

Scientific paper

# Evaluation of Adsorption Capacity of Montmorillonite and Aluminium-pillared Clay for $\text{Pb}^{2+}$ , $\text{Cu}^{2+}$ and $\text{Zn}^{2+}$

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Received: 21-07-2015

## Abstract

Adsorption capacity of the two adsorbents was investigated as a function of contact time between adsorbent and heavy metal ions solutions, the initial heavy metals concentration of the synthetic wastewater, pH value, temperature and adsorbent mass. Preliminary experiments at different pH values between 2.0 and 7.0 were performed, and were observed that maximum adsorption occurs at pH 5 for copper ( $q_{\text{max}} = 92.59 \text{ mg} \cdot \text{g}^{-1}$ ), 6.0 for lead ( $q_{\text{max}} = 97.08 \text{ mg} \cdot \text{g}^{-1}$ ) and 6.5 for zinc ions ( $q_{\text{max}} = 73.52 \text{ mg} \cdot \text{g}^{-1}$ ), respectively. The sorption capacity of studied adsorbents for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  was calculated using Langmuir and Freundlich models. Thermodynamic parameters – enthalpy change ( $\Delta H^0$ ), entropy change ( $\Delta S^0$ ) and free energy ( $\Delta G^0$ ) – were calculated for predicting the nature of adsorption. Scanning electron micrograph (SEM) revealed changes in the surface morphology of the adsorbent as a result of heavy metal ions adsorption. EDS characterization confirmed qualitatively the presence of adsorbed species in the samples. On the basis of the obtained results the adsorption it was proposed an ordered adsorption:  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , on the sorbents we investigated.

**Keywords:** aluminium pillared clay, adsorption, heavy metals, montmorillonite-K10, wastewater purification application.

## 1. Introduction

Heavy metals are present in aqueous waters wastes of many industries, such as nonferrous metal industry, metal plating, mining operations, paint industry, oil refining, radiator manufacturing, smelting, plastic industries, storage batteries industries, etc.

The removal of heavy metals from contaminated water represents a major research subject due to the toxicological aspects. Lead (Pb), copper (Cu), cadmium (Cd), zinc (Zn), chromium (Cr), arsenic (As) and nickel (Ni) are common pollutants found in industrial effluents. As microelements, some heavy metals (e.g. copper, selenium, zinc) are essential in the maintenance of the human body metabolism, but in high concentrations they can be dangerous.

The level of heavy metals in residual waters has considerably increased in last period due to a rapid development of industrial activities. Heavy metals can damage li-

ver, kidney, bone and nerves by blocking functional groups of vital enzymes.<sup>1–3</sup>

Various physical and chemical treatment processes such as chemical precipitation,<sup>4,5</sup> ion exchange,<sup>6,7</sup> membrane filtration,<sup>8</sup> coagulation, and adsorption<sup>9–12</sup> have been widely used to reduce heavy metal content from industrial wastewaters. Nevertheless, most of these methods have several disadvantages, such as complicated treatment process, energy consumption, and are expensive. Adsorption of heavy metals from aqueous solutions is an effective method that has good results in the removal of contaminants from aqueous effluents. The main advantages of adsorption over conventional treatment methods consist of low cost, high efficiency, minimization of chemical and/or biological sludge, regeneration of adsorbent, and possibility of metal recovery.

Among the treatment technologies, the biosorption is a high selective, efficient, cost effective and easy to apply. Different types of biomass have been tested for the re-

removal of heavy metals from residual waters, such as: maize cob,<sup>13</sup> banana pit,<sup>14</sup> fungi,<sup>15–17</sup> bacteria.<sup>18,19</sup>

The present investigations regard two adsorbents: montmorillonite-K10 and aluminium-pillared clay removal ability of Pb<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup> ions from synthetic wastewaters.

## 2. Experimental

All the chemicals used in our experiments were analytical reagent grade products from Sigma Aldrich, USA. For the preparation of synthetic heavy metals wastewater, Cu(NO<sub>3</sub>)<sub>2</sub>·5H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O salts were used to make a 250 mg/L solution, which was diluted to 50, 75, 100, 125, 150, 175, 200 and 225 mg/L. The sorbents were purchased from Sigma Aldrich and were used without any supplementary treatment.

The pH of the solutions was measured using a HANNA pH/temperature meter HI 991001 with a micro pH electrode calibrated with pH 4.01, 7.01, and 10.01 buffers.

The concentration of heavy metal ions in aqueous solution after sorption experiments was determined by flame atomic absorption spectroscopy (FAAS) on a continuum source atomic absorption ContrAA® –300 device equipped with an Echelle double monochromator with a high resolution. The wavelengths at which measurements were made are: λ<sub>Pb</sub> = 217 nm, λ<sub>Cu</sub> = 324.75 nm, respectively, λ<sub>Zn</sub> = 213.85 nm. Scanning Electron Microscopy (SEM) characterization was performed using a JEOL JSM 6362LV electron microscope in high vacuum mode at 15 kV acceleration voltage on uncoated samples. EDS characterization was performed using the INCA-ActX detector (Oxford) present on the SEM at 20 kV.

The textural properties of all samples were investigated by nitrogen sorption on a NOVA 2200e (Quantachrome instrument) automated gas adsorption system. The BET equation was used to estimate the specific surface area.

The characteristic of the used adsorbent are presented in Table 1.

Adsorption studies were performed by batch technique at different temperatures (30, 35, 40, 45 °C), various adsorbent mass (0.0025, 0.005, 0.0075, 0.01, 0.02, 0.03,

0.04, and 0.05 g, respectively), and a pH range between 2 and 7 (2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, and 7). The pH values were adjusted with 0.1 M NaOH and, respectively, HNO<sub>3</sub> solutions.

For sorption experiments, a weighed amount of adsorbent was equilibrated with a definite volume of solution of known concentration at a pre-established temperature. After different contact time (10 min., 20 min., 30 min., 40 min., 50 min., 60 min., 70 min., 80 min., 90 min., 100 min., 110 min., and 120 min., respectively), the supernatant was filtered and the filtrate was analysed by FAAS.

All experiments were carried out in duplicate and standard deviations were found to be less than 5.0%.

The percentage of retained metal ions on the adsorbents was calculated using the formula:

$$\text{sorption (\%)} = \frac{C_0 - C_e}{C_0} \cdot 100 \quad (1)$$

The amount of metal absorbed per unit mass by the adsorbent,  $q$ , was calculated with the equation (2)

$$q = \frac{(C_0 - C_e) \cdot V}{m} \quad (\text{mg / g dry adsorbent}) \quad (2)$$

where  $C_0$  is the initial concentration of solution, (mg · L<sup>-1</sup>),  $C_e$  is the equilibrium concentration (mg · L<sup>-1</sup>),  $V$  is the volume of solution (L), and  $m$  is the adsorbent mass (g).

The adsorption constant  $K_d$  is defined as the ratio of the concentration of metal in the adsorbent and the one in the solution at equilibrium. It was calculated with equation (3).

$$K_d = \frac{(C_0 - C_e) \cdot V}{C_e \cdot m} \quad (\text{mL} \cdot \text{g}^{-1}) \quad (3)$$

## 3. Results and Discussion

### 3.1. Effect of Contact Time on the Adsorption Process

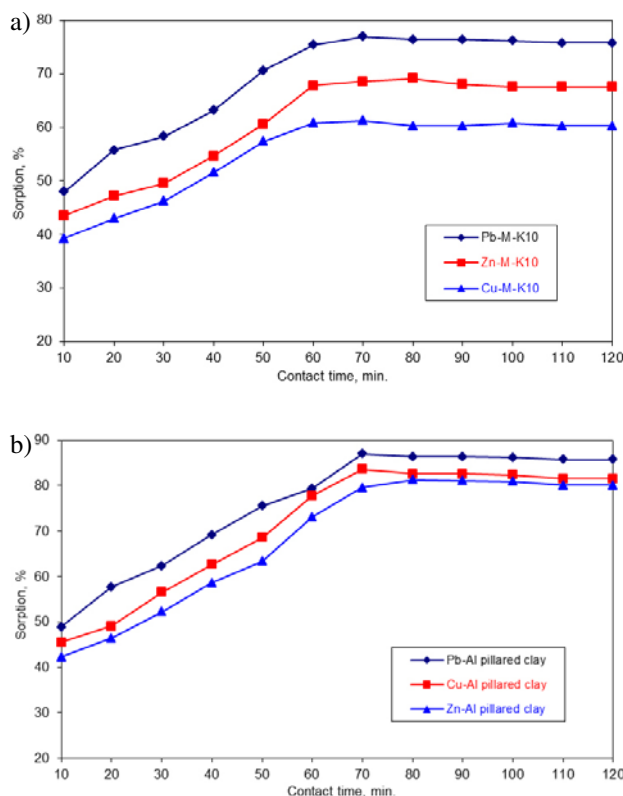
The influence of the contact time on the adsorption process of lead, copper and zinc ions on the two selected adsorbents was studied varying the contact time in the range of 0–120 minutes.

All experiments were carried out at a pH of 5 for the copper, 6.0 for the lead and 6.5 for zinc ions at a constant temperature of 25 °C and at a concentration of 150 mg · L<sup>-1</sup>.

The results (Fig. 1) show that the amount of the retained ions increases rapidly with the contact time, up to 10 min. and after this faster step, the adsorption becomes slower. The fast adsorption in the initial stage was, probably, due to the initial concentration gradient between

**Table 1.** Characteristics of the adsorbent.

Parameter	Sorbent	Value
BET surface area (m <sup>2</sup> · g <sup>-1</sup> )	montmorillonite	220
	aluminium pillared clay	250
Total pore volume (cm <sup>3</sup> · g <sup>-1</sup> )	montmorillonite	0.193
	aluminium pillared clay	0.383
Pore size (nm)	montmorillonite	4.32
	aluminium pillared clay	15.77



**Fig. 1.** Effect of contact time on Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> adsorption onto montmorillonite-K10 (a) and Al-pillared clay (b); V = 50 mL, m = 0.05g.

the adsorbate in solution and the number of vacant sites accessible on the adsorbent surface. The achievement of equilibrium adsorption might have been due to a decreasing in the available adsorption sites on the adsorbent with time, result a limited mass transfer of the adsorbate molecules from the liquid to the external surface of adsorbent.

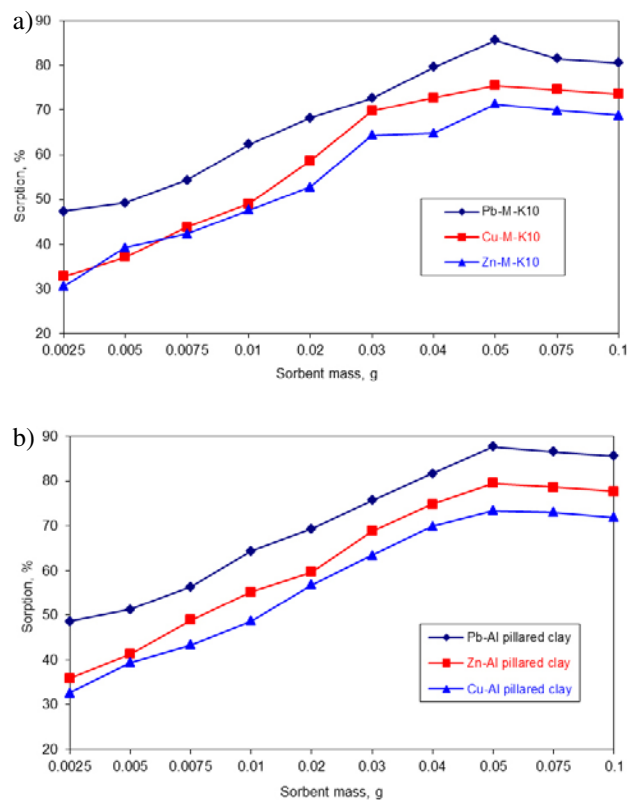
The equilibrium is reached in 75 minutes after which the sorption remains constant. It was found that the adsorption process onto Al-pillared clay is more intense in comparison with montmorillonite-K10 and has higher efficiency in the case of lead ions.

### 3. 2. Dependence of Adsorption Process on the Adsorbent Mass

An important factor influencing the effectiveness of the adsorption process from an economic point of view is the mass of adsorbent to be used. The adsorption is inefficient if it requires a substantial amount of adsorbent. The effect of the adsorbent mass on the adsorption process was studied at a fixed concentration of 150 mg · L<sup>-1</sup> metal ion solution, pH of 5.0 (copper), 6.0 (lead) and 6.5 (zinc), at a temperature of 25 °C, and volume of solution of 50 mL.

Figure 2 shows an increasing of the percentage of retained metal with the increase of adsorbent mass ran-

ging from 0.0025 g to 0.1 g. The reason could be that a larger mass of adsorbent involves a larger number of accessible active centres on his surface. An increase in the mass of adsorbent of more than 0.05 g leads to a decrease in the retention of metal ions. A number of researchers have explained that this variation by the adsorbent agglomeration at higher concentrations, which could lead to a decrease in the surface of contact between the adsorbent and the solution.<sup>20</sup> Özer et al.<sup>21</sup> have shown that the interaction of the particles at a greater concentration of the adsorbent can be a factor to partially desorption of the metal ions that is weakly bound to the surface of the adsorbent.

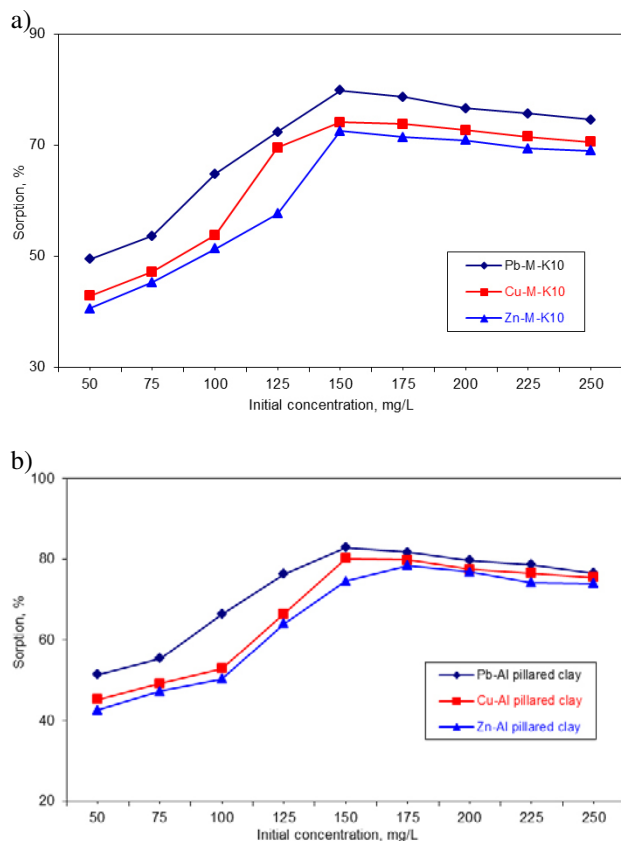


**Fig. 2.** Effect of adsorbent mass on adsorption process of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> onto montmorillonite-K10 (a) and Al-pillared clay (b).

### 3. 3. Influence of Initial Ions Concentration on Adsorption Process

The effect of the initial concentration on the adsorption process of lead, copper and zinc ions were also investigated.

These studies were carried out at 25 °C. The concentrations of copper and zinc ions in solutions range from 50 to 250 mg · L<sup>-1</sup>, while all the other parameters were maintained constant (pH 5, 6.0 and 6.5, the contact time – 75 minutes, the adsorbent mass – 0.05 g, volume of solution in contact with the adsorbent – 50 mL).



**Fig. 3.** Effect of initial ions concentration on adsorption of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> on montmorillonite-K10 (a) and Al-pillared clay (b).

It was observed that the adsorption process increases with the increasing concentration of the metal ions to an amount of 150 mg · L<sup>-1</sup> followed by a slow decrease in the adsorption process (Fig. 3).

This variation could be explained by the fact that with the increasing concentration, the binding centers of adsorbent are becoming saturated and no more ions can be adsorbed. Also, the increasing metal ions concentration has the effect of increasing of the amount of metal ion adsorbed due to increasing driving force of these ions towards the active sites of adsorbent. Another explanation could be that in dilute solutions the metal ions have high mobility and, therefore, their interaction with the adsorbent is high.

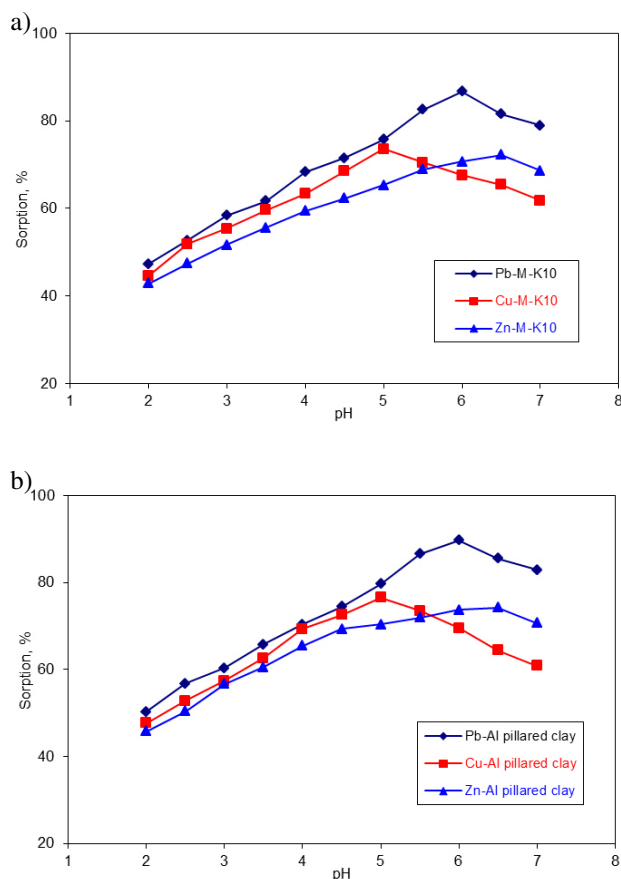
### 3. 4. pH Dependence of Adsorption Process

The adsorption of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> ions strongly dependent on the initial pH of heavy metal ions solution because it affects the species of metal ions that are present in solution.<sup>22</sup> These experiments were carried out at a fixed concentration of 150 mg · L<sup>-1</sup> metal ion solution, at a temperature of 25 °C with a 0.05 g adsorbent and volume of solution of 50 mL.

In this study, the adsorption experiments were performed in the initial pH range of 2–7 (Fig. 4). At pH > 6,

Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> ions precipitate as insoluble hydroxides which makes impossible the study of the adsorption process.<sup>23,24</sup>

We analyzed the possibility of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> to precipitate as hydroxides at pH of experiment during adsorption process. In agreement with the studies of Adebowale et al.<sup>25</sup> we used the solubility product constant ( $K_{sp}$ ) to calculate the pH values at which the hydroxides of the metal ions start to formulate. Therefore, we found that the pH values for precipitation of these ions from 150 mg · L<sup>-1</sup> solution are 6.71 for Pb<sup>2+</sup>, 4.86 for Cu<sup>2+</sup> and 7.26 for Zn<sup>2+</sup>, respectively.



**Fig. 4.** Dependence of adsorption process on pH value: montmorillonite-K10 (a), Al-pillared clay (b).

Consequently, the pH of heavy metal ion solutions was varied from 2 to 7.

As an example, in the case of lead ions at pH values greater than 6 can form species such as: Pb(OH)<sub>2</sub>, Pb(OH)<sub>3</sub><sup>-</sup>, Pb<sub>2</sub>(OH)<sub>4</sub><sup>2+</sup>, Pb<sub>4</sub>(OH)<sub>4</sub><sup>4+</sup>, leading to a decrease of the adsorption process.<sup>26</sup>

Increasing the amount of retained metal with increasing pH can be explained by the decreasing of the competition between metal ions and protons present on the adsorbent surface.

### 3. 5. Dependence of Adsorption Process on the Temperature

The temperature influence on the adsorption of heavy metal ions studied on the two sorbents was investigated in a temperature range between 25–45 °C, all the other parameters being kept constant. The obtained results are shown in Figure 5.

The continuous increase in percentage removal with temperature shows that the adsorption process was endothermic in nature. This was supplementary supported by calculating thermodynamic parameters. The change in free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy

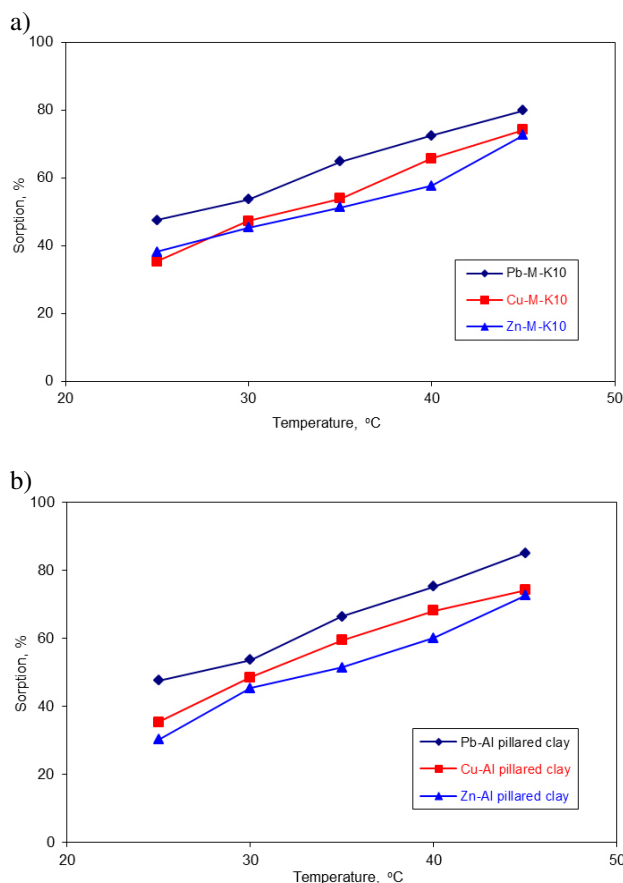


Fig. 5. Dependence of adsorption process on temperature: montmorillonite- K10 (a) Al-pillared clay (b).

( $\Delta S^\circ$ ) of adsorption was calculated using the following equations:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (4)$$

$$\Delta G^\circ = -RT \ln K_d \quad (5)$$

where  $K_d$  is the adsorption constant, calculated with equation (3).

The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated from the slope and intercept with the ordinate using the representation of  $\ln K_d$  versus  $1/T$ . The obtained results are shown in Table 2.

From Table 2 one can observe that  $\Delta H^\circ$  and  $\Delta S^\circ$  have positive values indicating that the adsorption is an endothermic process and suggest that a large amount of heat is consumed to transfer ions from aqueous solution into the solid phase, respectively the good affinity of the investigated adsorbents for the metal ions. According to Nunes and Airoidi<sup>27</sup> the metal ions must lose much of the hydration water before they could enter into the cavities adsorbent. Such a release of water would cause the positive values of  $\Delta S^\circ$ . This mechanism is supported by positive values of this parameter obtained in such investigations showing that metal ions are less hydrated in adsorbent layers than in aqueous solutions. Also, the positive values of this parameter indicate an increase in the degree of disorder in the system with the changes in the hydration of the adsorbed ions. The negative values of Gibbs energy indicate the spontaneity of the adsorption process, and the decrease of values with the increasing of temperature indicated a more efficient adsorption at higher temperatures.

### 3. 6. Adsorption Isotherms

In order to investigate the adsorption of lead, copper and zinc ions on the two types of adsorbent were used Langmuir and Freundlich models.

Langmuir isotherm assumes a monolayer adsorption and supposes that the maximum adsorption takes place when the adsorbed forms a saturated layer on the surface of the adsorbent.<sup>28,29</sup>

Table 2. Thermodynamic parameters for the adsorption of  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  onto montmorillonite-K10 and Al-pillared clay.

Adsorbent	Ion	$\Delta H^\circ$ , $kJ \cdot mol^{-1}$	$\Delta S^\circ$ , $J \cdot mol^{-1} \cdot K^{-1}$	$\Delta G^\circ$ , $kJ \cdot mol^{-1}$					Mean	S.E.(±)
				25 °C	30 °C	35 °C	40 °C	45 °C		
Montmorillonite K10	$Pb^{2+}$	31.59	68.66	-17.87	-18.6	-19.52	-20.46	-21.26	-19.42	0.611
	$Cu^{2+}$	34.91	67.41	-17.72	-18.55	-19.39	-20.07	-20.94	-19.33	0.563
	$Zn^{2+}$	36.94	66.70	-17.62	-18.44	-19.31	-19.96	-20.68	-19.20	0.541
Al-pillared clay	$Pb^{2+}$	28.26	69.23	-18.02	-18.75	-19.62	-20.64	-21.42	-19.69	0.615
	$Cu^{2+}$	31.59	68.49	-17.89	-18.57	-19.47	-20.41	-21.24	-19.51	0.604
	$Zn^{2+}$	39.90	67.92	-17.74	-18.55	-19.41	-20.15	-21.10	-19.39	0.588

$$q_e = \frac{q_m \cdot b \cdot C_e}{1 + b \cdot C_e} \quad (6)$$

The linearized Langmuir isotherm was applied:

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot q_m} + \frac{C_e}{q_m} \quad (7)$$

where  $q_e$  is the amount of adsorbed metal per sorbent unit ( $\text{mg} \cdot \text{g}^{-1}$ ) at equilibrium;  $q_m$  is the parameter that denotes the maximum adsorption capacity ( $\text{mg} \cdot \text{g}^{-1}$ );  $K_L$  is constantly referring to the adsorption energy ( $\text{g} \cdot \text{L}^{-1}$ ).

$K_L$  and  $q_m$  values were calculated from the intercept and the slope of the straight line obtained by plotting  $C_e/q_e$  versus  $C_e$  (Fig. 6).

According to Hall et al.<sup>30</sup> the important characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor,  $R_L$ , which is defined by the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (8)$$

This separation factor,  $R_L$ , indicates the isotherm profile and whether the adsorption process is favorable or not, according to the below criteria (Table 3).

**Table 3.** Range of  $R_L$  factor.

$R_L$ values	Adsorption process
$R_L = 0$	Irreversible
$0 < R_L < 1$	Favorable
$R_L = 1$	Linear
$R_L > 1$	Unfavorable

In the present investigations the  $R_L$  obtained values were less than one (Table 2) which shows that the adsorption process was favorable.

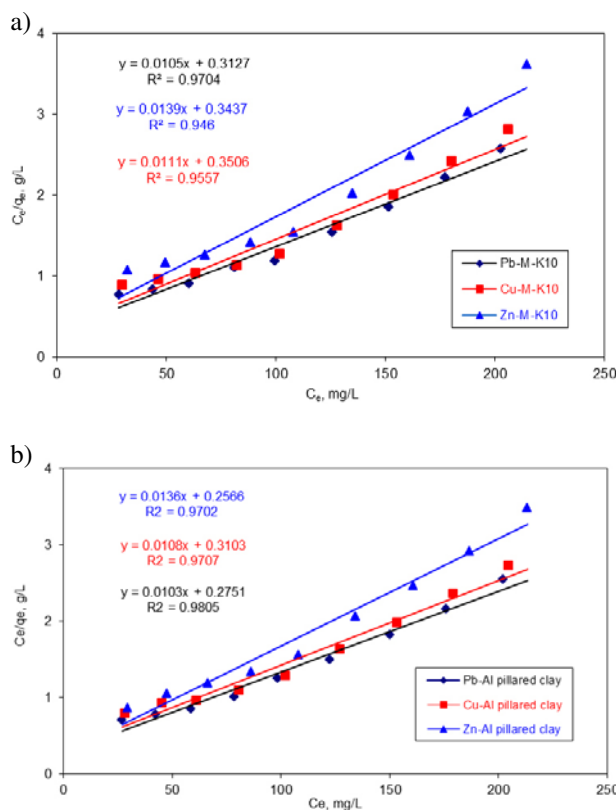
Freundlich isotherm is another mathematical model extensively used to describe the adsorption process of the metal ions from the solution on the solid surface that assumes a heterogeneous surface adsorption.

$$q_e = K_F \cdot C_e^{1/n} \quad (9)$$

The linear form is given by equation (10):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (10)$$

In this equation,  $K_F$  ( $\text{mg}^{(1-1/n)} \cdot \text{L}^{1/n} \cdot \text{g}^{-1/n}$ ) and  $1/n$  are the constants that relate the Freundlich adsorption capacity of the sorbent, and the adsorption intensity, respectively.



**Fig. 6.** Langmuir adsorption isotherms: montmorillonite – K10 (a), Al-pillared clay (b).

The  $1/n$  and  $K_F$  parameters were calculated from the slope and intercept of the linear representation of  $\log q_e$  versus  $C_e$  (Fig. S1) and are presented in Table S1. The subunit values obtained for  $1/n$  indicates a favorable adsorption process. In all investigated cases, the  $n$  values which represented the favorability of the adsorption process were more than one, indicating that the adsorption process is favorable. A smaller  $1/n$  value indicates more heterogeneous surface while a value closer to or even one indicates that the adsorbents have relatively more homogeneous binding sites.<sup>31</sup>

On the basis of regression coefficient of the obtained experimental data on the adsorptive behavior of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions on montmorillonite-K10, and Al-pillared clay, it may be concluded that the adsorption behavior of these ions on the studied adsorbents is in good agreement with Langmuir model.

Based on the presented results it can be established a series in terms of the metal ion adsorption on two sorbents:



It is known that in aqueous solution the metal ions are hydrated, and the obtained series can be correlated well with the variation of the hydrated ion radii, that is shown in Table 5.

**Table 4.** Parameters and correlation coefficients calculated for Langmuir adsorption model for Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> on montmorillonite-K10 and Al-pillared clay.

Adsorbent	Ion	q <sub>m</sub> (mg · g <sup>-1</sup> )	K <sub>L</sub> (L · g <sup>-1</sup> )	R <sup>2</sup>	R <sub>L</sub>
Montmorillonite- K10	Pb <sup>2+</sup>	95.23	0.033	0.970	0.168
	Cu <sup>2+</sup>	90.90	0.031	0.955	0.215
	Zn <sup>2+</sup>	71.94	0.040	0.946	0.166
Al-pillared clay	Pb <sup>2+</sup>	97.08	0.037	0.980	0.180
	Cu <sup>2+</sup>	92.59	0.034	0.970	0.196
	Zn <sup>2+</sup>	73.52	0.053	0.970	0.125

**Table 5.** Hydrated ion radii.

Metallic Ion	Radius(Å)
Pb <sup>2+</sup>	4.01
Cu <sup>2+</sup>	4.19
Zn <sup>2+</sup>	4.30

In order to establish the efficiency of these adsorbents towards Pb<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup> there was performed a comparison with the results from the literature for other adsorbents, and the results are presented in Table 6.

### 3. 7. SEM Characterization

SEM images recorded before and after adsorption process of heavy metals on montmorillonite-K10 and aluminium pillared clay are presented in Figure 7. Both sorbents and metal-absorbed samples proved to be quite conductive. Images of ×1000 magnification for each sorbent-metal absorbed series of samples are presented in the following images.

Images 7a–d show the sorbent montmorillonite-K10 microscopic aspect followed by the images of Zn, Pb and Cu modified. SEM micrographs present generally a granular structure. According to SEM observations Zn presence seems to promote agglomerations compared with the sorbent structure and it seems to have a slightly improved conductivity.

Pb and Cu presence seems that don't change significantly the microscopic characteristics of the sorbent material.

Images 7e–h show the sorbent Al-pillared clay microscopic aspect followed by the images of Zn, Pb and Cu modified. SEM micrographs present generally a granular structure. Al-pillared clay structure is quite different of montmorillonite –K10 sorbent structure. It seems „fluffier” and containing lamellar structures. According to SEM observations metal presence seems to promote agglomeration and perhaps hardening compared with the Al-pillared clay sorbent initial structure and it seems to have a slightly improved conductivity. Zn, Pb and Cu modified Al-pillared clay sorbent shows a larger grain size distribution, irregular grains and large agglomerations.

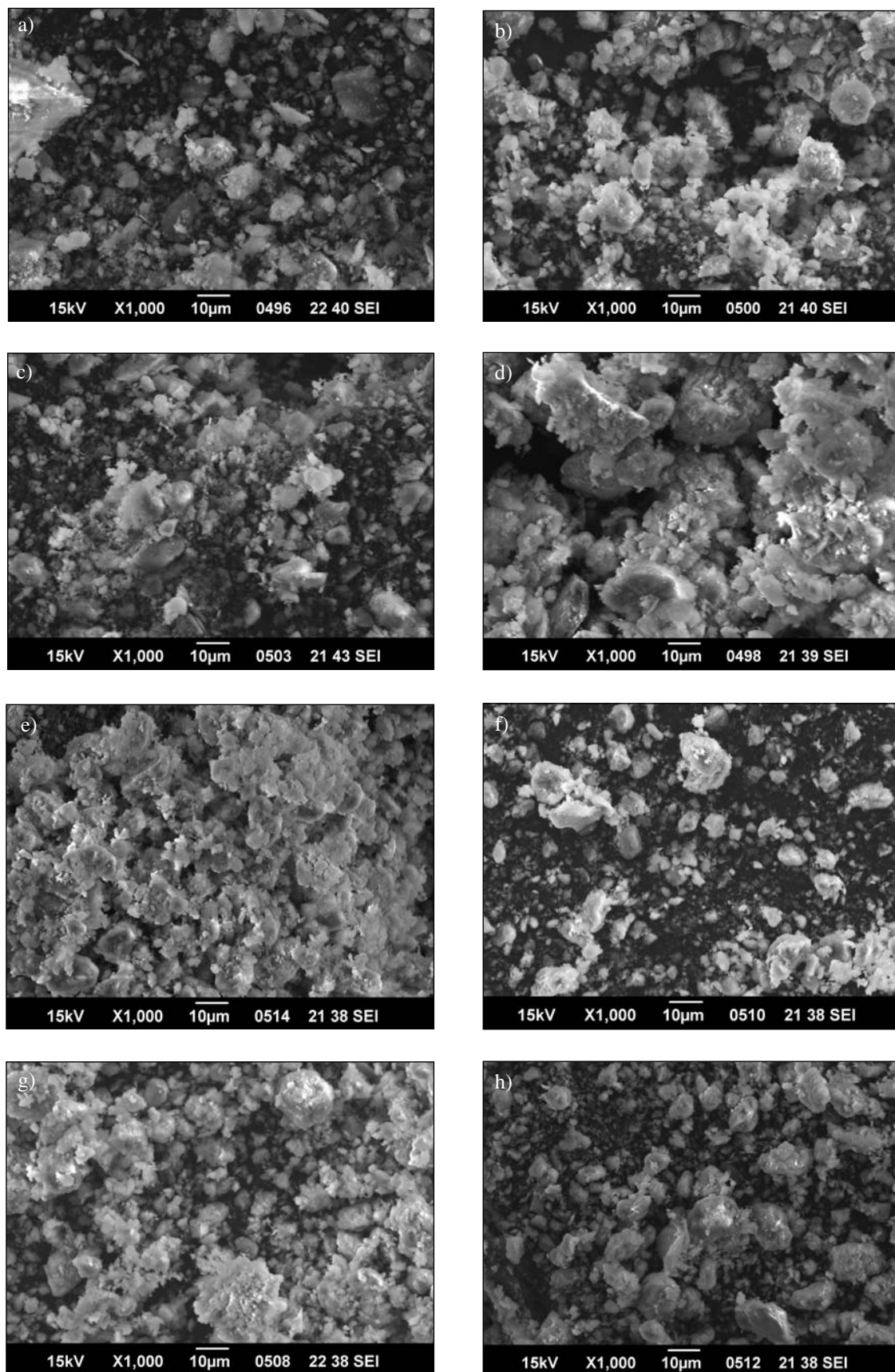
Due to the fact that samples are not enough conductive and not enough stable to stand 20kV accelerated electron beam for long enough time to have a decent number of counts collected, the results of EDS analysis are only **qualitative** in this case. EDS analysis shows the presence of Cu, Pb and Zn in both Al-pillared clay structure and montmorillonite –K10 sorbents.

The following table shows an example of elemental composition (weight and atomic %) for each type of studied material for a 65 seconds collection time (20kV).

EDS analysis confirmed the highest retention rate for Pb<sup>2+</sup> (larger in K10) but shows higher Zn<sup>2+</sup> retention than Cu<sup>2+</sup> in both Al-pillared clay structure and montmorillonite –K10 sorbents.

**Table 6.** Comparative analysis of adsorption efficiency of different adsorbents for Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> ions.

Adsorbent	q <sub>m</sub> (mg · g <sup>-1</sup> )			Reference
	Pb <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	
Maghemite	–	26.8	57.21	8
TiO <sub>2</sub>	81.3	–	15.3	9
HMO	324.32	–	57.21	11
BENT–PAAm	–	33	–	12
Al <sub>2</sub> O <sub>3</sub> modified	100	16.3	–	32,33
Lignin	89.42	23.04	11.18	34
SBA-15	–	10.5	6.9	35
Functionalised SBA-15	1.24	0.2208	0.845	36
Nordmann fir	29.3	–	18.4	37
Montmorillonite-K10	95.23	90.90	71.94	This study
Al-pillared clay	97.08	95.29	73.52	This study



**Table 7.** Example of elemental composition (weight and atomic %) for each type of studied material for a 65 seconds collection time (20kV).



**Table 7.** Example of elemental composition (weight and atomic %) for each type of studied material for a 65 seconds collection time (20kV).

Al pillared clay			Zn-Al pillared clay			Cu-Al pillared clay			Pb-Al pillared clay		
Element	Wt%	At%	Element	Wt%	At%	Element	Wt%	At%	Element	Wt%	At%
<i>CK</i>	03.49	05.55	<i>CK</i>	03.06	05.03	<i>CK</i>	04.76	07.72	<i>CK</i>	02.90	04.79
<i>NK</i>	01.53	02.09	<i>NK</i>	01.79	02.53	<i>NK</i>	01.50	02.08	<i>NK</i>	01.16	01.64
<i>OK</i>	53.08	63.37	<i>OK</i>	47.48	58.71	<i>OK</i>	47.95	58.30	<i>OK</i>	48.63	60.32
<i>MgK</i>	01.65	01.30	<i>MgK</i>	00.93	00.76	<i>MgK</i>	01.58	01.27	<i>MgK</i>	01.59	01.30
<i>AlK</i>	11.61	08.22	<i>AlK</i>	07.84	05.75	<i>AlK</i>	12.18	08.78	<i>AlK</i>	12.41	09.13
<i>SiK</i>	28.65	19.48	<i>SiK</i>	38.45	27.08	<i>SiK</i>	31.20	21.61	<i>SiK</i>	32.16	22.72
			<i>ZnK</i>	00.44	00.14	<i>CuK</i>	00.83	00.25	<i>PbM</i>	01.15	00.11
M-K 10			Zn-M-K 10			Cu-M-K 10			Pb-K 10		
Element	Wt%	At%	Element	Wt%	At%	Element	Wt%	At%	Element	Wt%	At%
<i>CK</i>	03.55	05.62	<i>CK</i>	06.91	10.98	<i>CK</i>	06.34	10.16	<i>CK</i>	09.06	14.45
<i>NK</i>	01.56	02.12	<i>CK</i>	06.91	10.98	<i>NK</i>	01.40	01.93	<i>NK</i>	01.42	01.94
<i>OK</i>	54.23	64.42	<i>OK</i>	47.47	56.64	<i>OK</i>	47.70	57.42	<i>OK</i>	45.40	54.32
<i>AlK</i>	11.66	08.21	<i>MgK</i>	01.60	01.26	<i>MgK</i>	00.86	00.68	<i>MgK</i>	00.93	00.73
<i>SiK</i>	29.00	19.63	<i>AlK</i>	11.85	08.38	<i>AlK</i>	06.65	04.75	<i>AlK</i>	06.89	04.89
			<i>SiK</i>	30.31	20.60	<i>SiK</i>	36.17	24.80	<i>SiK</i>	34.49	23.51
			<i>ZnK</i>	00.37	00.11	<i>CuK</i>	00.88	00.26	<i>PbM</i>	01.81	00.17

Elemental mapping was not possible at a publishable resolution due to already mentioned reasons. Longer collection time leads to irreversible deterioration of material at the 20kV electron beam exposure.

### 3. 8. Desorption Studies

The desorption processes are important to recover the metal ion and its subsequent use in industrial field and, secondly, to reuse of the regenerated sorbent. The desorption experiments were carried out in batch system by immersing the sorbent after adsorption in different eluents solutions (HCl, HNO<sub>3</sub> and NaHCO<sub>3</sub> 0.1 M solutions) for 24 hours with stirring at 250 rpm.

The metal ion concentration in the supernatant was determined using AAS method. The percentage of desorbed metal ion was calculated using the following equation:

$$\text{desorbed ion \%} = \frac{\text{amount}_{\text{des}}}{\text{amount}_{\text{ads}}} \cdot 100 \quad (11)$$

where: amount<sub>des</sub> represents the amount of desorbed metal ion and amount<sub>ads</sub> is the amount of the retained metal ion.

The obtained results are presented in Table 8.

The results show that the adsorption process is reversible and also there is the possibility to reuse chosen

**Table 8.** Desorption results.

Ion	Desorption, %			
	H <sub>2</sub> O	HCl	HNO <sub>3</sub>	NaHCO <sub>3</sub>
Pb <sup>2+</sup>	20.17	91.53	89.16	85.37
Cu <sup>2+</sup>	18.48	87.49	85.39	84.62
Zn <sup>2+</sup>	17.35	86.38	83.46	81.57

adsorbents taking into account the high recovery level of the metal ions.

## 4. Conclusions

The experimental results obtained in this study demonstrate a possible use of the investigated adsorbents for Pb<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> ions from wastewaters.

The positive value of enthalpy (ΔH°) confirmed the endothermic nature of the adsorption process while the negative value of free energy (ΔG°) indicated the possibility and the spontaneous nature for the adsorption of lead, copper and zinc ions onto investigated sorbents.

The obtained values for maximum adsorption capacity place the two adsorbents in the limits obtained by other researchers, with higher values compared to the case when using TiO<sub>2</sub> and lignin as sorbent, and lower than hydrous manganese dioxide (HMO), Al<sub>2</sub>O<sub>3</sub> modified were used.

It was noted that Al-pillared clay has a higher adsorption capacity than montmorillonite – K10. This is in agreement with other data from the literature, because it is known that the pillaring process increases the specific surface of a material.

Based on the results it can be established an order in terms of the metal ion adsorption on two sorbents, order that is in good agreement with the variation of the hydrated ion radii.

## 5. Acknowledgements

This work was partially supported by a grant of the Romanian National Authority for Scientific Research,

CNCS – UEFISCDI, project number PN-II-RU-TE-2012-3-0202

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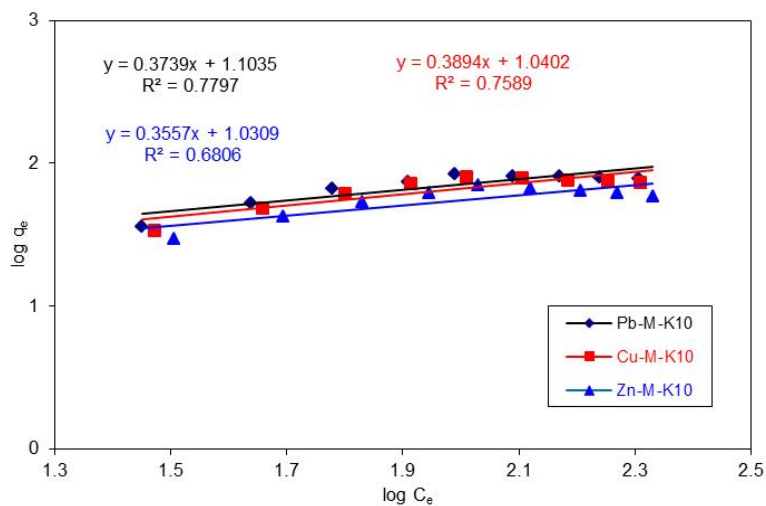
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## Povzetek

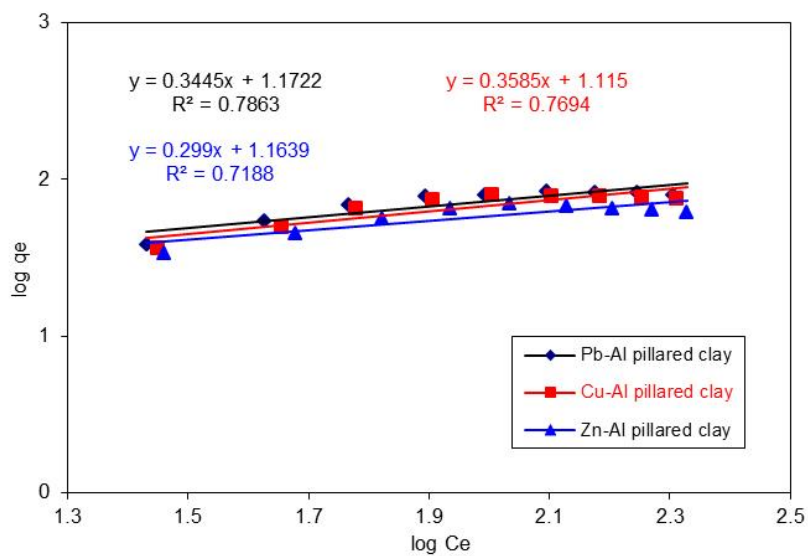
Proučevana je bila adsorpcijska kapaciteta dveh različnih adsorbentov v odvisnosti od kontaktnega časa med adsorbentom in raztopino ionov težkih kovin v sintetični odpadni vodi, začetne koncentracije, vrednosti pH, temperature in mase adsorbenta. V preliminarnih raziskavah je bilo ugotovljeno, da se maksimalna adsorpcija pojavi pri pH 5.0 za bakrove ( $q_{\max} = 92.59 \text{ mg} \cdot \text{g}^{-1}$ ), pri pH 6.0 za svinčeve ( $q_{\max} = 97.08 \text{ mg} \cdot \text{g}^{-1}$ ) in pri pH 6.5 za cinkove ( $q_{\max} = 73.52 \text{ mg} \cdot \text{g}^{-1}$ ) ione. Adsorpcijske kapacitete za  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  in  $\text{Zn}^{2+}$  so bili obdelane z Langmuirjevim in Freundlichovim modelom. Za napoved narave adsorpcije so bili določeni termodinamski parametri kot so sprememba entalpije ( $\Delta H^0$ ), sprememba entropije ( $\Delta S^0$ ) in prosta energija ( $\Delta G^0$ ). Vrstična elektronska mikrofografija (SEM) je pokazala spremembe na površini adsorbenta kot posledico adsorpcije. EDS karakterizacija je v vzorcih kvalitativno potrdila prisotnost adsorbiranih specij. Na osnovi dobljenih rezultatov v predstavljenih raziskavah je predlagan vrstni red adsorpcije  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ .

# Evaluation of Adsorption Capacity of Montmorillonite and Aluminium-pillared Clay for $Pb^{2+}$ , $Cu^{2+}$ and $Zn^{2+}$

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a.



b.

**Fig. S1.** Freundlich adsorption isotherms montmorillonite – K10 (a), Al-pillared clay (b).

**Table S1.** Parameters and correlation coefficients calculated for Freundlich adsorption model for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  on montmorillonite-K10 and Al-pillared clay.

Adsorbent	Ion	$K_F$	N	$R^2$
Montmorillonite-K10	$\text{Pb}^{2+}$	12.69	2.68	0.779
	$\text{Cu}^{2+}$	10.97	2.57	0.759
	$\text{Zn}^{2+}$	10.74	2.81	0.681
Al-pillared clay	$\text{Pb}^{2+}$	14.86	2.90	0.786
	$\text{Cu}^{2+}$	13.03	2.78	0.769
	$\text{Zn}^{2+}$	14.58	3.34	0.719