

# TECHNOLOGICA ACTA

SCIENTIFIC/PROFESSIONAL JOURNAL  
OF CHEMISTRY AND TECHNOLOGY

FACULTY OF TECHNOLOGY  
UNIVERSITY OF TUZLA

ISSN 1840-0426 (P)  
ISSN 2232-7568 (E)

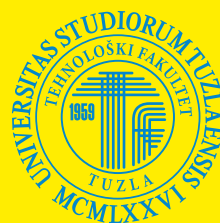
Vol. 14

No. 2

Pages 1-48

December 2021

Tuzla, Bosnia and Herzegovina



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<https://hrcak.srce.hr/ojs/index.php/technologicaacta>

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Vol. 14, No. 2, December 2021

Pages 1-48

- Publisher** Faculty of Technology, University in Tuzla
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- Cover Photo** Offshore wind turbines at Barrow Offshore Wind Farm off Walney Island in the Irish Sea; by Andy Dingley, CC BY-SA 3.0 <<https://creativecommons.org/licenses/by-sa/3.0/>>, via Wikimedia Commons
- Editorial Office** Nermina Jahić (Technical Secretary)  
Faculty of Technology, University in Tuzla  
Urfeta Vejzagića 8, 75000 Tuzla, Bosnia and Herzegovina  
Phone/fax: +387 35 320 740 / +387 35 320 741
- Printing** OFF-SET d.o.o. Tuzla
- Circulation** 100
- Available online at:** <http://tf.untz.ba/technologica-acta>  
<https://hrcak.srce.hr/ojs/index.php/technologicaacta>
- Technologica Acta is indexed in** CAB Abstracts, COBISS, Index Copernicus Journal Master List, EBSCO, HRČAK, ROAD, Directory of Journal Quality Factor, Publons, Norwegian Register for Scientific Journals, Series and Publishers... Also recognized by Google Scholar, ResearchGate, OpenAIRE etc.

Technologica Acta is being published twice a year.

This number of Technologica Acta is supported by the Federal Ministry of Education, Science and Culture of Bosnia and Herzegovina

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# INFLUENCE OF NUTRITIONAL SUPPLEMENTS ON MICROBIOLOGICAL COMPOSITION OF RAW SHEEP MILK

ORIGINAL SCIENTIFIC PAPER

Aida Džaferović<sup>1</sup>✉, Azra Bakrač<sup>1</sup>, Huska Jukić<sup>2</sup>,  
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DOI: 10.5281/zenodo.6371114

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## ABSTRACT:

The aim of this study is to examine the effect of plant fat sources in sheep feed on somatic cells and the total number of microorganisms in raw milk samples obtained from 210 sheep, breed Pramenka in Una-Sana Canton. The research was conducted in three periods: winter, spring and summer. The herd was divided into experimental and control groups of sheep. In the experimental groups of sheep in each period of the study, omega-3 supplements were added to the diet, namely extruded flaxseed in the amount of 3.5%. The influence of added omega-3 supplements on the microbiological parameters of raw sheep milk, which was milked from experimental and control groups of sheep every fifteen days of the experiment in all periods of the study, was examined. Analysis of variance (ANOVA) found that during the winter and summer feeding period there is a statistically very significant influence of both experimental factors (treatment and period) on the total number of microorganisms and somatic cells in raw sheep milk ( $p < 0.001$ ). In the spring diet in somatic cells, factor treatment did not show a statistically significant effect (ns).

**KEYWORDS:** Sheep milk, microbiological analysis, somatic cells, total number of microorganisms

## INTRODUCTION

Due to its specific composition, milk is a suitable environment for the growth and development of various bacteria. Milk from the farm can contain from several thousand to several million bacteria/ml, depending on the sanitary conditions on the farmstate that coliform bacteria are very often contaminants of raw milk, and the presence in milk indicates on fecal contamination as well as soil and water contamination<sup>1</sup>. When coliform bacteria are present in large numbers, they cause defects in the appearance and taste of milk, because they create gas and increase acidity. The basic indicators of the hygienic correctness of milk are the total number of microorganisms and the number of somatic cellsstate that the quality of milk is determined by its chemical composition, physical properties and hygienic correctness<sup>2</sup>. Milking is the most important process in milk production that affects the quality of milk. The milking has a significant influence on the daily amount of milk, the content of dry matter and milk fat, the freezing point and the hygienic quality of milk. Sanitary conditions during milking are especially important and affect the quality of milk<sup>3</sup>. The number and type of microorganisms present in raw milk are

determined by season, hygienic production conditions and diet.

## MATERIALS AND METHODS

Two herds of sheep were selected for the research (a herd of pure Pramenka and a herd of crossed sheep) in the Una-Sana Canton. Groups of 35 experimental and 35 control sheep were formed in the herds, which were kept in identical conditions. In addition to the regular diet, the concentrates were added to the sheep in a daily amount of 300 g / head. A concentrate mixture with the addition of omega - 3 supplements (diet treatment) was added to the experimental group (Og) of sheep. In addition to the regular meal, a concentrate mixture without the addition of omega-3 preparations (diet treatment) was added to the control group of sheep (Kg). Experimental studies were done during three different periods. The first period of winter (February and March, analyzes performed every 15 days - four sampling dates). The second period of the spring diet (May, analyzes done every 15 days - two sampling dates).

The third period of the summer diet (July, analyzes performed every 15 days - two sampling dates). Microbiological analysis of raw sheep's milk was

performed according to "Official Gazette of BiH" No. 21/11<sup>4</sup>, where the number of somatic cells and the total number of bacteria was determined. The somatic cell number of raw sheep milk was determined on a „Fossomatic™ Minor“ instrument by the fluoro-opto-electronic method EN ISO 13366-2: 2006 / AC: 2007, IDT<sup>5</sup>. Electronic somatic cell counters work on the principle of epifluorescence microscopic technique. Somatic cells, after staining the nucleus (DNA) with fluorescent dye under ultraviolet light, fluoresce. This method is based on mixing a milk sample with a buffer and a staining solution. The total number of raw sheep's milk bacteria was determined on a BactoScan™ FC 50 instrument, by flow cytometry EN ISO 21187: 2004, IDT<sup>6</sup>. In the process of determining the bacteria are stained with fluorescent dye, then the individual components of the milk are sprayed so that the bacteria can be counted. The detector in the device registers fluorescent light emitted by the DNA of colored bacteria. Light impulses are converted into

electronic impulses that are registered with a high-sensitivity pass-through detector. Analysis of variance (ANOVA) was used to examine the influence of factors (period and treatment) on the observed properties.

## RESULTS AND DISCUSSION

Table 1. presents the results of statistical analysis of the value of microbiological properties of raw sheep's milk in the winter diet period (four times). Analysis of variance (ANOVA) found that there is a statistically very significant impact of both experimental factors (treatment and term) on the total number of microorganisms and somatic cells in raw sheep milk ( $p < 0.001$ ). There was also a statistically very significant influence of factor interaction on somatic cells ( $p < 0.001$ ), while for the total number of microorganisms, the level of significance of factor influence was 99% ( $p < 0.01$ ).

**Table 1.** Results of statistical analysis of the average value of microbiological properties of raw sheep milk - period winter diet

Milk parameters		Winter (february,march)				Level of significance ( <i>p</i> )		
		I(15)	II (30)	III (45)	IV (60)	period	treatment	Interaction
Somatic cells	Og	557x10 <sup>3</sup>	183x 10 <sup>3</sup>	31 x 10 <sup>3</sup>	105 x 10 <sup>3</sup>	***	***	***
	Kg	85 x 10 <sup>3</sup>	86 x 10 <sup>3</sup>	58 x 10 <sup>3</sup>	287x 10 <sup>3</sup>			
Total number of microorganisms	Og	108 x 10 <sup>3</sup>	23 x 10 <sup>3</sup>	27 x 10 <sup>3</sup>	110x 10 <sup>3</sup>	***	***	**
	Kg	8 x 10 <sup>3</sup>	26 x 10 <sup>3</sup>	20 x 10 <sup>3</sup>	70 x 10 <sup>3</sup>			

*p*– significance level: \* $p < 0,05$ ; \*\* $p < 0,01$ ; \*\*\*  $p < 0,001$ ; ns –no statistical significance

Og – experimental group

Kg – control group

I, II, III, IV- periods of sampling(15, 30, 45, 60 day)

In our results in the experimental group of sheep, the number of somatic cells ranged from 31x10<sup>3</sup> in the third sampling period to 557 x 10<sup>3</sup> in the first. The number of microorganisms was highest in the fourth term (110 x 10<sup>3</sup>) and lowest in the second (23 x 10<sup>3</sup>). Other values between (Og) and (Kg) as well as within the sampling period were in the values allowed by the legislation ("Official Gazette of BiH" No. 21/11)<sup>4</sup> but with significant variations both among herds and within the period.

In European countries, sheep milk can be processed into cheese if the number of bacteria is  $< 1 \times 10^6$  ml with pasteurization of the milk before processing. To make cheese from fresh milk, the number of bacteria must be  $< 500,000$  / ml, but the values of the number of somatic cells for sheep milk processing are not given<sup>7</sup>.

The results of statistical analysis of the average value of microbiological parameters of raw sheep milk in the spring period of feeding (grazing) are shown in Table 2.

**Table 2.** Results of statistical analysis of the average value of microbiological parameters of raw sheep milk in the spring period of feeding

Milk parameters		Spring(grazing,may)		Significance level ( <i>p</i> )		
		I(15)	II (30)	period	treatment	interaction
Somatic cells	Og	182 x 10 <sup>3</sup>	207x 10 <sup>3</sup>	***	ns	ns
	Kg	192x 10 <sup>3</sup>	103x 10 <sup>3</sup>			
Total number of microorganisms	Og	21x 10 <sup>3</sup>	15x 10 <sup>3</sup>	***	***	***
	Kg	11x 10 <sup>3</sup>	9x 10 <sup>3</sup>			

*p*– significance level: \**p*<0,05; \*\**p*<0,01; \*\*\* *p*<0,001; ns –no statistical significance

Os – experimental group

Ks – control group

I, II- periods of sampling (15, 30 day)

Analysis of variance (ANOVA) it was determined that there was a statistically very significant influence of the factor (period) on the total number of microorganisms (*p* <0.001) in raw sheep milk, while in somatic cells the factor treatment did not show a statistically significant influence (ns). A statistically very highly significant influence of factor interaction on the total number of microorganisms was also found (*p* <0.001), while in somatic cells it did not show statistical significance (ns). Sheep milk, unlike cow's milk, contains significantly more microorganisms and mechanical impurities, which is conditioned by the way it is kept, fed and milked.

Microorganisms enter the milk from the udder or from the external environment (body, air, dishes, dust). There are a large number of microorganisms and

impurities on the suction opening. Numerous microorganisms in milk can cause desirable changes, eg in cheese production (*Lactobacillus* spp., *Lactococcus* spp., *Streptococcus* spp.,). While harmful ones can cause various human diseases (*Listeria*, *Salmonella*, *Brucella*) or problems during the ripening of dairy products (*Coliform* , *Psychrotrophs*, *Clostridium* spp., *Enterobacteriaceae*)<sup>8</sup>. The obtained values between (Og) and (Kg) as well as within the sampling period were in the values allowed by the legislation ("Official Gazette of BiH" No. 21/11)<sup>4</sup> but with significant variations both among herds and within the period. The results of the statistical analysis of the average value of microbiological parameters of raw sheep milk in the summer grazing period are shown in Table 3.

**Table 3.** Results of statistical analysis of the average value of microbiological parameters of raw sheep milk in the summer grazing period

Milk parameters		Summer(grazing,july)		Significance level( <i>p</i> )		
		I-a	I-b	period	treatment	Interactio
Somatic cells	Og	680 x 10 <sup>3</sup>	362x 10 <sup>3</sup>	***	***	***
	Kg	814x 10 <sup>3</sup>	1274x 10 <sup>3</sup>			
Total number of microorganisms	Og	40x 10 <sup>3</sup>	159x 10 <sup>3</sup>	***	***	***
	Kg	45x 10 <sup>3</sup>	1707x 10 <sup>3</sup>			

*p*– significance level: \**p*<0,05; \*\**p*<0,01; \*\*\* *p*<0,001; ns –no statistical significance

Os – experimental group

Ks – control group

I, II –periods of sampleing (15, 30 day)

Analysis of variance (ANOVA) revealed that there was a statistically very significant influence of both factors (period and treatment) on somatic cells and the total number of microorganisms (*p* <0.001) in raw sheep milk. A statistically very highly significant influence of factor interaction (*p* <0.001) on the total number of microorganisms and on the number of somatic cells was also determined. Direct comparisons of individual studies are not always possible because

they depend on whether analyzes of individual or total milk samples have been performed<sup>9</sup>. The average number of somatic cells (SCC) determined in this study was 680 x 10<sup>3</sup>, in the first period (summer), in the experimental herd, and in the control 814 x 10<sup>3</sup>. The total number of microorganisms (CFU) in the experimental herd was 40 x 10<sup>3</sup> and in the control 45 x 10<sup>3</sup>. The sampling date did not significantly affect the number of somatic cells in the milk, although higher



values were found in the second term<sup>10</sup>, however, a significantly higher number of somatic cells was found in sheep milk of breed Pramenka, at the beginning than at the end of lactation. One of the causes of increased number of bacteria in milk can be bacterial inflammation of the udder, which causes a significant increase in the number of somatic cells above the physiological limit, and occurs due to the body's immune response to inflammation<sup>11</sup>.

## CONCLUSION

Based on the conducted tests on samples of raw sheep milk to whose food concentrate mixtures with omega-3 supplements in the form of extruded flaxseed and concentrate mixtures without the addition of the following conclusions can be drawn:

- Additions of omega-3 supplements to the diet of dairy sheep in the examined feeding periods (winter, spring and summer) did not have harmful effects on the microbiological composition of sheep milk.
- During the winter diet, it was found that there is a statistically very significant influence of both experimental factors (treatment and period) on the total number of microorganisms and somatic cells in raw sheep milk ( $p < 0.001$ ).
- During microbiological analyzes of raw sheep milk in the diet in the spring period (grazing), it was found that there is a statistically very significant influence of factors (term) on the total number of microorganisms ( $p < 0.001$ ), but somatic cells the factor treatment did not show a statistically significant influence (ns).

In the summer diet (grazing) of sheep, it was found that there is a statistically very significant influence of both factors (period and treatment) on somatic cells and the total number of microorganisms ( $p < 0.001$ ) in raw sheep milk.

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# INFLUENCE OF PROCESS PARAMETERS ON THE PRODUCTION OF *TRICHODERMA* BIOCONTROL AGENT

ORIGINAL SCIENTIFIC PAPER

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DOI: 10.5281/zenodo.6371166

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## ABSTRACT:

Maize is an agricultural crop that is susceptible to infections by various phytopathogenic fungi, producers of mycotoxins harmful to humans and animals. Since this agricultural crop has an important place in the human diet, its health safety is very important. *Trichoderma* genus has great potential in the biocontrol of various phytopathogens however, the medium composition as well as the cultivation conditions, have a significant impact on the efficiency of the produced *Trichoderma* bioagents. In this work, influence of medium pH, temperature and mixing speed on the productivity of *Trichoderma* bioagent effective against two maize pathogens, *Fusarium graminearum* and *Aspergillus flavus*, was investigated. The results obtained by statistical processing show that the best productivity of *Trichoderma harzianum* bioagent was achieved when the pH of the medium was 6, the temperature was 28°C and the mixing speed of the rotary shaker was 180 rpm. By applying these cultivation conditions, the largest inhibition zone diameters of *F. graminearum* and *A. flavus* mycelial growth were formed. Also, the results show that the maize pathogen, *F. graminearum*, was more sensitive to the produced *Trichoderma* biocontrol agent compared to the other maize pathogen, *A. flavus*.

**KEYWORDS:** *Trichoderma harzianum*; Bioprocess; Process parameters; pH; Temperature; Mixing.

## INTRODUCTION

The primary goal of maize production is to achieve stable and high grain yields of high nutritional value, which is at the same time healthy. However, maize is susceptible to attack by a number of pathogens. *Fusarium* and *Aspergillus* species are mentioned among the most important causes of maize disease. A big problem is the fact that these species are producers of mycotoxins harmful to human health and their presence on maize must be controlled [1]. Zearalenone is one of the most prevalent mycotoxins, mainly produced by *Fusarium* fungi (*F. graminearum*, *F. cerealis*, etc.) and has been proven to affect the reproductive capacity of animals [2]. Also, deoxynivalenol is one of several mycotoxins produced by certain *Fusarium* species that frequently infect maize, wheat, oats, barley, rice, and other grains in the field or during storage [3]. This mycotoxin leads to a number of side effects in animals and humans, but above all cytotoxicity [4]. On the other hand, according to the classification of the International Agency for Research on Cancer, aflatoxin is classified in group 1a of carcinogenic compounds for humans and animals [5]-[7].

The emergence of overpopulation and the growing number of people around the world has led to the intensification of agricultural activities aimed at direct food production and increased need for food has led to increased use of chemical pesticides and fertilizers [8]. One of the acceptable alternatives to the use of chemical plant protection products and the control of plant diseases caused by various microbiological phytopathogens is biological control [9]. Biological control, according to one of the most widely accepted definitions, represents the purposeful use of living organisms and their metabolites to suppress the activity and reduce the population of one or more phytopathogens [10]. Due to low toxicity to humans and the environment and a high degree of efficiency against phytopathogenic fungi, the biotechnological production of antifungal agents is progressively increasing with an emphasis on *Trichoderma* species as production microorganisms.

Fungi of the *Trichoderma* genus are used in various branches of biotechnology and in agriculture. *Trichoderma* genus inhabit different ecosystems, but are predominantly present in different types of soil, from agricultural to forests, pastures, orchards, but also deserts [11]. *Trichoderma harzianum* most often

inhabits the rhizosphere of different agricultural crops, where due to the exchange and recognition of signaling molecules, physiological and biochemical changes can occur in *Trichoderma*, but also in plants [12].

Among the first, their antagonistic ability should be emphasized, which is why they occupy a significant place in the biological control of plant pathogens. In addition to the interaction of *Trichoderma* - pathogen, certain isolates of this fungus have other positive effects on plant growth and development [12]. Products based on fungi of the genus *Trichoderma*, which are known as biocontrol agents, make up about 60% of the total number of registered biofungicides. *T. harzianum* stands out as the most used species in commercially available preparations [13].

The metabolic activity of the selected production microorganism in the medium with optimal composition significantly depends on the environmental conditions such as the pH value, oxygen content in the cultivation medium and the temperature of the bioprocess. *Trichoderma* species require special conditions in terms of the mentioned process parameters, so it is important to examine the impact of each factor on the production of the *Trichoderma* biological agents. In accordance with this fact, the influence of temperature, pH of the cultivation medium and mixing on the production of *Trichoderma harzianum* biocontrol agent effective against phytopathogenic fungi *Fusarium graminearum* and *Aspergillus flavus*, was examined in this paper.

## MATERIALS AND METHODS

### Microorganisms.

The isolate *T. harzianum* obtained from soil sample is kept as a pure culture in the Microbiological Collection of cultures of the Institute of Field and Vegetable Crops, Novi Sad, Serbia.

Within the work, phytopathogenic isolates, *F. graminearum* and *A. flavus* were isolated from maize with typical symptoms of infection. Isolation of phytopathogenic fungi was performed according to the method described in the study by Tančić Živanov et al. [14]. Microorganisms are stored at the PDA medium in the Microbial Culture Collection of Faculty of Technology Novi Sad, Serbia.

### Inoculum preparation.

Isolates were initially grown on PDA (potato dextrose agar) [15] for seven days at 25°C. A small amount of mycelium of each isolate was taken to inoculate 50 cm<sup>3</sup> of PDB. The Erlenmayer flakes were

then incubated for 72 h on a rotary shaker (150 rpm) at 25°C.

Obtained *T. harzianum* inoculum was further used to inoculate experimental flasks for each individual experiment. On the other hand, after three days of cultivation, obtained cultivation broth of *F. graminearum* and *A. flavus* was filtered through double layer of sterile cheesecloth and used for *in vitro* testing.

### Experiments.

Selection of the optimal pH of the medium, optimal cultivation temperature and optimal mixing speed on a rotary shaker were realized on a medium containing: dextrose (10 g/dm<sup>3</sup>), soy flour (7 g/dm<sup>3</sup>), K<sub>2</sub>HPO<sub>4</sub> (3 g/dm<sup>3</sup>), KCl (0.5 g/dm<sup>3</sup>) and MgSO<sub>4</sub> x 7H<sub>2</sub>O (0.5 g/dm<sup>3</sup>).

The influence of medium pH on production was monitored through seven experiments with different pH (3-9 ± 0.1). Medium pH values were adjusted using HCl (1 M) and NaOH (1 M) before sterilization. The influence of cultivation temperature on the production of *T. harzianum* biocontrol agent was monitored through six separate cultivations (24, 26, 28, 30, 32 and 34°C). Examination of the effect of mixing on the production of *T. harzianum* bioagent was followed by change of rpm (rotation per minute) of the rotary shaker in five separate experiments (120, 150, 180, 210 and 240 rpm).

Experiments to select the optimal pH value of the medium were performed in Erlenmeyer flasks with a volume of 100 cm<sup>3</sup> with 40 cm<sup>3</sup> of culture medium. Cultivation was continued for 7 days at 26 ± 1°C on a rotary shaker with a stirring speed of 150 rpm.

Experiments to select the optimal value of the cultivation temperature were performed in 100 cm<sup>3</sup> Erlenmeyer flasks with 40 cm<sup>3</sup> of cultivation medium. Cultivation lasted 7 days on a rotary shaker with a mixing speed of 150 rpm.

Experiments aimed at selecting the optimal mixing speed on a rotary shaker were performed in 100 cm<sup>3</sup> Erlenmeyer flasks with 40 cm<sup>3</sup> of cultivation medium. Cultivation lasted 7 days at 26 ± 1°C.

### Antifungal activity testing.

The antifungal activity of the produced *T. harzianum* bioagent was examined on the test phytopathogenic isolates, *F. graminearum* and *A. flavus*, in accordance with the method described in the paper Grahovac et al. [16].

### Data analysis.

The results obtained in *in vitro* tests were performed in three replicates under identical

conditions, and the obtained results are presented as mean values with standard deviations. The results obtained in this experiment were processed by one-way ANOVA using Software Statistica, version 13.0 (StatSoft Inc., USA). Duncan multiple range test was used to test significance of differences ( $p \leq 0.05$ ) between mean values of measured diameter of inhibition zones.

## RESULTS AND DISCUSSION

The results shown in Figures 1-3 represent the mean values of the inhibition zone diameters of the tested isolates *F. graminearum* and *A. flavus*, obtained by the activity of *T. harzianum* biocontrol agent. For each test isolate, obtained diameters were statistically processed. Homogeneous groups and the significance of differences between the mean values of the groups were determined by post-hoc testing using the Duncan multiple range test. Results of the Duncan test are also shown in Figures 1-3 and the differences in significance are indicated with lowercase letter.

### pH.

The results presented in Figure 1 show that production of *T. harzianum* bioagent effective against *F. graminearum* was successful on medium with all applied pH (all results are greater than 22 mm in diameter of the mycelial growth inhibition zone) [17]. Certainly, at the highest level of statistical significance are three medium pH marks with lowercase letter *a* (pH 5-7). However, the largest formed diameter of the inhibition zone was formed by cultivating *T. harzianum* on medium with a pH value of 6 (50.67 mm).

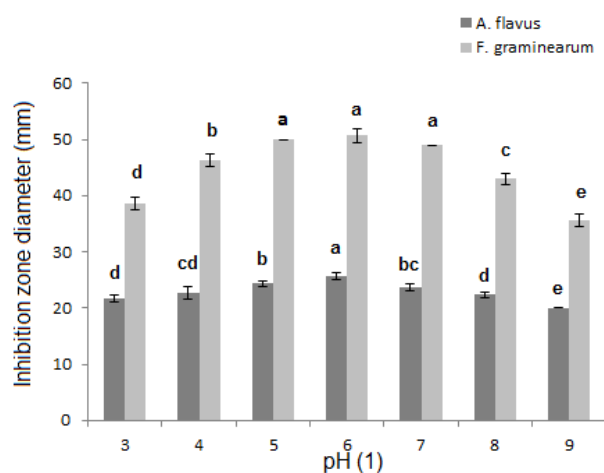


Figure 1. Variation of medium pH. Duncan multiple range test: mean values of inhibition zone diameter formed around wells for isolates *A. flavus* and *F. graminearum*.

On the other hand, observing the effect of *T. harzianum* bioagent against *A. flavus*, the conclusion is different. Namely, the pH values of the medium from 4 to 8 (diameters higher than 22 mm) are considered suitable for the production of *T. harzianum* bioagent. Medium pH values of 3 and 9 do not show adequate activity. In this case, the pH 6 of the medium was the most suitable for the production of *T. harzianum* bioagent effective against *A. flavus* isolate and this pH value is at the statistically highest level of significance for this tested isolate (25.67 mm).

In accordance with the obtained results, a slightly acidic medium (pH of  $6 \pm 0.1$ ) was most suitable for the production of *T. harzianum* bioagent effective against *A. flavus* and *F. graminearum*. These results coincide with the research of Singh et al. In their research they have found that the production of *Trichoderma* spp. was the most suitable on medium with pH range of 5.5 to 7.5 [18].

### Temperature.

Temperature is one of the most important parameters that affect the growth of microorganisms. The optimal temperature is the temperature at which cells multiply, grow and produce the appropriate metabolites. For the production of high value products using *Trichoderma* spp. the optimum temperature ranges from 25°C to 30°C. However, some members of this genus can inhabit areas with temperatures up to 40°C and even extreme areas with low temperatures (0°C) [18].

The results presented in Figure 2 show that at all applied bioprocess temperatures, the desired production of *T. harzianum* bioagent effective against isolate *F. graminearum*, occurs. However, at the highest level of statistical significance is only the inhibition zone obtained by activity of *T. harzianum* bioagent produced at a temperature of 28°C (marked with lowercase letter *a*) forming a zone diameter mean value of 61.33 mm. On the other hand, the weakest activity against *F. graminearum* isolate was formed by the production of *T. harzianum* bioagent at a temperature of 34°C (indicated by a lowercase letter *f*) and 24°C (indicated by a lowercase letter *e*).

Depending on the applied bioprocess temperature, the zones range from 19.33 mm (indicated by a small letter *d*) to 28 mm (indicated by a small letter *a*) was formed by activity of produced *T. harzianum* bioagent against *A. flavus*. The largest diameter of the inhibition zone was formed by applying a temperature of 28°C and this diameter is at the highest level of statistical significance together with the diameter formed at a temperature of 30°C. Thus, for isolate *A. flavus* two temperature values were at the highest level of

statistical significance. In these cases, a lower temperature is generally chosen to reduce the cost of producing *Trichoderma* bioagent.

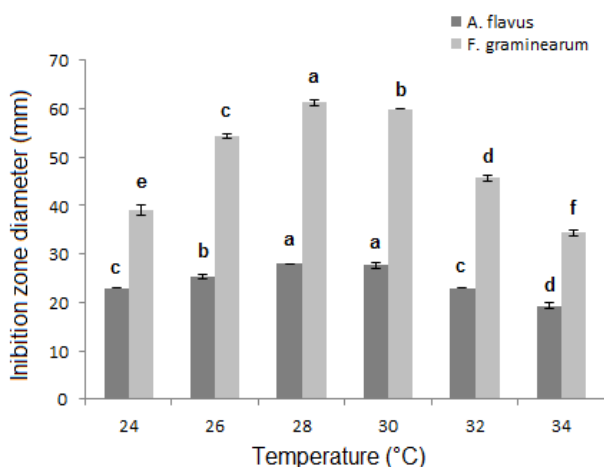


Figure 2. Temperature variation. Duncan multiple range test: mean values of inhibition zone diameter formed around wells for isolates *A. flavus* and *F. graminearum*.

Considering that in both cases the temperature of 28°C proved to be the most suitable for the production of *T. harzianum* bioagent effective against isolates *F. graminearum* and *A. flavus*, this temperature was selected as optimal for production.

#### Mixing.

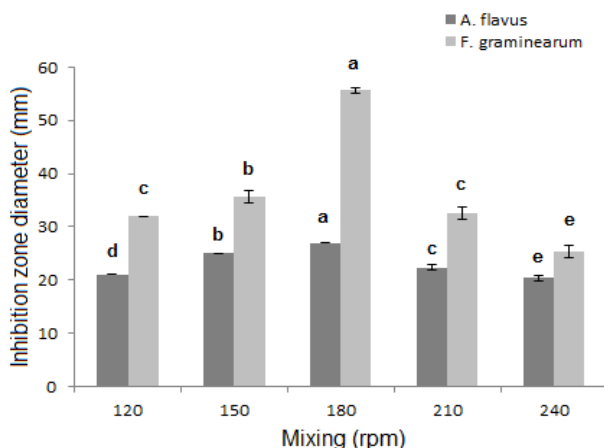


Figure 3. Mixing variation. Duncan multiple range test: mean values of inhibition zone diameter formed around wells for isolates *A. flavus* and *F. graminearum*.

Mixing of the cultivation medium enables dispersion of the gas phase, homogenization of the composition (nutrient and metabolite content), pH and temperature, suspension of solid ingredients (cells of the production microorganism and insoluble ingredients) and dispersion of liquid ingredients that do not mix with water.

The desired degree of homogenization is achieved by mixing that provides turbulent movement throughout the volume of the cultivation medium.

For the production of *T. harzianum* on an enlarged scale, mixing over 200 rpm [19] and even up to 500 rpm [20], have been obtained as optimal in the scientific literature. Certainly, the mixing of the cultivation fluid on a rotary shaker cannot be fully compared with the conditions in enlarged scale (laboratory bioreactors). However, obtaining the optimal mixing speed on a small scale can be an indicator of the microorganism's need for oxygen. Figure 3 shows the influence of the rotational shaker speed on the production of *T. harzianum* bioagent effective on phytopathogenic isolates *F. graminearum* and *A. flavus*. The figure shows that isolate *F. graminearum* was more sensitive to produced *T. harzianum* bioagent in relation to isolate *A. flavus*.

At the highest level of statistical significance for both tested isolates, marked is a mixing speed of 180 rpm. This means that at this speed of shaker rotation the best production of *T. harzianum* bioagent occurs. By applying these conditions, the maximum formed diameter of the mycelial growth inhibition for isolate *F. graminearum* was 55.67 mm and 27.00 mm for isolate *A. flavus*. Higher and lower mixing speeds than this, show a decrease in the efficiency of the produced *T. harzianum* bioagent on the tested pathogenic isolates.

## CONCLUSION

The results obtained in this study indicate that for the production of *Trichoderma harzianum* agent for biological control of maize pathogens, *F. graminearum* and *A. flavus*, the optimal process conditions were: medium pH 6, bioprocess temperature 28°C and rotary shaker mixing speed of 180 rpm. Application of these cultivation conditions leads to the highest production of *T. harzianum* bioagent, which also affects the formation of the maximum inhibition zone diameters of *F. graminearum* and *A. flavus* mycelial growth.

## ACKNOWLEDGEMENTS

This work was supported by the Ministry of Education, Science and Technological development of the Republic of Serbia (451-03-9/2021-14/200134), and the Provincial Secretariat for Higher Education and Scientific Research, Autonomous Province of Vojvodina, Republic of Serbia (142-451-3213/2020-03).

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# EQUILIBRIUM SORPTION OF DIRECT DYE ON POLYAMIDE

ORIGINAL SCIENTIFIC PAPER

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DOI: 10.5281/zenodo.6371191

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## ABSTRACT:

In this paper, the equilibrium sorption of dyeing polyamide 6.6 fabric with direct dye is presented. Polyamide is a chemical fiber obtained from synthetically produced polymers, while direct dyes are most often sulfonated azo compounds: which are derived from bendisidine and its derivatives. Samples of 100% raw polyamide 6.6 fabric were used in the experiment. The direct used dye is called Solophenyl blue 4GL. The samples were dyed at different dye concentrations: 5, 10, 20, 30, 40, 50 mg/l. The temperature at which the samples were dyed was 40, 60 and 98 °C. Citric acid was added to the dye solution to achieve a certain pH of the solution. A spectrophotometer (Cary 100 Conc UV-VIS, Varian) was used to measure the absorbance of aqueous stained solutions and to calculate the unknown dye concentration in the solution and to construct a calibration curve. The degree of dye exhaustion and the amount of absorbed dye were calculated. Two models of adsorption isotherms were used: *Langmuir* and *Harkins-Jura*. The high functionality of the variable was observed in the *Langmuir* model.

**KEYWORDS:** polyamide, dyeing, sorption, direct dye

## INTRODUCTION

Polyamides (PA) or nylons were among the first synthetic polymers used for fiber applications. Polyamide fibers are used for a variety of different applications ranging from textiles and carpets to reinforcement of tires. PA's are polymers where the repeat units are held together by an amide linkage. PA can be classified into aromatic polyamides and aliphatic polyamides. Aliphatic PA's consist of only aliphatic chains whilst aromatic PA consist of aromatic rings in the main chain. Most of the aliphatic PA's are synthesized by either condensation polymerization or ring opening polymerization. Aromatic PA's are difficult to synthesize using diacids and diamines due to the lower reactivity of aromatic amines compared to aliphatic amines, and therefore aromatic PAs are usually made from diamine and diacid chloride [1-4].

Polymer blends are a class of polymeric systems, which can allow obtaining "new" materials with a suitable range of properties, with a relatively good performance/cost ratio. Unfortunately, when chemically different polymers are blended, incompatibility leads to a final product with poor properties, often worse than those of the corresponding neat polymers [5, 6].

In order for direct dye to be used for dyeing, it must be possible to change the solubility of the

compound, and groups may be included which will make the agent soluble in water. The type of interaction, whether physical or chemical, will depend on the groups on the dye molecules and in the fiber chains. Direct dyes are synthesized with sulfonic acid groups to give them solubility in water, separating and giving sodium cations. This allows the dye to bind to the chains in the fiber, often through intermolecularly hydrogen bond. They are used in dyeing in an aqueous solution containing sodium chloride. Salt reduces the electrical repulsive forces between the negative charge on the fiber surface and the type of anionic dyes [7, 8].

Most direct dyes are azo compounds, which often contain two or three azo groups. Azo groups have the potential to form hydrogen bonds with hydroxyl groups in polyamide. Vital substituents of direct dyes are said sodium sulfonate group,  $-\text{SO}_3\text{Na}$ , bound to benzene or naphthalene rings. It is a sulfonate group that gives most direct dyes the solubility property in water which is very important for dyeing. Dyes containing these groups ionize into sodium cations and dyed sulfonate anions that are positively and negatively charged [9].

In this paper, the equilibrium sorption of direct dye on polyamide 6,6 fabric was investigated. The aim of the research is to expand the spectrum of polyamide dyes.



## MATERIALS AND METHODS

In the experimental part, 100% raw polyamide 6,6 fabric (Jumko, Vranje) was used. The dyeing was performed in Erlenmeyer in which samples of polyamide fabric in a solution of citric acid and direct dye were placed. The Erlenmeyers were heated for 60 minutes. The amount of citric acid was 5 g/ml, pH = 3. The dye used is Solophenyl blue 4GL (Huntsman, Texas, United States), whose chemical structure is shown in figure 1.

The used dye has practically 3 azo groups, one benzene ring, three naphthalene nuclei, four sulfonate groups, there is also an aniline residue attached to naphthalene. Active places for binding, ie. contact, in molecules, are negatively charged hydrophilic sulfonate groups, as well as electron donor and acceptor groups. The active groups in the polyamide structure are the amino, carboxyl and amide groups. When immersed in an acidic aqueous solution, PA fibers receive a positive charge (amino, amide groups) which are then neutralized by dye anions (sulfonate groups).

The samples were dyed at different dye concentrations, as follows: 5, 10, 20, 30, 40, 50 mg/l. The temperature at which the samples were dyed was 40, 60 and 98 °C. Upon completion of dyeing, the solution was cooled and absorbance was measured using a spectrophotometer (Cary 100 Conc UV-VIS, Varian). The absorption maximum for the used dye is 580 nm. Also, a calibration curve was made to determine the unknown dye concentration during dyeing.

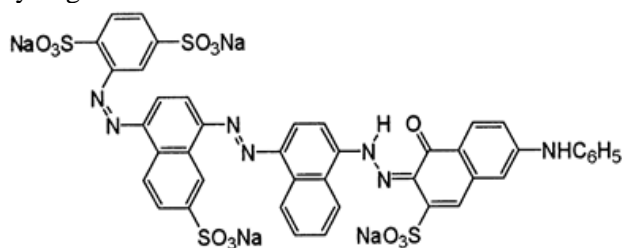


Figure 1. Chemical structure of Solophenyl blue 4GL

The degree of dye exhaustion was calculated using the form [10]:

$$\text{Degree of dye exhaustion} = \frac{C_0 - C_t}{C_0} \times 100(\%) \quad (1)$$

where:  $C_0$  and  $C_t$  (mg/l), initial and dye concentration at time  $t$ .

The amount of absorbed dye per unit mass of adsorbent (absorption capacity) was obtained using equation [9]:

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

where  $q_t$  (mg/g), mass of absorbed dye per unit mass at dye time  $t$ ;  $q_e$  (mg/g), mass of absorbed dye per unit

mass in equilibrium,  $C_0$  (mg/l), initial dye concentration;  $C_t$  (mg/l), dye concentration in solution at dye time  $t$ ,  $C_e$  (mg / l), equilibrium dye concentration in solution;  $w$  (g), mass of sample and  $V$  ( $\text{dm}^3$ ), volume of dyeing solution.

The *Langmuir* equation is applicable to a homogeneous surface where the adsorption of each adsorbate molecule has the same sorption activation energy. The linear form of this isotherm is represented by equation [11]:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \left[ \frac{1}{b \cdot Q_0} \right] \cdot \frac{1}{C_e}$$

where  $C_e$  is the equilibrium dye concentration (mg/g),  $q_e$  is the equilibrium amount of adsorbed dye (mg/g),  $Q_0$  is the maximum single layer coating capacity (mg/g),  $b$  is the adsorption energy.

The *Harkin-Jura* (H-J) isotherm model assumes the possibility of multilayer adsorption on the surface of an adsorbent having a heterogeneous pore distribution. Mathematically, this model can be expressed by equation [11]:

$$\frac{1}{q_e^2} = B / A - \left( \frac{1}{A} \right) \log \log C_e$$

where  $B$  and  $A$  are *Harkin-Jura's* constants.

## RESULTS AND DISCUSSION

The effect of initial dye concentration on adsorption – the degree of dye exhaustion when dyeing polyamide 6.6 fabric with direct dye, at different temperatures, is given in figure 2. There is continuity in changes during the growth of initial dye concentration. As the concentration increases, the degree of dye exhaustion decreases.

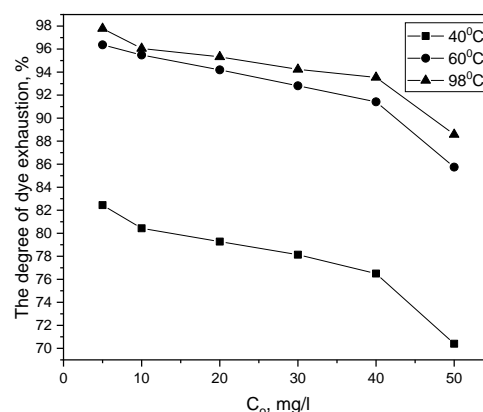


Figure 2. Influence of initial dye concentration on adsorption – the degree of dye exhaustion

At lower concentrations of dye in the solution, at the beginning there is a slightly larger drop in the percentage of exhausted dye, and at the end of dyeing

this drop was somewhat milder. At the highest dyeing temperature, ie. 98°C, the higher degree of dye exhaustion occurs. As the temperature rises, the degree of dye exhaustion increases, which is to be expected because is this conventional dyeing for polyamide fibers. At a temperature of 40°C, there is a sharp drop in the degree of dye exhaustion at an initial dye concentration of 40 mg/l. At a temperature of 60°C, the degree of dye exhaustion is balanced, however, at an initial dye concentration of 40 mg/l, there is a sharp drop in the degree of dye exhaustion at all temperatures, where the curve is the steepest.

The diagram in figure 3 shows the results of the change in the adsorbed amount of adsorbate (dye) on the adsorbent (polyamide 6.6 fabric) for different initial concentrations and temperatures. As the initial dye concentration increases, the dye absorption on the polyamide 6.6 fabric increases sharply. The curve is steeper at the highest applied dye concentration applied. As the initial dye concentration in the solution increases, better dye absorption occurs on the polyamide 6.6 fabric.

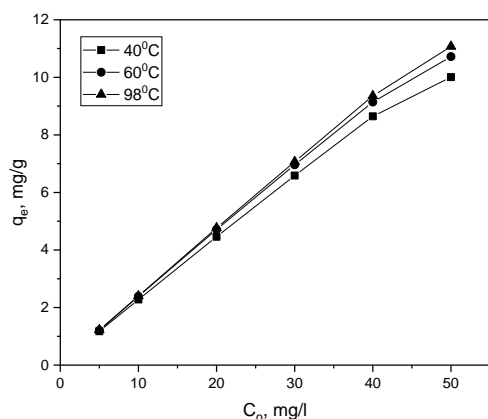


Figure 3 Adsorbed amount of direct dye per unit mass of PA 6.6 fabric in relation to the initial concentration for different times

Figure 4 shows the *Langmuir* isotherm for different dyeing temperatures, which is derived under the assumption of surface heterogeneity with uneven heat sorption distribution on the surface. From this diagram, the high functionality of the variables ( $R^2 = 0.980$  - 40 °C), ( $R^2 = 0.996$  - 60 °C) and ( $R^2 = 0.966$  - 98 °C) is noticeable. Based on the slope and section, the *Langmuir's* constants were determined, and the suitability of the model for describing the adsorption process of the used dye on polyamide 6.6 fabric was evaluated through them.

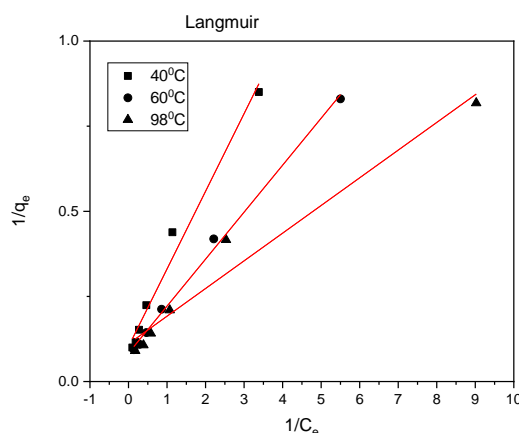


Figure 4 Graphical representation of the linear shape of the *Langmuir* adsorption isotherm for dyeing polyamide 6,6 fabric at different temperatures

By analyzing the isothermal data by fitting it, one comes across different isothermal equations by finding a suitable model that can be used to control the dyeing process. In the given research, the *Harkin-Jura* isothermal model was used for fitting experimental points with the help of OriginPro software.

In the *Harkin-Jura* model, multilayer adsorption at a relatively large distance from the surface is not noticeable. The diagram in figure 5 presents *Harkin Jura* isotherms for dye adsorption on the adsorbent. The high functionality of the variables is not noticeable, ie.  $R^2 = 0.779$  for 40 °C,  $R^2 = 0.707$  for 60°C and  $R^2 = 0.769$  for 98°C, so based on this diagram, *Harkin Jura's* constants were determined, as well as the coefficient of determination over which the inadmissibility of this model for describing was assessed. The process of adsorption of the used dye on the adsorbent-fabric at different temperatures (figure 5).

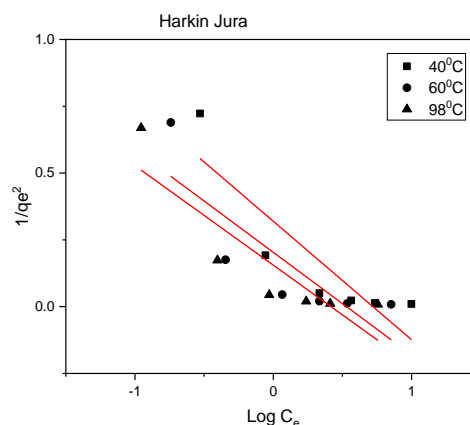


Figure 5 Graphic representation of *Harkin Jura* adsorption isotherm for dyeing polyamide 6.6 fabric at different temperatures

Table 1 shows the values, adsorption parameters, analytical expressions of adsorption isotherms, and values of the coefficient of determination  $R^2$ . According to the results from table 1, a high value of the coefficient of determination is observed, which indicates a large percentage of the sum of the squares of the deviation of the value of the variable from the arithmetic mean.

$Q_o$  and  $b$  are Langmuir constants. The maximum adsorption capacity  $Q_o$  increases with temperature, thus increasing the mobility of the dye ion. This led to a higher chance of direct dye being adsorbed on the adsorbent, resulting in an increase in its adsorption capacity in increasing pore size or activating the adsorbent surface area. The observed linear relationship is statistically significant (at the 95% confidence level) which proves high  $R^2$  values (which are closest to 1). This indicates the applicability of the *Langmuir* isotherm.

The adsorption energy  $b$  varies with increasing temperature. In general, the parameter  $b$  usually has

the value 1. This parameter is a measure of the heterogeneity of the system and a more homogeneous system would have  $b$  value approaching one, a more heterogeneous system would have a value of  $b$  approaching zero. The value of  $R_L$  indicates the shape of the isotherms that should be unfavorable ( $R_L < 1$ ), linear ( $R_L = 1$ ), favorable ( $0/R_L/1$ ) or irreversible ( $R_L = 0$ ).

The *Harkin Jura's* constants  $A$  and  $B$  were calculated from the linear ratio  $1/q^2e$  and  $\log C_e$ , and the values of the constants are presented in table 1. The value of the coefficient of determination for Solophenyl blue 4GL is  $R^2 = 0.779$  for 40 °C,  $R^2 = 0.707$  for 60 °C and  $R^2 = 0.769$  for 98 °C, which indicates that the model is poorly adapted to the obtained data. The model showed that there is no heterogeneous pore distribution. Constant  $A$  increases with increasing temperature and constant  $B$  decreases with increasing temperature. This explains the heterogeneous nature of both adsorbents.

**Table 1.** Analytical expressions of linear isotherms with coefficients for the system Solophenyl blue 4GL - polyamide 6.6 fabric

Models	Temperature (°C)	Analytical equations of models	Parameters of models		$R^2$
<i>Langmuir</i>	40	$\frac{1}{q_e} = 0.10 + 0.23 \cdot \frac{1}{C_e}$	$Q_o$	9.75	0.980
			$b$	0.45	
			$R_L$	0.04	
	60	$\frac{1}{q_e} = 0.08 + 0.14 \cdot \frac{1}{C_e}$	$Q_o$	11.98	0.996
			$b$	0.60	
			$R_L$	0.03	
	98	$\frac{1}{q_e} = 0.11 + 0.08 \cdot \frac{1}{C_e}$	$Q_o$	9.04	0.966
			$b$	1.36	
			$R_L$	0.01	
<i>Harkin Jura</i>	40	$\frac{1}{q_e^2} = 0.32 + 0.44 \log \log C_e$	$B$	0.72	0.779
			$A$	2.25	
	60	$\frac{1}{q_e^2} = 0.20 + 0.38 \log \log C_e$	$B$	0.53	0.707
			$A$	2.61	
	98	$\frac{1}{q_e^2} = 0.15 + 0.37 \log \log C_e$	$B$	0.42	0.769
			$A$	2.69	

## CONCLUSION

Based on the obtained experimental results, it was concluded that the addition of citric acid to the dye solution results in better dye adsorption on the polyamide 6,6 fabric, given the bonds established in the interactions of (+) and (-) charged functional groups.

The dyeing process at a higher temperature gives better results than at a lower temperature. As the concentration increases, the degree of dye exhaustion per unit mass of adsorbent (polyamide) decreases. At the highest applied dye concentrations and the highest temperature, the highest dye adsorption occurs.

The *Langmuir* isotherm is effective in simulating isothermal adsorption of brown direct dye on a polyamide 6.6 fabric. It was found that staining - adsorption depends on the temperature and the initial dye concentration.

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# SPECIFICS AND QUALITY OF DOMESTIC COOKED CHEESES FROM UNA-SANA CANTON

ORIGINAL SCIENTIFIC PAPER

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DOI: 10.5281/zenodo.6371214

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## ABSTRACT:

Una-Sana Canton with geographical and climatic characteristics abounds in different types of cheese produced from cow's milk. In this paper presents the production process and the results of chemical and sensory analysis of three types of domestic cow's cheeses, where acetic acid and whey were used for milk coagulation, and the heating temperature of milk ranged from 90°C to 95°C. For the third type of cheese, the milk coagulated using its own microflora, and the heating temperature ranged from 50°C to 55°C. Cheeses produced by coagulation of milk using their own microflora and whey could be classified as semi-soft cheeses, and cheese obtained by coagulation of milk with acetic acid in the group of semi-hard cheeses. Sensory analysis of the cheeses showed that the cheese produced by coagulation of milk with acetic acid had the highest total score of 94.10 points; then followed the cheese obtained coagulation of milk by its own microflora with 84.16 points, and the lowest number of points 81.92 had the cheese produced by coagulation of milk using whey.

**KEYWORDS:** domestic cooked cheeses, Una-Sana Canton, chemical and sensory properties

## INTRODUCTION

Production of cheese is one of oldest way of milk storing which has take place to present days. It is assumed that cheese as foodstuff was arised as 7000. to 6000. B.C. by spontaneous conversion of milk constituents, primarily casein and milk fat [1, 2]. According to Rulebook on dairy products and starter cultures in Article 29 [3], cheese is defined as fresh product or product with different of degree of maturity, and it is produced by separating of whey after milk coagulation (cow's, shep's, goat's, buffalo milk an/or their mixtures), from skimmed or partially skimmed milk, or by combination of the above listed raw materials. In the production of cheese is allowed the use of starter cultures, rennet and as so as appropriate coagulation enzymes. Cheese is very popular food product because of its richness in nutritional components like proteins, vitamins (riboflavin, thiamin, cyanocobalamin), minerals (calcium, phosphorus), and short-chain fatty acids [4]. Mechanical, rheological and cooking properties of heated and unheated cheese depend on the structure of cheese [5]. The main structural component of cheese casein, is present in the form of a three-dimensional network, where fat globules, water, minerals, bacteria and dissolved solutes such as lactose, lactic acid, soluble salts and peptides are presents in the cheese matrix [6].

In some countries and some areas of these countries are developed different ways of cheese

production, and different climat zones and kind of milk cattles influence on the existense of different types of cheeses. One of classification of cheeses is according to way of coagulation of milk [7] so there are: sour cheeses (made by the lactic acid fermentation), sweet cheeses (produced by the action of enzyme additions), fresh soft cheeses, semi-hard and hard cheeses, mixed cheeses (produced whit acid and rennet). According to the water content in the non-fat dry matter of the cheese and to the consistency, pursuant to the above listed Rulebook [3], cheeses are produced and placed on the market as: extra hard, hard, semi-hard, soft cheese and fresh cheese.

Cheese produced by heat treatment of milk, so-called cooked cheese is a representative of traditional cheese making and has a marginal importance. Cooked cheese can be produced from whey (albumin cheese), from milk and from fresh cheese [8]. In the production of cooked cow's cheese for coagulation is most commonly used 9% acetic acid which is added in quantity of 2-3% in the heat milk on 98°C-99°C. Except acetic acid, whey and buttermilk also be used for acidification. After coagulation of proteins, the mass is calmed down and in this moment the heating of the milk begins at the temperature 88°C -98°C in duration of 10-20 minutes. The cheese curd put into the molds and then pressed [1]. Cheese can be consumed immediately after production or after prolonged storage [9]. Cooked cheeses are less sour

than cheeses produced by fermentation with lactic acid [10].

Cooked cheese made from fresh cheese is produced of raw cow's milk that leave to sour spontaneously for 2 to 3 days, whereby the separated cream on the surface is skimmed, and the remaining milk is gently heated for 2 to 3 hours and coagulation. The created coagulum is cut into equal parts to separate the whey, and then put into gauze where it is drained [8]. Cooked cheese from whey is produced with acidification of whey (pH 4.5) and heating at 90°C to 95°C, whereby come to flocculation of whey proteins and milk proteins. The most famous cheese from whey is Italian Ricotta [9].

On the Una - Sana Canton there are casein cheeses made from cow's, shep's and goat's, milk, and consider to way of milk coagulation there are: fresh cheeses made with coagulation of milk using their own microflora and heating on the temperature to 55°C, then the cheeses made with coagulation of milk using acetic acid or whey and heat to the temperature of boiling [11].

Domestic cow's cheese produced by heat treatment of milk is very represented in Bosnia and Herzegovina and has a characteristics of tradicional speciality due to its long-term way of production and traditional composition. Food would have to be traditionally produced and marketed for at least 25 years in order to receive the traditional speciality label [12].

The main goal of this paper was to describe the production process and the results of chemical and sensory analysis of three types of domestic cooked cheeses from Una-Sana Canton. In the cheese production, for milk coagulation, acetic acid and whey were used with the heating temperature from 90°C to 95°C. Where milk was coagulated using its own microflora, the heating temperature ranged from 50°C to 55°C.

**MATERIALS AND METHODS**

In this experiment, three types of cow's milk cheese were made with the following labels: (A1), (A2) and (A3). Five liters of fresh milk were used to make each of these cheeses. For the cheese marked as (A1), 80% acetic acid was used to curd the milk; into the milk was added a teaspoon of salt (cca. 10 g), then the milk was heated at the temperature about 95°C, and a spoon of acetic acid was added (cca. 15 ml) in the milk. After addition of acid, the visible curd appeared in the cheese bowl. The curd is transferred to a strainer to separate the whey, and after squeezing, the curd is transferred to a wooden mold to acquire a round shape. For the cheese marked as (A3), the

production process was the same, only whey (cca.2 l) was used for the milk coagulation.

Figure 1. shows the production process of the cheeses marked as (A1) and (A3).

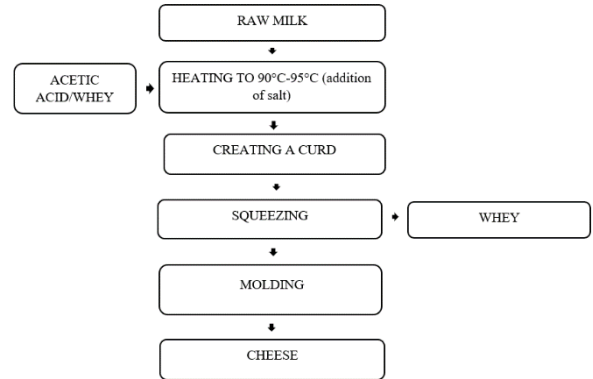


Figure 1. Production process of the cheeses marked as (A1) and (A3)

For the cheese marked as (A2), the milk was coagulated using its own microflora where the heating temperature ranged from 50°C to 55°C. Figure 2. shows the production process of the cheese marked as (A2).

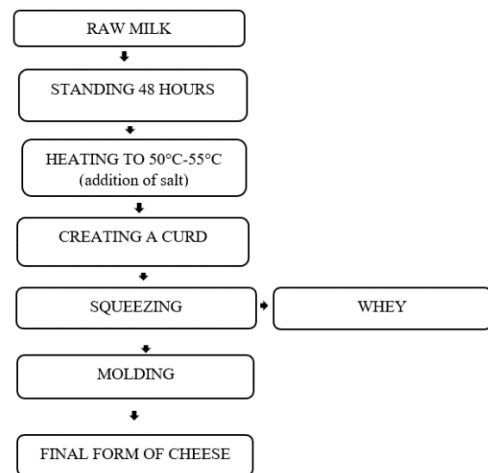


Figure 2. Production process of cheese marked as (A2)

Chemical and sensory analyzes were performed in the Laboratory for Control and Quality of the Biotechnical Faculty in Bihać. Of chemical analyses were done the following: water content, degree of acidity [13], and the content of sodium-chloride [14].

Sensory evaluation of cheeses was performed by the Sensory assessment panel of 5 evaluators. With the grades from 1 to 5, the following properties were evaluated: Appearance, Color, Smell, Taste and Consistency. Each of these properties was multiplied by a coefficient of importance: 1 for Appearance, 2 for

Color, 3 for Smell, 10 for Taste, and 4 for Consistency [15].

The results of this study are presented as the mean values accompanied with their standard deviations. One factor analysis of variance (ANOVA) was performed using statistical software SPSS (VER.20). When the main impact was significant, averages were

split by Tukey's test of the smallest significant deviations at 5% level.

## RESULTS AND DISCUSSION

Table 1. shows the results of chemical analysis of cheese samples.

**Table 1.** Results of chemical analysis of cheese samples

Parameters	Sample A1	Sample A2	Sample A3
Water %	53.20±0.30 <sup>b</sup>	66.15±0.72 <sup>a</sup>	65.63±0.44 <sup>a</sup>
Acidity °SH	11.12±0.06 <sup>a</sup>	24.56±1.03 <sup>b</sup>	10.65±1.16 <sup>a</sup>
NaCl %	0.92±0.09 <sup>a</sup>	0.77±0.06 <sup>b</sup>	0.80±0.07 <sup>ab</sup>

Data are expressed as mean ± standard deviation. Means with the same letter in the same row do not differ statistically at 5% ( $p > 0.05$ ).

The results of chemical analysis of samples show that the highest water content was found in the sample (A2) 66.15%, then followed the sample (A3) 65.63%, and the sample (A1) with a water content of 53.20%. As reported by Kirin [9], domestic cooked cheeses produced with milk coagulation using whey or acid and then heated at 95°C, had the average water content 51.04% and dry matter content 48.96%. The water content in cooked cheeses without the use of microorganisms was 48.86%; these cheeses can be consumed immediately after production [1]. Domestic semi-hard cheeses obtained by coagulation of milk using 80% acetic acid and heated to 95°C had a water content in range from 31.56% to 36.56% [16]. Considering the water content, (A2) and (A3) cheeses could be classified as semi-soft/ soft cheeses, while (A1) cheese could be classified as semi-hard cheese according to Tratnik [7]. The moisture content is very important for increasing the storage life of cheese [17].

Salt is added in cheese ranging from 0.5% to 6.0%, mainly for flavor and preservation [18]. The highest content of sodium chloride was recorded in the sample (A1) 0.92%, followed by the sample (A3) 0.80%, and the lowest content of sodium chloride had the sample (A2) 0.77%. According to Kirin [9], the NaCl content in the samples of cooked cheese was 1.23%, and since it is a traditional way of making cheese, table salt is

added according to one's own taste when making cheese.

Acidity has a strong influence on the texture, rheological, and cooking properties of cheese because of its impact on the interactions of casein-casein, mineral-casein, and casein-water [6]. Strong casein-casein interactions increase the firmness of the cheese matrix, and as a consequence, cheese becomes more firm and elastic [19]. The highest acidity was in the sample (A2) 24.56°SH, which is a significantly value compared to the samples (A1) 11.12°SH and (A3) 10.65°SH. Cheese (A2) produced by coagulation of milk using its own microflora had the highest water content which could be the cause of higher acidity compared to the other two methods of production. As reported Sabljak et al. [20], the acidity of fresh cheese obtained by coagulation of milk using its own microflora varies from 4.44 to 4.68 pH on the first day of storage. Pračić et al. [16] recorded values of acidity from 25.83°SH to 36.86°SH in domestic semi-hard cheeses. Kirin [21] states that due to the non-uniformity of the chemical composition of cooked cheeses, it is necessary to adopt regulations on the range of parameters of the chemical composition of cheese.

Table 2. shows the results of sensory analysis of cheese samples.

**Table 2.** Results of sensory analysis of cheese samples

Sensory properties	Sample A1	Sample A2	Sample A3
Appearance	4.38±0.30 <sup>a</sup>	4.02±0.05 <sup>b</sup>	3.46±0.26 <sup>c</sup>
Color	9.00±0.14 <sup>b</sup>	8.04±0.09 <sup>a</sup>	8.08±0.11 <sup>a</sup>
Taste	47.40±1.82 <sup>b</sup>	42.40±0.96 <sup>a</sup>	41.60±2.07 <sup>a</sup>
Smell	14.28±0.55 <sup>a</sup>	12.78±0.75 <sup>a</sup>	12.90±0.77 <sup>a</sup>
Consistency	19.04±0.73 <sup>b</sup>	17.12±1.11 <sup>a</sup>	16.08±1.25 <sup>a</sup>
Total	94.10±1.47 <sup>b</sup>	84.16±1.78 <sup>a</sup>	81.92±3.62 <sup>a</sup>

Data are expressed as mean ± standard deviation. Means with the same letter in the same row do not differ statistically at 5% ( $p > 0.05$ ).



After food consumption, flavour compounds are released from the food matrix and mixed with saliva, which need to be transported to the flavour receptors in the mouth and nose [22]. Overall flavour is influenced by perceptual interactions between various sensory modalities such as aroma, taste and texture. According to Visschers et al. [23], intensity of aroma perceived by subjects decreased with increasing firmness of the food.

After Sensory panel assessment, sample (A1) had a total of 94.10 points, which is the highest total number of points, followed by sample (A2) with 84.16 points, and sample (A3) 81.92 points. According to the results of Sabljak et al. [20], cheeses sampled from different producers had an uneven consistency, softer structure, while Kirin [8] found that cooked cheeses generally had a homogeneous and pliable dough, without sticking to the blade of the knife, with a specific lactic-sweet-sour combination of flavors. Lukač Havranek [1] describes samples of fresh cheese to have a soft consistency, a characteristic pale yellow color, with a slightly sour smell and taste, but a very uneven chemical composition. In this experiment, sample (A1) had a good surface appearance, harder consistency, easier slicing ability, characteristic pale and yellow color, with moderate salty taste and pleasant aroma. The sample (A2), where its own microflora was used for milk coagulation had more pronounced cavities on the surface, a rather soft consistency, and desintegrated during slicing, which is a characteristic of cheeses produced in this way. Compared to the other two cheeses, the taste of milk was more intense in this sample, the acidity was more pronounced, as well as the salty taste. During heating of the cheese, the proportion of liquid fat increases, and according to Lopez et al. [24], at the temperature higher than 40°C, almost all fat in cheese is in a liquid state. Liquid fat acts as a plasticizer between casein strands, making cheese more soft and flexible [25]. Sample (A3) had a moist cheese surface, softer consistency, more intense taste of milk, moderate acidity and less salinity compared to the other two cheeses. Increasing the ratio of moisture to non-fat substances in cheese, weakens the firmness in cheese and influences on the textural characteristics [5]. Content of fat, cheese yield, moisture, as well as coagulants plays an important role in cheese texture [26].

## CONCLUSION

By the chemical analysis was determined statistically significant difference ( $p < 0,05$ ) between samples for water and sodium chloride content, as well as acidity. These variations in chemical composition

could be due to the different way of coagulation and the heating temperature of milk. Cheeses produced by milk coagulation using whey, and with the help of their own microflora had a higher water content compared to cheese obtained by coagulation of milk using 80% acetic acid. Uneven acidity was found between the samples, and the highest acidity was found in cheese produced by coagulation of milk using its own microflora.

The Sensory panel rated the cheese produced by coagulation of milk with 80% acetic acid as the best, and awarded the highest number of total points, followed by the cheese produced by coagulation of the using its own microflora. The lowest number of total points received cheese produced by coagulation of milk with whey.

Due to the growing competition in the food market, among which cheese occupies a significant place, traditional products are especially valued for their special quality, and in addition they are a reflection of the cultural heritage that is passed down from generation to generation. As there are different approaches in the technology of domestic cooked cheese production, the results of chemical and sensory analysis in this paper could serve as a recommendation to producers to achieve even better results in the future and get products that could be placed on the market of Bosnia and Herzegovina, as well as wider.

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# EFFICIENCY OF DEGREASING BY DISHWASHING DETERGENTS

ORIGINAL SCIENTIFIC PAPER

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DOI: 10.5281/zenodo.6371252

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## ABSTRACT:

Consumption of agents for manual and machine washing of dishes is constantly increasing. Although the growth of the use of dishwashers is evident, hand dishwashing is still dominant in our region. A good dishwashing detergent must effectively remove food residues and degrease the surface of dishes, made of different materials, while the surfaces of washed dishes should remain smooth, shiny with a pleasant smell of freshness. The requirements of consumers-users of these funds are, in addition to the listed basic functions, also practicality of handling and dosing, pleasant smell and mild action on the hands and acceptable price. The aim of this paper is to examine the degreasing efficiency of commercial detergents from our market on four types of fats. In addition to commercial dishwashing detergents, whose composition is known only roughly indicated in the producer declaration, was tested a laboratory prepared sample with exactly known composition. All tests of the degreasing ability of dishes with different types of impurities were performed under the same conditions with a change in the concentration and type of detergent, and according to the method used by some industrial detergent manufacturers. It was found that in addition to the concentration of detergent in the washing solution, the degreasing efficiency is affected by the type and concentration of surfactants, as well as auxiliary components that are part of the product.

**KEYWORDS:** degreasing; fat; dishwashing detergents; surfactant

## INTRODUCTION

Liquid detergents play a very important role in our daily lives for personal care, household surface care and fabric care. Due to faster dissolution than powder detergents and easier dosing, liquid detergents are gaining more and more popularity [1].

Detergents can be classified as hard surface cleaners, laundry detergents, and dishwashing detergents according to their application.

Liquid dishwashing detergent is defined as an aqueous solution of a mixture of surfactants, in combination with other specific materials whose function is to increase the foam, stabilize and homogenize the formulation, and provide adequate viscosity [2]. Commercial products of liquid dishwashing detergents are foaming mixtures of surfactants (about 20%) and various additives (about 80%), most of which are water. Primarily used for washing glasses, cutlery, plates, kitchen utensil and other dishes.

Mixtures of anionic, nonionic and amphoteric surfactants are mainly used in the production of detergents in order to improve the cleaning performance and the ability to have a beneficial effect

on the skin of the hands. Anionic surfactants, in waters of high hardness, lead to the deposition of divalent ions  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , thus reducing the ability to clean with detergent. For this reason, amphoteric and nonionic surfactants are added, the combination of which increases temperature stability and the ability to thicken without the use of thickeners [3]. Amphoteric surfactants are characterized by gentleness to eyes and skin, very low toxicity, biodegradability, foam stability and water solubility, emulsification, temperature stability, hard water resistance and degradation by oxidation and reduction resulting from molecular structure [4]. Liquid detergent formulations are usually based on sodium salts and surfactants due to their low cost and high capacity to increase viscosity [5].

The surfactant properties used in these products should have the following characteristics: reduction of surface tension, good ability to wet and foam, non-toxicity and biodegradability, mild and harmless effect on the skin and mucous membranes, emulsifying ability, ability to disperse impurities and possibility of easy application.

The ability to clean detergents is attributed to the specific structure of surfactant molecules, which consists of hydrocarbon chains (hydrophobic part) attached to the active group (hydrophilic part). The removal of dirt from dishes is caused by the affinities of the hydrocarbon chain to dissolve grease (dirt) and hydrophilic groups for dissolve in water.

Many detergents suppress the growth of various bacteria that can cause odor, skin infection, food poisoning, intestinal diseases and other diseases. One study was conducted to determine the antibacterial efficiency of different brands of commercial dishwashing detergents on two tested microorganisms *E. coli* and *Staphylococcus aureus* and was confirmed in four samples [6].

Detergents represents the second largest category of products in the Middle East whose total annual consumption is estimated at about 700,000 tons [2].

## MATERIALS AND METHODS

The experiments have been carried out in Laboratory for organic and inorganic chemical technology at the Faculty of Technology, University of Banja Luka. This research consists of examining the influence of different types of commercial dishwashing detergents on the degreasing efficiency.

Nine commercial samples of detergents were obtained from the domestic market and one sample of detergent was prepared in the laboratory (Figure 1). A series of solutions of different concentrations (5 g/L, 10 g/L, 20 g/L, 50 g/L and 100 g/L) was prepared from these dishwashing detergents.



Figure 1. Detergents: laboratory prepared sample (left) and commercial (right)

In order to examine the influence of the type and concentration of components present in the detergent on the degreasing effect, six formulations were prepared, shown in Table 1.

Table 1. Composition of formulations

Type of component (%)	Formulation I	Formulation II	Formulation III	Formulation IV	Formulation V	Formulation VI
anionic surfactants (AS)	10	10	3	7	10	10
amphoteric surfactants (AMS)	7	3	7	10	3	3
nonionic surfactants (NS1)	3	7	10	3	7	-
nonionic surfactants (NS2)	-	-	-	-	-	7
auxiliary component (NaCl)	-	-	-	-	2	-

The degreasing effect was examined on the following fats: fat from roasting a pigs (F1), homemade

processed fat (F2), restaurant fat (F3), and fresh unused fat (F4), showed on Figure 2.



Figure 2. Fat samples

Physico-chemical characteristics of detergents and greases were determined and that characteristics are shown in the Table 2.

Table 2. Examined characteristics of detergent and grease samples

Characteristic of detergent	Characteristic of fat
Content of anionic surfactants (%)	Iodine number (g/100g)
Content of NaCl (%)	Peroxide number (mmol/kg)
Dry residue (%)	Acid number (mg KOH/g)
Content of total surfactants (%)	Index refraction on 20 °C
Other surfactants (%)	
Density on 20 °C (g/mL)	

Determination of the content of anionic substances in the sample was performed by two-phase titration, by dissolving the detergent sample, from which an aliquot was taken and 15 mL of chloroform and 10 mL of mixed indicator (dimidium bromide and disulphine blue) were added and titrated with benzenthonium chloride solution. The appearance of a gray-blue color of the lower phase of the solution mean end of titration.

The chloride content of the detergents was determined by dissolving the precise mass of the sample in a 50% solution of acetone, with an indicator of potassium chromate and titration with a solution of silver nitrate until the first deviation from the pure yellow color of the solution (light brown).

The dry residue was determined by drying the exact mass of the sample in an oven at 105 °C to constant weight, and weighing after cooling in a desiccator.

From the difference between the content of dry residue and the content of sodium chloride, the value

of total surfactants was obtained. By subtracting the content of anionic substances from the total surfactants, the value of other surfactants is calculated. The density was determined by thermostating the sample at 20 °C and reading the density values using a hydrometer.

A certain mass of the sample was dissolved in chloroform, Hanus reagent was added, mixed carefully and left in a dark place for 30 minutes to make the reaction of addition. Potassium iodide solution and distilled water are then added. Titration is performed with sodium thiosulfate solution until a yellow color appears when starch is added, shake vigorously and titration continues, until a blue color of the solution appears.

The peroxide number was determined by dissolving the exact mass of the fat sample in a mixture of glacial acetic acid and chloroform (3:2) and then adding 0.2 mL of saturated KJ solution. After stirring, distilled water and starch as an indicator are added to the flask and titrated with 0.1 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution until the blue color is lost.

The determination of the acid number is based on dissolving the exactly known mass of the fat sample in a neutralized mixture (diethyl ether: 95% ethanol = 1:1) and titrating with 0.1 M KOH solution, with the phenolphthalein indicator until a pink color appears. The refractive index was determined at a temperature of 20 °C using an Abbe refractometer.

The detergent solution is thermostated at 43 °C. The grease sample is also thermostated for one hour at a temperature of 60 °C and after reaching the set temperatures, about 3 g of grease is transferred to the beakers and 50 mL of detergent solution is added. The beaker with its contents is thermostated in a water bath (memmert) for an hour at 60 °C, after which about 5 g of paraffin is added and these beakers are placed again on the water bath so that the paraffin melts faster (about 15 minutes). When all the paraffin has melted, the beakers are placed in the refrigerator in order to make the best possible separation of the aqueous phase from the fat that has not been removed and is located on the surface of the solution. The aqueous phase is decanted and the solid phase-paraffin cake is washed with ethanol and dried in an oven at a temperature of 60 °C, to constant weight, cooled and weighed. Subtracting the mass of paraffin from the mass of the dried residue gave the mass of unremoved fat. When the mass of unremoved fat is subtracted from the initial mass of fat, the mass of fat removed by this degreasing process is obtained. Based on that, the degreasing efficiency is calculated:

$$\text{Degreasing efficiency (\%)} = \frac{m_1 - m_2}{m_1} * 100 \quad (1)$$

$m_1$  – weight of fat sample, (g) and  
 $m_2$  – weight of unremoved fat, (g).

## RESULTS AND DISCUSSION

The results of this research are presented in tables and graphs through diagrams. Table 3 shows the results of the analysis of the tested fats.

**Table 3.** Results of physico-chemical properties of fat samples

Characteristic	Fat			
	F1	F2	F3	F4
Iodine number (g/100g)	56.716	56.256	54.920	48.210
Peroxide number (mmol/kg)	0.871	1.794	1.810	0.516
Acid number (mg KOH/g)	1.077	0.178	2.394	0.764
Index refraction on 20 °C	1.4687	1.4741	1.469	1.472

The value of the iodine number is lower in fresh fat (F4) compared to the fats used. Determining the iodine number gives an insight into the degree of unsaturation of a fat. Fats with a high content of unsaturated fatty acids have an iodine number greater than 130, and those with a lower content less than 80.

Fresh and carefully purified fats and oils have a low acid number because they contain very small amounts of free fatty acids. Standing increases the content of free fatty acids, and thus the value of the acid number increases. As can be seen from the table, the value of the acid number for fat F1 and F3 is higher due to the presence of water and various impurities as well as the higher number of uses. Free acids are formed as a result of hydrolysis, ie cleavage

of triglycerides in the presence of water, so according to this fact, the fat F3 has the highest acid number because it is a used fat that has repeatedly come into contact with water.

The peroxide number of quality edible oil is zero and usually remains low under normal storage conditions. As the peroxide number indicates the degree of rancidity of some fat, fat F3 and F4 were used for prepare food, the obtained higher values are expect.

The refractive index is a parameter that is characteristic for certain groups of oils or fats, because it depends on the composition of fatty acids and can be used to identify fats and oils. The obtained results are in accordance with the properties of the used fats.

**Table 4.** Results physico-chemical properties of detergent samples

Characteristic	Detergent									
	1	2	3	4	5	6	7	8	9	10
Content of anionic surfactants (%)	4.28	6.59	8.97	5.94	8.97	4.01	10.89	5.84	4.77	12.85
Content of NaCl (%)	3.40	1.46	1.30	2.36	0.51	2.19	0.54	1.01	1.95	1.68
Dry residue (%)	12.70	14.42	15.74	14.14	18.19	7.71	17.04	13.61	9.79	22.10
Content of total surfactants (%)	9.30	12.96	14.44	11.78	17.68	5.52	16.50	12.60	7.84	20.42
Other surfactants (%)	5.02	6.37	5.47	5.84	8.71	1.51	5.62	6.77	3.07	7.58
Density on 20°C (g/mL)	1.059	0.955	1.020	1.035	1.030	1.030	1.030	1.020	1.025	1.030

The content of total surfactant is very different and ranges from 5.52% to 20.42%. However, the highest content of active substance does not necessarily mean

that this sample will work best on fat and will give the best degreasing efficiency. In addition to anionic surfactants, detergents contain other active substances

(amphoteric and nonionic surfactants) which are also responsible for removing fat during the degreasing process.

In order to increase the viscosity and reduce the cost of these formulations, NaCl is added to liquid dishwashing detergents, and the thickening effect depends on the concentration of surfactants. By higher content of NaCl compensated for the lower content of active substance.

The content of the basic active substance in these products is not limited by standard and regulations. However, in order to fulfill the basic function of these

products, a certain minimum content is necessary, which depends on the type of active substance and the content of other components, and this is defined by each manufacturer in the development phase.

The Figure 3 show the dependences of the fat removal efficiency on the detergent concentration. Degreasing efficiency values increase with increasing detergent concentration for both types of fat: F3 and F4. The dependence of degreasing efficiency on detergent concentrations is a linear function, which is confirmed by their correlation factors.

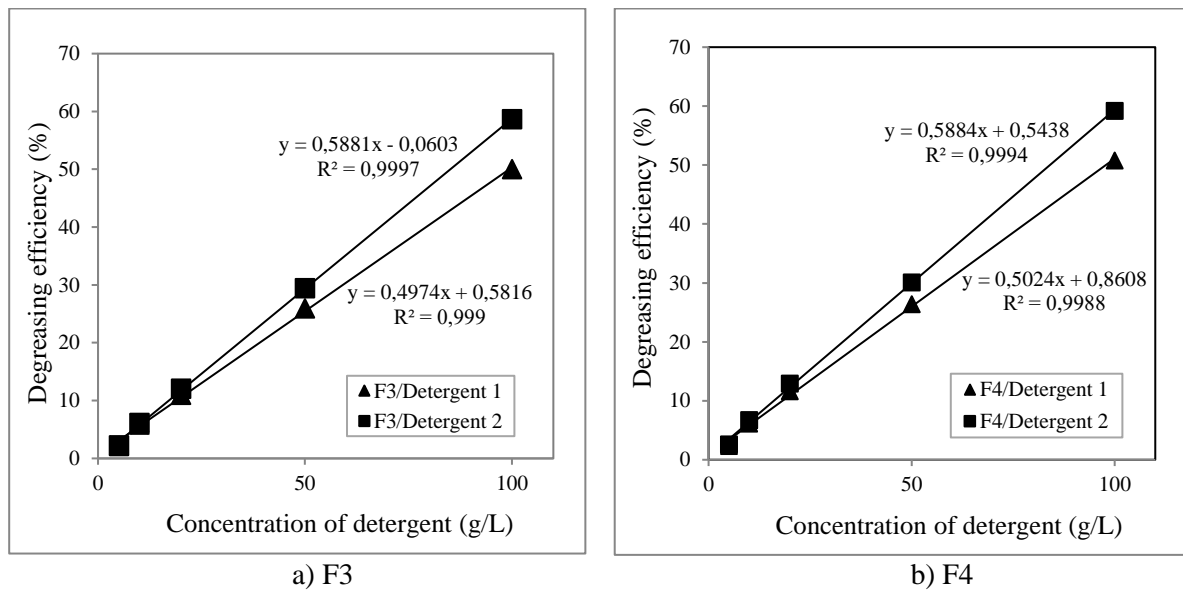


Figure 3. Dependence of degreasing efficiency on detergent concentration

Detergent 2 shows a greater ability of removing the mentioned fats than detergent 1 of the same concentration, while the difference in the degreasing efficiency of these fats with a solution of the same detergent is very small (less than 1%).

F3 and F4 fats are much better removed with detergents 1 and 2 than other fats: F1 and F2, which show twice the values of degreasing efficiency (Figure 4).

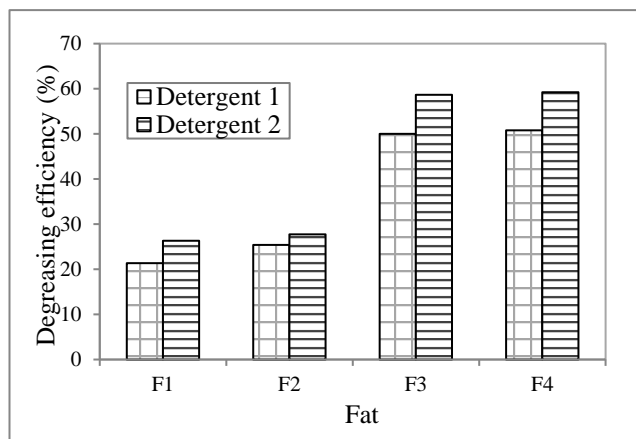


Figure 4. Efficiency of removal fats by detergent 1 and 2 (c=100 g/L)

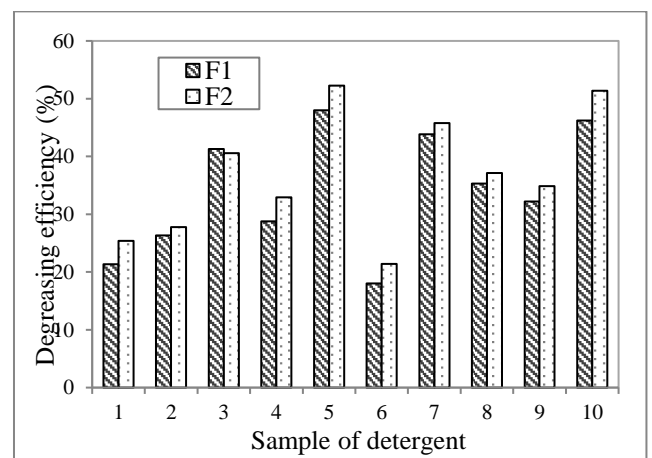


Figure 5. Dependence of degreasing efficiency and type of detergent (c=100 g/L)



All tested detergent samples show a stronger effect on F2 fat than on F1, due to the presence of mechanical impurities present in the F1, which is presented by Figure 5. The Figure 6 shows the dependences of the degreasing efficiency of F1 and F2 fat on the concentration of anionic surfactants (AS) and total surfactants (TS).

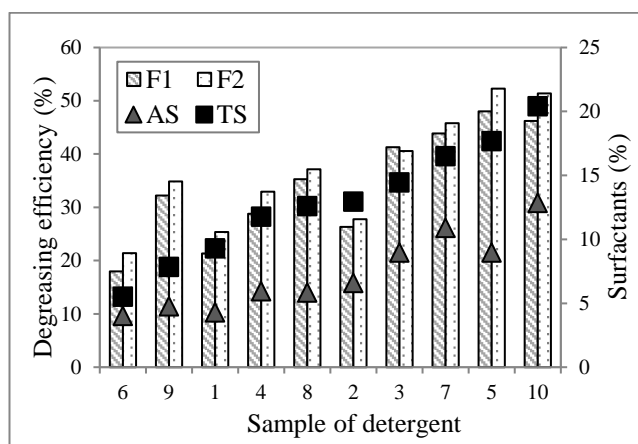


Figure 6. Influence of surfactants concentration on fat removal

From this diagram, it is clear that the content of surfactants present in the detergent affects the efficiency of fat removal. The growth trend of degreasing efficiency agrees with the growth trend of total surfactants and while with the growth trend of the concentration of anionic surfactants in detergents it shows less agreement. The concentration of anionic surfactants in detergent samples is not the main factor in the degreasing process because the presence of other active substances (nonionic and amphoteric surfactants) play a significant role in the fat removal process. For the same value of the concentration of anionic surfactants, sample 5 achieves better degreasing efficiency compared to sample 3 thanks to the other active substances present in it.

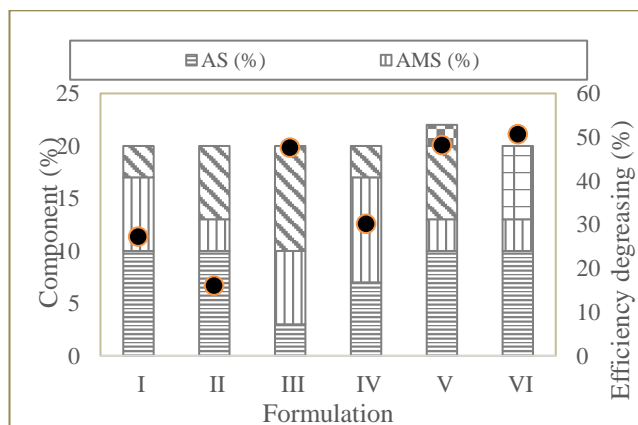


Figure 7. Efficiency degreasing fat F4 by laboratory detergent formulations

The laboratory sample of detergent (sample 10) has the highest content of total surfactants, but not the best washing effect, which means that the type of surfactant plays a major role in the degreasing process.

Figure 7 shows the influence of the composition of the prepared detergent formulations on the degreasing efficiency.

At the same concentration of anionic substance in detergent formulations (I and II), a stronger effect of degreasing is shown by a formulation with a higher concentration of amphoteric active substance. A higher nonionic surfactant content and a lower anionic surfactant content, along with the same amphoteric surfactant content in III lead to a significant increase in degreasing efficiency compared to I because in the micelles of ionic surfactants, there are also forces that tend to destroy the micelles, which are created due to the repulsion between the hydrophilic polar groups of the same charge. The presence of salt affects the degreasing efficiency because it reduces the repulsive forces of polar groups of surfactants. Due to the suppressed dissociation, the critical micellar concentration decreases and the micelle size increases, thus increasing the ability to remove fat, which can be seen from the degreasing efficiency values of formulations II and V. The formulation of detergent with ethoxylated fatty amide (NS1) leads to easier removal of fat than the combination containing a nonionic surfactant with a glycerine group (NS2).

## CONCLUSIONS

Degreasing efficiency depends on the concentration and composition of the detergent. The described method is very selective because other factors such as: different temperatures and process time, mechanical action in removing grease from the contaminated surface and rinsing with water, influencing the degreasing efficiency, are constant during the experiments. The degreasing effect would be much higher if these effects were taken into account and it would be more difficult to assess the degreasing ability of the tested detergents.

The tested dishwashing detergents show different ability to remove grease, and the concentration of removed fat is directly proportional to the concentration of detergent.

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# THE POTENTIAL OF CORN (*ZEA MAYS*) FOR PHYTOREMEDIATION OF SOIL CONTAMINATED WITH HEAVY METALS

ORIGINAL SCIENTIFIC PAPER

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DOI: 10.5281/zenodo.6371284

RECEIVED  
2021-10-18

ACCEPTED  
2021-11-17

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## ABSTRACT:

Heavy metal pollution is a significant environmental problem and has a negative impact on human health and agriculture. Phytoremediation has recently emerged as an efficient heavy metal remediation technology. To examine the phytoremediation potential, an experiment was conducted, where the influence of high and low concentrations of heavy metals, lead, cadmium and zinc (Pb, Cd and Zn) on the phenological characteristics of corn (*Zea mays*), as well as their accumulation in the underground and aboveground part was monitored. The experiment was carried out in outdoor conditions in pots in which corn was planted and the soil was contaminated with heavy metals in concentrations below and above the maximum allowable concentration prescribed by the Ordinance. The experiment lasted 45 days. By processing the results, statistically significant differences in plant development were determined. The highest concentration of Zn was recorded in the aboveground part of the plant, the stem in the amount of 24.443 mg/kg, and the lowest concentration in the leaf 0.216 mg/kg. The highest concentrations of Cd and Pb were recorded in the root, for lead 26.610 mg/kg and in the stem for cadmium 30.490 mg/kg, which is a statistically significantly higher established value compared to other parts of the plant.

**KEYWORDS:** phytoremediation, Corn (*Zea mays*), heavy metals

## INTRODUCTION

Phytoremediation has recently emerged as an efficient heavy metal remediation technology. If phytoremediation of urban areas is taken into account, pruning-tolerant species are preferred. Plant species useful for phytoremediation must meet some requirements: rapid growth, high-yield biomass production, pollution tolerance.

If phytoremediation of urban areas is taken into account, pruning-tolerant species are preferred. The species recommended for phytodegradation, which is usually found in the root, should have a large and dense root system. Root systems with a sufficiently large surface area are also preferred for microbial communities that take place together with the plant phytostimulation process [1].

The grass family (*Poaceae*) is one of the most important for the phytoremediation of heavy metals and organic pollutants such as PAH (polyaromatic hydrocarbons) and petroleum hydrocarbons. The advantage of the plant from this family is that after cutting and drying, the plant material is not brittle. They have a rather shallow root system, but they are very dense and penetrate well into the soil, so these

plants are very effective in phytoextraction of the upper part of the soil level.

The goal of remediation of contaminated areas due to human activity is to restore such ecosystems to their original state. Due to the application to a large number of pollutants, as well as the possibility of implementation on various surfaces, and due to lower environmental impact and lower costs, phytoremediation is considered a green technology. The toxicity of heavy metals in plants varies depending on plant species, metal specificity, metal content, chemical form, soil composition and pH. Some metals, including Cu, Mg, Co, Zn, and Cr, are essential for plants in trace amounts, but only when metals are present in bioavailable forms, and in increased amounts can become toxic to plants [2]. Others, such as Mg, Co, and Zn, have unknown biological functions and can cause disturbances even at relatively lower concentrations [3].

Phytoremediation consists of four different technologies used by plants and each has a different mechanism for remediation of soils, sediments and waters contaminated with heavy metals. These include:

1. Phytoextraction - the use of plants, with large biomass and the ability to accumulate metals and appropriate soil additives to transport and concentrate metals from the soil to the aboveground parts of plants, which will then be removed through conventional agronomic measures.
2. Phytostabilization - the use of plants to reduce the bioavailability of pollutants in the environment; in this case the plants stabilize the contaminated soil rather than clean it.
3. Rhizofiltration - the use of the root system of plants for the absorption and adsorption of pollutants, mainly metals, from water.
4. Phytovolatilization - the use of plants for the extraction of certain, volatile, metals from the soil, and then their release through the leaves into the atmosphere.

Zinc (Zn) is an essential trace element necessary for all living things while cadmium (Cd) is toxic and has no physiological or biological role in the body. They have very similar chemical properties and their uptake into the root and acropetal movement can be controlled by the same mechanisms [4].

Mojiri [5], was chosen cadmium, zinc as pollutants because they are widespread in the environment, especially as soil pollutants. The experiments were performed under natural environmental conditions where the reaction to *Zea mays* stress conditions, caused by the presence of heavy metals, was monitored. Today, the environment is filled with large amounts of toxins, including heavy metals of various shapes. Heavy metal pollution is a significant environmental problem and harms human health and agriculture. Heavy metals from the soil accumulated in plants enter the food chain and their excessive amount can be toxic to humans and animals.

Recently, a lot of work has been done on finding plants that can absorb, distribute and accumulate heavy metals in the aboveground part of plants. During several years of growing these plants, the concentration of heavy metals in the soil is reduced to the allowed value, thus cleaning the soil, and will create conditions for normal agricultural production. Therefore, in order to recultivate such and similar soils, in the last twenty years, the method of biological reclamation - phytoremediation, ie cultivation of annual and perennial herbaceous plants to reduce concentrations of heavy metals (extraction into the aboveground part of plants), increasing numbers and activities soil microflora as well as their detoxification (conversion of metals into forms that are not harmful to plants).

Plants growing on soils damaged by heavy metals may not accept metals, ie be tolerant to high concentrations of metals in the soil; to absorb metals, and to accumulate them in the root system and mycorrhizal root flora; to adopt metals and accumulate them in the aboveground part [6].

Currently, phytoremediation is an efficient and affordable technological solution used to extract or remove inactive metals, such as soil and water pollutants. This technology is environmentally friendly and potentially cost-effective [7].

Zinc (Zn) and cadmium (Cd) are elements with very similar chemical properties. They have similar ionic structures, a similar degree of electronegativity and a relative density above 5 g cm<sup>-3</sup>, based on which they are included in the group of "heavy metals". Both metals are present in very low amounts (mg/kg, and Cd and less) in almost all soils and most living organisms. They can be classified in the group of trace elements. Despite the chemical similarity, the biological and physiological importance of these elements is very different. Zn belongs to the group of metals necessary for more plants and mammals while Cd is unnecessary and toxic. To date, no physiological role of Cd in plant tissue has been established. The presence and accumulation of Cd, even in very low concentrations, significantly affect a number of physiological and biochemical processes in plant tissue, and its toxicity is ultimately manifested through slowed and impaired growth and development and reduced yields [8]. Wangstrand et al. [9], state that in humans the primary source of Cd is food. It is estimated that about 80% of Cd in the human diet comes from grains, vegetables and potatoes.

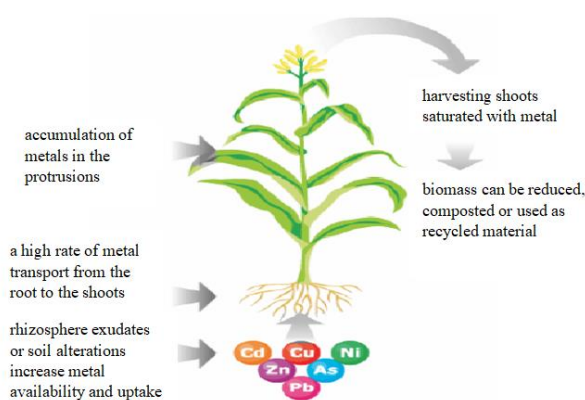
Unlike Cd, Zn is essential for a number of enzymes in nitrogen metabolism, energy transfer, and protein synthesis. Zn is biochemically and physiologically involved in several processes in the plant, ranging from water uptake and transport, through membrane stability and ion transport to the biosynthesis of auxins, RNA, DNA, protein, and carbohydrate and lipid metabolism. However, at too high concentrations like other heavy metals and Zn can be toxic, inhibiting cell growth and photosynthesis.

Zn is present in almost all cells of the human body, it is necessary for the immune system and the smooth functioning of cellular functions, and its deficiency causes hair loss disorders, skin health problems, memory loss, weakening of intellectual abilities, weakness and decreased immunity, fetal development problems, male infertility and congenital diseases. It is estimated that almost 60% of the world's population has health problems due to micronutrient malnutrition,

among which the most critical iron, zinc and vitamin A deficiency [4].

### Corn (*Zea mays*)

Is a genus from the family *Poaceae*, generally known as the grass family. "Zea" is derived from the ancient Greek name for food grass. The genus *Zea* has four species, the most economically significant of which being *Zea mays* L. Maize has been shown to accumulate significant amounts of heavy metals when induced by the addition of metal chelates. The crop is tolerant to heavy metals, has a high ability to accumulate metals in foliar parts with moderate bioaccumulation factor. Because of such characteristics, maize may continuously phytoextract metals from polluted soil by transporting them from roots to shoots [10].



**Figure 1.** Schematic representation of phytoextraction of metals from soil, adapted, [11]

The aim of this study was to determine:

1) The ability of maize, (*Zea mays*) genus from the family *Poaceae*, as a phytoremediator of soil contaminated with lead (Pb), zinc (Zn) and cadmium (Cd).

2) Possibility of accumulation of heavy metals (Pb and Cd) in its underground or aboveground parts Zn.

## MATERIALS AND METHODS

Plastic containers had been used to set up the experiment, volume 5 liters, filled with soil, from the experimental plots of the Biotechnical Faculty of the University of Bihać, then left in external conditions, of the Biotechnical Faculty. The soil in the containers has been contaminated with high and low concentrations of heavy metals (Pb, Cd, and Zn), and the maximum permitted amounts of pollutants prescribed by the Ordinance on determining the permitted amounts of harmful and dangerous substances in the soil and methods of their examinations were used as criteria

(Official Gazette of the Federation of B&H, 72/09). For experimental research, a plant culture was selected, corn (*Zea mays*), which shows a very rapid adaptation to conditions in the new and foreign environment, but also a great ability to reproduce. It is adaptable to almost all possible habitats conditions. Corn seeds were left to germinate in a petri dish on a moist substrate, and four days later were planted in plastic containers. Solutions of the corresponding salts were prepared; solution of lead nitrate  $Pb(NO)_3$ , 0.1 mol/L, cadmium sulfate  $CdSO_4$  0.05 mol/L zinc sulfate  $ZnSO_4$  0.1 mol/L, and then diluted and adjusted to the mass of the earth to define the exact mass concentrations of ions present, which are eliminated by a remediation process. Low concentration (LC) of lead ions ( $Pb^{2+}$ ) was 1000 mg, high concentration (HC) of lead ions ( $Pb^{2+}$ ) was 2000 mg, low concentration (LC) of cadmium ions ( $Cd^{2+}$ ) 20 mg, high concentration, cadmium ions ( $Cd^{2+}$ ) 100 mg per kilogram of soil, low concentration (LC) of zinc ions ( $Zn^{2+}$ ) was 1000 mg, high concentration (HC) of zinc ions ( $Zn^{2+}$ ) was 5000 mg, per kilogram of soil. LC, low metal concentrations, were 5 to 10 times higher than the maximum allowable concentrations, according to regulations [12]. HC, high metal concentrations, were 20 to 25 times higher than the maximum allowable concentrations, according to regulations [12]. Containers with soil without the addition of heavy metals were treated as a control. The prepared metal solutions were applied directly to plastic containers, each of which contains 5 kg of soil with known chemical properties. (Table 1). The plants were grown for 45 days from mid-July to the end of August under natural light temperature conditions. All treatments in three replications (HC, LC, Control) were tested after 45 days.

## PLANT GROWTH MONITORING, MEASUREMENTS AND

### ANALYSIS OF HEAVY METAL CONCENTRATIONS

During the experiment, the growth and development of *Zea mays* were monitored. After the experiment (45 days) plants were less than 30 cm tall. The concentration of heavy metals in the aboveground organs (stem and leaves) and underground organs (roots) was determined following the instructions [13]. The concentration of heavy metals in the aboveground organs (stem and leaves) and underground organs (root) was evaluated after air-drying the collected and treated plant components. Samples of accurately weighed mass (about 1 g), previously homogenized dry plant material, were transferred to a porcelain pot and heated in an electric oven for 8 hours, afterward the temperature was kept constant for the next 12

hours. The samples are then calcined to determine the mineral content in a muffle furnace at a temperature of 600 ° C until white or pale green ash is obtained. The cooled sample was dissolved in 4 ml of 10% HNO<sub>3</sub>, filtered through filter paper (blue stripe), and made up to 50 ml with deionized water. In the sample prepared in this way, the values on the Atomic Absorption Spectrophotometer, Perkin Elmer AAS 800, were read by flame technique. The analyzes were performed in the Laboratory of the Biotechnical Faculty of the University of Bihać.

## RESULTS AND DISCUSSION

Before conducting the experiment, a chemical analysis of the soil was performed (from the experimental plots of the Biotechnical Faculty), the results are shown in Table 1.

**Table 1.** Chemical analysis of the soil used in the research

Parameters	Unit of Measurement	Results
Depth	cm	0-30
Hygroscopic moisture (Hy)	%	4.70
Organic matter	%	21.42
Mineral matter	%	78.58
Humus	%	0.54
Active acidity		7.07
pH KCl-u		6.95
NH <sub>3</sub> -N	mg/ kg	3.68
NO <sub>3</sub> <sup>-</sup> -N	mg/ kg	7.05

NO <sub>3</sub> <sup>-</sup>	mg/ kg	30.38
P	mg/ kg	1.62
PO <sub>4</sub> <sup>3-</sup>	mg/ kg	4.88
P <sub>2</sub> O <sub>5</sub>	mg/ kg	3.79
SO <sub>4</sub> <sup>2-</sup>	mg/ kg	27.13
K <sub>2</sub> O	mg/ kg	9.22
K	mg/ kg	7.59
Ca <sup>2+</sup>	mg/ kg	553.48
Mg <sup>2+</sup>	mg/ kg	81.39

The obtained results of the analyzed plant material with standard deviation and the results of statistical data processing (One-Way ANOVA and Tukey test) depending on the applied concentration and part of the plant are presented in Tables 2, 3, and 4.

The plants looked healthy during the control treatment in the first stages of growth and development. By monitoring the parameters of plant growth and development, no significant changes were observed on the young leaves of the plant, while the plants were grown in soil contaminated with low concentrations of metals, which developed normally and achieved the expected development characteristic of the mentioned species.

Based on a one-way analysis of variance (One-Way ANOVA and Tukey test), a significant effect of metal concentration (High Concentration-HC and Low Concentration-LC) on phytoremediation potential depending on the part of the plant (root, stem and leaf) was determined, ( $p \leq 0,05$ ).

**Table 2.** Values of tested heavy metal, lead, Pb in plant material (mg/kg)

Pb	Root	Stem	Leaf
Control	15,123±0,38 <sup>a</sup>	3,982±0,99 <sup>b</sup>	4,082±0,98 <sup>c</sup>
Low concentration, LC	21,66±0,19 <sup>b</sup>	16,19±0,03 <sup>a</sup>	13,59±0,73 <sup>a</sup>
High concentration, HC	26,610±0,29 <sup>b</sup>	16,47±0,03 <sup>a</sup>	16,12±0,59 <sup>b</sup>
ANOVA	$p \leq 0,05$	$p \leq 0,05$	$p \leq 0,05$

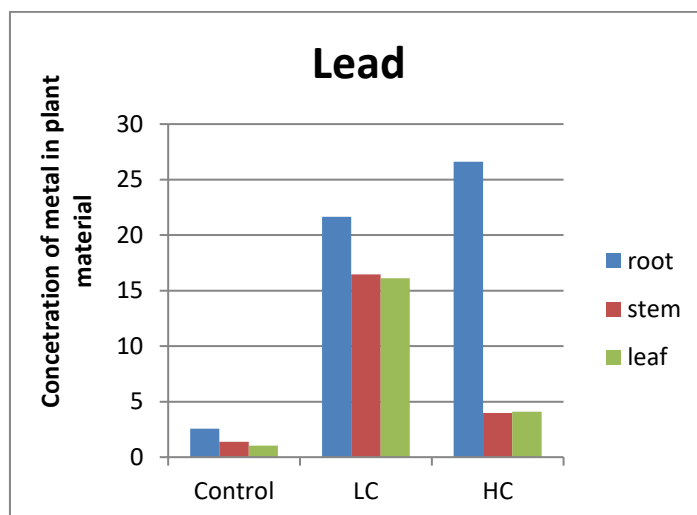


Figure 2. Concentration of Lead, Pb in plant material

Table 3. Values of tested heavy metal, cadmium, Cd in plant material (mg/kg)

Cd	Root	Stem	Leaf
Control	2,231±0,64 <sup>a</sup>	12,52±1 <sup>a</sup>	5,904±0,97 <sup>a</sup>
Low concentration, LC	19,18±0,07 <sup>b</sup>	13,94±0,71 <sup>a</sup>	12,40±0,95 <sup>b</sup>
High concentration, HC	20,398±0,54 <sup>b</sup>	30,490±0,09 <sup>b</sup>	13,09±0,87 <sup>b</sup>
ANOVA	p≤0,05	p≤0,05	p≤0,05

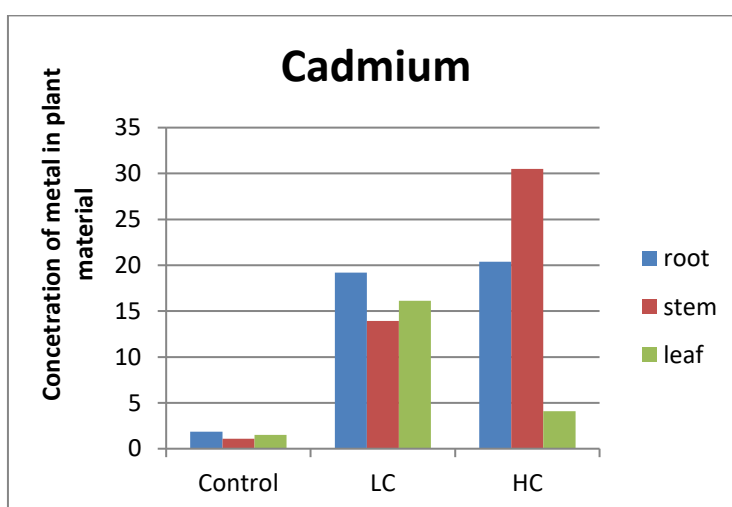


Figure 3. Concentration of cadmium, Cd in plant material

Table 4. Values of tested heavy metal, zinc, Zn in plant material (mg/kg)

Zn	Root	Stem	Leaf
Control	4,37±0,382 <sup>a</sup>	9,06±1,01 <sup>a</sup>	0,216±0,97 <sup>a</sup>
Low concentration, LC	9,421±0,662 <sup>b</sup>	9,50±0,910 <sup>a</sup>	5,46±0,95 <sup>b</sup>
High concentration, HC	11,426±0,762 <sup>b</sup>	24,443±0,080 <sup>b</sup>	6,15±0,92 <sup>b</sup>
ANOVA	p≤0,05	p≤0,05	p≤0,05



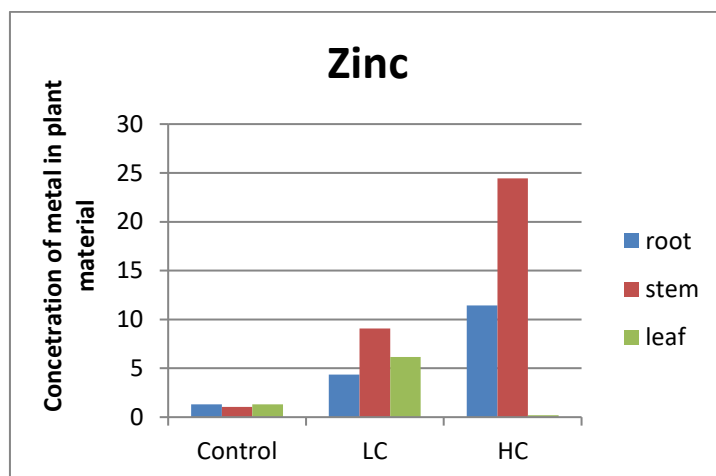


Figure 4. Concentration of zinc, Zn in plant material

Plants with phytoremediation ability are characterized by the accumulation of lead in the root system, and according to [14], this in a way represents a form of protection of the aboveground part. Natural concentrations of lead in plants range from 5 to 10 mg/kg, [15]. Lead concentrations in the tested plants during treatment with low and high concentrations are significantly higher. Lead belongs to the metals that accumulate in the underground parts of plants. Generally, the lead content in plant organs tends to decrease in the following order: roots > leaves > stems > flowers [16]. Factors that most affect the accessibility of Cd and Zn plants are concentration of Cd and Zn in the soil and the form in which they are, soil pH, content of organic matter, clay and calcium carbonate, microbiological activity in the rhizosphere, soil moisture, soil temperature, concentration of other elements, especially phosphorus and climate. The root helps the plant to absorb cations by secreting low molecular weight compounds, which function as metal chelators in the soil. Depending on the plant species, these are most often organic acids, which dissolve inaccessible forms of nutrients in the soil and phytosiderophores, which affect the enhanced work of the microflora and the faster transition of metals into the accessible form. An increase in the concentration of Cd in the soil can reduce the availability of certain metals from the soil as well as reduce the number of populations of soil microorganisms. Such action of Cd can reduce the uptake of Zn into the root, which is not an example of direct competition of Cd and Zn, but the reduced uptake of Zn is a consequence of the creation of unfavorable conditions for the uptake of Zn. It is well known that iron (Fe) in plants of the *Poaceae* family is absorbed into the root by phytosiderophores [17] found that Zn, except in the form of  $Zn^{2+}$  is adopted.

Several studies indicate that ZIP proteins play a significant role in the uptake of Zn in cereals [18], [19], [20] play a significant role in the uptake of Zn in cereals. hence  $Cd^{2+}$ , but that each transporter is specifically controlled by one particular metal [21]. Since Cd is a non-essential toxic element, it was considered that this is the reason why plants do not have a specific system for its adoption. It has been hypothesized and confirmed by numerous studies [21], [22] that Cd, like other toxic cations, is adopted together with essential elements, and because of its chemical similarity to Zn, it is assumed that they are adopted into the plant by the same mechanisms [23], [24]. In addition to common uptake mechanisms with other cations, the existence of Cd-specific transporters has been established [4]. Lead mainly accumulated in the underground parts of corn while the aboveground parts contained smaller amounts of this metal.

Among the studied metals, the concentration of Cd was found in the largest quantities, in the aboveground part of the stem.

Furthermore, the results of the research showed that corn shows tolerance to heavy metals. Even high concentrations of heavy metals (Cd and Pb) in the soil did not completely eliminate the ability to grow. Some metals such as Pb did not have a negative effect on maize growth and maize grew at a similar rate as control plants. Only at higher doses of Cd (100 mg/kg) was growth-retarded observed, indicating symptoms of "metal stress" in plants involving morphological and structural changes in aboveground shoots, such as leaf deformation and chlorosis, leaf necrosis, red and purple leaf color, brown leaf edges, reduced leaf number and size, reduced biomass, inhibited growth and eventual death [25].

Conducted research [26], have shown that *Helianthus annuus L.* has the ability to accumulate Pb,

Cd and Zn in its tissue (shoots and root) depending on the type of metal and the applied concentration. The highest concentrations of Pb were recorded in the root of the plant (24.03 mg / kg), while higher concentrations of Cd (16.13 mg / kg) and Zn (14.696 mg / kg) were recorded in the aboveground part of the plant (leaf). The accumulation of heavy metals and their distribution depends on the type of plant, plant organs, phenological phase, degree of contamination and combination of metals in the soil. Some research, [27] showed that the increased concentration of heavy metals in the soil stimulated the growth of the Japanese knotweed, *Reynoutria japonica*. This fact proves that *R. japonica* accumulates heavy metals efficiently when, it is grown in soils contaminated with heavy metals. This was especially observed in the case of Cd. In the aboveground parts of the plant from the samples with the addition of high concentration (HC), Cd 100 mg kg<sup>-1</sup>, 537 times more Cd was found compared to the control.

According to [15], 3-8 mg/kg Cd in the soil is a critical concentration for plant growth. Analysis of metal concentrations in plant tissues showed a high potential of corn for the uptake of heavy metals and their intensive accumulation in aboveground parts (in the case of Cd, Zn) and underground parts (in the case of Pb).

Translocation factor is defined as the ratio of the metal concentration in the aboveground part of the plant with respect to the metal concentration in the root and is used to determine the efficiency of the plant in translocating heavy metal from root to aboveground part. The translocation factor indicates an enhanced ability of plants to bioaccumulate heavy metals compared to the control sample.

**Table 5.** Translocation factor (TF)

Element	Low Concentration	High Concentration
Pb	0,76	0,14
Cd	0,72	1,49
Zn	2,07	2,14

$$TF = \frac{\text{metal (shoot)}}{\text{metal (root)}}$$

Translocation factor is defined as the ratio of the mass fraction of metal in the aboveground part of the plant with respect to the share of metal in the root and is used to determine the efficiency of the plant in translocating heavy metal from root to aboveground part. The translocation factor indicates an enhanced ability of plants to bioaccumulate heavy metals compared to the control sample. The obtained values

for TF are the most important test that can be used to assess the phytoremediation potential of the plant [28].

Plants that have a translocation factor less than 1, can be used as photo stabilizers (metal concentration in the underground part of the plant), and as phytoextractors if they have a translocation factor greater than 1, transport and concentrate metals from soil to aboveground parts of plants [29].

The results of this study show that in maize from the control sample for all three heavy metals TF is greater than 1, and based on this indicator, corn can be classified as an accumulator of these heavy metals (Pb, Cd and Zn).

## CONCLUSIONS

The experimental study was conducted to identify the ability of maize (*Zea mays*) to remove heavy metals (Pb, Cd and Zn) from contaminated soil. The main mechanism of remediation of heavy metals using the corn (*Zea mays*) is based on the extraction of contaminants from the soil (phytoextraction, followed by translocation and accumulation of contaminants in the aboveground part of the plant).

Analysis of the collected and processed data proved that corn (*Zea mays*) has the ability to accumulate Pb, Cd and Zn in its tissue (shoots and root system) depending on the type of metal and the applied strength of concentration. The highest concentrations of Pb were recorded in the root system of the plant (26.61 mg/kg), while higher concentrations of Cd (30.49 mg/kg) and Zn (24.43 mg/kg) were recorded in the aboveground part of the plant (stem). The accumulation of heavy metals and their distribution depends on the type of plant, plant organs, phenological stage, degree of contamination and combination of metals in the soil.

Based on the obtained results, it can be concluded that corn (*Zea mays*) is a tolerant plant species in soils contaminated with heavy metals (Pb, Cd and Zn) and can be successfully used in the phytoremediation of soil contaminated with these heavy metals.

## ACKNOWLEDGMENT

This research was realized within the scientific research project financially supported by the Federal Ministry of Education and Science of Bosnia and Herzegovina, number: 05-39-2412-1/17 entitled "Remediation of land contaminated with oil and heavy metals".

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# REMOVAL OF ACETALDEHYDE FORM INDOOR AIR USING NAA ZEOLITE AND MODERNITE

ORIGINAL SCIENTIFIC PAPER

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DOI: 10.5281/zenodo.6371332

RECEIVED  
2021-10-19ACCEPTED  
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## ABSTRACT:

Indoor pollution nowadays can have serious effects on people's health. The most common indoor pollutants in urban and industrial areas are volatile organic compounds – VOCs, which include acetaldehyde. Acetaldehyde vapors cause eye irritation, lung or respiratory tract problems and are considered cancerogenic. The aim of this research was to examine the adsorption properties of type NaA zeolite and Na-Form of modernite. Adsorption isotherms of acetaldehyde on the examined adsorbents were obtained by simulating adsorption in an indoor environment. The simulation chamber was set to the atmospheric pressure, the temperature of 25°C, and air humidity of 65%. The non-linear Langmuir model gave higher coefficients of determination (0.9675 and 0.9350, respectively) than those obtained using the Freundlich model (0.9563 and 0.9332, respectively), which is indicative of single-layer adsorption. Higher values of the Langmuir constant for the samples tested shows that there is only low affinity between the adsorbents examined and acetaldehyde. Maximum adsorption capacity ( $Q_m^0$ ) in the monolayer obtained using the Langmuir model is 3.387 mg/g for NaA zeolite and 2.5293 mg/g for modernite. From this it can be fairly assumed that NaA zeolite as an adsorbent, is more suitable for removing acetaldehyde from indoor air.

**KEYWORDS:** acetaldehyde; zeolites; adsorption isotherms; maximum adsorption capacity

## INTRODUCTION

Indoor air quality has become the focus of much research in recent years. Research has shown the presence of a large number of different pollutants which can have serious impact on human health. According to the World Health Organization, indoor air pollution – IAP, is responsible for 3.8 million deaths each year [1].

Indoor air pollution comes from various sources, and these are most commonly the materials that release pollutants into the air of the indoor environment. The sources can also come from different everyday activities, such as cooking, room heating, and similar human activities [2]. The most common indoor air pollutants present are carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), particulate matter (PM), aerosol, volatile organic compounds (VOCs), *etc.* VOCs are particularly dangerous due to their low boiling points, which allows them to be released into the air rather quickly. The most frequently occurring VOCs are toluene, acetaldehyde, methanol, ethanol, benzene, formaldehyde, *etc.* [3]. The presence of VOCs is recorded mostly in exhaust fumes [4], [5]. Apart from these, VOCs can come from different paints, varnishes, adhesives, wood preservatives, waxing and

cleaning products, air fresheners, *etc.* [6], [7]. Acetaldehyde is one of the volatile organic compounds most commonly emitted into the air in urban and industrial areas. It is a product from incomplete combustion, mostly present in cigarette smoke, gases released from roasting coffee, automobile exhaust fumes, burning different organic waste material, *etc.* It is also, interestingly enough, the product of metabolic processes in plants. According to the research conducted so far, acetaldehyde vapors can cause eye and respiratory tract irritation, and are considered cancerogenic [8].

Reducing the content of volatile organic compounds in indoor environments has become one of the primary goals in air quality improvement. The simplest method for indoor VOC reduction is the use of natural ventilation or structural ventilation systems. Natural ventilation does not always give best results, especially during winter months. During winter, when the use of private incinerators is increased and the content of VOCs in the air is higher, natural ventilation can have the opposite effect. Structural ventilation systems also require outdoor air of good quality. This is the reason for an increased use of adsorbents (*e.g.*, activated charcoal) in removing certain air pollutants. Apart from that, the reduction of the content of VOCs

in indoor air is increasingly achieved using adsorption processes, or by introducing suitable adsorbents.

An adsorption mechanism consists of dissolving VOCs in organic layers of adsorbents with large active surface areas [9], [10]. Much research is dedicated to the adsorption of VOCs on zeolites or activated charcoal in the absence of moisture. Under real conditions, water vapor is always present, and its content may sometimes exceed that of VOCs. Research in the past couple of years has shown that the presence of water vapor (moisture) affects the adsorption of gases and volatile compounds [11], [12]. For example, investigations into the adsorption of dichloroethane, ethyl acetate and benzene on metal-organic frameworks (MOFs) show that the adsorption of these volatile organic compounds decreases in the presence of humidity [13], [14].

The choice of the adsorbent depends on numerous factors, such as temperature, velocity, affinity of the adsorbent towards another adsorbent, *etc.* It is not easy to choose the right adsorbent because the choice is governed by the conditions in which the adsorbent is to be used, as well as by its characteristics (adsorption capacity, stability, hydrophilicity, hydrophobicity, *etc.*). The most commonly used adsorbents are activated charcoal, natural and synthetic zeolites, silica gel, and activated alumina [15].

The adsorbents chosen for the purpose of this research are hydrophilic synthetic NaA type zeolite (NaA zeolite) and Na-Forma modernite (Modernite), which were activated, *i.e.*, dehydrated prior the experiments. Zeolites are microporous hydrated aluminosilicates of the elements in the first and the second groups of the periodic table, built up from an infinitely extended three-dimensional framework of  $[\text{SiO}_4]$  and  $[\text{AlO}_4]$  tetrahedra inter connected through a shared oxygen atom. Variations in the geometry of tetrahedra within the structure result in different forms of zeolites, characterized by cavities and/or canals. The cavity/canal size is determined by the "rings" made up from the aluminum and silicon tetrahedra. The rings can be four-membered, five-membered, six-membered, *etc.* Type NaA zeolite is characterized by a three-dimensional system of canals with an opening in the form of an eight-membered ring, 4.1 Å in diameter. Modernite is characterized by the main canal of elliptical shape made up from a twelve-membered ring whose dimensions are of 6.5x7.0 Å, and the so-called "side pockets" in the form of eight-membered rings whose dimensions are 2.6x5.7 Å [16]-[18].

The focus of investigation here is the efficiency of using type NaA zeolite and modernite to remove the acetaldehyde vapors from indoor air. The paper, therefore, presents the results of a simulation of an

adsorption process in an indoor environment (atmospheric pressure, particular temperature and humidity) using the free diffusion mechanism.

## MATERIALS AND METHODS

Adsorption of acetaldehyde was conducted on NaA zeolite and modernite  $m \approx 0.5\text{g}$  in  $2.5\text{ dm}^3$  adsorption chambers (Table 1). The adsorption chambers were first filled with humid air (relative humidity of  $RH=65\%$ ), and then acetaldehyde in batches of varying volumes (10-250 $\mu\text{l}$ ) was injected. The temperature of the chambers was set at  $25^\circ\text{C}$  for an hour in order to allow for acetaldehyde to evaporate completely. After that, zeolite was subjected to the adsorption of acetaldehyde from the indoor environment prepared as described previously. The process of adsorption was conducted for three hours at the set temperature in the chambers. After the process completed, the gas phase analysis was conducted on a high sensitivity device which calculates total organic carbon (Shimadzu TOC high sensitive). The samples of zeolite were dried at  $400^\circ\text{C}$  for 2 hours in a vacuum prior to the experiment [15].

**Table 1.** Physical and chemical properties of NaA zeolite and modernite

Parameters	NaA zeolite	Modernite
Loss on ignition, w (%)	2.4	6.9
L Grey index	90.0	84.5
$d(10)$ ( $\mu\text{m}$ )	1.4	2.3
$d(50)$ ( $\mu\text{m}$ )	3.4	8.8
$d(90)$ ( $\mu\text{m}$ )	5.7	-
$\text{SiO}_2/\text{Al}_2\text{O}_3$	1.98	13.5
Sodium content (Na), w (%)	22	4.3
pH(5%)	-	9-11.5
Water adsorption (WA), $25^\circ\text{C}/65RH/24\text{h}$ , w (%)	24,61	12,80

From the concentration of the organic carbon and acetaldehyde, it was possible to calculate the amount of adsorbed acetaldehyde using the following equation (1):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where:

$q_e$  – the amount of the adsorbed acetaldehyde per gram of zeolite (mol/g)

$C_0$  – acetaldehyde concentration at the beginning of adsorption (mol/m<sup>3</sup>)

$C_e$  – equilibrium concentration of acetaldehyde (mol/m<sup>3</sup>)

$V$  – chamber volume (m<sup>3</sup>)

$m$  – mass of the adsorbent (g)

Equation (2) was used to calculate the constant for the Langmuir isotherm in a non-linear form:

$$q_e = \frac{Q_{max}^0 \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (2)$$

where:

$q_e$  (mg/g) – adsorption capacity (equilibrium concentration of the adsorbed ions on the adsorbent),

$Q_{max}^0$  (mg/g) – maximum adsorption capacity of the adsorbent,

$K_L$  (L/mg) – Langmuir adsorption equilibrium constant, referring to the adsorption energy.

Maximum adsorption capacity,  $Q_{max}^0$ , gives an insight into the saturation of the monomolecular layer on the surface of the adsorbent, whereas the Langmuir constant,  $K_L$ , refers to the adsorption energy [19].

Equation (3) was used to calculate the constant for the Freundlich isotherm:

$$q_e = K_F \cdot C_e^{\frac{1}{n}} \quad (3)$$

where:

$q_e$  (mg/g) – adsorption capacity (equilibrium concentration of the adsorbed ions on the adsorbent),

$n$  – function of the adsorption intensity (the higher  $n$  – the higher the adsorption intensity),

$K_F$  (mg/g)(L/mg)<sup>1/n</sup> – Freundlich adsorption equilibrium constant, referring to the adsorption energy.

“Microsoft Excel” program was used to calculate the parameters in the non-linear models of the adsorption isotherms. In order to determine the regression analysis error, we used the non-linear Chi-square test ( $\chi^2$ ) according to Equation (4) [19], [20]:

$$\chi^2 = \sum_{i=n}^n \frac{(q_{e,observed} - q_{e,expected})^2}{q_{e,expected}} \quad (4)$$

## RESULTS AND DISCUSSION

Modernite and NaA zeolite are very active hydrophobic zeolites with high thermal stability, widely used for removing undesirable tastes and odors. Due to its open three-dimensional structure modernite is also very efficient in removing larger molecules. These very properties are the reason why it was decided to perform the adsorption of acetaldehyde with these two types of zeolites for the purpose of this paper. Water adsorption on zeolites (modernite and NaA zeolite) was performed under conditions:  $t=25^\circ\text{C}$ ,  $RH=65\%$ , atmospheric pressure and time of adsorption 24 hours. Obtained the results of water adsorption in Table 1. indicate that NaA zeolite has a higher affinity for water ( $WA=24.61\%$ ). Acetaldehyde adsorption was conducted in an experimental chamber under specific conditions:  $t=25^\circ\text{C}$ ,  $RH=65\%$ , at the atmospheric pressure. The isotherm data were analyzed using the two most commonly used equilibrium models – Langmuir and Freundlich. The Langmuir isotherm is based on the assumption that a monomolecular layer of the adsorbent is formed and that there is no side interaction between the adsorbed molecules. On the other hand, the Freundlich isotherm is based on a multilayer adsorption on a heterogeneous surface [20].

The coefficients for determining the isotherm adsorption according to the Langmuir and the Freundlich models for the adsorbents tested are given in Table 2.

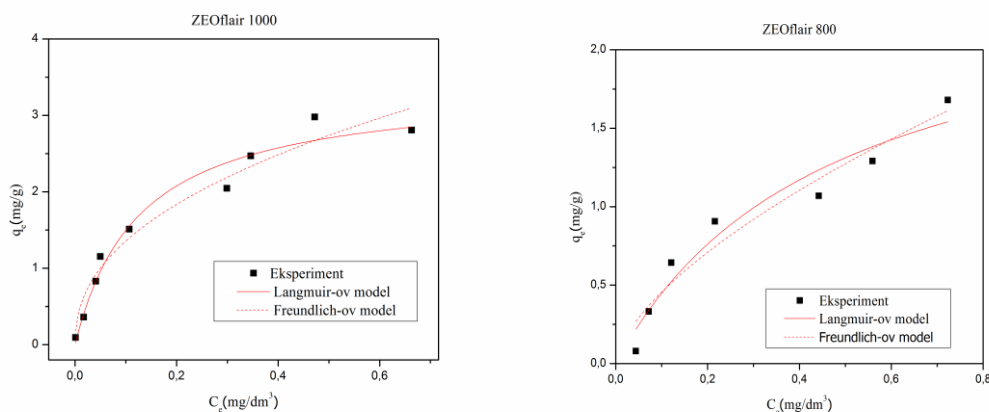
**Table 2.** Adsorption isotherm constants for Modernite and NaA zeolite using non-linear models ( $t=25^\circ\text{C}$ ,  $RH=65\%$ , adsorption time=3h)

Model	Parameter	Adsorption parameter values	
		Modernite	NaA zeolite
Langmuir	$K_L$ (dm <sup>3</sup> /mg)	2.1538	7.915
	$Q_m^0$ (mg/g)	2.5293	3.387
Adsorption parameter values	$R^2$	0.9350	0.9675
	$R_L$	0.1-0.9	0.2-0.9
	$\chi^2$	0.322	0.17
Freundlich	$N$	1.5649	2.291
	$K_F$ (mg/g)/(mg/dm <sup>3</sup> ) <sup>n</sup>	1.9832	3.705
Adsorption parameter values	$R^2$	0.9332	0.95632
	$\chi^2$	2.86	8.66

Coefficients of determination obtained from the Langmuir model for NaA zeolite and modernite

samples are high (0.9675 and 0.9350, respectively), *i.e.*, they are approaching 1 (Table 2). Coefficients of

determination obtained from the non-linear Freundlich model ( $R^2$ ) were somewhat lower (0.9563 and 0.9332, respectively). From this it can be concluded that this is a monolayer adsorption. The higher values of the Langmuir constant ( $K_L$ ) for the tested samples show that the affinity between the tested adsorbents and acetaldehyde is pretty low. It can also be concluded that the tested adsorbents do not have much capacity



**Figure 1.** The use of non-linear Langmuir and Freundlich models for the adsorption of acetaldehyde on the adsorbents NaA zeolite and modernite ( $t=25^{\circ}\text{C}$ ,  $RH=65\%$ , adsorption time =3h)

The results of the analyses ( $R_L=0.1-0.9$  for modernite and  $R_L=0.2-0.9$  for NaA zeolite) lead to the conclusion that both models are favorable. Figure 1 shows the use of non-linear Langmuir and Freundlich models for the experimental data of the equilibrium concentration of the adsorbed acetaldehyde on the adsorbents NaA zeolite and modernite.

The adsorption of acetaldehyde on NaA zeolite and modernite adheres more to the non-linear Langmuir model (Table 2, Figure 1).

## CONCLUSION

Based on the results obtained from the adsorption of acetaldehyde vapors at the relative humidity of 65%, temperature of  $25^{\circ}\text{C}$ , the adsorption time of 3h and the atmospheric pressure, it can be concluded that the adsorption on modernite and NaA zeolite is a monolayer adsorption. This is confirmed by the obtained coefficients of determination, which are higher for the non-linear Langmuir model than those for the Freundlich non-linear model (According to Table 2).

Maximum adsorption capacity ( $Q_m^0$ ) in the monolayer obtained according to the Langmuir model is 3.387 mg/g for NaA zeolite and 2.5293 mg/g for modernite. From this it follows that NaA zeolite is the more suitable of the two adsorbents for removing

for acetaldehyde adsorption because maximum adsorption capacity ( $Q_m^0$ ) in the monolayer obtained based on the Langmuir model is 3.387 mg/g for NaA zeolite and 2.5293 mg/g for Modernite. The values of the  $R_L$  factor were in the interval of  $0 < R_L < 1$ , which can confirm if the process is favorable. If  $R_L=0$  the process is irreversible, if  $R_L=1$ , then it is linear, whereas  $R_L > 1$  means that it is unfavorable.

acetaldehyde from indoor air. It can also be concluded that, although zeolite has a higher affinity for water (water sorption capacity), the presence of water vapor, did not reduce the absorption capacity of acetaldehyde.

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ISSN 1840-0426



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