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Adsorption efficiency of fired clay materials in removal of copper ion from printing developer waste

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Abstract: The paper analyses the application and adsorption efficiency of fired clay pellets (whole, half-pellets and their powder), produced from a pozzolanic material, waste glass, suitable surfactant and wooden dust, in removal of copper ion from a printing developer waste. The obtained results indicated that the copper ion removal reached the highest quantity after 30 min of contact. The experimental data have been fitted to Freundlich, Dubinin–Kaganer–Radushkevich and Temkin isotherm models. The obtained correlation coefficients were subjected to two-way ANOVA statistical method in order to investigate the statistical significance among the isotherm models. The comparative analysis of correlation coefficients showed that the Freundlich model is the most suitable one. The adsorption efficiency of the copper ion removal increases significantly with the increase of the adsorbent mass. The maximum obtained efficiency was 63%. Considering the size of the used adsorbents, the following order was noticed: whole pellet > powder > half-pellet. The results of performance tests present a good basis for the selection of column fill in the case of the purification of printing developers waste.

Key words: clay materials, cooper ion, adsorption process, printing developer, purification

1. INTRODUCTION

In the light of more popular appreciation of environmental issues, pressures have arisen to minimize the production of contaminants, and to remove contaminants already present in natural systems from past anthropogenic activities (Agathokleous et al., 2015; Turan and Ozgonenel, 2013; Abate et al., 2015). Various toxic heavy metals released into natural waters from graphic industry, chemical manufacturing, electroplating and metal finishing (Bedford, 2015; Omotoso and Ojo, 2015) present a great threat. Apart from being hazardous to living organisms, specific limits are exceeded, heavy metals accumulate in nature as they cannot be biodegraded or destroyed (Veli and Alyuz, 2007).

One of the most common heavy metals is copper. In graphic industry, it is frequently found in a printing developer waste originating from dye residue (Kiurski et al., 2012). Due to the fact that the copper is one of the substances present on the list of priority pollutants proposed by the Environmental Protection Agency (EPA), evidently there is a need to remove copper from industrial wastewaters (Veli and Alyuz, 2007). Copper can be transported via food chain to the human body through bioaccumulation, causing brain, skin, pancreas and heart diseases (Sdiri et al., 2014; Turan and Ozgonenel, 2013). The printing ink industry uses copper metal and copper/zinc alloy (brass), as well as their compounds for certain purposes (Siegwerk, 2015). In particular, all inks cyan, green and reddish blue color, and some pink and purple colors contain up to 3% copper. Copper salts and compounds are potentially dangerous for some living organisms, if they are, depending on their solubility, released via wastewater into the environment.

There are different physico-chemical methods for the removal of heavy metals from wastewaters. Adsorption, ion exchange, chemical settling and reverse osmosis are the most common. Among them, adsorption shows considerable efficiency (Veli and Ozturk, 2005). This process provides flexibility in design and operation of the treatment systems and in many cases generates high-quality effluent (Gimenes et al., 2013a). For this reason, many studies have been carried out in order to find out effective and low cost adsorbents (Ahmaruzzaman, 2011; Ngah and Hanafiah, 2008; Kiurski et al. 2012; Kiurski et al. 2013; Salam et al., 2011). Recently, researchers have focused on using clay materials as new efficient and recyclable adsorbents for the removal of metals (Ghorbel-Abid and Trabelsi-Ayadi, 2015; Padilla-Ortega et al., 2013; Zhao and He, 2014), organic compounds (Nguemtchouin et al., 2015; Tireli et al., 2014) and dyes (Errais et al., 2011).

The use of natural clays in the process of copper ion removal from aqueous solutions is of particular interest for environmental clean-up, since the use of natural adsorbents is particularly beneficial for the development of cost-effective processes. The chemical and mechanical stability of clays allow their application in various states (green or fired) and improve the consistency of adsorption relative to less stable materials. Relatively large specific surface area of these materials compared to their mass gives a wide range of available sites for ion adsorption. Moreover, clays are materials that can act as Lewis and Brönsted acids and offer a large cation exchange capacity in a layered structure that presents chemical and physical stability (Bedford, 2015; Gimenes et al., 2013b; Veli and Alyuz, 2007).

In continuation of our previous work (Kiurski et al., 2014a, 2014b, 2014c, 2014d; Kiurski et al., 2015), this study aimed to:

1. evaluate the potential of fired clay pellets in the removal processes of copper ion from a printing developer waste;
2. examine the influence of pellet form on adsorption efficiency; and
3. determine a statistical significance of the applied isotherm models.

2. MATERIALS AND METHODS

The sample of printing developer waste was taken from an offset printing facility, Novi Sad, Serbia. The role of the printing developer in the plate or film development is to convert the latent images to visible ones. The frequently used components of the fresh printing developer are potassium silicate, sodium silicate, sodium carbonate, potassium hydroxide, D-sorbitol, sodium sulfite, potassium bromide, metol (4-(methylamino)phenol sulfate), hydroquinone and pentasodium diethylene triamine penta acetic acid solution (DTPA).

The lightweight aggregate based on natural pozzolanic and waste materials was used as the adsorbent in the experiments described below. The raw mixture of this product consisted of natural pozzolanic material, waste glass, surfactant and wooden dust. The clayey material was shaped by extrusion, dried at 105 ºC during 24 h and fired at 1,020 ºC in laboratory conditions (Ranogajec et al., 2013). The fired clay pellets, i.e., whole pellets (diameter size of 5 mm), half-pellets and powders, were chosen for the adsorption experiments.

The adsorptions of Cu^{2+} ion onto the fired clay materials were studied in a batch mode. Determination of the equilibrium time experiments were carried out by shaking 0.2 g of adsorbents with 25 mL of aqueous working solution of Cu^{2+} ion (3.059 mg/L) at a speed of 160 rpm and shaking times of 15, 30, 45, 60, 75, 90, 105 and 120 min. The obtained solutions, at the end of the predetermined time intervals, were centrifuged for 10 min at 3000 rpm and then filtered through an Advantec quantitative cellulose filter paper (grade 5C). The equilibrated Cu^{2+} ion concentrations were determined with the ICP-MS method (PerkinElmer Elan 5000 mass spectrometer). The experimental results showed that the equilibrium is established at 30 min of shaking. Further, the adsorption experiments were performed by shaking various masses (0.04–0.24 g with the increment of 0.04 g) of each adsorbent (whole, half-pellets and powder) with an aliquot of a printing developer waste, within the determined contact time of 30 minutes. The Cu^{2+} ion concentrations were determined in the same way as in the equilibrium time experiment. Ambient temperature (23.4 °C) and pH value (13.0) were constant during the experiments.

In this study, a statistically significant difference between the isotherm models was investigated by using the software Excel 2007 with two-way ANOVA without replication. Two-way ANOVA is a multiple regression with two categorical explanatory variables or factors. In general, ANOVA is a special case of regression, where there is a quantitative response variable and one or more categorical explanatory variables. The response variable is modeled as varying normally around a mean that it is a linear combination of the explanatory variables. A design has replication if multiple observations exist for some of the treatment combinations. Without replication, there is only one observation per treatment combination (Bret, 2003). The advantage of this method lies in the fact that the model inputs, as well as their impact, possess all variability which otherwise would be impossible to assess (Hadži Stojković, 2006). In the majority of experiments, it is necessary to define and test the statistical hypothesis. Once the formed hypothesis is used to draw conclusions about the observed problems with the help of appropriate statistical methods, the hypothesis represents an assumption based on certain facts, mostly scientific or experimental. Within the ANOVA method, the null and alternative hypothesis must be formed and tested. The null hypothesis is the assumption that there will be no differences between the tested groups, and therefore, no significant results will be revealed. The alternative hypothesis, on the other hand, states that there will be a difference between the groups, performed on the collected data. In alternative hypotheses, at least two arithmetic means are different (Hadži Stojković, 2006). A decision about the acceptance or the rejection of the null hypothesis is based on the comparison of the experimentally obtained values of the parameter F for each factor, with theoretical (critical) value, F_{crit}, that is obtained from the table of the limit values of F distribution for certain degrees of freedom. If the value of the parameter F is less than F_{crit}, the null hypothesis is accepted and it brings to the conclusion that between the observed groups does not exist statistically significant differences. This means that independent variable has no effect. Otherwise, some of the alternative hypothesis will be accepted, and the mean values of some or of all the studied groups differ significantly. In this case, the test factor has an effect on the mean value of those data sets that differ significantly (Reimann, 2008).

3. RESULTS AND DISCUSSION

3.1 Equilibrium time experiments

The effect of equilibrium time on the copper ion adsorption was analyzed kinetically over a range of 15 - 120 min by shaking an aqueous solution of copper ion (3.059 mg/L) with constant mass of the fired clay pellets (whole pellets, half-pellets and their powders).

From theoretical point of view, the adsorption process requires long equilibrium time, while the practical approach needs a short contact time (Sdiri et al., 2014). The results indicate that more than 95% of the total adsorbtion capacity for all fired clayey materials (whole pellet, half-pellet and powder) occurred within 30 minutes (Figure 1). After this time, there was no significant removal of copper ion from the aqueous solution, suggesting that the equilibrium has been established. Faster removal of copper ion by the fired clayey materials confirms the significant role of chemisorption as a removal mechanism.

3.2 Adsorption isotherm models

Freundlich, Dubinin–Kaganer–Radushkevich (DKR) and Temkin isotherm models were used in this study to establish the relationship between the amount of adsorbed copper ion onto the fired clayey materials and their equilibrium concentration in a printing developer waste. The corresponding parameters of copper ion adsorption onto the fired clayey materials (the three analyzed systems) are presented in Table 1. The whole pellets showed the maximum capacity of copper ion adsorption (66.18 mg/kg), which was almost 37 times higher than in the case of the half-pellets (Table 1). The values of Freundlich adsorption capacity, K_f, indicate the best copper ion removal from a printing developer waste. According to the X_m values, the highest adsorption capacity (226.41·10^3 mg/kg) was also obtained with the whole pellets, forming the following decreasing order: whole pellet > powder > half-pellet, as in the case of Freundlich adsorption capacity. The maximum value of DKR adsorption energy (*E*) for copper ion removal was also obtained with the whole pellets used as adsorbents (42.03 kJ/mol) (Table 1). Temkin isotherm constant B showed that the whole pellets have the highest adsorption energy (4.74·10^3 J/mol) (Table 1).

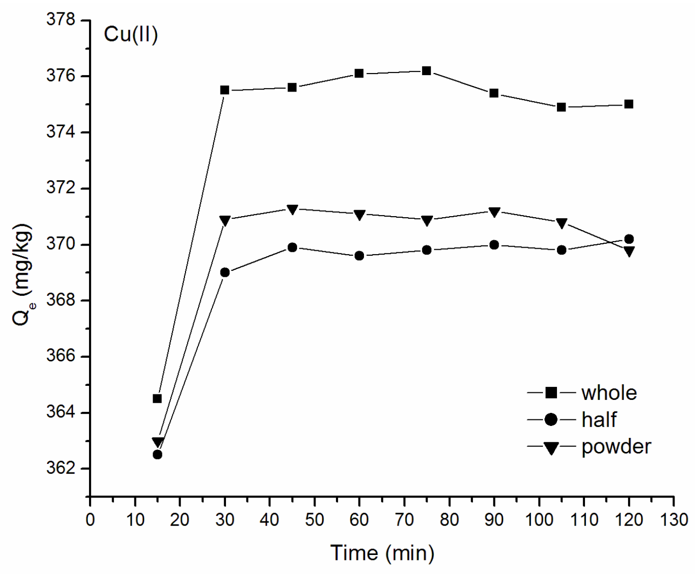

Figure 1. Equilibriumium contact time of Cu (II) ion on clay materials.

Table 1. Adsorption isotherm constants for copper ion adsorption onto the fired clayey materials.

Isotherm model	Isotherm parameter	Fired clay pellets		
		Whole pellet	**Half-pellet**	**Powder**
Freundlich	K_f (mg/kg)	66.18	1.78	15.44
	n	0.11	0.10	0.10
	R^2	0.956	0.900	0.918
DKR	$X_m \cdot 10^3$ (mg/kg)	226.41	111.29	224.06
	$\beta \cdot 10^{-10}$ (mol^2/J^2)	-2.83	-4.48	-3.47
	E (kJ/mol)	42.03	33.41	37.96
	R^2	0.949	0.880	0.902
Temkin	*A* (L/kg)	0.91	0.65	0.80
	$B \cdot 10^3$ (J/mol)	4.74	3.44	4.46
	R^2	0.841	0.747	0.761

The validation of Freundlich, DKR and Temkin isotherm models to the experimental data showed that the highest coefficient of determination, R^2, is obtained for Freundlich model in comparison with the DKR and Temkin models (Table 1). The high values in the coefficient of determination indicate the best model fitting with the experimental data (Ho et al., 2002; Sdiri et al. 2014). The obtained R^2 values (Table 1) suggest that Freundlich model is the most suitable one for describing copper ion removal from a printing developer waste using fired clay pellets as adsorbents. Therefore, the applicability of the used isotherm models follows the decreasing order: Freundlich > DKR > Temkin.

As the linearization plots may not be a significant basis to reject or accept the isotherm model, the suitability of these models is analyzed based on their fitness to the experimental data. The fitness of the data was established using a coefficient of determination, R^2, which represents the percentage of variance in the dependent variable that has been explained by the regression line (Ho et al., 2002; Sdiri et al. 2014). However, the obtained R^2 values was also subjected to two-way

ANOVA without replication at the significance level $\alpha = 0.05$. The comparative analysis of R^2 values (Table 2) indicates which model is suitable for describing the adsorption process based on the average correlation coefficients and how the experimental results fit the applied models. The obtained values in Table 2 also suggest that Freundlich model is the best one for the observed adsorption systems. Also, the data of copper ion adsorption onto whole pellets exhibit a better fitting to Freundlich, DKR and Temkin models. The value of $R^2 = 0.915$ indicates that the experimental data fit well with the isotherm models.

Table 2. The comparative analysis of R^2 values.

A. Summary				
	Count	*Sum*	*Average*	*Variance*
Freundlich	3	2.774	0.927	8.17×10^{-4}
DKR	3	2.731	0.910	1.24×10^{-3}
Temkin	3	2.349	0.783	2.57×10^{-3}
whole	3	2.746	0.915	4.16×10^{-3}
half-pellet	3	2.527	0.842	6.92×10^{-3}
powder	3	2.581	0.860	7.46×10^{-3}

The analysis of variance – ANOVA (Table 3) presented by the *F-values*, indicates whether there is a statistically significant difference between the applied models and the obtained results. As the *F-values* are higher than the F_{crit} (6.944), there is evidently a statistically significant difference between Freundlich, DKR and Temkin models in describing copper ion adsorption onto the three fired clayey pellets (Table 3).

Table 3. The analysis of variance – ANOVA.

B. ANOVA						
Source of Variation	*SS**	*df***	*MS****	*F-value*	*P-value*****	F_{crit}
Models	36.49×10^{-3}	2	18.24×10^{-3}	124.676	0.00025	6.944
Adsorbents	8.68×10^{-3}	2	4.34×10^{-3}	29.651	0.0040	6.944
Error	0.58×10^{-3}	4	0.15×10^{-3}			
Total	45.75×10^{-3}	8				

* Sum of squares; ** Degrees of freedom; *** Mean square; **** Statistical significance

3.3 The influence of pellet form on the adsorption efficiency

The structure of green and fired clays makes them popular as adsorbent materials. From this perspective, recycling industrial wastes gain added relevance, and a number of potential applications have been proposed in the production of clay-based materials (Acchar et al., 2006; Huang et al., 2001; Oliveira et al., 2007; Qi et al., 2010). A large specific surface area relative to their mass gives a wide range of available sites for the metal ion adsorption. The chemical and mechanical stability allow their application in various states and improve the consistency of adsorption relative to less stable materials (Abd-Allah et al., 2007; Bedford, 2015; Karapinar and Donat, 2009).

The presence of water in interlayer zones of green clay materials greatly reduces cohesion within these materials, thus allowing the adsorbate greater access to available active sites for cation exchange and adsorption (Bedford, 2015).

The adsorption efficiency of the system ($R_{eff}\%$) is calculated as in equation (1):

$$R_{eff}\% = \frac{C_i - C_e}{C_i} x100 \quad (1)$$

where C_i and C_e are the initial and the final concentration of the metal ions present in the solution (mg/L) (Turan and Ozgonenel, 2013).

The increase of the copper ion adsorption with the usage of fired clayey materials can be attributed to the increased surface area and the availability of more adsorption sites (Bedford, 2015). The results shown in Figure 2 indicate that the removal of copper ion from a printing developer waste also increases with the increase of the adsorbent mass. The maximum adsorption efficiencies of the copper ion removal by using whole pellet, half-pellet and the powder were 63.6, 48.9 and 58.8%, respectively (Figure 2). Therefore, the values of R_{eff} decreased in the following order: whole pellet > powder > half-pellet.

The whole pellets, as adsorbents, have higher surface functionality, hence a great number of sites that are available for the interaction with the copper ion present in a printing developer waste. Beside the availability of the surface sites, the observed trend of adsorption efficiency is also related to the clay structure.

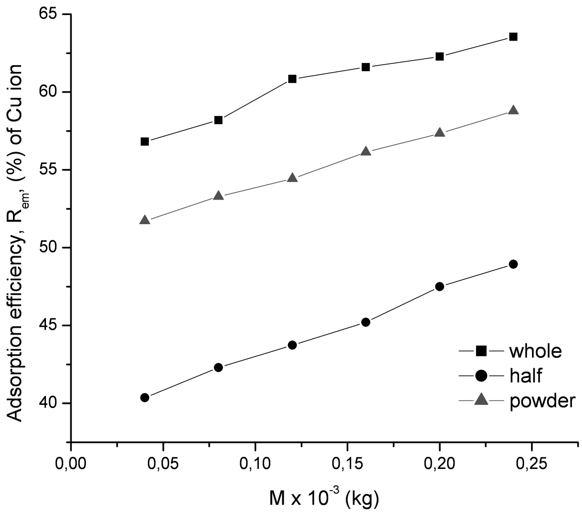

Figure 2. Efficiency of copper ion removal using fired clayey materials.

The results of the performance tests present a good basis for the selection of column fill in the case of the purification of printing developers wastes.

4. CONCLUSIONS

The adsorption capacity of the used fired clay pellets (whole pellets, half-pellets and their powders), produced from a mixture of pozzolanic material, waste glass, suitable surfactant and wooden dust, was tested in order to remove copper ion from a printing developer waste.

The obtained results indicated that the removal of copper ion was effective within the first 30 minutes of contact. The adsorption data were evaluated by using Freundlich, Dubinin–Kaganer–Radushkevich and Temkin isotherm models. The validation of the coefficient of determination (R^2) showed that the applicability of the used models follows the decreasing order: Freundlich > DKR > Temkin. The Freundlich model gave the best agreement during the whole adsorption range (with correlation coefficient $R^2 > 0.900$). The results of two-way ANOVA without replication at significance level $\alpha = 0.05$ pointed out that there was a statistically significant difference between Freundlich, DKR and Temkin models in describing the copper ion adsorption onto all the analysed forms of the fired clayey pellets.

The whole pellets showed the highest adsorption capacity of the copper ion adsorption, 66.18 (K_f value) and $226.41 \cdot 10^3$ mg/kg (X_m value), in relation to half-pellets and their powder. The whole pellets affected better removal of copper ion from the printing developer waste. The maximum adsorption efficiencies of 63% were achieved by using whole pellets.

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