of heavy metals in the soil, it is noticed that only two chemical elements, respectively *chromium* (Cr) and *nickel* (Ni) are above the recommended values, thus becoming a major factor of soil pollution, and all other heavy metals are within the recommended parameters (Howsam and Jones, 1998).

Elbasan city has always been one of the most polluted cities in Albania. The reason for this considerable and continuous pollution that comes mainly from heavy metals, we think is dedicated to the release into the environment from smelting and refining industries, technological industries and waste incineration that contain these elements. After being released into the atmosphere through the air, water and soil, they can easily pass into the food chain, through daily life processes such as: drinking water, inhaling air and consuming food, whether of plant or animal nature (Gaszo, 2001).

Factors that affect soil pollution can be grouped (even based on the analysis performed) in:

- Bacteriological sewage discharge
- Physico-chemical pollution of agricultural land from indiscriminate use of pesticides
- Heavy metals deposits coming from industrial activity in Elbasan.

Conclusion

- Soil pollution in Elbasan city we are of the opinion that it is not dedicated only to human activity related to agriculture, wastewater treatment, but above all industrial activity carried out by leading companies in Elbasan area.
- Elbasani town soil is considered polluted based on the analysis:
 - 1. Microbiological: *Enterococci* and *Coliform bacteria* are above the recommended norms.
 - 2. Physico-chemical: *Nitrates and Ammonium* are significantly above the allowed norms.

3. Toxicological: *Chromium* and *Nickel* appear above the recommended norms.

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Original scientific article

DATA ABOUT SOIL POLLUTION AND THE IMPACT ON AGRICULTURAL CULTURES IN ELBASAN, ALBANIA

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Abstract

In this paper are given chemical data of the soil composition in Elbasan city. The distribution of heavy metals that are presented above the allowed norm cause soil pollution, were obtained by analyzing soil samples that as geographical location includes the industrial area of the Elbasan city.

The purpose of this paper is to provide the link between chemical soil pollution caused by the productive activity of heavy industries and the impact of these pollutants on agricultural crops. To achieve this goal, we have taken soil samples, during April - June 2020. It should be noted that the area of Elbasan, especially in recent years has been the epicenter of air pollution, both chemical and microbiological nature, a fact that is dedicated to the heavy industries that have been operating in this city for a long time.

Based on the analysis of the obtained results we consist of a considerable level of chemical pollution of the soil mainly for the element Chromium (Cr) which is above the standard values set by the EU Regulation.

Keywords: Heavy metals, Chemical, Chromium, Agricultural cultures, Elbasan.

Introduction

Soil pollution caused by heavy metals concentrated in them (especially in cities where industry has a primary role) has been devastating in addition to agricultural land also in forests and pastures. Accumulations of Fe, Cu, Ni, Zn, Pb, As, Co, etc. on agricultural lands as well as in forest ecosystems, always near industrial areas, have drastically changed the plant community.

Heavy metals have always been part of the Earth's crust. Among the heavy metals we mention Lead (Pb), Mercury (Hg), Cadmium (Cd), Arsenic (Si), Chromium (Cr), Selenium (Se), etc. Heavy metals have a toxic effect if they are present in the

soil above the permissible concentrations. In this case they lead to degradation and inevitably serious consequences in the agricultural crops grown on that land. Like trace elements, heavy metals (eg copper, selenium, zinc) are of a primary character to maintain the human body's metabolism, so that the human body functions properly. (Wolfendem and Lewin, 1977; Lacatusu, 1998). It should be noted that in small quantities they pass to the human body, mainly obtained through food, drinking water and air (Mantovi et al. 2003).

Concentrations beyond the recommended norms of heavy metals cause serious damage to public health and the environment (Berglund and Davis, 1984; Jason, 2004). In the case of concentrations above the set norms, the presence of heavy metals in the soil can lead to poisoning of the human body. This hazard caused by heavy metals comes as a result of its bio-accumulation property (Censi et al. 2006). Bioaccumulation can be defined as an increase in the concentration of chemical elements in a biological organism over time, compared to its concentration in the environment (Bogoev et al. 2010; Jançe, 2015). The concentration of heavy metals in the soil depends directly on factors such as: pH, redox potential, organic matter content. Heavy metals have low solubility in normal soils. (McBride, 1994; Flint et al. 2000).

In this scientific paper we have tried to provide information on soil pollution for Elbasan city, during the period May - June 2020. For the most efficient analysis of the level of heavy metal pollution are determined 9 monitoring points in the north, east and southwest direction of study area. The first monitoring point is defined at a distance of 100 m from the base study area and the last point goes at a distance of up to 3 km.

Based on the data obtained as a result of the analysis, it was found that the concentrations of all elements are below the recommended critical values, with the exception of nickel and especially chromium, which are found in higher levels than the defined criteria. All the lands where the samples were taken are cultivated mainly with fodder products, cereals (corn and wheat) and fruit trees (Jançe, 2015). This paper through the study of the present amount of heavy metals for the analyzed samples of the city of Elbasan gives us preliminary information on the impacts and possible factors that have led to soil pollution.

Materials and Methods

All the pre-treated samples were digested with the 4-acid method, which consists in the digestion of 0.1 g of sample initially by 2.5 ml HNO₃. The soil samples with the weight varied from 20 g to 200 g were dried at 40°C, separated in a porcelain mortar, homogenized and sieved. More than 95% of the sample consisted of <2 mm fraction.

After dividing into four parts, one part was crushed to fine powder for total analysis, while the rest of the sample was stored in plastic bags and set aside for additional analysis.

Twice jointly 5 ml HF and 1.5 ml HClO₄ were added and as the last process was added, after partial evaporation 2.5 ml HCl. The total concentrations of Cr, Ni, Zn, Cu, Cd, Co, As and Pb were defined by Flame Atomic Absorption Spectrometry (FAAS, types Varian AA6 and Varian AA-1475). The insoluble residue from the 4-acid digestion varied between 1-3% of the initial sample weight. The detection limit for most of the trace elements varied around 0.1 and 1 mg/kg. Therefore the term "total concentrations" will be used for the geochemical results obtained from the 4-acid digestion. Determination of the colors in dry soil/sediments was made in laboratory conditions based on the Munsell (Munsell, 1997).

Soil-pH was measured in a suspension solution of 10 g of sediment (<2 mm) in 25 ml demineralised water after magnetic stirring for 30 min and 5 minutes sediment settling. When sufficient sample was available, measurements of pH and grain size were also carried out. Grain size analyses (Gee and Bauder, 1986) were carried out on composite samples, and were determined by laser diffraction.

Results and Discussion

Based on the results obtained for the analyzed samples during the period May -June 2020 in Elbasan area, it is found that there are elements that are present above the allowed norms, thus leading to soil pollution. The results for each of the two months are grouped together in order to understand the performance of soil pollution by comparing them with the basic parameters.

Color analyzes in dry soil/sediments according to Munsell (1997) determine the soil samples taken from us in *Gray Brown Soils*. Grain size analyzes performed allow us to judge that more than 95% of the soil sample are <2 mm fraction.

The pH value found for the soil samples analyzed in the Elbasan region is at the average value of 7.95 - classifying them in the soils type with *Slight alkalinity* (moderate).

Table 1 shows the average values presence of chemical elements in two months, as well as the recommended content. Also presented is the value of the standard deviation for each element for all nine samples taken in the field and analyzed in the laboratory. With the exception of chromium and nickel, all other elements are below the allowable norm. Figure 1 is constructed from the data provided in Table 1. This figure shows the level of soil pollution by chemical elements compared to the recommended content.

No.	Chemical elements	Recommended content	Content found	Stadard
		mg / kg soil sample	mg / kg soil	deviation
			sample	
1	Lead (Pb)	300	35.6	0.90
2	Zinc (Zn)	300	104.3	1.33
3	Chromium (Cr)	200	285	2.87
4	Copper (Cu)	140	31	4.68
5	Nickel (Ni)	75	103.5	1.28
6	Cobalt (Co)	75	28.4	0.85
7	Arsenic (As)	30	9	0.98
8	Cadmium (Cd)	3	1.8	1.09

Table 1. Average value presence of heavy metals in soil samples

<u>Lead</u> (Pb) in the amount of 10 mg/kg is included in the normal soil content while for 100 mg/kg the soil is called toxic, namely it is in the value of 35.6 mg/kg of 300 mg/kg which constitutes the limit permitted by the European Directives, so its presence can be considered almost *normal*.

<u>Zinc</u> (Zn), for the amount of 10 mg/kg is the normal soil contents and for the amount of 100 mg / kg the soil is called toxic, in our case it is in the value of 104.3 mg/kg of 300 mg/kg constituting the limit permitted by European directives, so its presence can be considered *normal*.

<u>Copper</u> (Cu) for 2mg/kg quantifies normal soil type and for 60-125 mg/kg soil is classified as toxic, currently it is measured at 31 mg/kg from 140 mg/kg constituting the permissible limit of European directives, so its presence can be considered *normal*.

<u>*Cobalt*</u> (Co) for the amount of 10 mg/kg is introduced into the normal soil content while for the amount of 60-200 mg/kg the soil is called toxic. It is present at a value of 28.4 mg/kg of 75 mg/kg; so its presence can be considered *normal*.

<u>Arsenic</u> (As) for the amount of 1 mg/kg is introduced into the normal soil content while for the amount of 20-50 mg/kg the soil is called toxic. It is present at a value of 9 mg/kg of 30 mg/kg; so its presence can be considered almost *normal*.

<u>Cadmium</u> (Cd) in the amount of 0.1 mg/kg is included in the normal soil content while for 3-8 mg/kg the soil is called toxic; in particular it is in the value of 1.8 mg/kg of 3 mg/kg constituting the limit permitted by the EU, so its presence can be considered almost *normal*.

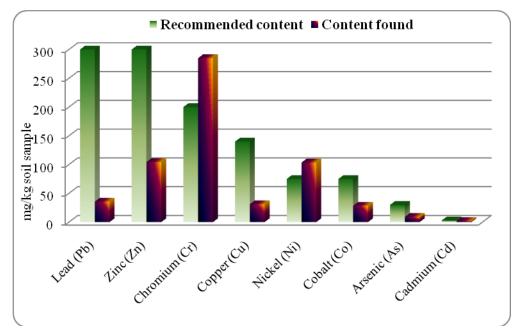


Figure 1. Soil pollution level by chemical elements in relation to the recommended amount

<u>Chromium</u> (Cr) for the amount of 5 mg/kg is included in normal soil content and for the presence of 75-100 mg/kg the soil is considered toxic, currently it is present in the value of 285 mg/kg out of 200 mg/kg which constitutes the limit permitted by the Directives. European, so its presence can be considered *much higher than the allowed parameters*.

Chromium is absorbed by plants mainly through sulfate. Symptoms in plants that result from Cr toxicity include: reduced germination, reduced growth, inhibition of enzymatic activities, impaired photosynthesis and oxidative imbalances. (Barnhart, 1997; .Zayed and Terry, 2003).

<u>Nickel</u> (Ni) for the amount of 10 mg/kg is introduced into the normal soil content while for the amount of 70-400 mg/kg the soil is called toxic. It is present at a value of 103.5 mg/kg of 75 mg/kg which constitutes the limit permitted by the European Directives; *this means that it is at a higher level than the European standard*.

As Nickel is an essential nutrient for the normal growth and development of the plant as well as being required for the activation of certain enzymes such as urease and glycoxalase-I It plays an important role in a wide range of physiological processes including germination seed, vegetative and reproductive growth, photosynthesis, and nitrogen metabolism. Therefore, plants can not realize their biological cycle without adequate supply of Ni. (Gajewska and Skłodowska, 2005; Hussain et al. 2013)

It should be noted that heavy metals are present in the environment mainly by technological processes, the development of smelting and refining industries, scrap, plastics and rubber industries, various consumer products and combustion of waste. They can reach the food chain through drinking water supply, air intake and consumption of plant-based foods (Gaszo, 2001).

Regarding the Elbasan city where the analyzed results were obtained, it must be said that it has always been ranked among the most polluted cities in Albania over the years. This drastic pollution is mainly due to: lack of green areas, urban traffic, infrastructure, high concentration of population and above all the development of heavy industry activity in this city as well as poor management related to the technical control performed by the state.

Finally, we can say that the soil of Elbasani town, for the time period when the samples were taken, turns out to be polluted by heavy metals, especially Chromium but also Nickel.

Conclusion

- 1. All heavy metals except Chromium and Nickel are within the allowed parameters.
- 2. The soil of Elbasani town has in its composition elements of heavy metals, most of which do not show any level of pollution except for nickel components and especially chromium that are present above the standards set by EU regulation.
- 3. Elbasan city is presented with significant soil pollution, and the reason for this we think is the storage of raw materials in the ground from the activities of heavy industries.

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