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CONTENT


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TUZLA
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SENSORY PROPERTIES OF DAIRY PRODUCTS BASED ON FRESH CHEESE AND FRUIT

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT: Fermented dairy products are the favorite food of most consumers of all ages. To increase nutritional value, many fermented dairy products are mixed with grains and other additives. Fresh cheeses can be mixed with canned or dried vegetables and fruits and spices. The aim of the work was to produce a cheese dessert with different fruits in order to bring this product closer to the younger population, especially children. Fresh cheese samples were produced from skimmed milk (0.9% milk fat) and partially skimmed milk (1.5% milk fat). The obtained fresh cheese was mixed with compote fruit pineapple, peach and pear, in order to obtain the cheese dessert. Poppy, peach and poppy compositions were used as fruit additives. The sensory properties of the cheese dessert were evaluated by a group of 15 analysts. Dessert samples were evaluated after 1, 5 and 10 day of storage.

Samples of fermented dairy products from the milk with 1.5% milk fat had a better consistency, pronounced aroma and a fuller taste during the storage.

Sensory properties of the dairy products based on fresh cheese and pineapple were most pronounced, with the sum of points ranging from 18.15 to 19.65, compared to the addition of peach and pear. Statistically analysis showed that the best samples were based on fresh cheese and pineapple.

KEYWORDS: fresh cheese, fruit, sensory properties

INTRODUCTION

Fresh cheeses are cheeses produced by coagulation of milk, cream or whey by acid, a combination of acid and rennet, or a combination of acid and heat. Fresh cheeses are ready for consumption immediately after production. The type of fresh soft cheese often mixed with cream and sometimes with fruit or spices is referred to as creamy cheese (quark, orchard and others). The standard for this cheese is different, so it can be produced with 14 - 24% dry matter. Quark (Quarg) is a fresh cheese originating in Eastern Europe. It is a soft white cheese, usually containing less fat (roughly like yogurt) than cheese cream[1]. Microorganisms play an essential role in cheese production because they contribute to the formation of sensory properties due to their metabolism[2]. Fresh cheeses have high moisture content, mild flavour, soft and smooth texture[3]. Many dairy fermented products are mixed with grains and other additives to provide higher nutritionally balanced food[4]. During the production, fresh cheeses can be mixed with canned or dried vegetables or fruits and spices. Vegetables can be added in fresh state, pasteurized or sterilized, in pieces or as a casserole. Choi et al.[5] examined the properties of Gouda cheese with the addition of fruit liqueur, which was added during production. They came to the conclusion that the addition of fruit liqueur did not affect ($P>0.05$) the appearance or sensory characteristics of the cheese produced, but the higher values of ashes, minerals and flavonoids ($P<0.05$) were observed than in the control sample of the cheese. Also, the results of their work indicate that such supplements in cheese provide additional nutrients, retaining taste and quality. According to Khalifa and Wahdan[6] cranberry extract can be used as a functional ingredient that improves cheese stability during storage. During the study, the influence of addition of three different concentrations of cranberry extract (500, 750 and about 1000 ppm) was investigated on chemical composition, maturation index, oxidation stability and microbiological as well as organoleptic properties of white soft cheese. The research has shown that the addition of the cranberry extract at a concentration of 750 ppm significantly improves and maintains cheese quality. Various polyphenolic compounds to cheese, individual phenolic compounds, including catechins, epigalocatein galata (EGCG), tannic acid, homovanilic acid and flavones together with natural compounds such as grape extracts, green tea extract and dehydrated cranberry powder are added as functional ingredients during the process of cheese production[7]. According to a study conducted by Yerlikaya and Karagozlu[8], the Caper berry supplement in white cheese positively affects some of the physical-chemical properties of cheese, while some have no positive influences. Berries were

added to the cheese after cutting the cheese, in an amount of 8 g of berries/100 g of raspberries. The results showed significant differences in the content of salt, lactic acid and mineral constituents ($P<0.05$), in contrast to the sample in which no berries were added.

In this paper, the fruit pineapple, peach and pear is added to fresh cheese in order to obtain cheese desserts of different flavour variations and thus offer a product that would approach consumers, especially children, who are eating more and more unhealthy foods at the time.

MATERIAL AND METHODS

MATERIALS

Production prototypes of milk based products with fresh cheese and fruits were conducted in the laboratory of Food Technology, Faculty of Technology, University of Tuzla. For the production of fresh cheese, commercial UHT cow milk (Meggle) with 0.9% (M1) and 1.5% (M2) milk fat was used. For direct inoculation of milk, FD-DVS cultures were used: CHN-22, XT-303 and combination CHN-22 and Lyofast SAB 440B in ratio 2:1.

CHN-22 in composition: *Lactococcus lactis* ssp. *lactis*
Lactococcus lactis ssp. *cremoris*
Lactococcus lactis ssp. *lactis* biovar *diacetylactis*
Leuconostoc mesenteorides ssp. *cremoris*
Streptococcus thermophilus

XT–303 in composition: *Lactococcus lactis* ssp. *lactis*
Lactococcus lactis ssp. *cremoris*
Lactococcus lactis ssp. *lactis* biovar *diacetylactis*
Leuconostoc mesenteorides ssp. *cremoris*
Leuconostoc pseudomesenteorides

CHN – 22 : Lyofast SAB 440B = 2:1

Lyofast SAB 440 B in composition: *Streptococcus thermophilus*
Lactobacillus acidophilus
Bifidobacterium animals ssp.*lactis*

As fruit supplement, pasteurized compote of pineapple (V_1), peach (V_2) and pear (V_3), in light syrup (Iska Qualität, I. Schroeder KG, Germany) was used. The addition of fruit was carried out by a selected formulation (25% of fruit to the weight of cheese). The milk was thermally processed at a temperature of 75°C/30 sec, cooled to an inoculation temperature (25°C), primed with microbial starter cultures. The fermentation lasted between 11 and 12 hours at 25°C until a pH value of 4.6-4.7 was reached. Subsequently, curd was cut, cooled and squeezed through cotton fabrics for about 8 hours at 20°C. After finishing the curd draining, the fresh cheese was well homogenized in the mixer and divided into 3 parts. One type of chopped fruit was added into each part, pineapple, peach and pear, respectively. The obtained products were stored in a refrigerator in a plastic container for 10 days at + 4°C. The sample markings, milk fat content, type of microbial crops and the types of fruit used in the laboratory production of cheese desserts are shown in Table 1.

Table 1. Samples of dairy products based on fresh cheese and fruit

Samples	Milk fat (%)	Starter culture	Fruit
M_1K_1A	0.9	CHN -22	Pineapple
M_1K_1B			Peach
M_1K_1K			Pear
M_1K_2A		XT - 303	Pineapple
M_1K_2B			Peach
M_1K_2K			Pear
M_1K_3A		CHN – 22: Lyofast SAB 440 B = 2:1	Pineapple
M_1K_3B			Peach
M_1K_3K			Pear
M_2K_1A	1.5	CHN -22	Pineapple
M_2K_1B			Peach
M_2K_1K			Pear
M_2K_2A		XT - 303	Pineapple
M_2K_2B			Peach
M_2K_2K			Pear
M_2K_3A		CHN – 22: Lyofast SAB 440 B = 2:1	Pineapple
M_2K_3B			Peach
M_2K_3K			Pear

The sensory properties of samples of milk products based on fresh cheese and fruits were evaluated by a group of 15 assessors using a scoring method (Table 2), after 1, 5 and 10 days of storage[9].

STATISTICAL ANALYSIS

Analysis of variance (ANOVA) was carried out using SPSS software (version 22). Duncan test was used to determinate which samples were statistically different by all the sensory properties and acceptability of product ($P<0.05$).

RESULTS AND DISCUSSION

The acidic coagulation of milk from the laboratory production of fresh cheese, irrespective of the proportion of milk fat, was approximately equal in all samples (11:50 - 12 hours) as shown in Figure 1.

Table 2. Sensory properties of dairy products based on fresh cheese and fruit

Properties	Characteristics	Score
External appearance	The surface of the cheese is uniformly white to light-colored and completely pure without ripening, does not release whey, with noticeable fragments of fruit.	2
	On the surface there is barely noticeable impurities. It releases a little bit of whey. Poor noteful pieces of fruit.	1
	On the surface noticeable impurities. Appearing on the side of the paint, it releases the whey with no fragments of fruit. More white stains, molds and mucus.	0
Consistency	A dough of cheese without chops, with tiny pieces of fruit	4
	Dough of cheese with little bushes, slightly dull, slightly sticky, conductive pieces of fruit	3
	Dough of cheese with little bushes, stronger gum, stronger sticky, slightly mushy, trace fruit	2
	Dough of cheese with little bruise, stronger gum, stronger sticky, very fleshy	1
	Consistency errors are very pronounced.	0
Smell	Pure, characteristic of the type of fruit added, slightly acidic and without foreign appendage	3
	Clean, characterized by the type of fruit added and no foreign appendages	2
	With foreign admixtures, stronger acidity and weaker fruity aroma	1
	Errors smell more pronounced and without fruity flavor	0
Taste	Pure, slightly acidic, pronounced taste of added fruit, very aromatic	9
	Slightly sweet, aromatic and slightly less pronounced taste of fruit	8
	Strongly acidic, indefinite, the taste of fruit is poorly expressed	7
	Acidy, a bit unclean, little by the cook, the taste of fruit is not present	6
	Slight bitter taste	4-5
	Bitter, metallic, musty	2-3
	Errors taste are very pronounced	0-1
Colour	The cheese has a uniform white to pale yellow, free of impurities.	2
	Uneven white to light-colored color without impurities.	1
	The mistakes are more pronounced, with foreign colors, very unclean.	0

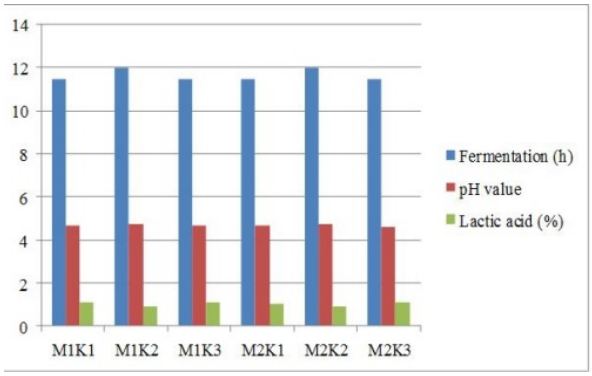

Figure 1. Parameters of laboratory fermentation of milk samples with 0.9% and 1.5 % milk fat

The shorter fermentation time had variations of the fresh cheese produced using the starter culture CHN-22 and the mixture of CHN - 22 and Lyofast SAB 440 B in the ratio of 2:1. Slightly longer fermentation and higher pH at the end of the fermentation showed cheese variations with the microbial starter culture XT - 303 (pH 4,7) irrespective of the proportion of milk fat in milk from which fresh cheese was produced. This may be due to a reduced activity of the microbial starter culture since the fermentation lasted for a long time.

The average values of sensory properties of milk product samples based on fresh cheese and fruits are shown in Tables 3, 5, 7, 9, 11.

The variance analysis - data of sensory properties are shown in Tables 4, 6, 8, 10, 12 and 14. Structural and textural properties of dairy products are the primary criterion of their quality assurance. Sensory properties such as appearance, taste, smell, texture and consistency are essential quality parameters that change during storage due to the composition of milk, fatty acid content, production conditions and the like[10]. In many markets, fruit, sweeteners and spices are added and largely determine the sensory properties of these products[11]. The variance analysis (Tables 4, 6, 8, 10, 12 and 14) shows that there is a statistically significant difference between the samples for exterior appearance, consistency, odour and taste, since the calculated F-quotient has a greater value than the limit value read from the statistical tables, the fact that $P<0.05$ is also supported. Considering the statistically significant difference ($P<0,05$), the Duncan test was conducted by which it was determined which samples were the best by certain sensory properties also during the storage. Almost all of the samples had a good external appearance throughout 10 days of storage.

Table 3. Average values of sensory properties of milk product based on fresh cheese and fruits using milk with 0.9 % milk fat after 1 day of storage

Samples	External appearance (2.0)	Consistency (4.0)	Smell (3.0)	Taste (9.0)	Colour (2.0)	Σ (20.0)
M_1K_1A	2.00^{2}	3.16^{3}	3.00^{5}	8.16^{5}	2.00	18.32
M_1K_1B	2.00^{2}	3.00^{2}	$2.5^{1,2}$	$7.5^{1,2}$	2.00	17.00
M_1K_1K	1.93^{1}	3.00^{2}	$2.58^{2,3}$	7.69^{3}	2.00	17.20
M_1K_2A	2.00^{2}	3.66^{4}	2.83^{4}	8.24^{5}	2.00	18.73
M_1K_2B	2.00^{2}	3.66^{4}	$2.91^{4,5}$	7.41^{1}	2.00	17.98
M_1K_2K	2.00^{2}	3.66^{4}	3.00^{5}	7.83^{4}	2.00	18.49
M_1K_3A	2.00^{2}	2.83^{1}	2.66^{3}	8.66^{6}	2.00	18.15
M_1K_3B	2.00^{2}	3.00^{2}	2.41^{1}	$7.58^{2,3}$	2.00	16.99
M_1K_3K	2.00^{2}	2.83^{1}	2.83^{4}	8.25^{5}	2.00	17.91

^{1,2,3,4,5,6} - Mean values in the same column, with different superscript are significantly different (P<0.05)

Table 4. Analysis of variance of data from Table 3

		Sum of Squares	Df	Mean square	F	p
External appearance	Between Groups	0.065	8	0.008	1470,00	0.000
	Within Groups	0.007	126	0.000		
	Total	0.072	134			
Consistency	Between Groups	15.453	8	1.932	93.538	0.000
	Within Groups	2.602	126	0.021		
	Total	18.055	134			
Smell	Between Groups	5.676	8	0.709	27.166	0.000
	Within Groups	3.291	126	0.026		
	Total	8.967	134			
Taste	Between Groups	21.459	8	2.682	82.043	0.000
	Within Groups	4119	126	0.033		
	Total	25.578	134			
Colour	Between Groups	0.000	8	0.000		
	Within Groups	0.000	126	0.000		
	Total					

$F_{0.05}(8/126)=0.063$

Table 5. Average values of sensory properties of milk product based on fresh cheese and fruits using milk with 0.9 % milk fat after 5 day of storage

Samples	External appearance (2.0)	Consistency (4.0)	Smell (3.0)	Taste (9.0)	Colour (2.0)	Σ (20.0)
M_1K_1A	1.96^{2}	3.26^{1}	2.89^{4}	8.37^{5}	2.00	18.48
M_1K_1B	2.00^{2}	3.16^{1}	2.50^{1}	7.16^{1}	2.00	16.82
M_1K_1K	2.00^{2}	$3.58^{2,3}$	2.91^{4}	7.83^{3}	2.00	18.32
M_1K_2A	2.00^{2}	$3.58^{2,3}$	$2.66^{2,3}$	$8.50^{5,6}$	2.00	18.74
M_1K_2B	2.00^{2}	3.66^{3}	2.75^{3}	7.41^{2}	2.00	17.82
M_1K_2K	1.91^{1}	$3.58^{2,3}$	2.91^{4}	8.08^{4}	2.00	18.48
M_1K_3A	2.00^{2}	3.66^{3}	2.91^{4}	8.66^{6}	2.00	19.23
M_1K_3B	2.00^{2}	3.50^{2}	$2.58^{1,2}$	$7.91^{3,4}$	2.00	17.99
M_1K_3K	2.00^{2}	$3.58^{2,3}$	3.00^{4}	8.33^{5}	2.00	18.91

^{1,2,3,4,5,6} - Mean values in the same column, with different superscript are significantly different (P<0.05)

Table 6. Analysis of variance of data from Table 5

		Sum of Squares	df	Mean square	F	p
External appearance	Between Groups	0.113	8	0.014	5.160	0.000
	Within Groups	0.344	126	0.003		
	Total	0.457	134			
Consistency	Between Groups	3.695	8	0.462	12.456	0.000
	Within Groups	4.672	126	0.037		
	Total	8.368	134			
Smell	Between Groups	3.681	8	0.460	15.968	0.000
	Within Groups	3.630	126	0.029		
	Total	7.311	134			
Taste	Between Groups	30.358	8	3.795	39.034	0.000
	Within Groups	12.249	126	0.097		
	Total	42.607	134			
Colour	Between Groups	0.000	8	0.000	.	.
	Within Groups	0.000	126	0.000		
	Total	0.000	134			

$F_{0.05}(8/126)=0.063$

Table 7. Average values of sensory properties of milk product based on fresh cheese and fruits using milk with 0.9 % milk fat after 10 day of storage

Sample	External appearance (2.0)	Consistency (4.0)	Smell (3.0)	Taste (9.0)	Colour (2.0)	Σ (20.0)
M_1K_1A	1.93^{2}	3.41^{2}	$2.83^{3,4}$	8.40^{5}	2.00	18.57
M_1K_1B	1.93^{2}	3.33^{1}	2.50^{1}	7.50^{2}	2.00	17.26
M_1K_1K	1.93^{2}	3.58^{3}	3.00^{5}	7.75^{3}	2.00	18.26
M_1K_2A	1.58^{1}	3.75^{4}	$2.75^{2,3}$	8.58^{6}	2.00	18.66
M_1K_2B	1.50^{1}	3.83^{4}	2.66^{2}	7.25^{1}	2.00	17.24
M_1K_2K	1.58^{1}	3.75^{4}	$2.91^{4,5}$	$8.25^{4,5}$	2.00	18.49
M_1K_3A	2.00^{2}	3.82^{4}	2.99^{5}	8.74^{6}	2.00	19.55
M_1K_3B	2.00^{2}	3.41^{2}	2.41^{1}	$7.58^{2,3}$	2.00	17.4
M_1K_3K	2.00^{2}	3.83^{4}	$2.91^{4,5}$	8.16^{4}	2.00	18.9

^{1,2,3,4,5,6} - Mean values in the same column, with different superscript are significantly different ($P<0.05$)

Table 8. Analysis of variance of data from Table 7

		Sum of Squares	df	Mean square	F	p
External apearance	Between Groups	5.258	8	0.657	56.148	0.000
	Within Groups	1.475	126	0.012		
	Total	6.733	134			
Consistency	Between Groups	5.029	8	0.629	58.623	0.000
	Within Groups	1.351	126	0.011		
	Total	6.380	134			
Smell	Between Groups	5.407	8	0.676	19.261	0.000
	Within Groups	4.421	126	0.035		
	Total	9.828	134			
Taste	Between Groups	32.751	8	4.094	67.136	0.000
	Within Groups	7.683	126	0.061		
	Total	40.434	134			

$F_{0.05}(8/126)=0.063$

Table 9. Average values of sensory properties of milk product based on fresh cheese and fruits using milk with 1.5 % milk fat after 1 day of storage

Sample	External appearance (2.0)	Consistency (4.0)	Smell (3.0)	Taste (9.0)	Colour (2.0)	Σ (20.0)
M_2K_1A	2.00	4.00^{3}	2.91^{2}	8.16^{3}	2.00	17.07
M_2K_1B	2.00	3.83^{2}	2.58^{1}	7.75^{1}	2.00	16.16
M_2K_1K	2.00	4.00^{3}	2.91^{2}	8.41^{4}	2.00	17.32
M_2K_2A	2.00	3.66^{1}	2.91^{2}	8.50^{6}	2.00	17.07
M_2K_2B	2.00	3.66^{1}	3.00^{2}	7.66^{2}	2.00	16.32
M_2K_2K	2.00	3.66^{1}	2.82^{2}	7.83^{2}	2.00	16.31
M_2K_3A	2.00	4.00^{3}	2.50^{1}	8.25^{4}	2.00	16.75
M_2K_3B	2.00	$3.75^{1,2}$	2.25^{1}	7.83^{2}	2.00	15.83
M_2K_3K	2.00	3.83^{2}	2.66^{1}	8.41^{4}	2.00	16.90

^{1,2,3,4,5,6} - Mean values in the same column, with different superscript are significantly different ($P<0.05$)

Table 10. Analysis of variance of data from Table 9

		Sum of Squares	df	Mean square	F	p
External appearance	Between Groups	0.000	8	0.000		
	Within Groups	0.000	126	0.000		
	Total	0.000	134			
Consistency	Between Groups	2.686	8	0.336	19.311	0.000
	Within Groups	2.191	126	0.017		
	Total	4.877	134			
Smell	Between Groups	7.353	8	0.919	82.506	0.000
	Within Groups	1.404	126	0.011		
	Total	8.757	134			
Taste	Between Groups	12.586	8	1.573	140.632	0.000
	Within Groups	1.410	126	0.011		
	Total	13.996	134			
Colour	Between Groups	0.000	8	0.000		
	Within Groups	0.000	126	0.000		
	Total	0.000	134			

$F_{0.05}(8/126)=0.063$

Table 11. Average values of sensory properties of milk product based on fresh cheese and fruits using milk with 1.5 % milk fat after 5 day of storage

Sample	External appearance (2.0)	Consistency (4.0)	Smell (3.0)	Taste (9.0)	Colour (2.0)	Σ (20.0)
M_2K_1A	2.00	3.83^{3}	2.91^{5}	8.33^{5}	2.00	19.07
M_2K_1B	2.00	3.66^{2}	2.66^{3}	7.83^{2}	2.00	18.15
M_2K_1K	2.00	3.83^{3}	2.75^{4}	8.16^{4}	2.00	18.74
M_2K_2A	2.00	3.58^{2}	2.91^{5}	8.58^{6}	2.00	19.07
M_2K_2B	2.00	3.66^{2}	2.91^{5}	8.00^{3}	2.00	18.57
M_2K_2K	2.00	3.66^{2}	2.91^{5}	8.16^{4}	2.00	18.73
M_2K_3A	2.00	3.58^{2}	$2.58^{2,3}$	8.00^{3}	2.00	18.16
M_2K_3B	2.00	3.58^{2}	2.50^{2}	7.66^{1}	2.00	17.74
M_2K_3K	2.00	3.41^{1}	2.33^{1}	8.16^{4}	2.00	17.90

^{1,2,3,4,5,6} - Mean values in the same column, with different superscript are significantly different ($P<0.05$)

Table 12. Analysis of variance of data from Table 11

		Sum of Squares	df	Mean square	F	p
External appearance	Between Groups	0.000	8	0.000	.	.
	Within Groups	0.000	126	0.000		
	Total	0.000	134			
Consistency	Between Groups	2.055	8	0.257	10.250	0.000
	Within Groups	3.158	126	0.025		
	Total	5.213	134			
Smell	Between Groups	5.534	8	0.692	53.873	0.000
	Within Groups	1.618	126	0.013		
	Total	7.152	134			
Taste	Between Groups	8.721	8	1.090	43.839	0.000
	Within Groups	3.133	126	0.025		
	Total	11.855	134			
Colour	Between Groups	0.000	8	0.000	.	.
	Within Groups	0.000	126	0.000		
	Total	0.000	134			

$F_{0.05}(8/126)=0.063$

Table 13. Average values of sensory properties of milk product based on fresh cheese and fruits using milk with 1.5 % milk fat after 10 day of storage

Sample	External appearance (2.0)	Consistency (4.0)	Smell (3.0)	Taste (9.0)	Colour (2.0)	Σ (20.0)
M_2K_1A	2.00^{3}	4.00^{3}	3.00^{4}	8.50^{5}	2.00	19.5
M_2K_1B	1.83^{1}	3.66^{1}	2.58^{2}	7.83^{2}	2.00	17.9
M_2K_1K	1.83^{1}	3.83^{2}	2.58^{2}	8.33^{4}	2.00	18.57
M_2K_2A	1.91^{2}	$3.91^{2,3}$	2.83^{3}	9.00^{6}	2.00	19.65
M_2K_2B	1.83^{1}	4.00^{3}	2.58^{2}	7.66^{1}	2.00	18.07
M_2K_2K	2.00^{3}	3.83^{2}	$2.91^{3,4}$	8.16^{3}	2.00	18.9
M_2K_3A	2.00^{3}	4.00^{3}	2.66^{2}	8.50^{5}	2.00	19.16
M_2K_3B	1.83^{1}	3.66^{1}	2.33^{1}	7.66^{1}	2.00	17.48
M_2K_3K	2.00^{3}	3.83^{2}	2.66^{2}	8.16^{3}	2.00	18.65

^{1,2,3,4,5,6} - Mean values in the same column, with different superscript are significantly different ($P<0.05$)

Table 14. Analysis of variance of data from Table 13

		Sum of Squares	df	Mean square	F	p
External appearance	Between Groups	0.867	8	0.108	13.840	0.000
	Within Groups	0.987	126	0.008		
	Total	1.854	134			
Consistency	Between Groups	2.159	8	0.270	20.365	0.000
	Within Groups	1.670	126	0.013		
	Total	3.829	134			
Smell	Between Groups	4.966	8	0.621	31.502	0.000
	Within Groups	2.483	126	0.020		
	Total	7.449	134			
Taste	Between Groups	23.396	8	2.924	173.866	0.000
	Within Groups	2.119	126	0.017		
	Total	25.515	134			
Colour	Between Groups	0.000	8	0.000		
	Within Groups	0.000	126	0.000		
	Total	0.000	134			

$F_{0.05}(8/126)=0.063$

Some samples had better ratings for the consistency, smell and flavour on the 10th day of storage. The cause of the lower estimate of the external appearance of some samples was due to the small amount of extracted whey on the surface of the sample, which was noticed after 10 days of storage. Consistency in most samples was enhanced during storage, as well as the smell, taste, which were typical by the types of fruit that was added. Reduced fat content in milk, later in the cheese resulted in a lower content of forming fatty acids and other aromatic compounds that are important for the taste and smell of cheeses[12]. The colour of all samples remained unchanged, regardless of the content of milk fat, type of microbial starter cultures or types of fruits present in samples, so it can be considered as most stable properties. Samples derived from milk with 1.5% milk fat were obtained using the mesophilic culture CHN-22 and a combination of mesophilic and probiotic Lyofast SAB 440B, achieved significantly higher scores compared to culture XT-303. Higher content of milk fat had a positive influence on consistency and better taste of the cheese dessert. The samples of products based on fresh cheese and pineapple were best assessed. The consistency of pineapple itself inside of a milk product was not altered during the storage. Some of them had a maximum scores for certain sensory properties of 10th day of storage (M_2K_1A i M_2K_3A). The samples of milk product based on fresh cheese and pear as well fresh cheese and peach achieved a bit lower scores, compared to the samples with pineapple. The consequence of that was hard and grainy texture of pear that did not fit in well with the overall feel of milk products. Smell and taste of pears were not fully expressed. Further, samples of milk products based on fresh cheese and peach had the lowest sum of total points for sensory properties (16.82-17.8). The reason of that was not sufficiently expressed smell and taste, a softer consistency of peaches that changed during storage of milk product.

CONCLUSION

For the production of a fermented milk product based on fresh cheese and fruits, skimmed milk with 0.9% milk fat and partially skimmed milk with 1.5% milk fat was used. Fermentation of milk was carried out at a temperature of 25 C up to pH 4.6 – 4.7, with implementation of FD-DVS starter cultures (CHN-22 iXT-303) and mixture of starter cultures CHN-22 and Lyofast SAB 440 B in ratio 2:1. Compotes of pineapple, peaches and pears were used as fruit additives. The samples of fermented milk product from milk with 1.5% milk fat had a better consistency, pronounced aroma and fuller taste during storage. Sensory properties of the milk product based on fresh cheese and pineapple were the most pronounced, with the sum of points between 18.18–19.65, compared to the addition of peach and pear. Addition of pineapple in samples, application of culture CHN-22 and combination with probiotic had most influence on the average scores of 8.66, compared to the peach (7.34) and pear (7.69).

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EVALUATION OF LOW-COST SORBENTS AS POTENTIAL MATERIALS FOR *IN SITU* REMEDIATION OF WATER CONTAMINATED WITH HEAVY METALS

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT: The aim of this paper was to examine the possibilities of using various *low-cost* sorbents as material for permeable reactive barrier for efficient removing of lead, cadmium, copper and zinc from contaminated water. Natural zeolite (NZ), iron-modified zeolite (IMZ), apatite, concentrated apatite, kaolin and raw bentonite were examined. The batch test evaluation was used to investigate capturing of heavy metals from contaminated water onto sorbents, as well as retention strength of saturated sorbent. The change of pH values during saturation and leaching of heavy metals was performed in a slightly acidic to neutral area, confirming buffering abilities and environmental acceptability of all investigated sorbents as a material in PRB for protection of groundwater as the most valuable natural resources. The highest saturation ability towards all examined heavy metals was detected with raw bentonite and IMZ. Leaching of heavy metals at pH=2.94-2.98 was confirmed in all saturated sorbents, while at pH=6.07-6.46 it was not detected, except of Pb and Cd in raw bentonite. From the obtaned results, the recommendation for selection of sorbent for treatment of water contaminated with lead, cadmium, cooper and zinc is given.

KEYWORDS: *low-cost* sorbent, leachability, permeable reactive barrier, heavy metals (zinc, copper, cadmium, lead)

INTRODUCTION

Groundwater is the most valuable natural resource that is extensively used for water supply, irrigation, industry and mining. This source is highly vulnerable to various anthropogenic pollution influences. Therefore, monitoring and maintaining the good quality of groundwater is of great public interest. At localized sources of pollution, a harmful substance is rapidly dispersed and spread out in the form of plumes in direction of groundwater flow. The remediation of such contaminated groundwater can be carried out using various "*in situ*" and "*ex situ*" techniques. Today, more attention is focused on the "*in situ*" technique of a permeable reactive barrier (PRB) due to simplicity of performance and economy benefits. PRB provides a barrier consisted of water-permeable material, set below the surface perpendicular to the groundwater flow. In the case of remediation of groundwater contaminated with heavy metals, by passing contaminated groundwater through the barrier, the reactive material in the barrier keeps heavy metals by different processes such as absorption, ion-exchange, oxidation, reduction, chemical precipitation. Each of mentioned processes is directly related to the pH of the system. In this regard, the groundwater geochemistry and reactivity of the material are control factors for PRB binding and retention of metal cations. The choice of materials for barriers is important and depends on the contamination source and the type of harmful substances. Material for PRB must demonstrate good binding properties towards contaminants, the ability of their retention, excellent hydraulic properties which allow smooth flow of groundwater through the barrier, and satisfactory mechanical properties for safety performance[1,2]. The recent investigations of many scientists have focused on investigation of materials which are abundant in nature or waste material from another process. These materials are usually called as "*low cost*" [2,3]. The purpose of this work is to explore testing of various natural materials such as zeolite, bentonite, kaolin and apatite and investigate the possibility of their use as a material for PRB, which would effectively remove heavy metals such as lead, cadmium, zinc and copper from contaminated groundwater. The results should give an answer which sorbent provides optimal removal of heavy metals from contaminated water and retention strength of saturated sorbent.

EXPERIMENTAL

REAGENTS

Metal aqueous solutions of zinc, copper, lead and cadmium were prepared from nitrates salts with similar initial metal concentrations of c_o(Zn) = 10.107 mmol/l, c_o(Cu) = 10.083 mmol/l, c_o(Pb)=10.172 mmol/l and c_o(Cd)=10.068 mmol/l. The following *low-cost* sorbent were used in this study: natural zeolite (NZ), iron-modified zeolite (IMZ), apatite, concentrated apatite, kaolin and raw bentonite. Natural zeolite was supplied from Zlatokop deposit in Vranjska Banja (Serbia), with clinotilolite as a major component, while feldspat plagioclase and quartz were in traces[4,5]. Bentonite originated from Šipovo deposit (Bosnia), in which montmorillonite was a major component with quartz and calcite in traces[4]. Apatite from ore deposit Lisina, near Bosilegrad (Serbia), prepared by washing and wet milling, with an average content of P_2O_5 of 17.73%[6]. Kaolin was obtained from a plant for production of quartz sand in Rgotina (Serbia), and kaolinite was found as a major component with quartz and mica in traces[7]. Iron-modified zeolite (IMZ) and concentrate apatite was prepared from original zeolite and apatite, respectively, according to well-known procedures[5,8]. Chemical composition of investigated sorbents is summarised in Table 1.

Table 1 Chemical composition (in %) of investigated low-cost sorbent

	K_2O	Na_2O	Al_2O_3	SiO_2	CaO	MgO	Fe_2O_3 %	TiO_2	L.I.	P_2O_5	Total
Apatite	3.18	0.08	9.96	27.95	35.28	0.98	2.42	0.51	1.88	17.73	99.97
Conc. apatite	0.63	0.05	2.40	9.51	49.09	0.16	0.70	0.17	1.67	36.21	100.59
Kaolin	0.79	0.07	28.5	48.29	10.81	0.20	0.83	0.84	9.65	-	99.98
Bentonite	0.38	0.16	25.04	49.24	5.07	1.57	5.67	0.84	11.99	-	99.96
Raw bentonite	0.25	0.16	25.23	51.31	4.54	3.23	3.78	0.34	11.12	-	99.96
NZ	1.26	1.60	13.58	65.15	4.15	0.62	2.27	0.30	11.07	-	100.00
IMZ	4.14	0.87	12.87	64.28	3.47	0.37	4.04	0.60	9.12	-	99.76

SATURATION EXPERIMENT

The saturation of sorbents with heavy metals solutions was examined using batch mode, at solid/liquid ratio of 10 g/l, during 48 hours at room temperature. As our previous experiments have shown that copper in the system of Cu-IMZ precipitates[9], the pH values of initial copper solutions in this system were adjusted at pH=2.52. During all experiments, pH values were recorded, and concentrations of heavy metals were determined before and after the experiment complexometrically, and checked by AAS. In all suspension, the precipitates were not observed.

LEACHING EXPERIMENT

After loading with heavy metals, leaching of heavy metals from saturated sorbents were performed by using an original approach based on a batch-pH static leaching experiment in ultrapure water of different initial pH values in ranges 2.94-2.98 and 6.07-6.46. The leaching experiments were performed at solid/liquid ratio of 10g/l, during 24 hours at room temperature. During the experiments, pH values of solutions were recorded, and concentrations of heavy metals after the experiment were determined.

RESULTS AND DISCUSSION

SATURATION EXPERIMENT

Saturation experiments were continuously monitored by measuring pH values of solutions and results are given in Figure 1.

The slight increase of pH of solutions in all examined systems is evident, which is related with decrease of metal concentration in solution and their hydrolyse reaction.

Metals removed quantity on different sorbents q_e (mmol/g) is calculated by equations (1):

$$q_e = (c_o - c_e)\frac{V}{m} \quad \text{.....(1)}$$

where c_o and c_e are initial and equilibrium concentrations of metal cations (mmol/l), V is the volume of the solution (l) and m is the mass of sorbent (g).

The results of metals removed quantity on different sorbents are given in Figure 2.

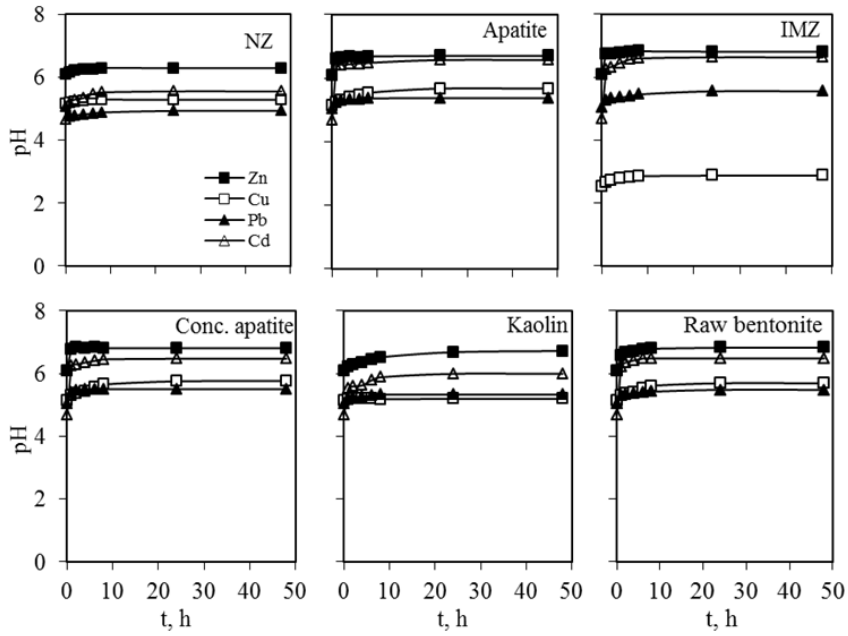

Figure 1. pH values of solution during sorption of zinc, copper, lead and cadmium onto investigated sorbents

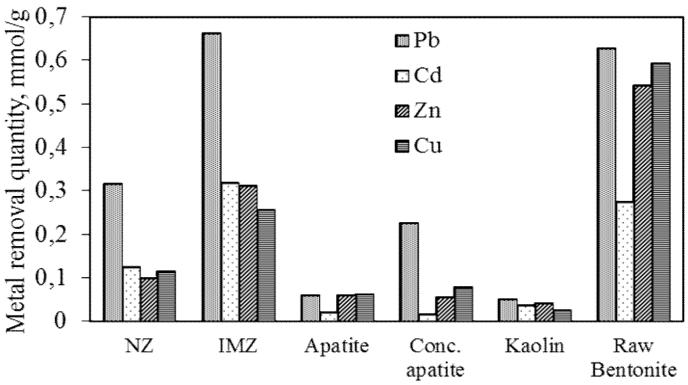

Figure 2. Amount of lead, cadmium, zinc and copper removal on different sorbents

The results indicate that lead was removed in the highest amount in all investigated sorbents, among which IMZ and raw bentonite dominates, followed by NZ and conc. apatite, while the smallest amount was removed by apatite and kaolin. Almost similar amounts of zinc and copper were sorbed onto investigated sorbents, confirming their similar affinities. However, twice higher amount of lead were removed onto investigated sorbent compared to cadmium.

Raw bentonite and IMZ can be selected as materials with the highest potential for removal of heavy metals. Affinity sequence of heavy metals on raw bentonite is in order Pb>Cu≥Zn>Cd, while for IMZ is in order Pb>Cd>Zn>Cu.

LEACHING EXPERIMENT

Leaching experiments were followed by measuring the pH values of solutions and results are given in Figure 3.

At pH=2.94-2.98, a slight increase of pH values is evident in the system of metal ions with IMZ, conc. apatite and raw bentonite. At pH=6.07-6.46, a slight increase is evident for all examined systems, and is most pronounced for conc. apatite.

The amount of metal cations leached from sorbent, q_l (mmol/g) is calculated by equations (2):

$$q_l = c_l \frac{V}{m} \qquad (2)$$

where c_l is the concentration of metal cations leached from sorbent (mmol/l).

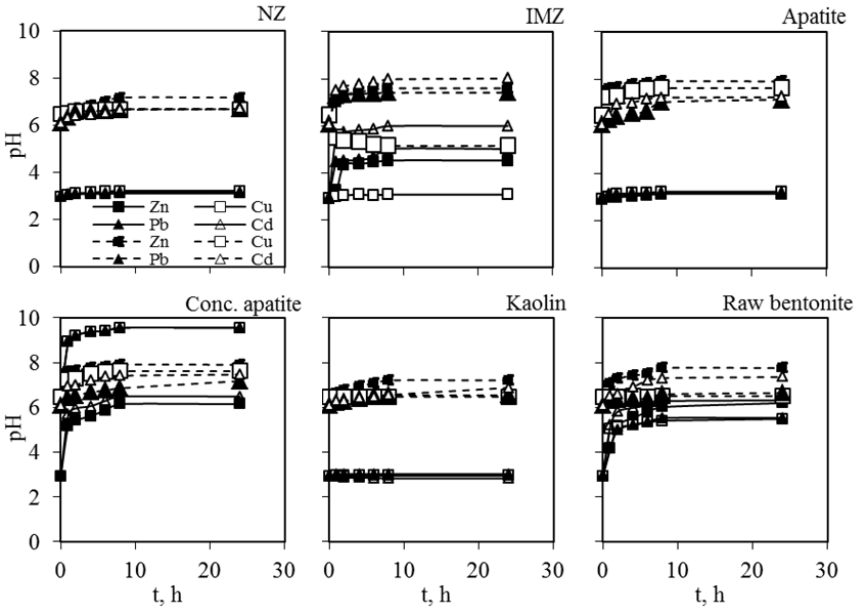

Figure 3. pH values of solution during metal leaching experiment from solution of pH=2.94-2.98 (full lines)and 6.07-6.46 (dash lines)

Leaching of heavy metals from metal-saturated sorbents in ultrapure water solution of pH=2.94-2.98 is given in Figure 4. Leaching in ultrapure water solution of pH=6.07-6.46 was only recorded for lead and cadmium from raw bentonite (thus graphical presentation of these results is not given).

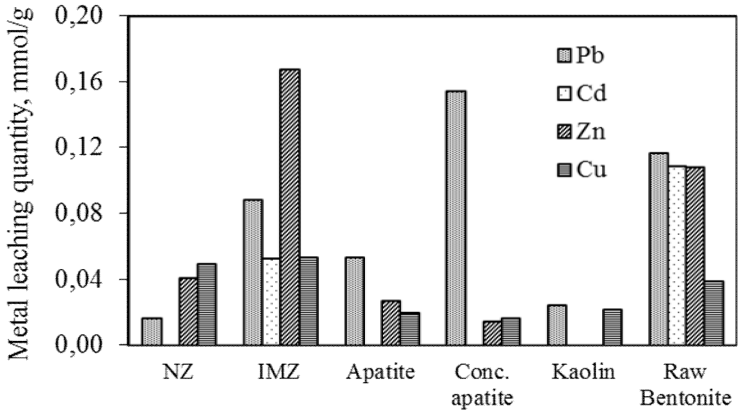

Figure 4. Leaching amount of heavy metals from saturated sorbents in solution of pH=2.94-2.98

At pH_o=2.94 leaching of zinc and cooper is evident for all examined sorbents except leaching of zinc from kaolin. Absence of zinc leaching from kaolin is a consequence of a lower amount of sorbed zinc during the saturation experiment.

Also, leaching of lead is evident from al all examined sorbent, while leaching of cadmium is evident from saturated IMZ and raw bentonite. Lower pH value encourages competition of H^+ ions, thus leaching of all examined heavy metals is more pronounced.

CONCLUSION

During saturation of zinc, copper, cadmium and lead on investigated sorbent, the highest removal of heavy metals was achieved by IMZ and raw bentonite. Leaching of heavy metal in acidic medium at pH=2.94-2.98 was recorded in almost all saturated sorbents, due to the presence and competition of higher amounts of H^+ ions. Leaching of heavy metals from slightly acidic to neutral medium at pH_o=6.07-6.46 was recorded for lead and cadmium from raw bentonite.

Thus, although raw bentonite has excellent removal properties toward lead and cadmium, recorded leaching at pH pH=6.07-6.46 indicate that this material is not suitable for PRB for removal of lead and cadmium.

Based on the obtained results, the following recommendations for the selection of investigated sorbents as materials for PRB for remediation of water contaminated with heavy metals can be given: for zinc removal, among examined sorbents, raw bentonite and IMZ show the highest potential as materials in PRB. As in the system of Cu-IMZ precipitates creates due to the increase of pH, raw bentonite can be selected as a material for PRB for copper removal. For removal of lead and cadmium, IMZ shows the potential to be used as a material in PRB.

Application of the "low-cost" sorbents as materials in a barrier makes the overall process economically and environmentally acceptable.

ACKNOWLEDGEMENT

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EFFECTIVENESS OF DOMESTIC WASTEWATER TREATMENT IN THE "GRMEČ" TEACHING CENTER USING PILOT - SCALE CONSTRUCTED WETLAND AS UNCONVENTIONAL METHOD

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT: Environmental care, higher requirements for quality of effluent, high cost of conventional wastewater treatment, and increased energy costs required for their work, have led scientists to more comprehensive research on a possibility of using a constructed wetland in wastewater treatment technology. Constructed wetlands are artificially shaped swamps with the aim of creating conditions conducive to the purification of wastewaters flowing through them. They are used for treatment of municipal wastewater from small settlements and a small industrial facility, as well as other types of wastewater.

The educational pilot - scale constructed wetland on which the research was conducted is located in the area of Bihać municipality, on a plot used by the Biotechnical Faculty in Bihać. The pilot - scale constructed wetland for wastewater treatment covers an area of 20 m^2 and is dimensioned for 10 equivalents of population. In this research we have examined the effectiveness of domestic wastewater treatment in the "Grmeč" Teaching Center using pilot - scale constructed wetland.

Plants planted in the constructed wetland were *Typha latifolia and Phragmites australis*, and the substrate was made of sand and pebbles of different granulations. The recipient of purified wastewater is the Drobnica stream, which is about 10 m away from the site. The research was conducted in May, with the flow varied depending on a weekly student workload.

Efficiency of purification using constructed wetland depended on flow rate and organic wastewater load, ranging from 37.15% at a minimum flow of 9.89x10-6 m^3/s and HPK values of 35 mgO_2/L, up to 89.48% at the highest flow value of 2.51x10-5 m^3/s, and HPK values of 189 mgO_2/L. The highest concentration of ammonia in the influent was 145.62 mg N/L, and the lowest concentration of ammonia in the effluent was 6.31. mg N/L.

KEYWORDS: wastewater, constructed wetland, efficiency of purification.

INTRODUCTION

Constructed wetlands are complex biological systems, made and built to use natural processes that occur in wetland soil and plants, including microorganisms that participate in water purification. They are designed to imitate processes that happen in natural wetlands, but under controlled conditions.[1,2] These systems mostly consist of certain vegetation, substrates, soil, microorganisms and water, and they use complex procedures that include physical, chemical and biological mechanisms for removing different pollutants or for improving the quality of water.[3] Simple work, high treatment efficiency and relatively low costs of polygons construction and maintenance, in regard to conventional purification technologies – are the characteristics of a constructed wetland (CW) as acceptable quality solutions for wastewater purification. Other factors that contribute to their attractiveness are aesthetic and ecological values (biological diversity of wetland habitats). CW are used mostly for utility wastewater purification in smaller places away from the urban environment. The main role in purification process belongs to microorganisms that live on plants whose leaves, trees and roots are filled with air holes whose role is to bring the oxygen from atmosphere to the root and surrounding ground. Decomposed organic matters are built into tissue of the plants and that is how waste water is purified.[4] Plants that are mostly planted within the wetland systems for wastewater purification are cane (*Phragmites australis*), cattail (*Typha latifolia*), bur-reed (*Sparganium erectum*), common clubrush (*Scirpus lacustris*), yellow iris (*Iris pseudacorus*), sedges (*Carex sp.*) etc.[5] The main characteristics of those plants are: widely spread and adaptive to different conditions, including very low temperatures as well (below 0°C). It is recommended to choose native wetland vegetation whenever it is possible.[6] In this research paper will be present the examination results of domestic wastewater treatment efficiency (water from Teaching Centre "Grmeč"), in a month of May 2017. The pilot - scale constructed

wetland was used. During this research, wastewater flow and organic loading varied on a daily basis, depending on the number of students. The plants that were used in a plant device were: cattail (*Typha latifolia*) and cane (*Phragmites australis*), and substrate consisted of sand and pebbles in various grain sizes. The aim of this research was to determine efficiency of domestic wastewater treatment with the pilot – scale constructed wetland. Efficiency of the work was confirmed by measuring the relevant standard physical-chemical and bacteriological parameters.

MATERIAL AND METHODS

The educational pilot - scale constructed wetland that was used for the research purposes is located in Bihać, on the lot that is currently used by Biotechnical Faculty. That device covers a total surface of 20 m^2, dimensioned for 10 ERU (equivalent unit), and intended for experimental purification of different kinds of wastewater for research purposes. Cattail (*Typha latifolia*) was planted in the first field of the CW, and cane (*Phragmites australis*) was planted in the second field. Domestic wastewater from Teaching Centre "Grmeč" was used for the research purposes, with the varying flow and the content of organic matter in wastewater, depending on the number of students. The research was done in a month of May, when vegetation was lush. The content of wastewater was monitored through specific parameters such as suspended solids, chemical oxygen demand (COD), biochemical oxygen demand (BOD), concentration of ammonia ion and salt, nitrate and nitrite, concentration of phosphorus etc. Determination of the physical-chemical parameters of the quality of a wastewater sample was performed according to standard APHA[7] methods and Uredba o uslovima ispuštanja otpadnih voda u okoliš i sisteme javne kanalizacije.[8] In order to measure general parameters like pH-value, temperature, electroconductivity, dissolved oxygen concentration and oxygen saturation – it used multiparameter SensoDirect 150, Lovibond, and the turbidimeter HANNA was used to measure the turbidity of water in the sample. Spectrophotometric method on Spectrophotometer photoLab® 6600 UV-VIS device was used for the determination of ammonia nitrogen, nitrite, nitrate and phosphorus, with help of Merck with special test kits from the Spectroquant®. The chemical oxygen demand was determined spectrophotometrically by the device called Spectrophotometer photoLab® 6600 UV-VIS. The method for determination of chemical oxygen demand is called a bichromatic method, and Merck tests Cod Cell Test C4/25 were used for this purpose. Microbiological analysis of the sample was determined by the membrane filtration method, and ready-made substrates for determination of total coliform bacteria and *Escherichia coli* were used for this purpose.

RESULTS AND DISCUSSION

This chapter presents the results of the physical, chemical and biological analysis of domestic wastewater at Teaching Centre "Grmeč", at the entry and exit of constructed wetland, depending on the flow rate. The research was done in a month of May 2017, and the results varied depending on the flow and workload of students.

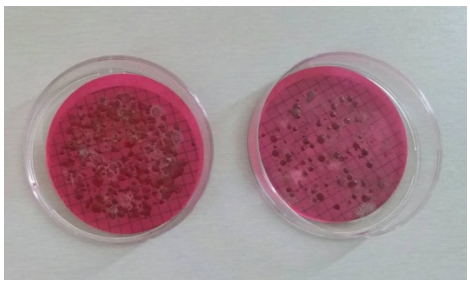

Figure 1. Total coliforms in influent and effluent at 37°C/24h (number/100 ml)

Figure 2. Colour of municipal wastewater in influent and effluent

Table 1. Physico-chemical quality indicators of municipal wastewater from Educational Centre "Grmeč" at the entry and exit of the educational pilot - scale constructed wetland

Parameter	I1	E1	I2	E2	I3	E3	Limits[8]
Flavour	Strong odour	Odourless	Strong odour	Odourless	Strong odour	Odourless	-
Colour	Light brown	Colourless	Light brown	Colourless	Yellow	Colourless	-
Fuzziness (NTU)	35.17	16.39	25.12	12.78	32.64	12.5	-
Temperature (°C)	15	14.2	13	14	14.5	15.3	30
pH	7.9	8.64	7.85	8.05	8.13	8.06	6.5-9.0
Conductivity (μS)	463	267	323	250	369	357	-
Oxygen saturation (%)	2	10.4	2.6	6.7	3.7	9.3	-
Dissolved oxygen (mg/L)	0.9	5	1.2	3.3	1.7	4.3	-
Evaporated residue (mg/L)	366	218	309	261	340	280	-
Annealed rest (mg/L)	243	115	267	188	199	165	-
Suspended solids (mg/L)	65	35	5	3	25	5	35
Ammonia (mg N/L)	48	19.04	21	6.77	42.64	6.31	10
Nitrites (mg N/L)	0.06	0.13	0.08	0.02	0.11	0.02	-
Nitrates (mg N/L)	0.7	0	0.1	0	0.05	0	10
Total nitrogen (mg N/L)	49	22.2	23.2	7.5	42.9	7.11	15
Phosphorus (mg/L)	1.73	0.66	1.52	0.64	1.57	0.62	2
Consumption of $KMnO_4$ (mg/L)	17.9	5.5	12.32	3.79	16.22	4.18	-
COD (mgO_2/L)	87	32	35	22	119	20	125
BOD (mgO_2/L)	38	14.3	15.7	10.4	44.8	17.5	25
Flow (m^3/s)	$1.54x10^{-5}$		$9.89x10^{-6}$		$1.83x10^{-5}$		
Efficiency of purification for COD (%)	63.22		37.15		83.2		

I1 – influent in the pilot - scale constructed wetland (CW) the first day; E1 – effluent from the CW, the fifth day after sampling
I2 – influent in the pilot - scale constructed wetland (CW) the second day; E2 – effluent from the CW, the fifth day after sampling
I3 – influent in the pilot - scale constructed wetland (CW) the third day; E3 - effluent from the CW, the fifth day after sampling

Table 2. Physico-chemical quality indicators of municipal wastewater from Educational Centre "Grmeč" at the entry and exit of the educational pilot - scale constructed wetland

Parameter	I4	E4	I5	E5	Limits[8]
Flavour	Strong odour	Odourless	Strong odour	Odourless	-
Colour	Yellow	Colourless	Yellow	Colourless	-
Fuzziness (NTU)	30.65	7.11	26.58	14.84	-
Temperature (°C)	14.1	15.6	14.8	16	30
Ph	8.35	8.2	8.26	8.23	6.5-9.0
Conductivity (μS)	406	348	446	334	-
Oxygen saturation (%)	5.5	12.1	2.1	7.2	-
Dissolved oxygen (mg/L)	2.5	4.7	1	3.3	-
Evaporated residue (mg/L)	260	200	360	260	-
Annealed rest (mg/L)	180	132	199	175	-
Suspended solids (mg/L)	15	10	78	25	35
Ammonia (mg N/L)	145.62	22.55	48.69	28,.3	10
Nitrites (mg N/L)	0.11	0.08	0.18	0.11	-
Nitrates (mg N/L)	0.05	0	0.09	0	10
Total nitrogen (mg N/L)	40.5	23.4	147.1	29.9	15
Phosphorus (mg/L)	1.53	0.64	1.8	0.72	2
Consumption of $KMnO_4$ (mg/L)	18.2	2.3	16.6	6.2	-
COD (mgO_2/L)	189	20	157	41	125
BOD (mgO_2/L)	88	28.6	69.8	26.6	25
Flow (m^3/s)	$2.51x10^{-5}$		$1.23x10^{-5}$		
Efficiency of purification for COD (%)	89.48		73.89		

I4 –- influent in the pilot - scale constructed wetland (CW) fourth day E4 – effluent from the CW, the fifth day after sampling
I5 - influent in the pilot - scale constructed wetland (CW) fifth day; E5 – effluent from the CW, the fifth day after sampling

Sampling of wastewaters was carried out in accordance with the wastewater sampling standards prescribed by the Pravilnik o izmjenama i dopunama pravilnika o prirodnim mineralnim i prirodnim izvorskim vodama[9], in accordance with the domestic legislation in this field. The hydraulic retention time (HRT) for plant device was 5 days. This period depends on the size of pollutant and default level of purification. The usual retention time for removing BOD is 2-5 days and 7-14 days to remove nitrogen. HRT can be calculated according to the following formula:[10]

$$HRT = V/Q = LW\,(dmn+dw)/Q$$
$$= A(dmn+dw)/Q\ (day) \quad (1)$$
$$HRT = 5\ DAYS$$

V – volume of water in a plant device (m^3); Q – medium flow through a plant device (m^3/days); A – surface of a plant device (m2); L – length of a plant device (m); W – width of a plant device (m); dm - the thickness of the medium that allows water to pass through (m); dw - depth of water from media surface (m); n – porosity.

The parameters were monitored for 5 days, and the flow varied depending on the workload of students. The flow was ranging from $9.89x10^{-6}$ m^3/s to $2.51x10^{-5}$ m^3/s. The final recipient was the stream called Drobnica, which is located near the teaching centre. The pH value at the inlet and outlet samples from the device ranged from 7.85 to 8.64, which is in the line with border pH value of wastewater that can be dropped into surface water bodies, as prescribed by the Decree on the conditions of discharge of wastewater to the environment and public sewerage systems.[8] Concentration of suspended substances in influent samples varied, and it had the highest value on the first and last day of sampling, where the concentration of the suspended substances exceeded the limit values prescribed by the legislation. Nitrogen compounds in water are an indicator of current pollution. In all influent samples, concentration of ammonia and total nitrogen exceeded the maximum permissible concentration. The content of organic matter in wastewater samples (expressed as COD and BOD) varied, and the highest COD value was measured on the fourth sampling day, during the maximum flow. The COD value in the influent samples 4 and 5 exceeded the limit values prescribed by regulation. The content of organic matter expressed as COD and BOD in all wastewater samples, after passing through the constructed wetland, was below the maximum permissible concentration prescribed by regulation.[8] Efficiency of wastewater purification while using a horizontal pilot constructed wetland, expressed through COD, varied depending on the concentration of organic matter and the flow. The highest efficiency happened on the fourth day and it amounted to 89.48%, during the highest concentration of organic matter and the highest flow rate. The lowest efficiency was in the sample that went through the device on the second day - 37.15%. At that time there was also the smallest flow and the smallest content of organic matter in the input sample expressed as COD. The highest removal efficiency of ammoniacal nitrogen was in sample 4 – 84.52%, and the lowest removal efficiency of ammoniacal nitrogen was in sample 5 – 41.41%. In the wastewater samples at the entrance and exit from the constructed wetland, microbiological analysis of sample was done while using the membrane filtration method. Pre-mixed substrates for determination of total and faecal coliform bacteria were used in that process. The largest number of grown colonies was in sample 4, which had the highest content of organic substances expressed as COD. Total number of grown coliform bacteria in all samples at the entrance to the device at 37°C/24h (number/100 ml) was >1000. This number was <80 cfu/100ml in effluent. The number of *Escherichia coli* bacteria present in all influent samples exceeded the maximum number allowed in water that is released into coastal and transitional waters. In effluent samples that number is in accordance with the legal regulation.

Many researchers have dealt with this particular problem - wastewater. Merlin and associates[11] did this research on a three-phase horizontal pilot constructed wetland with subsurface flow of wastewater. This plant device was used for domestic wastewater purification and it was dimensioned for 350 population equivalent (PE). Since we are talking about a three-phase constructed wetland, there were three plant species planted: *Typha latifolia, Phragmites australis* and *Scirpus maritimus*. The hydraulic retention time of water in the device was 4-5 days. With the usage of plant equipment throughout the year, high efficiency of removal of total suspended particles was achieved, on average about 96% in the first phase already. Efficiency of the removal of organic matters expressed as COD and BOD in the first phase was on average about 60%, and on constructed wetland exit was bigger than 90%. Efficiency of nitrogen removal was on average about 57% (±21%), phosphorus 69% (±27%), respectively. Removal of total coliforms and enterococci was more or less proportional to water retention in every part of the constructed wetland. Merlin and associates[11] found that 50% of enterobacteria was removed in the first part of the constructed wetland, around 90% in second part and 99% at the plant device exit. The overall

efficiency of the enterobacteria removal ranged from 90% to 99.98%. Baskar and associates[12] did the research on purification efficiency of constructed wetlands depending on the vegetation type. Two small pilot-scale constructed wetlands were used for this research. They planted *Typha latifolia* in the first device, and *Phragmites australis* in the second one. Then they let domestic wastewater to flow through those devices. The hydraulic retention time (HRT) was 2, 4, 6 and 8 days. In the constructed wetland which had *Phragmites australis* planted, with the mentioned retention time, the efficiency of organic ingredients removal expressed as COD was 39%, 44%, 64% and 69%. Efficiency of total nitrogen removal was 23%, 7%, 31% and 45%. In the plant device which had *Typha latifolia* planted, the efficiency of organic ingredients removal expressed as COD was 31%, 37%, 73% and 68%. Efficiency of total nitrogen removal was 26%, 17%, 34% and 36%. Collison and Grismer[13] did the research on a horizontal constructed wetland with subsurface flow of water which had polluted cattail (lat. *Typha latifolia*). They investigated the efficiency of nitrogen removal and organic components expressed as COD values from two types of wastewater: domestic wastewater and synthetic wastewater, starting from a month of November to a month of June. Statistical analysis of results for this time period showed that the efficiency of organic components removal expressed as COD value from domestic wastewater - was 79%, and nitrogen 94%.

Studies have shown that devices with two kinds of vegetation have better purification efficiency than devices with one kind of vegetation.[14]

CONCLUSION

This research contribute to the understanding of how horizontal pilot – scale constructed wetland with different flow functions.

- Efficiency of wastewater purification while using the horizontal pilot – scale constructed wetland, expressed through COD, varied depending on the concentration of organic matter and the flow. The highest efficiency was at 9.89×10^{-6} m^3/s (89.48%), with the highest concentration of organic matters. The lowest efficiency was at 2.51×10^{-5} m^3/s (37.15%), with the lowest concentration of organic matters in the input sample expressed as COD.
- The highest efficiency of total nitrogen removal (as indicators of current pollution) was in sample number 3 (83.43%). The lowest efficiency of total nitrogen removal was in sample number 1 (54.7%).
- Efficiency in suspended matter removal ranged from 40% to 67.95%.
- Efficiency in *E. Coli* removal during 5 days showed excellent results in this research. The number of bacteria decreased from >1000/100 ml to <20 cfu/100ml. Those results are consistent with what other investigators have reported.
- Studies have shown that devices with two kinds of vegetation have better purification efficiency than devices with one kind of vegetation.

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RECURRENT WATER FROM SLAG AND FLY ASH DISPOSAL PONDS AS A MEDIUM FOR CARBON CAPTURE AND STORAGE

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT: Due to the increased use of fossil fuels and industrial production, the concentration of carbon dioxide in the atmosphere increases, causing greenhouse effect and, consequently, climate change. Stationary CO_2 sources like coal power plants produce the bulk of the world's CO_2 emissions. Electricity and heat plants and other fuel transformation activities account for 40% of total global CO_2 emissions. Therefore, great interest in the possibilities of CCS systems to reduce CO_2 emission is evident, either through removal or reduction measures. The experimental part of this paper deals with the determination of the potential of alternative media for use in CCS technologies, describing the lab-scale investigation. The role of alternative media in that context has been assigned to recurrent water from fly ash and slag disposal pond Jezero II of Power Plant Tuzla. When choosing an alternative medium for CCS applications, the following features were considered: that the medium currently has a negative impact on the environment; that the medium is available in sufficient quantities; that the medium has a low price and that its final disposal causes costs. Hence, the ability of the selected media (recurrent water) for CO_2 capture has been confirmed and its capacity in that context roughly determined.

KEYWORDS: carbon dioxide, CCS technologies, recurrent water, power plant.

INTRODUCTION

CCS is a process that consists of separating CO_2 from industrial and energy sources, transporting to a storage location and long-term extraction from the atmosphere[1]. Spectrum of measures that need to be urgently implemented to mitigate climate change can play a decisive role because it can contribute to a 20% reduction of CO_2 that is considered necessary by 2050. According to Loš[2], carbon dioxide capture, extraction and storage technologies make a promising option that can significantly reduce emissions.

However, CCS systems will be difficult to apply as long as the policy that legally limits greenhouse gas emissions in the atmosphere does not change. Such political changes would lead to all new industrial fossil fuel plants being designed so that some of the CCS technologies can be used[3].

Simplified, CCS processes consist of three main components: capture, transport and storage (disposal)[4]. However, some technologies can be rather expensive and there are no reliable estimates of the total cost as well as the individual costs of the links in the technology chain, but it is considered that the major part of cost are related to CO_2 separation processes. Nevertheless, the wider application would be considered to lead to a reduction in separation costs, which would make the generating of electricity from fossil fuels still more cost-effective than the production from alternative, clean sources of energy.

CCS technologies are also needed in Bosnia and Herzegovina, but there is also the need for legal and regulatory framework regulating CCS. Development of ability to adopt new technology, additional efforts in order to solve transport, storage, location choices, monitoring, leakage responsibilities, property rights, environmental issues and public perceptions are the issues that require time and finance, which are mostly missing, so the technology implementation process is significantly slowed down. It has been shown that the necessary investments in the CCS will come only if there are adequate financial incentives and regulatory mandates[5].

The development of CCS technology can potentially provide developing countries, as well as Bosnia and Herzegovina, a shift away from fossil fuels energy and the gradual abolition of the same. Determining the potential of alternative media that represents an environmental load, which is available in sufficient quantities, with a low price, for whose disposal is currently paid, as a carbon extraction medium in CCS technologies, could be of great importance in this respect. Such an approach can also be helpful in terms of the environmental performance of the emitters, but also provide the basis for improving the implementation of CCS technology, and additionally

purchase the time needed to switch to other materials and technologies with low carbon contents.

The idea of using recurrent water from slag and fly ash disposal pond Jezero II of Thermal Power Plant Tuzla, as an alternative medium for capturing CO_2 has been imposed on itself, knowing the above stated desirable properties that such a medium should hold and which correspond to the properties of recurrent water.

MATERIALS

(1) Recurrent water was supplied from disposal pond Jezero II of Power Plant Tuzla. The samples were taken 2017, March 28.

Power Plant Tuzla uses water for various purposes. A very significant quantity of water, from 1200 to 1500 m^3/h is used as a transport fluid for the hydraulic transport of slag and ash from the thermal power plant to the disposal pond Jezero II. Waste water is largely free of suspended matter, it is relatively clear however, regular water analyses show:

– significant alkalinity expressed as $CaCO_3$ content (460-1900 mg/L),
– very high pH value from 10.5 to 13,
– pronounced toxicity.

This waste water is not in accordance with the criteria specified by the legal regulations, i.e. by the applicable ordinance[6]. Power Plant Tuzla has therefore started closing the circle of this water into recycle, so now water is not released into surface water in normal operation, and therefore does not represent a waste stream. However, under certain circumstances (especially in the case of high precipitation), recurrent water flows into the drainage to the surface water, so that its parameters become important from the environmental point of view. Additionally, the recurrent water is treated with additives in order to prevent the creation of fouling in the pipeline, so that the reduction in the content of the substances causing the fouling would be highly desirable from an economic point of view.

Hence, by hydraulic transport, suspension of slag, ash and water arrives to the disposal pond Jezero II, where the slag and ash are deposited with natural decantation, and the discharged water from the pond drainage system and the drainage channel (drain E3) in regular operation returns to the Thermal Power Plant and is reused for the same purpose; or it is discharged into the natural recipient – the River Jala[7] (in the event of an excessive amount, mainly due to high precipitation).

(2) Carbon dioxide was supplied from MESSER Ltd Tehnoplin (Schl. Nr. ELN 13891L10 Typ TG 400 Nr 11133 ND2 MM – 530) – 5 kg tank.

EXPERIMENTAL

The apparatus was assembled from:

– Glass beaker 3 L;
– Magnetic stirrer (Tehnica Železniki);
– pH-meter (WTW InoLab 720) with SenTix®41 electrode;
– Rotameter (MLW/ WEB MLW PRUFGERATE – WERK MEDINBGEN/ SITZ FREITAL 1 GDR) 3 L/h;
– Glass aspirator (Intos Boral Pula);
– Two diffusers (airstones).

The picture of apparatus is given in the Figure 1.

Figure 1. Assembled apparatus

A glass beaker with a sample of recurrent water, in an amount of 2 L was placed on a magnetic stirrer. In the same beaker, the immersed electrode was previously kept in 3 mol/L KCl, and washed with distilled water. From the CO_2 tank, gradually and very slowly moving the valve, gas was released, and through the rubber hose was passed through a glass aspirator, which actually serves as a buffer tank for preventing the flow fluctuation. The aspirator was connected to the rotameter with a rubber hose, and owing to its scale, the gas flow was monitored, read, and continuously maintained at 1 L/h. The rubber

hose, through which CO_2 flowed from the rotameter, was placed in the glass beaker containing the recurrent water. At the end of the hose that plunged into water, a Y-shaped extension was attached with two diffusers (airstones) on its two ends. The diffusers serve to form smaller bubbles of CO_2 as much as possible, thereby increasing the surface of the gas in contact with the aqueous medium, for the purpose of better gas dissolution in water, and at the same time prolonging its retention. A magnetic stir bar was also placed in the glass cup.

Three series of experiments were performed, with different setups:

- Series 1 - without installed gas diffusers;
- Series 2 - with installed gas diffusers;
- Series 3 - with installed gas diffusers, for shorter time.

Each series of measurement consisted of three consecutive measurements, with identical parameters.

The average values of experimental results are shown graphically.

RESULTS AND DISCUSSION

SERIES 1

During the measurements, pH and temperature values were monitored for every 60 and then 30 seconds. The initial pH value was 12.93, temperature 21.5°C with a volume flow of 1 L/h. At the end of the measurement, monitored pH value was 6.25 and temperature 22.4°C. A rise in temperature of 0.9°C corresponded to a decrease in pH to a value of 6.68. The pH was kept constant, until a sudden decrease of pH value below 7 at about 19 minute of experiment. Measured pH values were incorporated into formulas for expressing the concentration of $[H]^+/[OH]^-$ ions in order to graphically display the dependency of average concentrations of $[OH]^-$ ions from time *t*. In this regard, a shortened time scale is given, with the aim of a clearer representation of the important 'moment' of the measurement series, when a significant decrease in the pH value occurred.

Starting from the onset of the experiment, the initial concentration of $[OH]^-$ ions, 0.085 mol/dm^3, was decreasing for about 19 minute, after which the pH of the solution went to 'acidic' values, and it is to assume that from this moment, part of the formed residue was dissolved, which can be concluded from the fact that from that moment the solution began to clarify.

SERIES 2

Measurements were done, with monitored pH and temperature values, for every 60 seconds. The initial pH value was 12.86, temperature 21.5°C with a volume flow of 1 L/h. At the end of the measurement series, pH was 6.02 and temperature 23.5°C. While the temperature increased by 2°C, the pH value decreased by 6.84. The pH value was kept relatively constant, with a slight decrease until about the 9th minute, when the significant decrease in pH happened, leading to a 'drop' of pH below 7, after which pH was kept relative constant to about 6, and thus until the experiment was completed. pH values were translated to the concentration of [OH-] ions whose dependency of the average values of time *t* is shown graphically with a shortened time scale for the same reason as in the series 1, for a clearer view of the 'moment' of the measurement series when a significant 'drop' in pH values occurred.

From the very beginning of the experiment implementation, the initial concentration of $[OH]^-$ ions, 0.07 mol/dm^3, was decreasing until about the 11th minute of experiment, after which pH of the solution went into 'acidic' values. A part of the formed residue was dissolved, and the solution was slowly beginning to clarify.

SERIES 3

The third series of measurements was carried out for the purpose of indicating the potential of recurrent water for capturing CO_2. Measurements were carried out to the point of noticeable pH change, with an average time of 19 minutes, monitoring pH and temperature values every 60 seconds (the first 10 measurements), and then for 30 seconds until the end of the experiment. The initial pH value was 12.76, temperature 22.6°C, with a volume flow of 1 L/h. At the end of the measurement series, the pH was 7.9 and temperature 23.4°C. The increase in temperature of 1.8°C corresponded to a pH reduction of 4.86. The pH value was kept relatively constant, until about the 18th minute of the experiment, when a significant decrease was observed, and the pH dropped below 8, after which the experiment was stopped (after 19 minutes), in order to avoid the re-dissolution of the residue. At that moment, a total of 0.32 L CO_2 was transmitted. The pH values on the same principle as in the series 1 and 2 were translated to the concentration of $[OH]^-$ ions, for the same reason. The initial concentration of $[OH]^-$ ions, slightly less than 0.06 mol/dm^3, from the beginning of the experiment, decreased until about the 18th minute of experiment progression, when pH value of the solution went to the 'acidic' values.

After completion of the third series of measurements (shortest one), the resulting residue was filtered, dried, and weighed. The characterization of the

formed residue was not performed, but it was assumed that this 3.566 g of residue was mainly composed of calcium carbonate. If so, it could be concluded that the 2 L of recurrent water captured cca 1.57 g CO_2, which could be roughly taken as the minimal potential for CO_2 capture.

Carbon dioxide within the solution reacted with the molecules of the medium, but only a small part, so carbonic acid was formed in a small concentration. Water containing a lot of carbon dioxide has a low pH, 6-7. In relation to this, and according to the graphic presentation (Figure 2) where the pH dropped between 6 and 7, the used medium "captured" the maximum possible amount of CO_2, which would represent a breakthrough capacity for capturing CO_2.

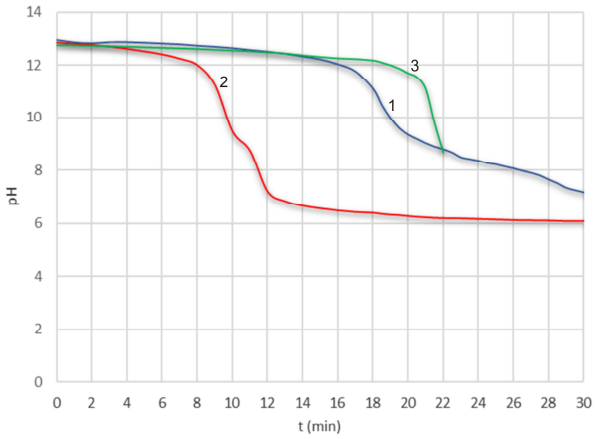

Figure 2. pH vs time for all three series together

Based on the determined concentrations of $[OH]^-$ ions, which decreased during all three series of measurements (Figure 3), it can also be determined that the used medium or wastewater shows a certain ability to capture CO_2.

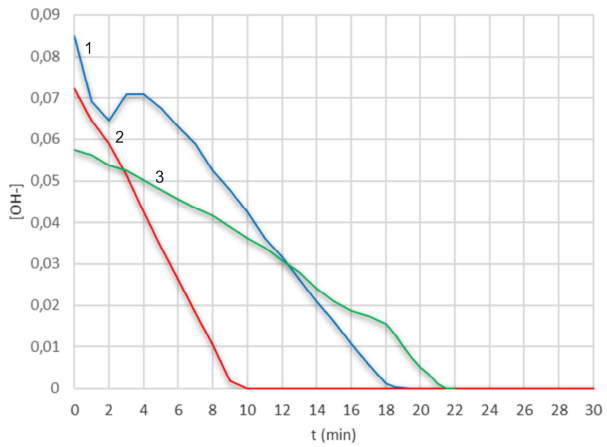

Figure 3. $[OH]^-$ vs time for all three series together

CONCLUSIONS

During all three series of measurements, with minor deviations, the recurrent water showed similar properties in contact with CO_2 gas. Therefore, it was possible to determine the capacity to capture carbon dioxide in all measurement series. Also, the recurrent water from the disposal pond Jezero II has shown satisfactory results in terms of application in CCS technologies, and has become a good candidate for consideration when it comes to wider application in the environment, perhaps not as an independent medium, but certainly in combination with other media, especially if CCS is combined with flue gas desulphurization by wet process.

Hence, recurrent water has a composition that is not in accordance with the legislation; certainly represents the load for the ecosystem; it is available in an ample amount without any costs; its disposal into the environment causes the costs and, according to the results of this research, it has a potential for capturing the CO_2. Taking all these facts into account, it could be concluded that the recurrent water from slag and fly ash disposal ponds of Power Plant Tuzla could be a convenient medium for use in CCS technologies.

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CONTROL OF HEAVY METAL CONTENT IN DIFFERENT TYPES OF VEGETABLES PRODUCED IN THE AREA OF ZENICA

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT: In this study, concentrations of lead Pb, cadmium Cd and arsenic As were tested in 177 samples of fresh vegetables produced in the area of Zenica. This locality is exposed to the strong influence of high emissions of various pollutants primarily originating from metallurgical and thermal power plants, but also from local heating plants. The accumulation of heavy metals is followed by the types of vegetables: tuber and root, bulb, leaf, fruiting and legume from the group of fruiting vegetables. Preparation of samples was done with microwave digestion. The concentration of the selected metals in solutions after digestion was determined on Induced coupled plasma mass spectrometry (ICP-MS). The percentage participation of contents Pb, Cd and As, either higher or lower than the maximum allowable amount prescribed by the applicable law, was calculated in all 177 samples. The results showed that different groups of vegetables have different ability to adopt and accumulate heavy metals. The largest number of samples containing Pb content above the maximum level (ML) was in the group of leaf vegetables, then in the roots and finally in bulb groups. Cd was at the very limit with the maximum level in the parsley sample, while all other tested samples were in compliance with the applicable regulations. Two of the tested samples of the parsley leaves group had an increased content of As according to the legal regulations.

KEYWORDS: heavy metals, vegetables, maximum level (ML)

INTRODUCTION

The development of technology has brought to progress and serious damage of the eco-system. The area of Zenica municipality is under a strong influence of high emissions of different pollutants which are primarily derived from metallurgical and thermal power plants as well as from local boilers and other smaller environmental pollutants. Emission of different gases and solid particles results in contamination of soil, water and plants. Particularly threatened is the quality of agricultural crops that are constantly exposed to unfavourable impacts, leading to the accumulation of certain toxicants in plants. That is why this aspect of the research devotes great importance to determination of accumulation and effects of toxic substances in the diet chain. The term "heavy metals" is often used for a group of metals and metalloids that are related to toxicity, potential toxicity and ecotoxicity[1]. According to toxicity, metals and metalloid ions can be divided into three groups[2].

The first group includes metals (metalloids) which are toxic regardless of their concentration (lead, cadmium, mercury). Metals of the second group (arsenic, bismuth, indium, antimony and thallium) are less toxic, i.e. they are toxic only at higher concentrations. In the third group are metals (metalloids) of essential importance, such as copper, zinc, cobalt, selenium and iron, which are necessary for various biochemical and physiological processes in the body, and are toxic only above the certain concentration.

Concentration of essential and toxic heavy metals in ecosystems is continually increasing due to anthropogenic processes of urbanization, industrialization, transport, agricultural production and military activities. Production and industrial processes and road traffic are the most important for the deposition of zinc, copper, lead, cadmium and nickel and thermal power plants for arsenic[3].

As it is related to toxic substances which in a very low concentrations have a harmful effect on human health (mutagenic, teratogenic and carcinogenic effects), regular control of their presence in vegetables is gaining ever greater significance, especially given the fact that vegetables are consumed on a daily basis. In order to protect the health of the consumer, in the world and even in our country, the maximum level (ML) of metals in vegetables is regulated by normative regulations.

Plant adopts heavy metals from the soil through the root system, but also through the shoot system. Heavy metals that are deposited on the surface can often be eliminated by the washing, while bioaccumulated are difficult to remove[4].

Depending on the fact which plant organ is used in the diet, the following groups of vegetable crops are distinguished: bulb, fruiting, leafy, root vegetables. The categorization of the ability to accumulate heavy metals in important cultivated plants has a practical value because it provides the choice of species in relation to the level of loading of soil by heavy metals. So on land that is contaminated with heavy metals, it is not desirable to grow salad, spinach and so on.

MATERIALS AND METHODS

177 vegetable samples (fruits, leaves, tubers and bulbs) were collected at a phase of useable value. The vegetables were sampled from the locations which were from 0.1 up to 18 km far from a steel plant in Zenica. All samples were analyzed on lead, cadmium and arsenic. They were grouped into the following types of vegetables:

- tuberous and rooted vegetables (potatoes, carrots, parsley),
- bulb vegetables (red onion, white onion, young onions, leek),
- leafy vegetables (chard, lettuce),
- fruiting vegetables (tomato, pepper, cucumber, eggplant),
- legume from the group of fruiting vegetables (beans, peas, green beans).

The reason for the isolation of vegetable crops of legume vegetables in a special group belonging to the fruiting vegetable group is the separation within the regulation according to which the maximum level of heavy metal is determined[5].

Analyzes were done according to the accredited method "Determination of Trace Elements - Lead, Cadmium and Arsenic in Fruit and Vegetable by ICP-MS Method, after microwave digestion"[8]. For this method, the quantification limits (LOQ) for lead is 0.020 mg/kg and for cadmium and arsenic 0.004 mg/kg.

Sample preparation was performed in a microwave oven for digestion (MDS-8, Sineo). Microwave sample preparation technology is widely used in modern laboratories worldwide, due to their high speed, high efficiency, with the necessary characteristics related to protection of the environment, etc.

Microwave digestion involves rapid heating by direct absorption of microwave energy. This technology applies the closed digestion vessels to achieve a high temperature and high pressure.

The sample for analysis was prepared by removing inedible parts such as claws, leaves, seeds and so on, and washing with water. Then, the complete homogenization of the sample was carried out, by milling in a mixer or a mill. The sample mass used for the analysis was 1 g of wet mass.

Exposition (disquisition) of samples was done in concentration of minimum 65% HNO_3 (suprapur) and H_2O_2 (suprapur) minimum 30%.

The presence of elements in samples was read on the Induced coupled plasma mass spectrometry (ICP-MS), Agilent Technologies 7700x.

For calibration of instruments, at least three different concentrations of calibration solutions were prepared and used. The concentration range was selected in relation to the expected concentration of the analyte in the investigated sample. For these analyses, Multi-Element Calibration Standard concentration of 10 mg/l and internal standard Mix 100 mg/l concentration were used.

Concentrations of heavy metals were monitored according to the current regulation "Ordinance on maximum permissible quantities for certain contaminants in food, BiH Official Gazette No. 68/2014"[5]. According to this Ordinance for vegetables, it is necessary to determine lead, cadmium and arsenic.

RESULTS AND DISCUSSION

Developments of the industry, agriculture, transport and urbanization have resulted in excessive emissions of heavy metals into the environment, which due to their bio-accumulative properties have their negative impacts on the environment and living organisms as a whole. In this paper, the presence of lead, cadmium and arsenic in grown vegetables in the area of Zenica is presented. All 177 samples were classified by vegetable groups and the percentage of samples with lead, cadmium, arsenic content higher and lower than the maximum level (ML) were calculated.

From 59 examined samples in the group of tuberous and rooted vegetables, 41 had content of lead below the limit of quantification. 14 samples ranged from 0.035 to 0.096 mg/kg, as permitted by the Regulations[5,6,7]. Four samples had lead content higher than allowed. The cadmium content in 16 samples was within the range of 0.019 to 0.050 mg/kg. Only one sample had higher concentration than ML, while 42 samples were below the limit of quantification. There were no samples with arsenic content higher than allowed in tuberous and rooted vegetables. 51 samples had the amount of arsenic below the detection limit, while eight samples varied from 0.020 to 0.083 mg/kg.

42 samples were analyzed in the group of bulb vegetables. The content of lead was below the limit of the quantification method in 36 samples. Four

samples had the concentration within the permissible limits of 0.043 to 0.064 mg/kg, while two samples had higher concentration than ML (0.523 and 1.296 mg/kg). According to the Regulations in this group of vegetables, the content of lead should not be higher than 0.10 mg/kg. The cadmium content in 37 samples was below the limit of quantification. Five samples had the concentration within the permissible limits (0.031 to 0.041 mg/kg). The samples with cadmium content higher than allowed did not exist. 36 samples had the arsenic content below the limit of quantification. In six samples the content was within the permissible limits and ranged from 0.018 to 0.234 mg/kg. The samples with high content of arsenic were not in bulb vegetables.

Table 1. Lead, cadmium and arsenic content in different vegetable groups (%)

Types of vegetables	Lead		Cadmium		Arsenic	
	n	%	N	%	n	%
Tuber and root	**59**					
<LOQ	41	69.49	42	71.19	51	86.44
Below ML	14	23.73	16	27.12	8	13.56
Above ML	4	6.78	1	1.69	0	0.00
Bulb	**42**					
<LOQ	36	85.71	37	88.10	36	85.71
Below ML	4	9.53	5	11.90	6	14.29
Above ML	2	4.76	0	0.00	0	0.00
Leaf	**28**					
<LOQ	5	17.86	7	25.00	8	28.57
Below ML	16	57.14	21	75.00	18	64.29
Above ML	7	25.00	0	0.00	2	7.14
Fruiting	**31**					
<LOQ	31	100	31	96.77	31	96.77
Below ML	0	0.00	1	3.23	1	3.23
Above ML	0	0.00	0	0.00	0	0.00
Fruiting - legume	**17**					
<LOQ	16	94.12	17	100.00	17	100.00
Below ML	0	0.00	0	0.00	0	0.00
Above ML	1	5.88	0	0.00	0	0.00

28 samples of leafy vegetables were collected and analyzed. Lead content in five samples was below the limit of quantification. In 16 samples lead content ranged from 0.040 to 0.209 mg/kg, and in seven samples it was higher than ML. The highest lead content was found in parsley leaves - 2,385 mg/kg, which is eight times more than the maximum permitted quantity in this type of vegetable and is 0.3 mg/kg. The lead content was increased in salad samples in the amount of 0.767 mg/kg and 0.618 mg/kg, in chard 0.345 mg/kg.

The cadmium in the seven samples was below the detection limit, while in others it ranged from 0.020 mg/kg to 0.156 mg/kg, which is permitted under the Regulations. There were no samples with cadmium content over ML. The amount of arsenic in two samples of parsley leaves was above ML in amounts of 0.563 mg/kg and 0.416 mg/kg. According to the current regulation, the permitted amount is 0.3 mg/kg. Eight samples were below the limit of quantification, and in 18 samples it ranged from 0.020 to 0.191 mg/kg.

Based on the data presented in Table 1, it can be concluded that the content of lead, cadmium and arsenic in fruit crops did not exceed the limit prescribed by the Regulations. In almost all samples the content of the examined elements was even below the limit of the quantification method.

According to the results of the analysis for the content of lead, cadmium and arsenic in legume vegetables from the group of fruiting vegetables it can be concluded that an increased amount of lead was found in only one sample. The content of lead in the pea sample was 0.472 mg/kg and ML was 0.20 mg/kg. All other samples of the legume vegetables from all three locations had the content of lead, cadmium and arsenic below the limit of quantification.

From the results shown, different types of vegetables have different ability to adopt and accumulate heavy metals. The intensity of adoption is primarily influenced by the concentration of heavy metals in the external environment, especially the concentration of dissolved (active) forms of metal, the pH value of the soil, the carbonate content and organic matter in the soil, the degree of soil moisture and so on.

CONCLUSIONS

The development of technology and industry has led to undoubted progress, but also to serious damage of the eco-system. Soil, water, plants, and then animals and humans are contaminated due to the emission of various gases and solid particles. Dominant polluters are spatially and ecologically strongly linked to the city and surrounding settlements and their emissions cause multiple ecological consequences in all components of the ecosystem of Zenica region (air, water, soil, vegetation).

The concentration of lead, cadmium and arsenic in different types of vegetables was as follows:

– In 4 out of 59 samples of tuber and root vegetables or in 6.78% of samples the lead content was above ML. The cadmium content in one sample (1.69%) was higher than allowed,

while the arsenic content of all samples was below ML.

- In 2 of 42 bulb samples or in 2.76% of samples, cadmium content was above ML. Cadmium and arsenic content was in all samples below the maximum permitted limit.
- In 7 of 28 leafy samples, or 25.00% of samples had the lead content higher than allowable. The cadmium content in all samples was below ML, while the arsenic content in two samples (7.14%) was above the maximum allowable amount.
- In 31 samples of fruiting crops, the content of lead, cadmium and arsenic did not exceed the limit prescribed by the Ordinance. In almost all samples, the content of the examined elements was even below the detection limit.
- In 17 samples of legume vegetables from the group of fruiting vegetables only one sample had the lead content above ML, while in other 16 samples the content of lead, cadmium and arsenic was below the detection limit.

From the results of the paper it can be seen that different types of vegetables have different ability to adopt and accumulate heavy metals. The largest number of samples with lead content above the maximum level was in the group of leafy vegetables (salad, leaf of parsley, chard) then in root (parsley, cabbage tail) and bulbous (leek). (Cadmium was at the limit of ML only in sample of root vegetable, while arsenic was above ML in two samples of leafy vegetables). The results of the study show that some cultures should be avoided near the emission centre. Special attention must be paid to the choice of cultures to be cultivated in this area because individual plants have a different affinity for heavy metals.

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POMOLOGICAL CHARACTERISTICS OF THE MOST REPRESENTED AUTOCHTHONOUS APPLE CULTIVARS FROM THE AREA OF NORTHEAST BOSNIA

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT:

Introduction:Autochthonous apple cultivars are present in the life of the population of almost every country. They have economic imporance, especially in the nourishment of the population, as well as very valuable genetic material in breeding process. There is little literature based on scientific methods related to the description of these varieties. Mostly the descriptions of local apple varieties are given through folk tales and poems.

Task of the paper: The aim of this research is the description of autochthonous apple cultivars and creation of preconditions for their registration and their placing in the Bosnian and Herzegovina's list of cultivars.

Results and discussion: Varieties of apples covered by this work were monitored for two years in an *ex situ* collection of autochthonous apple cultivars in Špionica, municipality of Srebrenik. The description of fruits is given through the following parameters: fruit weight, axis height and diameter, fruit index, length of fruit stalk, depth of calix end and firmness of fruits. The results are statistically processed and presented in tables and graphs.

Conclusion: Due to the diversity of the pomological characteristics of autochthonous apple cultivars, their quality and purpose of fruits and because of the longevity that is result of their resistance to unfavorable abiotic and biotic factors of growing, they represent a real small treasure because they are a source of genetic diversity and a factor of biodiversity

KEYWORDS: autochthonous apple cultivars, pomological descriptions, biodiversity

INTRODUCTION

Autochthonous varieties are those varieties that have been related to our region for centuries, whose origin is not known, or if it is known, origin is uncertain[1].

Autochthonous fruit varieties represent significant plant genetic resources that will be especially important in the future. The area of BiH has been exposed to different influences over time. The first recorded data about cultivation of fruit trees in our country originated from the Ottoman Empire[2], but the first official data appeared during the Austro-Hungarian empire[3].

Pomological characterization as the first determinant of fruit and then the morphological and ecophysiological characterisation of these genotypes will be the first evaluation and indetification of apple genetic pool which on at the level of BiH has status of autochthonous cultivars.

The pomological characterization defined with the purpose of research represent the basis for future scientific research work on the standardization of autochthonous genetic pool (pomological and genotypic standardization) and creation of new cultivars adapted to given conditions with certain resistance and predisoposition for the commercial and ecological production of apples in Bosnia and Herzegovina[4].

Detection, collation, characterization and identification of potentially valuable but threatened genetic resources is of primary interest in many countries[5].

The diversity of cultivated plant species is a basis for entire biodiversity in agriculture[6].

Over the past decades, several research on autochthonous fruit germplasm in Bosnia and Herzegovina has been carried out[7], in the review of the results of previous research conducted in the former Yugoslavia, provided that this area has 124 registered wild species of fruit trees and relatives. In this, very important research is done on spontaneous seedlings of fruit trees[7].

Characterization is regular activity in established collections and gene banks, with the aim of more detailed evaluation and removal of possible duplicates. In the available literature, there are data on the characterization of germplasm of autochthonous apple and pear varieties[5, 8, 9].

Traditional methods of cultivar characterization are based on agronomic and morphological parameters and most commonly they are used to distinguish varieties of one species[5]. Characterization of germplasm of one species has huge importance and is the subject of many contemporary researches.

MATERIAL AND METHOD

Assaying included 6 autochthoneous cultivars of apple planted in an *ex situ* collection in Špionica, the plants are 12 years old. The trees of these apples were maintained by usual agro and pomologycal measures as well as chemical protection against pests.

Domestic (autochthonous) genotypes that were the subject of research are some of the most famous and most widely used autochthoneous cultivars in BiH, collected from the five most important fruit regions in BiH (Bosanska Krajina, Posavina, North East BiH, Podrinje and Herzegovina).

Table 1. List of autochthonous apple cultivars of BiH in the collection Špionica – Srebrenik

No	CULTIVAR	CODE
1	Srebrenička	J- VII - 7
2	Senabija	J – X - 3
3	Bukovija	J- VIII - 3
4	Đulabija	J-VII - 1
5	Žuja-Ramićka	J – X - 10
6	Kanjiška	J – XI - 2

The fruits of autochthonous varieties for pomological analyzes are picked at the stage of physiological maturity (which is determined on basis of the number of days from bloom to harvest in the previous years of fruit bearing) from each of the 4 trees and from all parts of crown. The fruits were then transported to the laboratory, where pomological analyzes were performed. Fruit analysis includes the following parameters: fruit weight, axis height and diameter, fruit index, length of fruit stalk, depth of calix end and firmness of fruits.

The average weight of the fruit is determined by weighing 30 fruits of each variety, on a digital scale (Exacta 300 EB) and expressed in grams (g).

Fruit firmness was measured with a GY - 1 manual penetrometer, value expressed in kilograms (1 kg corresponding to a value of 10 N) and a cylindrical probe Ø 11 mm for measuring ranges from 0.5 to 12 kg / cm2

The axis height, diameter, length of fruit stalk and depth of calix were measured using the Vernier calipers, 150 x 0.05.

RESULTS AND DISCUSSION

FRUIT WEIGHT

The average weight of autochthonous apple cultivars in the northeastern BiH in the collection of plant Špionica - Srebrenik, in the period 2016 - 2017, is shown in table 2.

Table 2. Average fruit weight in g

Year / Variety	2016		2017		2016/2017	
	$\bar{x}\pm S\bar{x}$	Vk	$\bar{x}\pm S\bar{x}$	Vk	$\bar{x}$	t
Srebrenička	155.26 ± 3.566	12.37	149.98 ± 2.757	9.90	152.62	1.189
Senabija	92.19 ± 1.826	10.67	90.21 ± 1.492	8.91	91.20	0.853
Bukovija	76.03 ± 1.248	8.84	75.29 ± 1.333	9.54	75.66	0.412
Đulabija	90.01 ± 1.294	7.75	89.39 ± 1.296	7.81	89.70	0.342
Žuja-Ramićka	92.13 ± 1.804	10.55	91.28 ± 1.245	7.35	91.71	0.394
Kanjiška	103.13 ± 3.743	19.55	102.28 ± 1.928	10.15	102.70	0.206

On average, for the both years the largest weight of the fruit had the variety Srebrenička (152.62 g), and the smallest variety Bukovija (75.66 g). Based on the comparison of the average weight of the fruit according to the market criteria for the first class fruit (160-180 g) and the obtained results it can be concluded that the fruits of the analyzed varieties do not belong to the first class fruits.

The variation of the fruit weight, expressed by the coefficient of variation, shows that the variation in the weight of the fruit was more pronounced in 2016 (7.75% - 19.55%), which can be explained by poor climatic conditions.

In 2017, the variation in fruit weight was less pronounced (7.35% - 10.15%) which means that va-

rieties responded equally to favorable climatic conditions.

There were no statistically significant differences in the weight of fruits of the varieties examined in 2016 and 2017.

AXIS HEIGHT

The highest fruit axis height on average for both years had the variety Srebrenička (68.00), and the lowest fruits height on average had the variety Žuja (47.71). From the standpoint of axis height of the fruit of the observed varieties, compared with the standard varieties of apples it can be concluded that these autochthonous varieties do not have an attractive appearance which puts them in the other plan at choice of customers.

The variation of the fruit axis height, expressed by the coefficient of variation, shows that variation at the axis height of the fruit was slightly less in 2016, which indicates that the axis height of the fruit depends more on the hereditary characteristics of the variety than on the climatic conditions. Observing the significance of the differences in the fruit axis height of the varieties in 2016. and 2017. is observed that the variety Kanjiška had a statistically significantly lower fruit height, and the variety of Srebrenička highly significant lower fruit height than in 2017. In the case of other varieties these differences were not statistically significant.

Table 3. Average fruit axis height in mm

Year / Variety	2016		2017		2016/2017	
	$\bar{x}\pm S\bar{x}$	Vk	$\bar{x}\pm S\bar{x}$	Vk	$\bar{x}$	t
Srebrenička	71.60 ± 1.508	11.35	64.40 ± 1.703	14.25	68.00	3.218
Senabija	53.00 ± 0.734	7.45	51.59 ± 0.677	7.07	52.30	1.436
Bukovija	57.98 ± 0.931	8.65	57.61 ± 1.408	13.17	57.80	0.227
Đulabija	54.07 ± 1.256	12.52	52.77 ± 1.100	11.23	53.42	0.792
Žuja-Rami	51.17 ± 0.873	9.19	49.35 ± 0.848	9.26	50.04	1.520
Kanjiška	48.52 ± 0.690	7.67	46.91 ± 0.598	6.87	47.71	1.795

FRUIT DIAMETER

Fruit diameter of autochthonous apples in BiH, as well as axis height of the fruit, is important from the agronomic point of view and for the market of the fruits, because a harmonious relation of height and width of the fruit makes the fruit attractive for the market.

The average fruit diameter on average for both years had variety Kanjiška (78.305 mm), and the smallest fruit diameter on average had variety Bukovija (60.310 mm).

Table 4. Average fruit width in mm

Year / Variety	2016		2017		2016/2017	
	$\bar{x}\pm S\bar{x}$	Vk	$\bar{x}\pm S\bar{x}$	Vk	$\bar{x}$	t
Srebrenička	74.20 ± 1.830	13.28	72.59 ± 1.707	12.67	73.39	0.654
Senabija	76.57 ± 2.181	15.34	76.00 ± 2.062	14.61	76.28	0.193
Bukovija	61.20 ± 2.242	19.73	59.41 ± 2.241	20.32	60.31	0.574
Đulabija	68.30 ± 1.720	13.56	67.79 ± 1.700	13.51	68.04	0.217
Žuja-Ram	72.60 ± 1.535	11.39	72.59 ± 1.707	12.67	72.59	0.004
Kanjiška	79.80 ± 1.334	9.01	76.81 ± 1.529	10.72	78.31	1.499

The variation of the fruit diameter, expressed by the coefficient of variation, shows that variation of fruit diameter was less insignificant in 2016 indicating that the diameter of the fruit depends more on the hereditary characteristics of the variety rather than climatic conditions. Observing the significance of

differences in fruit diameter of the varieties in 2016 and 2017 it was noticed that it is not statistically significant.

Based on fruit diameter and criteria in the European market (65-90 mm I class), we can say that most of the investigated cultivars (except Bukovija) have the fruits of the I class. However, the ratio of axis height and diameter of the fruit that is expressed through the fruit index is unfavorable.

FRUIT INDEX

Fruit index represents the ratio of axis height and diameter of the fruit (table 4) and was used for the detection of the shape of the fruit by the following scale: less than or equal to 0.90 - flattened fruit, from 0.90 - 1.00 elliptical fruit and 1.0 and higher elongated fruit.

Table 5. Fruit index

SN	CULTIVAR	AXIS HEIGHT	DIAMETER	INDEX
1	Senabija	52,3	76,2	0,68
2	Srebrenička	73,4	69,4	1,05
3	Bukovija	60.3	57.8	1.04
4	Đulabija	53,4	68,0	0,78
5	Žuja-Ramićka	50,4	72,1	0,69
6	Kanjiška	47.7	78.3	0.61

On basis of the obtained results of measurements and given parameters, it can be concluded that cultivar Srebrenička and Bukovija have elongated fruit and all other have flattened fruit. According to agronomic and market criteria, the varieties with flattened fruit are not of high market value.

LENGTH OF FRUIT STALK

The length of the fruit stalk is presented in table 6. Besides being a good morphological indicator in the pomologycal description of fruit, it also represents an important pomological characteristic because it keeps the fruit on the tree and prevents fall of fruit. Varieties with longer fruit stalk are easier to harvest.

Table 6. Length of fruit stalk in mm

No	CULTIVAR	2016	2017	$\bar{X}$
		$\bar{x}$	$\bar{x}$	
1	Senabija	7.61	7.33	7.47
2	Srebrenička	10.53	10.76	10.65
3	Bukovija	8.92	8.64	8.78
4	Đulabija	7.84	7.61	7.73
5	Žuja-Ramićka	8.67	8.91	8.79
6	Kanjiška	9.23	8.87	9.05

From this table it can be seen that Srebrenička had the longest fruit stalk on the average (10.65 mm) and the Senabija variety had the shortest on average (7.47 mm). All the investigated varieties had a very short or short stalk. which is a negative characteristic.

FRUIT FIRMNESS

Fruit firmness was analyzed in the physiological maturity of the fruit. In this paper fruit firmness was observed as a significant pomological characteristic which indicates the predisposition of varieties for storage as well as their sustainability in the process of selling fruits. The fruit firmness is shown in table 7 as kg / cm²

Table 7. Fruit firmness

SN	CULTIVAR	2016	2017	$\bar{X}$
		$\bar{x}$	$\bar{x}$	
1	Senabija	7.50	7.40	7.45
2	Srebrenička	6.31	6.36	6.33
3	Bukovija	6.00	6.16	6.08
4	Đulabija	6.82	6.88	6.85
5	Žuja-Ramićka	7.43	7.52	7.47
6	Kanjiška	6.42	6.49	6.45

From the results in table 7 we can make conclusion that the fruits of these autochthoneous cultivars have soft and spongy fruit flesh. only the Senabija and Žuja-Ramićka cultivars have somewhat harder flesh. The Western European market is looking for hard and crunchy flesh of apple fruits. so it can freely be said that this is one of the reasons for reduced production of these cultivars. They are more of a local importance and are nostalgically related to our childhood.

CONCLUSIONS

1. A pomological analysis of fruit of autochthoneous apple cultivars creates the basis for the registration and placing of these varieties on the cultivar list. So far, very few papers have been published on this subject. and especially papers based on scientific methods.

2. The fruits of these varieties belong to a group of smaller fruits and are not attractive to the market

3. The relation between axis height and diameter of the fruit. or the fruit index. is not in accordance with market requirements.

4. They are of local importance and are used to make traditional apple product- pekmez.

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KINETIC MODELLING OF COOKIE BROWNING DURING BAKING

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT:
The modern food industry relies on the application of the Maillard reaction to produce many foods, e.g. coffee and bakery products that possess the colour and flavour demanded by the consumer. The aim of this study was kinetics modelling of cookie browning during 10 minutes of baking at 205°C in order to predict the cookie lightness variation during baking. Cookies were produced according to AACC Approved Method 10-50D from a commercial cookie plain white flour and wholegrain flour. Baking quality of used flours was determined using Alkaline water retention capacity (AWRC) and Solvent retention capacity (SRC) methods and by measuring width (W), thickness (T), W/T ratio (cookie spread factor) and volume of cookies. Both type of flour was used to make three types of mixing distinguished in water addition (standard-S; dry-D and wet-W formula). The colour of samples was measured using digital image analysis, and quantified using CIE*L*a*b colour model. Several mathematical model was proposed to predict the development of browning during baking (zero-, first- and second-order kinetics model). Lightness (*L**) variation were supposed to be representative of colour formation reaction. Comparing all the results of surface and bottom cookies lightness, the cookies with the plain white flour and standard addition of water had the lowest value of lightness change. The evolution of lightness appears to follow a second-order kinetic of cookies made from wholegrain flour, and evolution of lightness of cookies made from plain white flour followed zero-order kinetic. According to obtained results, all tested kinetics model can be used for modelling of cookie browning. Kinetic model is also suitable to suggest how baking profiles should be changed in order to obtain products with a different final lightness.**

KEYWORDS: cookies, colour, lightness, digital image analysis, kinetics model

INTRODUCTION

The colour is the first sensation that the consumer perceives. The overall appearance of any object is a combination of its chromatic and geometric attributes. Both of these attributes should be accounted for when making visual or instrumental assessment of appearance. Some of the instruments commonly used for colour determination are colorimeters, spectrophotometers, comparator charts or colour discs which proved to be useful tools for colour measurement. Colour measurement is an important tool for determining and monitoring quality of the bakery product[1]. Changes in bakery product colour can be associated with its previous heat treatment history. Various reactions such as pigment destruction (carotenoids and chlorophylls) and non-enzymatic browning reactions can occur during heating and therefore affect its colour[2]. The yellow-gold colour formation during baking is often called browning, and is the results of sugar degradation. Formation of coloured compounds during baking is product of chemical reactions specifically caramelisation and Maillard reactions. These reactions are activated by the higher temperature and lower water content in cookies during baking[3]. Direct heating of carbohydrates produces complex reactions namely as caramelisation reactions, were at high temperature sugars decompose into furfural compounds. Maillard reactions involve reducing sugar (glucose and fructose), protein (aminic compound) and some water. The Maillard reaction is influenced by temperature, pH, moisture content, presence or absence of metallic cations, and inner sugar structure. Particularly, the reaction is accelerated at medium moisture level and high temperature[2].

In recent years significant changes have occurred in objective colour measurement methods with advancements in computer hardware and software and digitalization technology. Image processing and image analysis are recognized as being the core of computer vision. This system known as computer vision has proven to be successful for objective measurement of various agricultural and food products. Computer vision includes the capturing, processing and analysing images[4]. Flatbed scanners, cameras and various software are finding increased applications

for colour measurement and monitoring. Scanner is a device that optically scans object and converts it to a digital image, which is then transferred to a computer. The scanner head (includes mirrors, lens, filter and Charge Coupled Device (CCD array) move over the document line by line by belt attached to steeper motor. Each line is broken down into "basic dots" which correspond to pixels. A captor analyses the colour of each pixel. The colour of each pixel is broken down into 3 components (red, green, blue). Each colour component is measured and represented by a value. For 8-bit quantification, each component will have a value between 0 and 255 (28-1=255). Scanners typically read red-green-blue colour (RGB) data from the array. The scanned result is a non-compressed RGB image. Flatbed scanning is fast, easy to use, cheap, robust, independent of external light conditions, and with good accuracy. Computer vision and image analysis, are non-destructive and cost-effective techniques for sorting and grading of agricultural and food products during handling processes and commercial purposes. Therefore, the objective of this research study was the mathematical modelling of cookie browning (made of different recipes) during baking in order to apply it for optimization of baking process.

MATERIAL AND METHODS

COOKIE BAKING AND EVALUATION OF BAKING QUALITY OF FLOUR

Cookies were produced according to AACC Approved Method 10-50D[5] from commercial cookie plain white flour (Belje d.d. Beli Manastir, Croatia) and wholegrain flour (Podravka d.d., Koprivnica, Croatia). The other ingredients were shortening, dextrose, sucrose, sodium chloride and sodium bicarbonate from a local market.

Cookie flour quality evaluation was conducted using Alkaline water retention capacity (AWRC) and Solvent retention capacity (SRC) methods (AACC Methods 56-10[6] and 56-11[7]). Sodium bicarbonate (5%) was used for AWRC determination and four solvents were independently used to produce four SRC values: water SRC, 50% sucrose SRC, 5% sodium carbonate SRC, and 5% lactic acid SRC.

The cookie doughs were prepared by weighing the appropriate mass of each constituent and mixing the ingredients using an electronic mixer (Gorenje MMC800W, Slovenia) with a flat beater. Three different amounts of water were used: standard (S) with 16 g water/225 g of flour (AACC Method 10-50D), dry (D) with 12 g water/225 g of flour and wet (W) with 20 g water/225 g of flour.

Baking process was conducted in a convection oven (WiesheuMinimat Zibo, Wiesheu GmbH, Germany) during 10 minutes at 205°C with the precision of ±1°C.

Baking quality of cookie flour was determined in six cookies (AACC Method 10-50D) by width (W), thickness (T), and W/T ratio (cookie spread factor). Cookie volume was measured with the use of Volscan Profiler (Stable Micro Systems, UK).

IMAGE ACQUISITION OF COOKIES

Computer vision (CV) was used to evaluate cookies browning variation during baking. The method was based on scanning cookies samples using a flatbed scanner, processing the colour images using ImageJ software, and representing results in CIE$L^*a^*b^*$ colour space as a function of the flour type, cookie recipe and baking time respectively. Acquisition is the first step in colour sample measuring. Images can be acquired by scanners and cameras etc. Appropriate lighting and high-quality optics and electronic circuitry are critical in acquiring high quality images. In this paper flatbed scanner (Epson V500 photo) was used for image acquisition. To avoid external light conditions, scanner were placed in black box. After acquiring image, the process of converting pictorial images into numerical form is called digitisation. For this purpose *ImageJ* software were used to analyse image file created after digital scanning for colour parameters. Since digital images are acquired in the RGB colour space, colour parameter were transformed from RGB to CIE$L^*a^*b^*$ parameters as reported by León et all.[8]. All data were presented as mean values of at least three replicates.

MATHEMATICAL MODELLING OF BROWNING KINETICS

The kinetic parameters (browning rate constant, k) are determined by least-square method implemented in *Mathcad* based on the experimental data of baking of cookies during 10 minutes at 205°C. The model which have the smallest RMSE and the highest R values were chosen for prediction of cookies browning during baking.

In this paper three kinetic models were used based on cookie lightness changes and determined corresponding kinetic parameters (reaction rate constant). We have use approach of applying simple kinetics zero-, first-, and second-order kinetics for browning, represented by the variation of cookies lightness L^* during cookies baking. In the form of a zero-order kinetics for browning, represented by the variation of surface lightness L^* following equation is:

$$L^* = L_0^* - kt$$

With L_0^* the initial lightness of the sample, k the reaction rate constant (rate of browning), and t time.

Zero-order reactions are rather frequently reported for changes in foods, especially for formation reactions when the amount of product formed is only a small fraction of the amount of precursors present[9]. A frequently reported example of a zero-order reaction is the formation of brown colour in foods as a result of the Maillard reaction.

Another frequently used equation is first-order equation:

$$L^* = L_0^* \cdot exp(-kt)$$

or in its logarithmic form:

$$\ln L^* = \ln(L_0^* - kt)$$

and finally a second-order equation is sometimes encountered:

$$\frac{1}{L^*} = \frac{1}{L_0^*} + kt$$

Second-order reactions are sometimes reported for changes of amino acids involved in the Maillard reaction.

RESULTS AND DISCUSSION

Alkaline water retention capacity (AWRC) and Solvent retention capacity (SRC) are frequently used methods for determining cookie flour quality, especially when we need quick results, if there is a lack of equipment for determination of dough rheological properties, or if only a small amount of sample is accessible. These methods are used to determine flour capacity of holding different solutions after centrifugation. Lactic acid SRC is associated with gluten characteristic, sodium carbonate SRC is associated with levels of damaged starch, sucrose SRC is associated with pentosane characteristics while water SRC and Alkaline Water Retention Capacity (AWRC) are influenced by all of those flour constituents combined[6, 7].

Table 1. Alkaline water retention capacity (AWRC) and Solvent retention capacity (SRC) of flour

Wheat flour	AWRC (%)	SRC (%)			
		Water	Sucrose	Sodium carbonate	Lactic acid
Plain white flour	61.6±0.4[b]	62.6±0.6[b]	141.0±3.9[a]	70.3±0.6[b]	140.2±0.5[a]
Wholegrain flour	70.1±0.4[a]	65.5±0.3[a]	134.3±0.6[b]	78.7±0.9[a]	131.2±1.8[b]

Values are means ± SD of five measurements. Values in the same column with different superscripts are significantly different ($p< 0.05$)

Results showed that AWRC, water and sodium carbonate SRC values increased and sucrose and lactic acid SRC decreased when wholegrain flour was used instead of commercial cookie plain white flour (Table 1). This can be explained with the higher water absorption and weaker gluten of the wholegrain flour. Also, use of wholegrain flour significantly increased width and spread factor of cookies while volume and thickness were not affected (Table 2) which can be also explained by higher water absorption and weaker gluten. These results are in accordance with previous studies conducted by several investigators[10,11].

Table 2. Baking quality of cookie flour

Wheat flour	Volume (cm^3)	Width (cm)	Thickness (cm)	Cookie spread factor W/T*10
Plain white flour	49.5±0.7[a]	6.79±0.13[b]	1.31±0.02[a]	51.8±0.6[b]
Wholegrain flour	49.0±0.9[a]	7.02±0.24[a]	1.31±0.07[a]	53.6±1.1[a]

Surface browning is a common phenomenon for cookies during baking. Colour development only begins when sufficient amount of drying has occurred in cookies and depends also on the drying rate and the heat transfer coefficient during the different stages of baking.

Three colour models can be used to define colour; those are RGB (red, green, and blue) model, the CMYK (cyan, magenta, yellow and black) model, and the CIE*L*a*b** model. The *L*a*b** model is an international standard for colour measurement developed by the CIE in 1976. Among the three models, the *L*a*b** model has the largest gamut encompassing all colours in the RGB and CMYK gamut's, and *L*a*b** values are often used in food research studies. Unlike the RGB and CMYK colour models, CIE*L*a*b** colour is designed to approximate human vision. It aspires to perceptual uniformity, and its*L** component closely matches human perception of lightness. The *L*a*b** colour space is perceptually uniform and the most complete model, device-independent, absolute model to be used as a reference. *L** is the luminance or lightness component, which ranges from 0 to 100, and parameters *a** (from green to red) and *b** (from blue to yellow) are the two chromatic components, which range from –120 to 120.

Formation of colour has been measured by computer vision, indirect method which quantify the amount of reflected light by the surface of the cookies and results are given in the CIE*L*a*b** colour space[8]. Colour formation is caused by group of complex chemical reactions, it can be simplified by assuming a general mechanism of browning, and followed by using colour models related to reflectance methods, for technological purposes[12].

In this study CIE*L*a*b** colour model was used to quantitatively describe the colour change of the cookies during baking[13]. Lightness is a good descriptor of the browning progress since it represents the intensity of images, and is decoupled from colour changes denoted by *a** and *b** values[13].

Table 3. Variation of cookie surface lightness (*L**) during baking

*L**	Plain white flour			Wholegrain		
Baking time [min]	**D**	**S**	**W**	**D**	**S**	**W**
0	78.28	77.06	78.12	51.30	55.05	57.81
1	72.39	71.86	72.74	49.16	52.14	53.43
2	74.03	75.26	75.46	51.84	54.98	55.73
3	75.79	76.77	77.57	58.41	57.14	60.59
4	76.88	78.19	78.93	60.77	61.63	61.76
5	78.02	77.83	77.94	61.16	62.13	61.36
6	74.27	72.96	73.80	60.02	59.94	60.08
7	71.86	68.01	68.96	58.84	58.22	56.79
8	65.93	63.83	65.21	55.56	55.49	54.21
9	64.55	59.11	61.05	53.90	53.39	53.39
10	61.39	56.37	57.99	52.06	50.67	52.40

Water addition: standard (S) with 16 g water/225 g of flour, dry (D) with 12 g water/225 g of flour and wet (W) with 20 g water/225 g of flour

Table 4. Variation of cookie bottom lightness (*L**) during baking

*L**	Plain white flour			Wholegrain		
Baking time [min]	**D**	**S**	**W**	**D**	**S**	**W**
0	76.71	77.58	79.33	50.83	55.05	52.40
1	74.24	73.87	75.06	49.36	52.14	56.34
2	75.92	76.31	75.61	57.13	54.98	54.20
3	75.36	73.18	70.06	57.53	57.14	58.41
4	74.12	67.03	62.71	55.09	61.63	58.20
5	63.09	61.37	58.31	52.48	62.13	56.01
6	58.12	55.70	55.52	50.82	59.94	54.84
7	56.78	52.96	52.86	49.39	58.22	50.75
8	53.45	51.57	50.15	47.62	55.49	49.51
9	52.99	49.57	48.71	46.24	53.39	47.98
10	51.35	47.10	46.61	45.30	50.67	46.49

Water addition: standard (S) with 16 g water/225 g of flour, dry (D) with 12 g water/225 g of flour and wet (W) with 20 g water/225 g of flour

Table 3 and Table 4 show the variation of lightness of cookies during baking. It can be seen that the colour intensity of samples increased with baking time, as is expected. Comparing results of plain white flour and wholegrain cookie samples, the cookies with wholegrain flour became darker during baking for all water additions (D, S and W). Similar results were reported byGökmenet all.[14, 15].

Experimental recordings of plain flour and wholegrain cookies surface lightness during baking showed first an enlightenment and subsequently a darkening phase. The darkening phase is initiated in 6th min of baking. The darkening phase of bottom lightness during baking is initiated in 2nd min of baking.

The development of browning in bakery products is the result of the Maillard reaction and caramelization of sugars. Ingredients of baked foods such as bread, cake and biscuit, i.e. carbohydrates, proteins and water, are actually the reactants for these chemi-

cal reactions, which are catalyzed by a low-medium moisture level and high temperature obtained at the product surface during baking[16].

With the aim of predicting and controlling the development of browning during baking, it is necessary to quantify the advance of browning reactions. The best approach to model the browning development would be to consider the actual mechanisms of non-enzymatic reactions and transport phenomena occurring in products during baking. The kinetic approach is widely used for modelling browning.Kinetic modelling establishes that a process can be mathematically described by means of kinetic parameters with the aim of understanding, predicting and controlling the quality changes in food processing[17].

Kinetics parameters should be estimated from experiments close to actual baking conditions. Based on these concept, and selecting cookie lightness (L^*) as browning index, a general model and related kinetic parameters (reaction rate constant) for colour development during baking can be stated. In order to describe the colour change during cookie baking, several kinetics model were used. Model validation can be seen in Tables 5 and 6.

Generally, the resulting modelled lightness profiles are in good agreement with the experimental results. The ability of the kinetic model to predict final lightness (important in terms of cookie sensory evaluation) values are given. Evolution of lightness of cookies surface and bottom made from plain white flour followed zero-order reaction. Browning rate constant k, varied from 1.2045 to 1.4072 min^{-1}. Prediction of lightness during baking was best described by zero-order kinetic model for plain flour cookies with standard water addition (S). Meanwhile, second-order kinetic model is more suitable for browning prediction of wholegrain cookies during baking.

Table 5. Variation of the browning rate of plain flourcookie samples

Sample	**Cookie surface**			**Cookie bottom**		
Water content	**D**	**S**	**W**	**D**	**S**	**W**
	Zero-order					
k_{CVS}**[min^{-1}]**	1.2045	1.5723	1.4072	2.5863	3.1462	3.5726
R	**0.7809**	**0.8045**	**0.7925**	**0.9357**	**0.9725**	0.9824
RMSE	3.3827	4.4443	4.2477	3.5537	2.5730	2.1155
	First-orderlinear					
k_{CVS}**[min^{-1}]**	1.6900E-02	2.2800E-02	2.0200E-02	3.9700E-02	4.9300E-02	5.5500E-02
R	0.7804	0.8007	0.7898	0.9350	0.9707	0.9883
RMSE	0.0485	0.0665	0.0623	0.0559	0.0430	0.0280
	First-order					
k_{CVS}**[min^{-1}]**	1.6300E-02	2.1600E-02	1.9100E-02	3.8500E-02	4.8200E-02	5.5400E-02
R	0.7689	0.7879	0.7774	0.9240	0.9642	0.9863
RMSE	3.4624	4.6073	4.3808	3.8512	2.9302	1.8651
	Second-orderlinear					
k_{CVS}**[min^{-1}]**	2.3799E-04	3.3341E-04	2.9182E-04	6.1681E-04	7.8401E-04	8.7832E-04
R	0.7795	0.7960	0.7867	0.9330	0.9652	**0.9878**
RMSE	6.9994E-04	1.0054E-03	9.2318E-04	8.9769E-04	7.7273E-04	4.7201E-04
	Second-order					
k_{CVS}**[min^{-1}]**	2.2054E-04	2.9533E-04	2.5987E-04	5.7058E-04	7.3291E-04	8.5052E-04
R	0.7573	0.7721	0.7630	0.9094	0.9503	0.9800
RMSE	3.5365	4.7547	4.5021	4.1892	3.4432	2.2515

Table 6. Variation of the browning rate of the wholegrain cookiesamples

Sample	Cookie surface			Cookie bottom		
Water content	**D**	**S**	**W**	**D**	**S**	**W**
	Zero-order					
k_{CVS}[min^{-1}]	0.0654	-0.1591	0.1544	0.1972	0.6749	0.9136
R	0.0728	0.0728	0.1829	0.2894	0.7256	0.8393
RMSE	3.9863	3.9863	4.7848	3.7740	3.0079	2.4786
	First-order linear					
k_{CVS}[min^{-1}]	1.2741E-03	-2.5334E-03	2.8300E-03	4.3404E-03	1.3400E-02	1.7700E-02
R	0.1219	0.1219	0.2128	0.3342	0.7393	0.8426
RMSE	0.0590	0.0590	0.0720	0.0722	0.0569	0.0475
	First-order					
k_{CVS}[min^{-1}]	9.6388E-04	-2.8063E-03	2.3094E-03	3.8552E-03	1.2700E-02	1.7100E-02
R	0.0718	0.0718	0.1811	0.2863	0.7163	0.8283
RMSE	3.9866	3.9866	4.7863	3.7777	3.0502	2.5539
	Second-order linear					
k_{CVS}[min^{-1}]	2.3643E-05	-3.9540E-05	5.0422E-05	9.4637E-05	2.6700E-04	3.4537E-04
R	**0.1576**	**0.1576**	**0.2395**	**0.3736**	**0.7501**	**0.8447**
RMSE	8.7606E-04	8.7606E-04	1.0895E-03	1.3888E-03	1.0885E-03	9.1886E-04
	Second-order					
k_{CVS}[min^{-1}]	1.4202E-05	-4.9522E-05	3.4555E-05	7.5379E-05	2.4063E-04	3.1928E-04
R	0.0708	0.0708	0.1794	0.2832	0.7072	0.8174
RMSE	3.9869	3.9869	4.7878	3.7813	3.0903	2.6259

CONCLUSIONS

During baking, complex chemical reactions take place in cookies, leading to the formation of heat-generated toxicants such as acrylamide. Comparing all the results of surface and bottom cookies lightness, the cookies with the plain flour and standard addition of water had the lowest value of lightness change. Several mathematical model was proposed to predict the development of browning during baking (zero-,first- and second-order kinetics model). The evolution of lightness appears to follow a second-order kinetic of cookies made from wholegrain flour, and evolution of lightness of cookies made from plainflour followed zero-order kinetic. Our experimental measurements also allowed us to use a kinetic model in order to predict colour formation (represented by lightness variations) of a cookies made by different recipes. According to obtained results, all tested kineticsmodel can be used for modelling of cookie browning. Kinetic model is alsosuitable to suggest how baking profiles should be changed in order to obtain products with a different final lightness. Advances in digital photography, flatbed scanners, and software for processing colour images provide a rapid, unbiased, and automated method for estimating the colorimetric parameters of coloured samples. With the developments in hardware and software for image analysis/processing, the applications of computer vision have been extended to the quality evaluation of diverse and processed foods, which has illustrated great advantages of using the technology for objective, rapid, non-contact and automated quality inspection and control.

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5th Scientific Symposium With International Participation „ENVIRONMENTAL RESOURCES, SUSTAINABLE DEVELOPMENT AND FOOD PRODUCTION" - OPORPH 2017

On the occasion of marking the 58th anniversary of the existence of the Faculty of Technology, University of Tuzla was in cooperation with Association of Chemists Tuzla's Canton organized the 5th Scientific Symposium with International Participation **„Environmental resources, sustainable development and food production" - OPORPH 2017**.

The two-day Symposium was held under the motto: "Sustainable development today is the change you want to see tomorrow". The significance of this Symposium is that it covers a wide range of scientific fields, such as: chemical-, biochemical- and food- engineering, environmental protection, applied chemistry and agronomy. The Symposium was attended by local eminent experts, as well as experts from the region and students, which contributed to the International Importance of the Symposium. Over 150 exhibitors participated at the Symposium from Germany, China, Croatia, Serbia, Montenegro, Slovenia, Macedonia, Bosnia and Herzegovina.

This year, the Scientific and Organizing Committee invited eight invited speakers:

- Bruno Zelić, Faculty of Chemical Engineering and Technology, University of Zagreb
- Ljubica Dokić, University of Novi Sad, Faculty of Technology Novi Sad, Serbia
- Zoran Jovović, University of Montenegro, Biotechnical Faculty Podgorica, Montenegro
- Elvis Ahmetović, University of Tuzla, Faculty of Technology, Bosnia and Herzegovina
- Jasmina Ibrahimpašić, University of Bihac, Biotehnical Faculty, Bosnia and Herzegovina
- Stanko Blatnik, IPAK Institut Velenje Slovenia ,
- Zdenko Lončarić, Josip Juraj Strossmayer of Osijek, Faculty of Agriculture Osijek, Croatia
- Mirna Habuda – Stanić, Josip Juraj Strossmayer of Osijek, Faculty of Food Technology Osijek

The aim of the Symposium was to promote scientific research through exchange of experiences and recent achievements in these fields.

This year, an electronic publication of the Book of the Abstracts was made on CD, and was cataloged by the National and University Library of Bosnia and Herzegovina (Book of Abstracts, Univerzitet u Tuzli, Tehnološki fakultet, Tuzla. ISSN 2566-3364).

Vahida Selimbašić,
President of the Scientific and Organizing Committee

INSTRUCTION FOR AUTHORS

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