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[1.] Jelena KIURSKI, [2.] Savka ADAMOVIC, [3.] Jelena KRSTIC,
[4.] Ivana OROS, [5.] Mirjana VOJINOVIC MILORADOV

ADSORPTION EFFICIENCY OF LOW-COST MATERIALS IN THE REMOVAL OF Zn(II) IONS FROM PRINTING DEVELOPER

■ ***ABSTRACT:***

The research objective in this study is to find solutions for immobilization of Zn(II) ions from spent printing developer in the printing industry by adsorption on natural, low-cost adsorbents: activated carbon (AC, Norit Row 0.8 Supra), natural zeolite (NZ, clinoptilolite) and their mixtures (AC+NZ); by doing this, environmentally-harmful metal Zn(II) would be eliminated. Because of the complexity of printing wastewater we studied the adsorption onto various adsorbents, to gain an insight into the influence of heavy metal Zn(II) on the sorption behavior of these adsorbents, the effect of their nature and optimal concentration, and determine the adsorption capacity and the appropriate contact time. Therefore, these adsorbents of the defined pore size and structure were applied to examine their adsorption efficiency in the removal of Zn (II) ions from the spent printing developer sample. Concentrations of Zn(II) ions in fresh and spent printing developers before and after the adsorption were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), using a PerkinElmer Elan 5000 mass spectrometer. The adsorption of Zn(II) ions onto activated carbon, clinoptilolite and there mixture was studied in laboratory batch mode. The adsorption equilibrium data for Zn(II) ions on AC, NZ and (AC+NZ) were analyzed in terms of the Freundlich isotherm model. The results provided strong support for the Zn(II) ions adsorption onto these adsorbents, and all the data fitted well to the Freundlich isotherm ($R^2 \geq 0.988$). The lowest correlation coefficient for Zn(II) ions was obtained using the mixtures of activated carbon and clinoptilolite. The adsorption capacities of Zn(II) ions decreased in the order: AC>NZ>AC+NZ.

■ ***KEYWORDS:***

Equilibrium; Adsorption; Adsorption isotherm; Spent printing developer; Clinoptilolite; Activated carbon; Printing industry

INTRODUCTION

Printing industry is at the top of industrial polluters according to the amount of highly emerging pollutants released into the ecosystem. Due to lack of wastewater treatment and recycling, highly polluted wastewater with emerging inorganic and organic pollutants is present in the printing industry. In Serbia, there is a great deficiency in the adequate facilities for treatment of printing plants wastewaters. Hence, the raw wastewaters are directly discharged into the municipal sewerage, threatening to endanger the water quality because of the potential increase in the concentrations of some metals and organic pollutants (Kiurski 2008; Kiurski 2009; Prica 2010).

In the printing industry waste is generated from the three basic phases of the technological process: pre-press, press and post-press. The offset pre-press process is a complex printing operation which involves the use of many toxic and hazardous chemicals, such as printing developer.

The role of printing developer in the plate or film development process is to convert the latent images to visible ones. The most present components of fresh printing developer are potassium silicate, sodium silicate, sodium carbonate, potassium hydroxide, D-sorbitol, sodium sulfite, potassium bromide, metol [4-(methylamino)phenol sulfate] and hydroquinone. After the development process, printing developer (spent developer) is enriched by plate surface compounds: novolac, organic polymeric binders, photosensitive compounds, dyes and some others. Heavy metal ions found in spent printing developer come from the dye residue. Therefore, in order to have a pollution-free environment, the toxic metals should be removed from wastewater before its disposal. The requirements for an adequate treatment of spent printing developer are to be met, to prevent increased the concentrations of heavy metals and organic pollutants (Shuiping 2003a; Shuiping 2003b;Vengris 2004; Llanes Monter 2007; Oliveira 2007;Vengris 2007; Malakootian 2009) from the printing industry.

Among all the approaches proposed, adsorption of heavy metal on low-cost effective adsorbents is one of the most popular methods, and it is currently considered as an effective, efficient and economic method for liquid waste purification. In the past two decades, researches have been carried out focused on using low-cost sorbents for heavy metal adsorption, like natural zeolites and activated carbon (Rao 2006; Kocaoba 2007). Clinoptilolite, as a most common natural zeolite, has a high sorption capacity and selectivity, resulting from its porosity and sieving properties. Activated carbon, due to its versatility and wide range of applications, is also used as a medium for removal of a variety of contaminants (Babel 2003; Genc Fuhrman 2007).

The aims of the study were to examine the efficiency of natural, low-cost adsorbents: activated carbon (AC, Norit Row 0.8 Supra), natural zeolite (NZ, clinoptilolite) and their mixture (AC+NZ) for immobilization of Zn(II) ions from spent printing developer and to investigate the equilibrium parameters involved in the adsorption process.

MATERIAL AND METHODS

The adsorption of Zn(II) ions from spent printing developer was investigated using activated carbon (AC, Norit Row 0.8 Supra), natural zeolite (NZ, clinoptilolite) and the mixture of AC and NZ (AC+NZ) as adsorbents. Samples of fresh and spent printing developer were taken from the pre-press unit of a Novi Sad (Serbia) offset printing plant.

The commercial powdered activated carbon (Row 0.8 Supra, Norit, USA) and clinoptilolite (High Tech zeolite producer, Turkey) were used in this study and their characteristics are presented in Tables 1 and 2.

Table 1. Physicochemical characteristics of activated carbon

Characteristic	Value
Iodine number	1050
Methylene blue adsorption (g/100g)	22
Total surface area (BET) (m^2/g)	1150
Apparent density (kg/m^3)	390
Density backwashed and drained (kg/m^3)	345
Particle size < 0.60 mm (wt %)	0.1
Ash content (wt %)	7
pH value	10.3
Moisture (as packed) (wt %)	2

Table 2. Chemical composition of clinoptilolite

Oxides	%
SiO_2	66.9
Al_2O_3	13.5
Fe_2O_3	0.98
MgO	0.69
CaO	3.85
K_2O	0.54
Na_2O	0.37
SO_3	1.18

All the chemicals used were of analytical reagent grade (Merck, Germany). Deionized water was used throughout the experiments. Working solution was prepared by diluting the stock metal solution (1000 mg/l) with deionized water to obtain 17.302 mg/l Zn(II) ions.

APPARATUS

Concentrations of Zn(II) ions were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), using a PerkinElmer Elan 5000 mass spectrometer. Before introducing the sample into the instrument, nitric acid (ρ =1.4 g/cm^3) was added to obtain pH 2. Every ICP-MS result given in Table 3 represents the average concentration of three measurements with relative deviations less than 5%.

Table 3. Concentrations of Zn(II) ions in the printing developer before and after adsorption

Heavy metal	Concentration (mg/l) ± RD		
	Before adsorption		
	Fresh developer	Spent developer	
Zn(II)	1.278 ± 0.064	17.302 ± 0.865	
Heavy metal	Concentration (mg/l) ± RD		
	After adsorption		
	AC*	NZ*	AC+NZ *
Zn(II)	6.233 ± 0.312	7.624 ± 0.381	9.567 ± 0.478

**Spent printing developer after adsorption on AC, NZ and (AC+NZ)*

The pH and temperature were measured on a Multi pH/Cond/Temp 340i handheld meter. Samples were shaken on a mechanical shaker (26 rpm), and the solid phase was separated by centrifuging at 3000 rpm (Tehtnica Železniki, Slovenia).

EQUILIBRIUM TIME EXPERIMENTS

The starting conditions of experiments were 0.2 g of the adsorbent, 25 ml of metal working solution with the concentration 17.302 mg/l for Zn(II) ions, pH = 5.7, temperature 24.1°C and shaking speed 26 rpm, while the time varied from 60 to 110 min. As can be seen from Fig. 1, the adsorption of Zn(II) ions increased first and then remained constant when the equilibrium was attained, which occurred after about 90 minutes for all the adsorbents. Based on the trend of the curves in Fig. 1, it can be predicted that the optimal contact time for adsorption on mixture (AC+NZ) would be also 90 minutes.

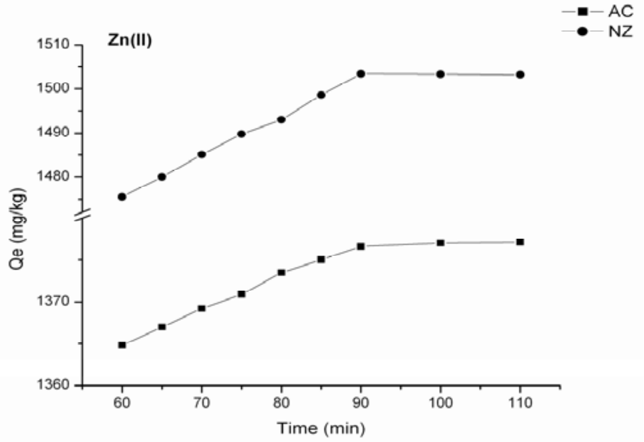

Fig. 1 Adsorption time dependence of Zn(II) ions on AC and NZ

EQUILIBRIUM ADSORPTION EXPERIMENTS

The equilibrium isotherms were obtained using the different amounts (0.04-0.24 g, with an increment of 0.04 g) of AC, NZ and (AC+NZ). The equilibrium amount of metal adsorbed from the aqueous solution was calculated from the equation (1):

$$Qe = \frac{V(C_0 - C_e)}{M} \tag{1}$$

where Q_e is the amount of metal ions adsorbed at equilibrium (mg/kg); C_0 is the initial concentration of metal ions (mg/l); C_e is the equilibrium concentration of metal ions (mg/l); M is the adsorbent mass (kg); and V is the volume of the aqueous solution (l) (Kocaoba 2007).

The distribution ratio was calculated using equation (2):

$$K_d = \frac{C_0 - C_e}{C_0}\frac{V}{M}, \tag{2}$$

where K_d is the distribution ratio (L/kg), C_0 is the initial concentration of metal ions (mg/L); C_e is the equilibrium concentration of metal ions (mg/L); M is the adsorbent mass (kg), and V is the volume of aqueous solution (L) (Erdem, 2004). It is evident that the values of distribution coefficient (K_d) increase with the decrease amount of adsorbent, as shown in Fig. 2. The K_d values depend on the type of the adsorbent, and they decrease for Zn(II) ion in the following order: AC>NZ>(AC+NZ).

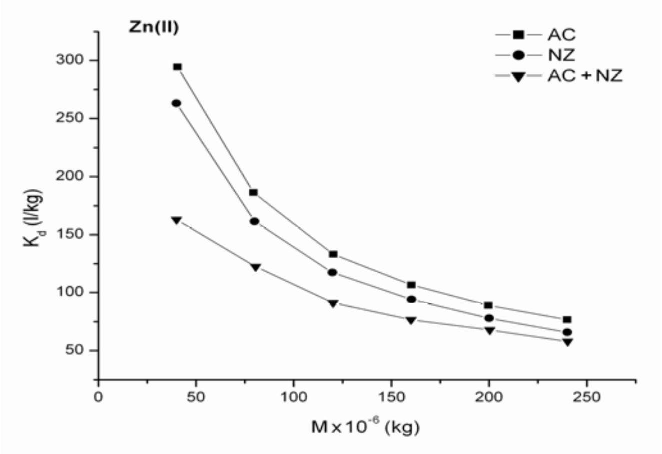

Fig. 2 Dependence of the distribution coefficient on the adsorbent amount for Zn(II) ions

ADSORPTION ISOTHERM MODELS

The adsorption equilibrium data for Zn(II) ions on AC, NZ and (AC+NZ) were analyzed in terms of the Freundlich, Langmuir and Dubinin-Kaganer-Radushkevich (DKR) isotherm models.

Thus the Freundlich isotherm is given by equation (3):

$$\log Q_e = \log K_f + \frac{1}{n}\log C_e, \tag{3}$$

where Q_e is the equilibrium removal, i.e. the amount adsorbed per unit weight of the adsorbent (mg/kg); C_e is the equilibrium metal ion concentration in the solution (mg/l).

The Freundlich isotherm constants, K_f and n, are related to the adsorption capacity and adsorption intensity, respectively.

The conventional Langmuir isotherm written in a linearized form as in equations (4) and (5):

$$\frac{C_e}{Q_e} = \frac{1}{Q_m k_L} + \frac{C_e}{Q_m} \tag{4}$$

or

$$\frac{1}{Q_e} = \frac{1}{Q_m k_L}\frac{1}{C_e} + \frac{1}{Q_m} \tag{5}$$

where the constants Q_m and k_L, are related to the adsorption capacity and the energy of adsorption, respectively (Rao 2006; Kocaoba 2007).

The DKR isotherm for describing the adsorption of metal ions on all adsorbents was used the following equation:

$$\ln Q_e = \ln X_m - \beta\varepsilon^2 \tag{6}$$

where Q_e is the amount of metal ions adsorbed per unit weight of the adsorbent (mg/kg); X_m is the maximum adsorption capacity (mg/kg); β is the coefficient of activity related to the mean sorption energy (mol^2/J^2), and ε is the Polanyi potential equation (7), which is equal to

$$\varepsilon = RT\ln(1 + \frac{1}{C_e}) \tag{7}$$

where R is the gas constant (J/mol K) and T is the temperature (K).

The adsorption energy (E) can be calculated using the following equation (Erdem et al. 2004):

$$E = \frac{1}{\sqrt{-2\beta}}. \tag{8}$$

RESULTS AND DISCUSSION

The adsorption isotherms for Zn(II) ions were obtained for different amounts of three adsorbents, with constant parameters: pH, temperature and shaking speed. Fig. 3 shows that all adsorption isotherms have similar trend, characteristic for the Freundlich isotherm. The corresponding adsorption parameters are summarized in Table 4, and point out that Zn(II) ions were adsorbed effectively on all adsorbents.

Table 4. Freundlich parameters in the equilibrium isotherms for AC, NZ and (AC+NZ)

		Freundlich adsorption isotherm constants		
		K_f (mg/kg)	n	R^2
AC	Zn(II)	60.20	0.50	0.9982
NZ		17.52	0.50	0.9963
(AC+NZ)		5.14	0.34	0.9879

According to the K_f values, the adsorption capacity of Zn(II) ions follows the sequence of adsorption efficiency: AC>NZ>(AC+NZ). It is evident that highest adsorption capacity for Zn(II) ions on AC was 60.20 mg/kg. On the other hand, the least effective was the adsorption of Zn(II) ions on mixture (AC+NZ).

The correlation coefficients (R^2) indicate that the adsorption data for Zn(II) ions on AC, NZ and (AC+NZ) fitted well to the Freundlich isotherm. It can be concluded that AC is most effective for the removal of Zn(II) ions from spent printing developer.

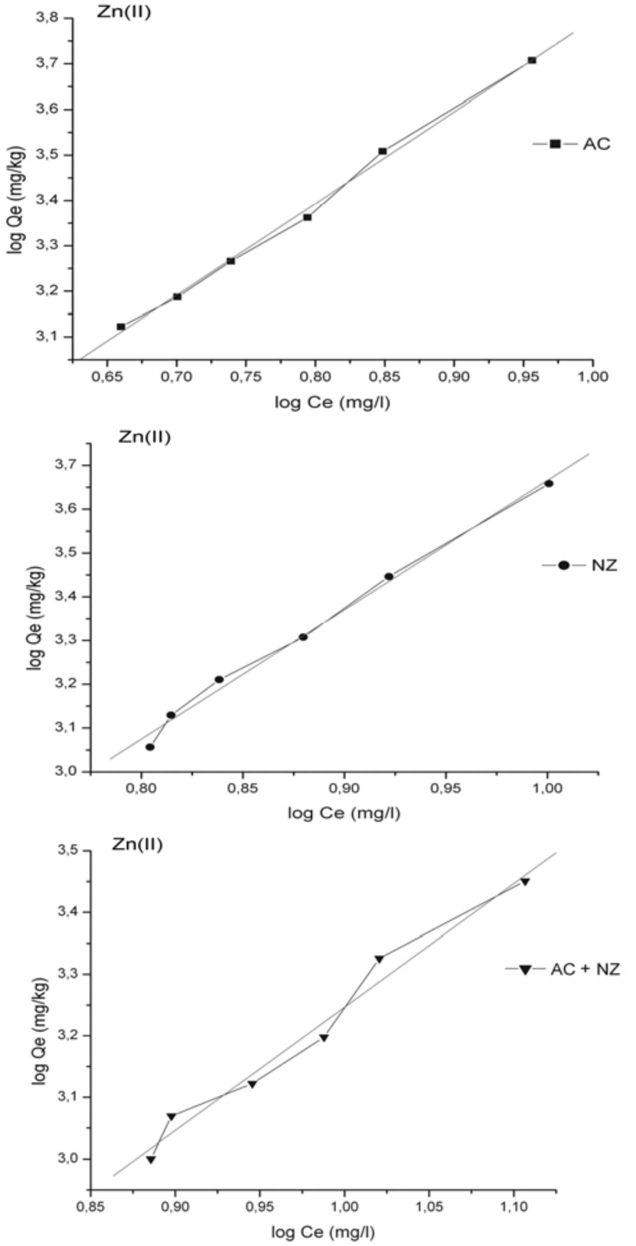

Fig. 3 Freundlich isotherms of Zn(II) ions on AC, NZ and (AC+NZ)

Table 5. Langmuir parameters in the equilibrium isotherms for AC, NZ and (AC+NZ)

		Langmuir adsorption isotherm constants		
		Q_m (mg/kg)	*k_L*	*R^2*
AC	*Zn(II)*	*-0.20*	*-869.56*	*0.9589*
NZ		*-0.11*	*-833.33*	*0.9332*
(AC+NZ)		*-0.18*	*-483.09*	*0.9572*

The experimental data from Table 5 did not fit to the Langmuir isotherm, giving negative slopes and intercepts, leading to the conclusion that the adsorption behavior of the tested systems does not follow the assumption on which the Langmuir approach is based.

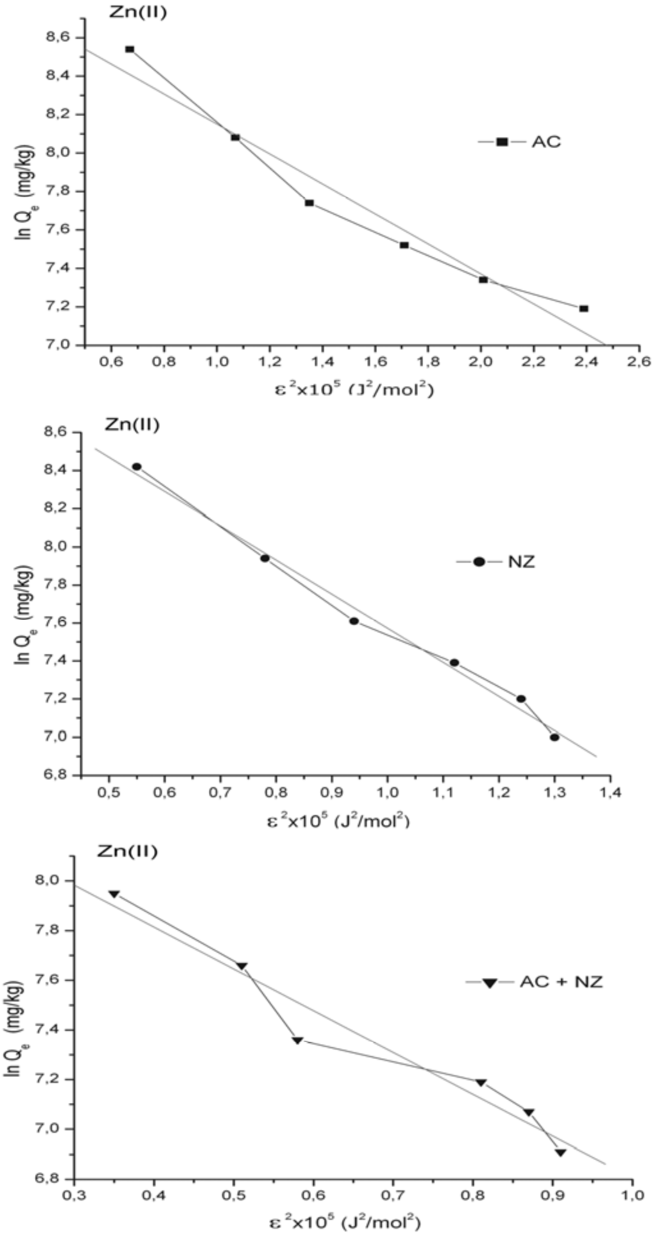

Fig. 4 DKR isotherms for Zn(II) ions on AC, NZ and (AC+NZ)

The DKR plots of ln Q_e against ε^2 for the adsorption of Zn(II) ions on the tested adsorbents are shown in Fig. 4. The DKR parameter (β) gives negative values for all the adsorbents and investigated metal ion, because it was calculated from a negative slope, while the parameter X_m was calculated from the intercept. The values of the DKR parameters and the corresponding correlation coefficients are summarized in Table 6. According to the X_m values, the adsorption capacities of Zn (II) ions show the following decreasing order: NZ>AC>AC+NZ.

Table 6. DKR parameters in the equilibrium isotherms for AC, NZ and (AC+NZ)

		DKR parameters			
		X_m (mg/kg)	*β (mol^2/J^2)*	*E (J/mol)*	*R^2*
AC	*Zn(II)*	*7562.07*	*-0.7799*	*0.80*	*0.9540*
NZ		*11698.20*	*-1.7948*	*0.53*	*0.9905*
(AC+NZ)		*4855.42*	*-1.6842*	*0.54*	*0.9534*

The influence of the different amount of the adsorbents (AC, NZ and their mixture) on the adsorption efficiency in the removal of Zn(II) ions is shown in Fig. 5. As can be seen, the adsorption efficiency of Zn(II) ions increases considerably with increasing the adsorbent amount. The maximum adsorption efficiencies were 73.6%, 62.9%, 55.1% for AC, NZ and (AC+NZ), respectively. Besides the amount of adsorbents, the removal efficiency of metal ions depends on adsorbent fraction size and physicochemical characteristics of metal ions.

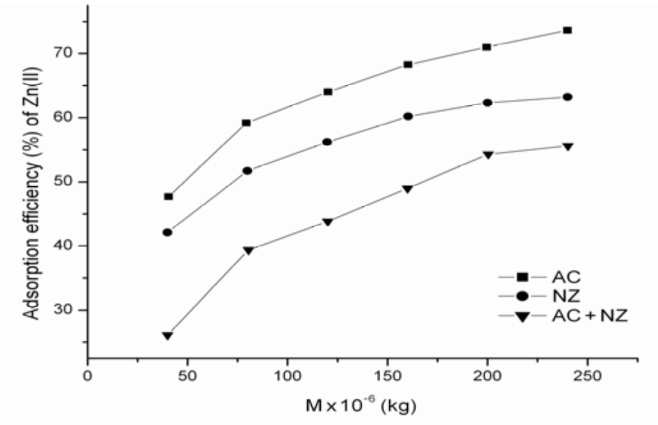

Fig. 5 The influence of the adsorbent amount on the adsorption efficiency of Zn(II) ions

The adsorption efficiency of the adsorbents used in the removal of Zn(II) ions is illustrated in Table 3, showing the corresponding decreases in the concentration in spent printing developer after adsorption. As can be seen, the concentration reduction of Zn(II) ions in the spent printing developer after adsorption is almost 2 to 2.5 times.

According to the Regulation of hazardous matters in water recipients ("Official Gazette of Socialist Republic of Serbia" No. 31/82), the maximum allowed concentration (MAC) for Zn(II) ions is 1.0 mg/l. It is evident that the concentrations of Zn(II) ions in the spent printing developer after adsorption are almost 6-9 times higher than the MAC values. Hence, spent printing developer must not directly discharge into sewerage, but it can be reuse in the development process by application of adequate treatments.

CONCLUSIONS

The study showed that the adsorption of Zn(II) ions from spent printing developer using adsorbents: activated carbon, clinoptilolite and their mixture was most effective within the contact time of 90 minutes. The adsorption process was interpreted in terms of the Freundlich, Langmuir and DKR isotherm models. It was found that the Freundlich isotherm gave the best agreement over the whole adsorption range and the corresponding correlation coefficients (R^2) for Zn(II) ions on activated carbon, clinoptilolite and their mixture being ≥0.988. These investigations showed that the use of low-cost adsorbents may be an effective way for removal Zn(II) ions from spent printing developer. The adsorption capacity of Zn(II) ions decreased in the following order: AC>NZ>(AC+NZ). The adsorption efficiency achieved was 55 - 74%. Thus, the application of AC was the most effective for the removal of Zn(II) ions, but spent printing developer still not enough to discharge into sewer, although it may be reuse in the development process.

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AUTHORS & AFFILIATION

[1.] Jelena KIURSKI,
[2.] Savka ADAMOVIC,
[3.] Jelena KRSTIC,
[4.] Ivana OROS,
[5.] Mirjana VOJINOVIC MILORADOV

[1-5] UNIVERSITY OF NOVI SAD, FACULTY OF TECHNICAL SCIENCES, TRG DOSITEJA OBRADOVICA 6, 21000 NOVI SAD, SERBIA

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