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THE REMOVAL EFFICIENCY OF HEAVY METALS FROM SPENT PRINTING DEVELOPER

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Abstract: This study was concerned with the possibility of removal of heavy metal ions, Cr(total), Zn(II) and Cu(II) from spent printing developer by adsorption using low-cost materials: natural zeolite (NZ, clinoptilolite), activated carbon (AC, Norit Row 0.8 Supra) and their mixture (NZ + AC). Concentrations of Cr(total), Zn(II) and Cu(II) were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), using a PerkinElmer Elan 5000 mass spectrometer. The adsorption of Cr(total), Zn(II) and Cu(II) onto clinoptilolite and activated carbon was studied in laboratory batch mode. Adsorption data have been interpreted in terms of the Freundlich, Langmuir and Dubinin-Kaganer-Radushkevich (DKR) equations. The results provided strong support for the heavy metals adsorption onto these adsorbents, and all the data fitted well to the Freundlich isotherm (R^2>0.97). The lowest correlation coefficient for all target ions was obtained using their mixture (NZ + AC). The adsorption capacities of NZ and (NZ + AC) mixture decreased in the order: Cu(II)>Zn(II)>Cr(total), while that of AC followed the order: Zn(II)>Cu(II)>Cr(total).

Keywords: heavy metals, adsorption, printing process, developer, adsorption isotherms, natural adsorbents

1. INTRODUCTION

The printing industry is a significant contributor of pollutant discharges to the environment. Urged by environmental and legislative pressure, it has reduced its environmental impacts to water, land and air over the recent decades by 80-90% in the world, (Thompson et al., 2001) but not in Serbia, since the environmental awareness of people in this country is low. Wastewaters from printing plants can be potentially very polluting, depending on the chemicals and technology used. The polluted water needs to be suitably treated before discharging into water recipients. In Serbia, there is a great deficiency in the adequate facilities for treatment of wastewaters from printing plants. 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 (Lyubchik et al., 2005; Kiurski et al., 2008; Kiurski et al., 2009b).

Wastewaters of printing industry are a very serious problem and require the coordinated work of graphic experts and manufacturers of raw materials, because they influence the further spreading of the contaminants in the environment, especially in the natural recipient. The wastewaters generated from the printing process are highly coloured and contaminated with organic and inorganic matters. Hence, the presence of colour in wastewaters reduces aquatic diversity by blocking the passage of light through water and has impact on human health and the environment (Tapas et al., 2003; Khenifi et al., 2007). One of the main pollutants of the offset prepress process is the spent printing developer, which contains elevated metal concentrations (Metes et al., 2004; Sprynskyy et al., 2006; Park et al., 2007; Prica et al., 2008a; Prica et al., 2008b; Kiurski et al., 2009a). Heavy metal ions such as copper, chromium and zinc are particularly common in wastewaters of the printing industry. They are harmful to humans and other biological systems if their presence exceeds the

corresponding tolerance levels. Heavy metals are not biodegradable, and they tend to accumulate in the organisms, causing numerous diseases and disorders (Shuiping, 2003; Kiurski et al., 2010; Ozer and Pirincci, 2006; Kubilay et al., 2007; Llanes Monter et al., 2007; Oliveira et al., 2007; Krstic et al., 2009; Malakootian et al., 2009). Therefore, heavy metals must be removed from the polluted streams in order to meet increasingly stringent environmental quality standards. Various treatment techniques and processes have been used to remove the pollutants from contaminated waters. Among all the approaches proposed, adsorption is one of the most popular methods, and it is currently considered as an effective, efficient and economic method for water purification (Babel & Kurniawan, 2003; Jiuhui, 2008; Oke et al., 2008; Özpinar 2011).

The aim of the present work was to examine the possibility of removal of toxic Cr(total), Zn(II) and Cu(II) ions from spent printing developer by adsorption on different adsorbents, clinoptilolite, activated carbon and their mixture, as well as to investigate the equilibrium parameters involved in this adsorption process.

2. MATERIALS AND METHODS

2.1. Materials

The possibility of the removal of heavy metal ions, Cr(total), Zn(II) and Cu(II), from spent printing developer was investigated using natural zeolite (NZ, clinoptilolite), activated carbon (AC, Norit Row 0.8 Supra) and the mixture of NZ and AC (NZ+AC) as adsorbents. Samples of fresh and spent printing developer were taken from the prepress unit of a Novi Sad (Serbia) offset printing plant.

Natural zeolites (NZ) are rock-forming, microporous silicate minerals, one of them being clinoptilolite. It consists of an arrangement of silica and alumina tetrahedra, forming a lattice structure with long channels comprising water molecules and alkaline earth ions. As these ions do not occupy fixed positions, they may move within the lattice. Also, they can be easily released and exchanged without changing the character of the crystal lattice, enabling clinoptilolite to have strong ion exchange properties (Grancaric et al., 2009; Özpinar 2011). The isomorphous replacement of Si(IV) by Al(III) produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation (sodium, potassium or calcium). These cations can be replaced by certain cations from solutions, such as lead, cadmium, zinc and manganese. The chemical and structural features of zeolites and the fact that the exchangeable ions (sodium, calcium and potassium) are relatively innocuous, make them particularly suitable for removing undesirable heavy metal ions (e.g. copper, chromium, zinc, lead, nickel, cadmium, silver and cobalt), organic solvents, inks and oils, from industrial effluent waters (Erdem et al., 2004; Kiurski et al., 2009a).

The natural zeolite sample used in this study was a commercial clinoptilolite rich tuff (High Tech zeolite producer, Turkey). In terms of mineralogical composition, the natural zeolitic tuff primarily contained clinoptilolite (minimum 90%) with trace amounts of feldspar, quartz and pyrite. The physical properties of clinoptilolite rich tuff are particle size of <0.63 μm, specific mass of 2.1-2.2 g/cm^3 and hardness (by Moss) of 3.5-4. The chemical composition of clinoptilolite (%) is given in table 1.

Table 1. 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
H_2O	11.88

Activated carbon (AC) is a highly porous carbon material whose amorphous skeleton consists of microcrystallites with a graphite lattice (Kumar et al., 2008). The adsorption effectiveness of activated carbon depends on the nature of the organic matter to be removed (substances with a high molecular mass and low water solubility are adsorbed better); the concentration of the substance to be removed (the higher the concentration, the more efficient the adsorption); the presence of other organic compounds, which results in competition for the available adsorption space; and the parameters of the liquid (temperature, pressure, humidity and pH). Activated carbon adsorption is considered to be a particularly competitive and effective process for the removal of heavy metals at trace quantities (Erdem et al., 2004).

The commercial powdered activated carbon (Row 0.8 Supra, Norit, USA) that was used in this study had the physicochemical characteristics presented in table 2.

Activated carbon/zeolite composites, formed by the zeolite growth on porous carbon supports, can possess the bifunctional properties of both carbon and zeolite, which can have potential applications in

air purification, wastewater treatment, filters in compressed air and gas purification, and many other applications in catalysis and separation (Kumar et al., 2008).

Table 2. 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

2.2. Reagents

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 3.059 mg/L Cu(II), 4.674 mg/L Cr(total) and 17.302 mg/L Zn(II).

2.3. Apparatus

Concentrations of Cr(total), Zn(II) and Cu(II) 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. The uncertainties of the results depended on the level of metal concentration in the analyzed developer sample, and the statistical accuracy of measurements increases with the increase in concentrations. Every ICP-MS result given in table 3 represents the average concentration of three measurements with relative deviation (RD) less than 5%.

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).

2.4. Equilibrium time experiments

The adsorption of Cr(total), Zn(II) and Cu(II) onto clinoptilolite and activated carbon was studied in laboratory batch mode. The experiments were carried out by shaking known amounts of NZ or AC (0.2 g of the adsorbent) in 100 mL stopper bottles, with 25 mL of aqueous working solution of target metals (3.059 mg/L for Cu, 4.674 mg/L for Cr(total) and 17.302 mg/L for Zn) at pH = 5.7, temperature 24.1°C, shaking speed 26 rpm, and shaking times of 60, 65, 70, 75, 80, 85, 90, 100 and 110 minutes. At the end of the predetermined time intervals, the solutions containing heavy metals were centrifuged for 10 minutes at 3000 rpm and then filtered through an Advantec quantitative cellulose filter paper (grade 5C). The equilibrated metal concentrations were determined in the filtrate acidified with cc. HNO_3 on the mentioned Elan 5000 mass spectrometer.

2.5. 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 NZ, AC, and (NZ + AC) mixtures. The bottles were shaken for 90 minutes to reach the adsorption equilibrium. At the end of the equilibrium adsorption process, the residual metal concentrations were determined in the same way as in the equilibrium time experiment.

The equilibrium amount of metal adsorbed from the aqueous solution was calculated from the equation:

$$Q_e = \frac{V(C_0 - C_e)}{M} \quad (1)$$

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).

Table 3. Concentrations of heavy metals in the printing developer before and after adsorption

	Concentration (mg/l) ± RD				
	Before adsorption		After adsorption		
Heavy metal	Fresh developer	Spent developer	NZ*	AC*	NZ + AC*
Cu(II)	0.517 ± 0.026	3.059 ± 0.153	2.094 ± 0.105	2.053 ± 0.103	1.679 ± 0.084
Cr(total)	1.528 ± 0.076	4.674 ± 0.234	3.258 ± 0.163	3.251 ± 0.163	3.122 ± 0.156
Zn(II)	1.278 ± 0.064	17.302 ± 0.865	7.624 ± 0.381	6.233 ± 0.312	9.567 ± 0.478

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

The adsorption efficiency was calculated from the following equation:

$$E = \frac{100V(C_0 - C_e)}{VC_0} \quad (2)$$

where E is the adsorption efficiency (%); C_0 is the initial concentration of metal ions (mg/L); C_e is the equilibrium concentration of metal ions (mg/L), and V is the volume of solution from which adsorption takes place (L) (Sprynskyy et al., 2006; Kocaoba et al., 2007).

The distribution ratio was calculated using the equation:

$$K_d = \frac{C_0 - C_e}{C_0}\frac{V}{M} \quad (3)$$

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 et al., 2004).

2.6. Adsorption isotherm models

The adsorption equilibrium data for Cr(total), Zn(II) and Cu(II) on NZ, AC and (NZ + AC) were analyzed in terms of the Freundlich, Langmuir and Dubinin-Kaganer-Radushkevich (DKR) isotherm models. The Freundlich and Langmuir isotherms are used most often to describe sorption equilibria in environmental samples, and they are expressed in the form of straight-line equations, obtained by mathematical transformation of the isotherms.

Thus the Freundlich isotherm is written as:

$$\log Q_e = \log K_f + \frac{1}{n}\log C_e \quad (4)$$

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. They are calculated from the slope (1/n) and intercept (K_f) of the linear plot of the log Q_e versus log C_e (equilibrium concentration of the metal ion in the solution, mg/L).

The conventional Langmuir isotherm written in a linearized form is:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m k_L} + \frac{C_e}{Q_m} \quad (5)$$

or

$$\frac{1}{Q_e} = \frac{1}{Q_m k_L}\frac{1}{C_e} + \frac{1}{Q_m} \quad (6)$$

where the constants Q_m and k_L are related to the adsorption capacity and the energy of adsorption, and their values are obtained from the slope and intercept of the linear plot of $1/Q_e$ versus $1/C_e$ (Rao et al., 2006; Kocaoba et al., 2007).

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

$$\ln Q_e = \ln X_m - \beta\varepsilon^2 \quad (7)$$

where Q_e is the amount of metal ions adsorbed per unit weight of 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, which is equal to

$$\varepsilon = RT\ln(1 + \frac{1}{C_e}) \quad (8)$$

where R is the gas constant (J/mol K) and T is the temperature (K). The values for β and X_m are obtained from the slope and intercept of the plot of ln Q_e versus ε^2.

The adsorption space in the vicinity of a solid surface is characterized by a series of equipotential surfaces having the same adsorption potential. The adsorption potential is independent of the temperature, but depends on the nature of the sorbent and sorbate. The adsorption energy can be calculated using the following equation (Erdem et al., 2004):

$$E = \frac{1}{\sqrt{-2\beta}} \quad (9)$$

3. RESULTS AND DISCUSSION

3.1. Characteristics of printing developer waste

The offset prepress process is a complex printing operation which involves the use of many toxic and hazardous chemicals and procedures, such as printing developer, printing fixing agent, photosensitive chemicals and photographic technique to transfer the images and texts from the original to printing plates. 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 metals (chromium, zinc and copper) found in spent developer come from the dye residue.

Spent printing developer needs a proper treatment and disposal, only if its pH value is strongly alkaline (≥12.5), and thus it may be a potential hazard if discharged into water recipients. Also, cumulative organics considerably increase the chemical oxygen demand and the toxicity of this waste. The requirements for an adequate treatment of spent developer are to be met, to prevent increased concentrations of some metals and organic pollutants from the printing industry (Vengris et al., 2004; Vengris et al., 2007; Krstic et al., 2009).

3.2. Adsorption

Among several removal technologies, the adsorption onto clinoptilolite and activated carbon, thanks to its simplicity and comparable low cost of application, is of great importance. Because of the complexity of printing wastewater we studied the adsorption onto NZ, AC and (NZ + AC) mixtures, to gain an insight into the influence of heavy metals 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 target heavy metals (Cu, Cr, Zn) from the spent printing developer sample.

The study of the equilibrium distribution of heavy metals between the adsorbents employed and the spent printing developer served to determine the capacity of the adsorbents. Because of the complexity of the wastewater studied and wide range of pore size and structure of the adsorbents, the analysis of the adsorption behavior is quite complex.

Generally, when discussing the adsorption process, the adsorption mechanism is postulated on the basis of the correlation of the experimental data with empirical adsorption isotherms, and these are most commonly the Freundlich, Langmuir and DKR isotherms.

3.2.1. Equilibrium time

The starting conditions were 0.2 g of the adsorbent, 25 mL of metal working solution with the concentrations of 3.059 mg/L for Cu, 4.674 mg/L for Cr(total), and 17.302 mg/L for Zn, 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 figures 1-3, the adsorption of all the metal ions increased first and then remained constant when the equilibrium was attained, which occurred after about 90 minutes for all the adsorbents.

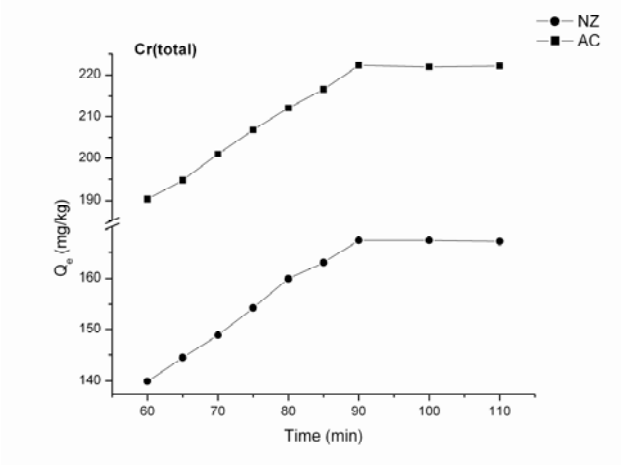

Figure 1. Time dependence of Cr(total) adsorption on NZ and AC

Based on the trend of the curves in figures 1-3, it can be predicted that the optimal contact time for adsorption on (NZ + AC) would be also 90 minutes.

3.2.2. Distribution coefficient

It is evident that the values of distribution coefficient (K_d) increase with the decrease amount of adsorbent, as shown in figures 4-6. The K_d values depend on the type of the adsorbent, and they decrease in the following order: (NZ + AC)>NZ>AC for Cr(total) and Cu(II) ion, while the order for Zn(II) ion is: AC>NZ>(NZ + AC).

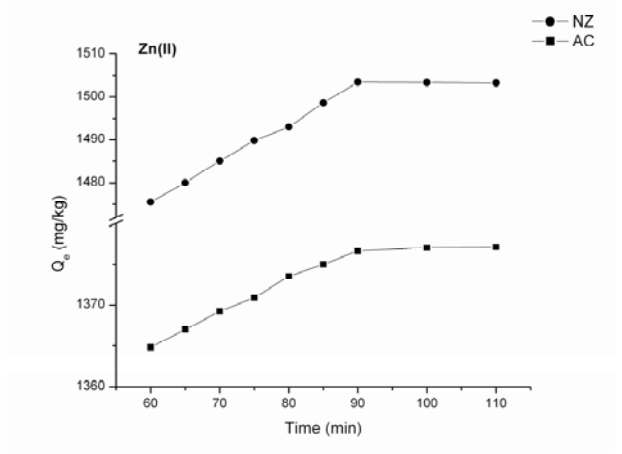

Figure 2. Time dependence of Zn(II) adsorption on NZ and AC

As can be seen from figure 4, the approximately same distribution coefficients were obtained using NZ and AC.

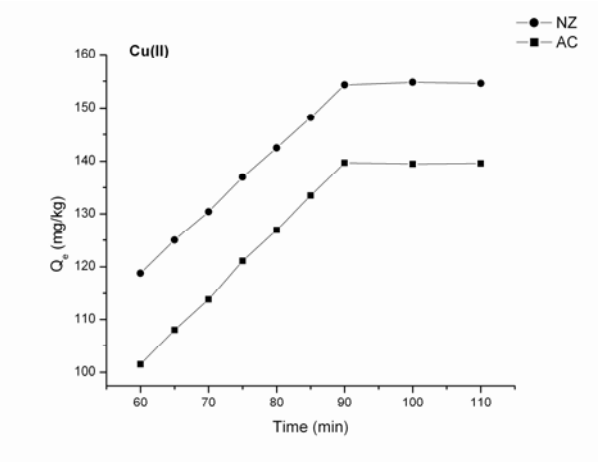

Figure 3. Time dependence of Cu(II) adsorption on NZ and AC

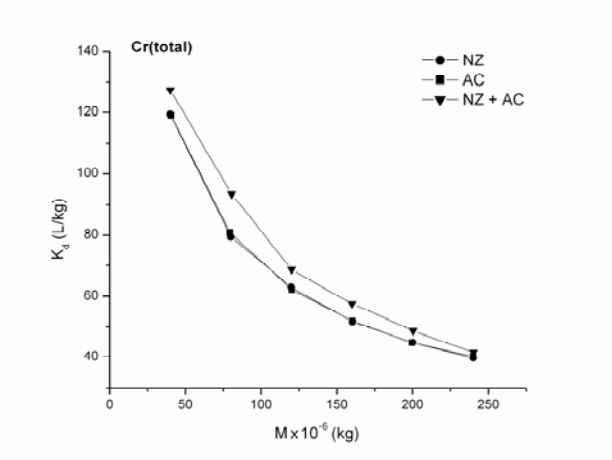

Figure 4. Dependence of the distribution coefficient on the amount of adsorbent for Cr(total)

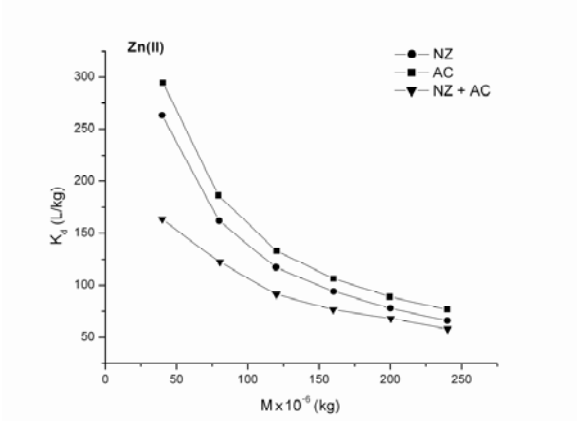

Figure 5. Dependence of the distribution coefficient on the amount of adsorbent for Zn(II)

3.2.3 Adsorption isotherms

The adsorption isotherms for Cr(total), Zn(II) and Cu(II) were obtained for different amounts (0.04-0.24 g with an increment of 0.04 g) of all three adsorbents, while keeping constant all other parameters (pH 10.9, temperature 23.4°C, and shaking speed 26 rpm). Figures 7-9 show that all three adsorption isotherms have similar shapes, characteristic for the Freundlich isotherms. The corresponding adsorption parameters are summarized in tables 4 and 5.

The values of the constants in table 4 show that all target metal ions adsorbed effectively on all three adsorbents. Judging from the K_f values, the adsorption capacity of NZ and (NZ + AC) follows the sequence of adsorption efficiency: Cu(II)>Zn(II)>Cr(total), while this sequence for AC is: Zn(II)>Cu(II)>Cr(total). Also, it is evident that highest adsorption capacity for Cu(II), of 9.09 and 150.85 mg/kg, had NZ and (NZ + AC), respectively, whereas the corresponding value for Zn(II) adsorption on AC was 60.20 mg/kg.

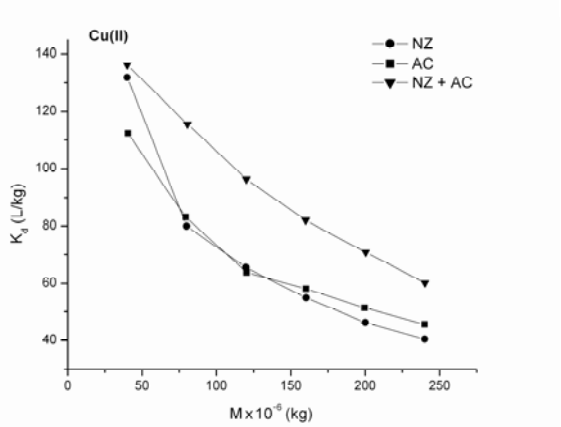

Figure 6. Dependence of the distribution coefficient on the amount of adsorbent for Cu(II)

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

Freundlich adsorption isotherm constants				
		K_f (mg/kg)	n	R^2
NZ	Cr(total)	2.42	0.25	0.9970
	Zn(II)	5.14	0.34	0.9963
	Cu(II)	9.09	0.24	0.9793
AC	Cr(total)	2.59	0.25	0.9958
	Zn(II)	60.20	0.50	0.9982
	Cu(II)	39.60	0.44	0.9815
(NZ + AC)	Cr(total)	3.73	0.26	0.9813
	Zn(II)	17.52	0.50	0.9879
	Cu(II)	150.85	0.83	0.9748

On the other hand, the least effective was the adsorption of Cr(total), the respective adsorption capacities of NZ, AC and (NZ + AC) being 2.42, 2.59 and 3.73 mg/kg.

The correlation coefficients (R^2) presented in table 4 indicate that the data for adsorption on NZ, AC and (NZ + AC) fitted well to the Freundlich isotherm, the highest values being: 0.9815, 0.9970 and 0.9982 for Cu(II), Cr(total) and Zn(II),

respectively. The lowest R^2 values were obtained for the adsorption of all three ions on the mixture (NZ + AC). It can be concluded that AC is the most effective for the removal of Cu(II) and Zn(II) and NZ for the removal of Cr(total).

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.

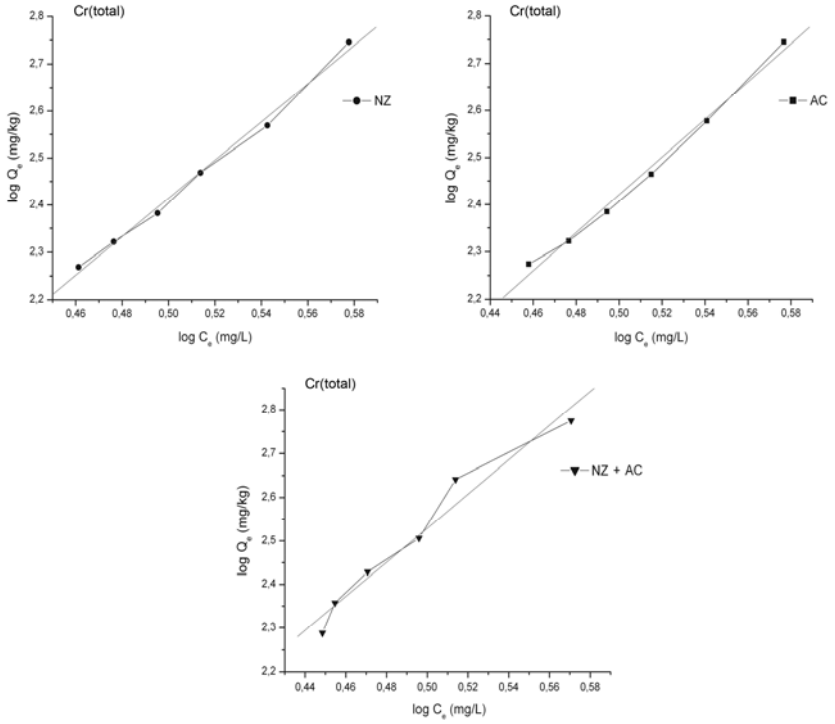

Figure 7. Freundlich isotherms of Cr(total) on NZ, AC and (NZ + AC)

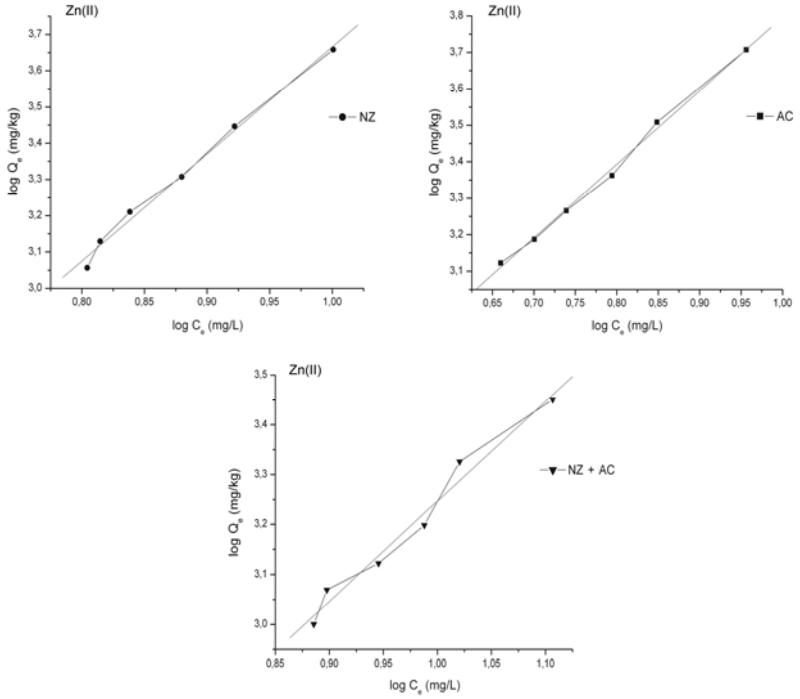

Figure 8. Freundlich isotherms of Zn(II) on NZ, AC and (NZ + AC)

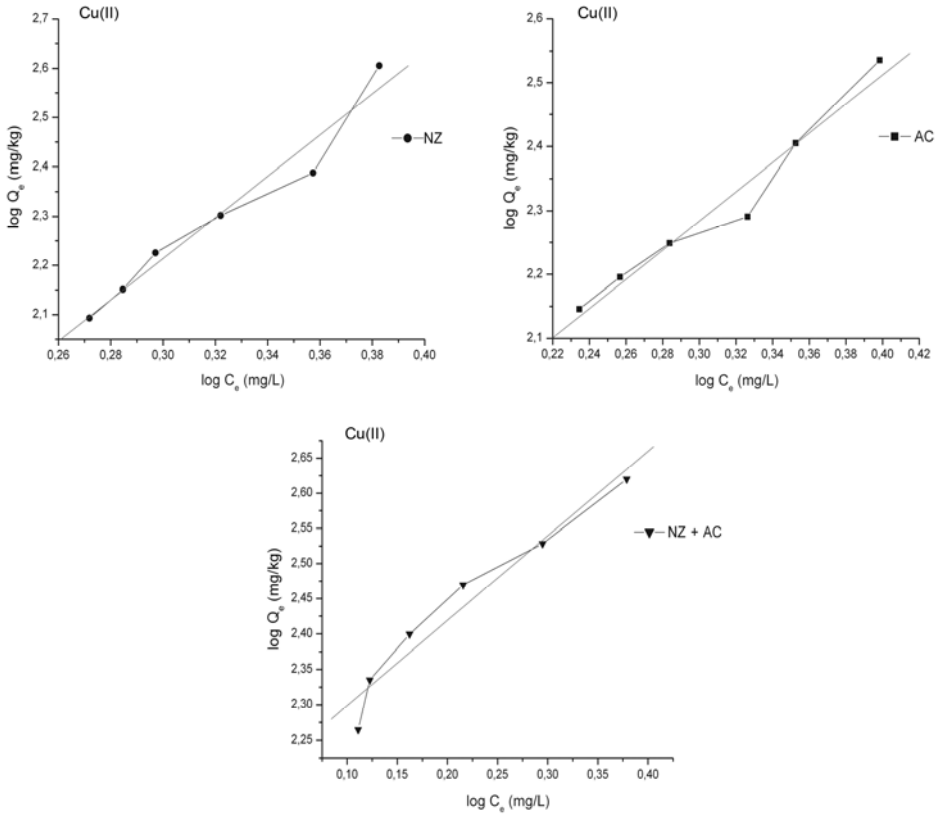

Figure 9. Freundlich isotherms of Cu(II) on NZ, AC and (NZ + AC)

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

		Langmuir adsorption isotherm constants		
		Q_m (mg/kg)	k_L	R^2
NZ	Cr(total)	-100.50	-0.23	0.9947
	Zn(II)	-0.11	-833.33	0.9332
	Cu(II)	-66.49	-0.35	0.9714
AC	Cr(total)	-102.35	-0.22	0.9961
	Zn(II)	-0.20	-869.56	0.9589
	Cu(II)	-170.65	-0.26	0.9784
(NZ + AC)	Cr(total)	-112.11	-0.23	0.9115
	Zn(II)	-0.18	-483.09	0.9572
	Cu(II)	-0.12	-1123.60	0.9269

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

		DKR parameters			
		X_m (mg/kg)	β (mol^2/J^2)	E (J/mol)	R^2
NZ	Cr(total)	3453.90	-0.5534	0.95	0.9877
	Zn(II)	11698.20	-1.7948	0.53	0.9905
	Cu(II)	2859.26	-0.2942	1.30	0.8572
AC	Cr(total)	3355.68	-0.5427	0.96	0.9691
	Zn(II)	7562.07	-0.7799	0.80	0.9540
	Cu(II)	816.22	-0.1381	1.90	0.9485
(NZ + AC)	Cr(total)	2903.38	-0.4525	1.05	0.9738
	Zn(II)	4855.42	-1.6842	0.54	0.9534
	Cu(II)	689.22	-0.0621	2.84	0.9760

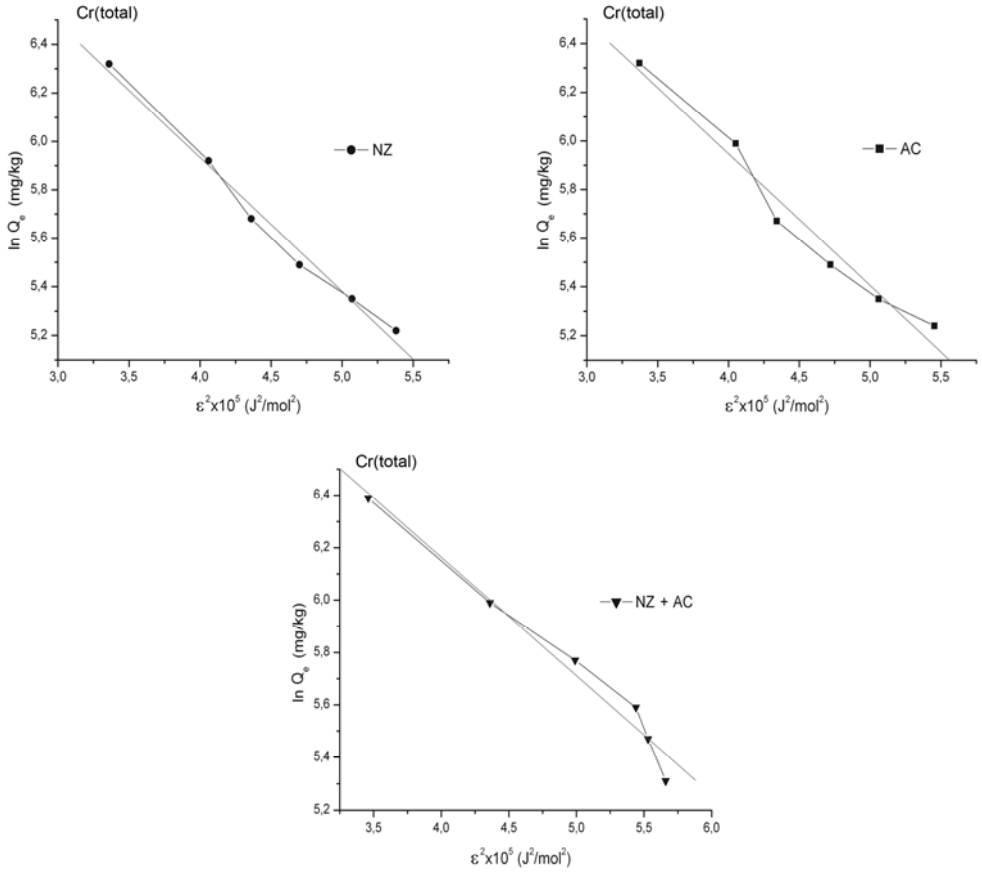

Figure 10. DKR isotherms for Cr(total) on NZ, AC and (NZ + AC)

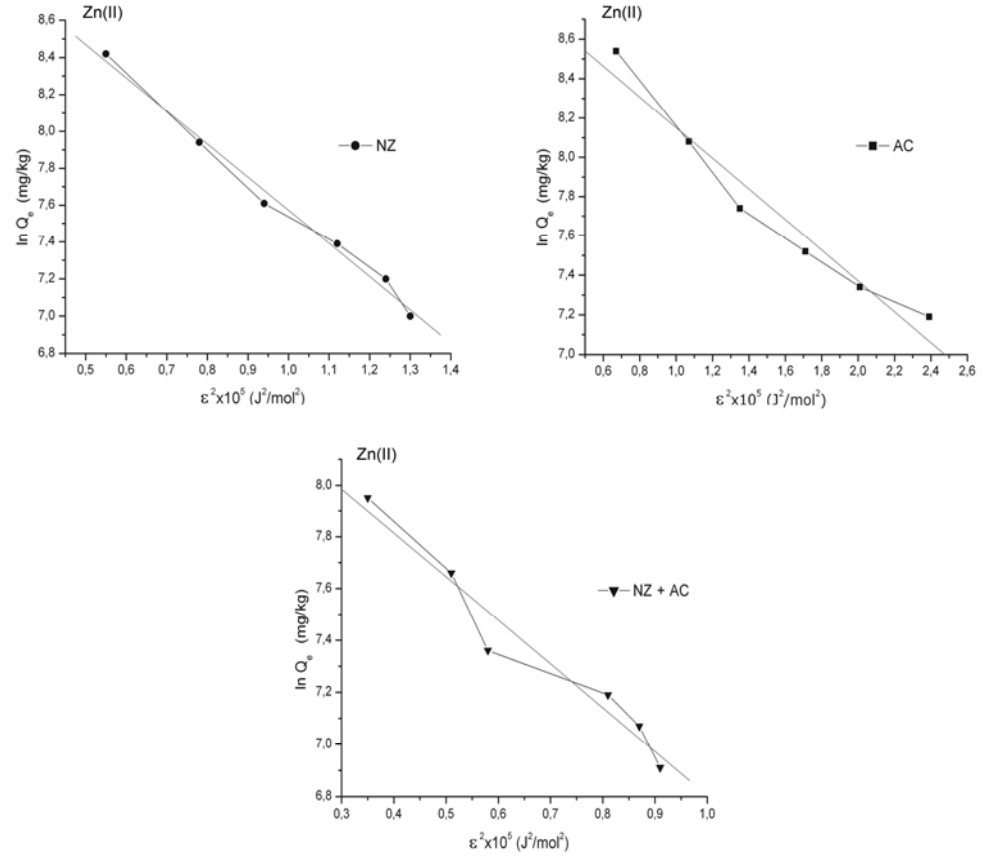

Figure 11. DKR isotherms for Zn(II) on NZ, AC and (NZ + AC)

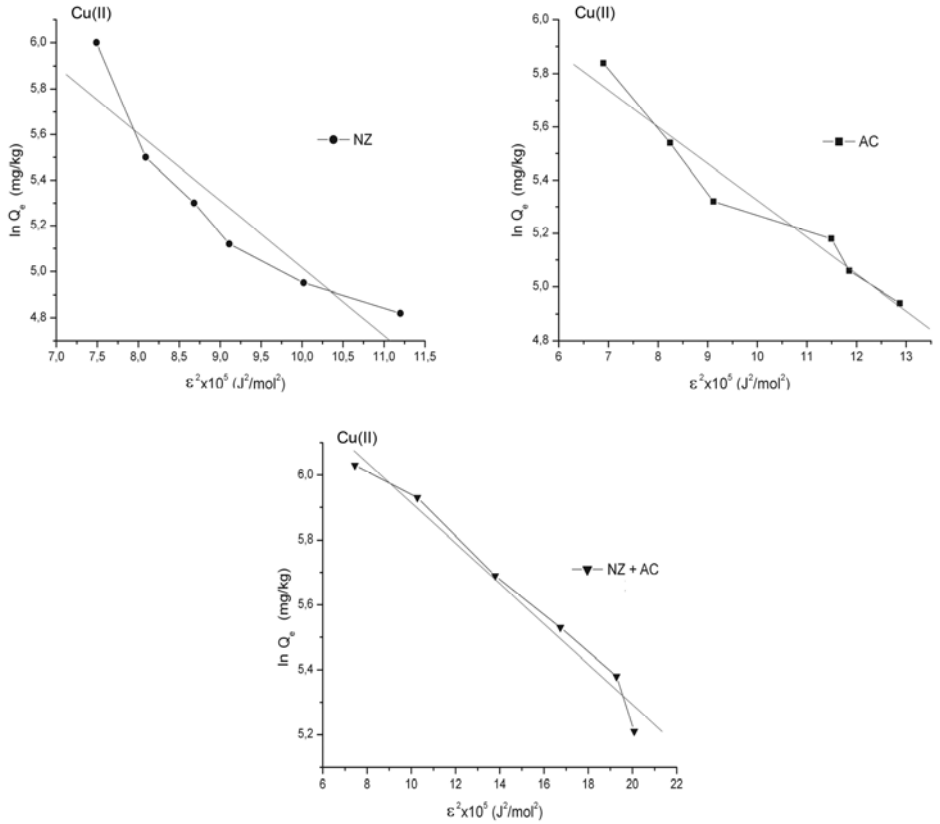

Figure 12. DKR isotherm for Cu(II) on NZ, AC and (NZ + AC)

The DKR plots of ln Q_e against ε^2 for the adsorption of investigated metal ions on the tested adsorbents are shown in Figures 10-12. The DKR parameter (β) gives negative values for all the adsorbents and investigated metal ions, 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. As can be seen from table 6, the maximum values of adsorption energy (E) was obtained for Cu(II) of 1.30, 1.90 and 2.84 J/mol for the adsorption on NZ, AC and (NZ + AC), respectively. According to the X_m values, the highest adsorption capacities of 11698.20, 7562.07 and 4855.42 mg/kg, were obtained for Zn(II) adsorption on NZ, AC and (NZ + AC), respectively. The adsorption capacities of all the adsorbents show the following decreasing order: Zn(II)>Cr(total)>Cu(II).

3.2.4. Adsorption efficiency

The dependence of the efficiency of NZ, AC and (NZ + AC) to adsorb target metal ions on the amount of the adsorbent is presented in Figures 13-15. As can be seen, the efficiency of Zn(II) adsorption increases considerably with increase in the adsorbent amount, while it does not depend much for Cr(total) and Cu(II).

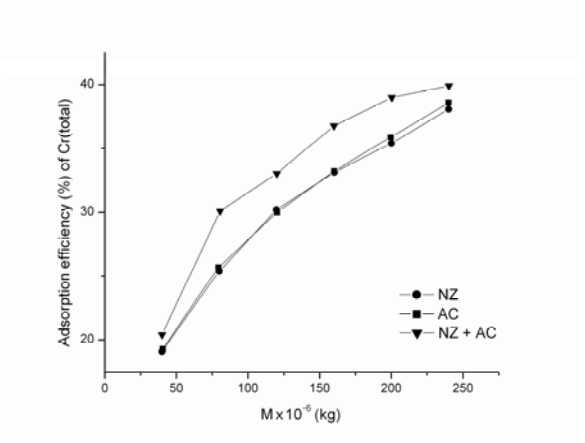

Figure 13. Dependence of the efficiency of Cr(total) adsorption on the amount of adsorbent

The maximum adsorption efficiencies for the removal of Cr(total) and Cu(II) using (NZ + AC) were 39.9 and 57.8%, respectively, while that for Zn(II) (73.6%) was obtained using AC. Besides the amount of adsorbent, the efficiency of metal removal depends on the adsorbent fraction size and physicochemical characteristics of metal ions. The fine-dispersion fractions of the NZ and AC adsorbents allowed the growth of their porosity and thus enhanced the accessibility of metal diffusion flows to adsorption centers. Hence the sorption capacity and selectivity of the adsorbents are related to the difference in the

physicochemical characteristics of heavy metals, such as covalent and van der Waals radii, electronegativity, and ionization potential.

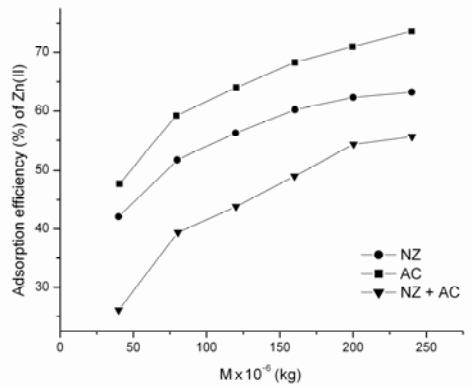

Figure 14. Dependence of the efficiency of Zn(II) adsorption on the amount of adsorbent

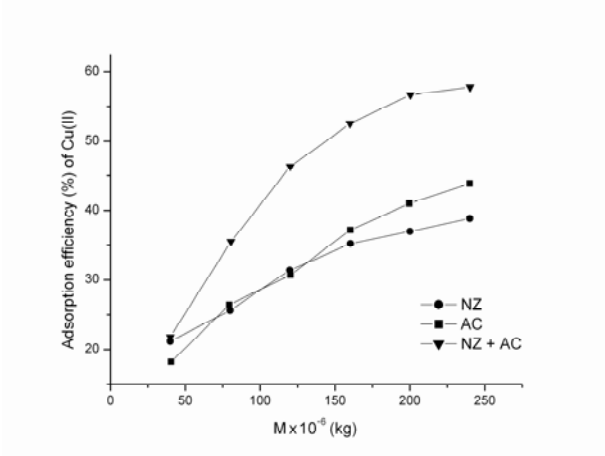

Figure 15. Dependence of the efficiency of Cu(II) adsorption on the amount of adsorbent

The adsorption efficiency of the adsorbents used in the removal of particular metal ions is illustrated in table 3, showing the corresponding decreases in the concentration in spent printing developer after the adsorption. As can be seen, the concentrations of all heavy metals in the spent printing developer after adsorption indicate the high adsorption capacity of all used sorbents. Evidently, all three adsorbents were most efficient in the removal of Zn(II).

The Regulation of hazardous matters in water recipients (Official Gazette of Socialist Republic of Serbia, 1982) gives the maximum allowed concentrations (MAC) for Cu(II), Cr(total) and Zn(II): 0.1 mg/L, 0.6 mg/L and 1.0 mg/L, respectively. It is evident that the concentrations of all heavy metals after adsorption exceed much the MAC level. This can be simply explained by the fact that the concentrations of heavy metals in the spent printing developer after adsorption are almost 5-15 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 application of adequate treatments.

4. CONCLUSIONS

This study showed that the removal of Cr(total), Zn(II) and Cu(II) from spent printing developer using all three adsorbents (NZ, AC and their mixture) was most effective within the first 90 minutes of contact time. The adsorption processes were interpreted in terms of the Freundlich, Langmuir and DKR theories. It was found that the Freundlich isotherm gave the best agreement over the whole adsorption range, the corresponding correlation coefficients (R^2) being 0.9815, 0.9970 and 0.9982, for Cu(II), Cr(total) and Zn(II), respectively.

These investigations showed that the use of inexpensive adsorbents may be an effective way to remove heavy metal ions from spent printing developer. The adsorption capacity of NZ and (NZ + AC) decreased in the following order of adsorption efficiency: Cu(II)>Zn(II)>Cr(total), while for AC the order was: Zn(II)> Cu(II)>Cr(total). The adsorption efficiency achieved using NZ were 25.7, 55.9 and 31.5% for Cr(total), Zn(II) and Cu(II), respectively; those using AC: 30.4, 64.0 and 32.9%, and those using (NZ + AC): 33.2, 44.7 and 45.1%. The application of (NZ + AC) was more efficient for the removal of Cr(total) and Cu(II), while AC was more effective in removing Zn(II), but spent printing developer still not enough to discharge into sewer although it may be reuse in the development process.

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