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APPLICATION OF FLY ASH/CHITOSAN COMPOSITES FOR HEAVY METAL ADSORPTION

The aim of this paper is to investigate the potential of modified fly ash (FA) as an adsorbent for the removal of heavy metal ions from polluted waters. The effectiveness of unmodified FA was compared to FA modified with chitosan. The FA and FA/chitosan particles were characterized by means of SEM, XRF and FTIR methods. The FA and FA/chitosan composites were investigated as adsorbents for Cu(II) and Pb(II) ions from aqueous solutions. Experiments were carried out in a previously optimized pH (pH = 6), at room temperature for 3 hours. Langmuir and Freundlich isotherms were used to determine the maximum adsorption capacities of the fly ash samples for Cu(II) and Pb(II) ions. The experimental data indicate that the Langmuir isotherm fits better than the Freundlich isotherm for all the investigated systems. The obtained values of the q_m, maximum adsorption capacity for the removal of Cu(II) and Pb(II) with the FA/chitosan composites were (1.068, 1.00, 1.042, 1.369 mg/g), and (2.532, 2.063, 1.036, 2.146, 2.482 mg/g), respectively. The efficiency trend was Pb(II) > Cu(II). The results indicate that the removal efficiency for Cu(II) and Pb(II) ions was 91.1 % and 99.7 %, respectively.

Keywords: adsorption, chitosan, composites, fly ash, heavy metals, modification

INTRODUCTION

Water pollution by toxic heavy metal ions (HMIs) is a problem of great global concern because of their toxicity, non-biodegradability, and possible carcinogenicity [1]. Heavy metal ions are persistent and toxic pollutants even at very low concentrations. They could be naturally present within the environment or could be introduced by anthropogenic activities such as mining, mineral processing, metallurgical operations, fuels, battery manufacturing, explosives manufacturing and others [2, 3]. Many heavy metals such as lead, copper, and cadmium are known to be toxic and carcinogenic for living organisms, causing several disorders and diseases [4, 5]. Copper has been proven to cause Wilson's disease (neurotoxicity) and kidney failure. In some cases, copper is known to cause an enlarged liver and jaundice [6]. Lead is ubiquitous in the environment and is hazardous at high levels. The long-term drinking of water containing high levels of lead will cause nervous system damage, renal kidney disease, mental retardation, cancer, and anemia [7]. Hence, there is a need to remove heavy metals from the aquatic ecosystem. Various methods such as chemical precipitation, membrane filtration, ion exchange, electrochemical processes, chemical coagulation and adsorption have been utilized to remove heavy metals from wastewater [8, 9]. Among these methods, adsorption is known to be the most efficient and economic one for water decontamination applications [10, 11]. Adsorption is a mass transfer process in which heavy metal ions are transferred from an aqueous solution to the solid surface through physical or chemical interactions [2]. In addition, owing to the reversible nature of most adsorption processes, the adsorbents can be regenerated by suitable desorption processes for multiple uses. However, the major problem in this field is to select novel types of highly efficient/low cost adsorbents. A number of adsorbents such as activated carbon, silica gel, zeolites, graphene, clays, chitosan, as well as industrial waste such as fly ash, red mud and agricultural residues have been used for the removal of heavy metal ions.

In the last few decades, several researchers have investigated chitosan as an adsorbent for the removal of heavy metals from aqueous streams. Chitosan has received considerable interest for heavy metal removal due to its excellent metal-binding capacities and low cost [12]. The excellent adsorption characteristics of chitosan for heavy metals are attributed to (1) high hydrophilicity owing to the large number of hydroxyl groups of glucose units, (2) the presence of a large number of functional groups (acetamido, primary amino and/or hydroxyl groups) that may form chelates with heavy metals (3), the high chemical reactivity of these

groups and (4) the flexible structure of the polymer chain [9]. Chitosan also has the disadvantages of being mechanically weak, soluble under acidic conditions and may leach carbohydrates when used in the raw form. Furthermore, chitosan-based composite materials can be used to enhance the surface properties and reduce the internal diffusion resistance of chitosan [13]. Various efforts have been made to stabilize chitosan using cross-linking agents.

Agarwal et al. worked with NaOH-treated FA particles modified by cethyl trimethyl ammonium bromide (CTAB) (FA/NaOH/CTAB) for the adsorption and removal of resorcinol in polluted waste waters. Based on the obtained results, the authors concluded that the resorcinol adsorption mechanism of FA/NaOH/CTAB from pH < 7 solutions was a combination of electrostatic attraction, hydrogen bonding, and organic partitioning [14]. Fly ash has potential applications in wastewater treatment because of its chemical composition, low cost and good adsorbent properties (porosity, large surface area, particle size distribution and water holding capacity) [15]. In this paper, fly ash was modified with chitosan to adsorb heavy metal ions such as Cu(II), and Pb(II), with highly efficiency.

MATERIALS AND METHODS

Materials

Three different types of fly ash obtained as metallurgical waste from the coal-fired power station in Oslomej (FA-OS) and metallurgical waste from the ferronickel smelting plant EURONICKEL (FA-EN, Electric furnace slag – EFS) in Kavadarci, North Macedonia were used. The six samples used were:

Sample 1 (FA-OS)
Sample 2 (FA-OS+NaOH)
Sample 3 (FA-EN)
Sample 4 (FA-EN+NaOH)
Sample 5 (EFS)
Sample 6 (EFS+NaOH)

Chitosan was obtained from Sigma Aldrich, Germany. The chitosan used in this study has a molecular weight of 50.000-190.000. All the chemicals used in this study were of analytical grade. Nitric acid, oxalic acid, EDTA, and sodium hydroxide were used.

Modification of fly ash/chitosan composites

The FA particles were treated with NHO_3 and 0.1 M EDTA for 24 h before being modified with the chitosan. The chitosan powder (0.2 g) was dissolved in 10 wt.% oxalic acid (200 mL). The acid and chitosan form a viscous mixture (gel), which must be heated to 40-50 °C to facilitate mixing. The chitosan gel was diluted twofold with water and heated to 40-50 °C. About 2 g of the acid-treated FA was slowly added to the diluted gel and stirred for about 36 h. The contents were filtered out, the composite bio sorbent was washed

twice with distilled water and dried in an oven at 55 °C for 24 h. The coating process was repeated on the coated bio sorbent to increase the loading of chitosan on the FA. The excess oxalic acid in the composite bio sorbent was neutralized by treatment with 10 wt.% aqueous NaOH (200 mL). The mixture was filtered, washed with ~ 500 mL of distilled water, and filtered again. The coated bio sorbent was then dried in an oven at 55 °C for about 48 h. After the modification of the fly ash with chitosan, the composites used were:

Sample 7 (FA-OS+Ch)
Sample 8 (FA-OS+NaOH+Ch)
Sample 9 (FA-EN+Ch)
Sample 10 (FA-EN+NaOH+Ch)
Sample 11 (EFS+Ch)
Sample 12 (EFS+NaOH+Ch)

The difference between the used samples is this: Samples 1-6 are raw fly ash. Samples 2, 4, 6 are the raw fly ash treated with NaOH, while samples 7-12 are modified fly ash with chitosan.

Characterization of adsorbent

The FA/chitosan composites were characterized by means of SEM, XRF and FTIR methods. SEM observation of the prepared samples was performed using a scanning electron microscope – JEOL JSM-IT200. The FTIR-ATR spectra were collected by a PerkinElmer Spectrum 100 machine at 64 scans, in ATR mode in the range from 400 cm^{-1} to 4000 cm^{-1}. The elemental composition for each used adsorbent was determined utilizing a Niton XL3t XRF analyzer.

Reagents and chemicals

The preparation of metal ion solutions was made with nitrate salts of copper and lead $Cu(NO_3)_2 \cdot 3H_2O$ and $Pb(NO_3)_2$; (MERCK) 0.1M NaOH and 0.1 M HNO_3 were applied to adjust the pH of the solutions. All the chemicals and reagents used in this adsorption experiment were of analytical grade.

Adsorption experiment

A batch adsorption experiment was performed to obtain the data for Cu(II) and Pb(II) removal efficiency of all the examined adsorbent materials. Metal solutions for all the adsorption experiments had the initial concentration of 5 mg/L. The researchers who worked on the adsorption of heavy metals using fly ash determined that the best results were obtained at pH 6, and consequently our adsorption tests were performed at this pH value of the solutions [15-17]. 0.3 g of the examined fly ash sample was placed in five Erlenmeyer flasks containing different volumes of the metal ion solutions ($50 \ cm^3$, $100 \ cm^3$, $150 \ cm^3$, $200 \ cm^3$ and $250 \ cm^3$). Continuous mixing of the solutions in a period of 3 hours, which is sufficient to reach equilibrium, was carried out utilizing a shaker (CERTOMAT R,

B. Braun by Biotech International) at 170 rpm at room temperature. An atomic absorption spectrophotometer (Agilent 55B AA) was employed to investigate the residual concentration of Cu(II) and Pb(II) ions in the filtrate after the adsorption.

RESULTS AND DISCUSSION

Structure characterization

Based on the theoretical facts, the physicochemical properties of the adsorbent materials have a dominant effect on heavy metal ion sorption. Hence, also the physical and chemical properties of the FA particles and chitosan (deacetylation degree, chemical composition, molecular mass etc.) have the main influence on heavy metal ion sorption onto fly ash and fly ash coated with chitosan. The results of the analysis of the chemical composition of the FA, presented in a previous paper [9], disclosed that FA-OS is Class F (50% + 30% + + 13% = 93%); FA-EN is Class C (37.2 % + 1.8% + + 30 % = 69 %); EFS is Class C (53 % + 2.0 % + 14 % = = 69 %), which is in agreement with the standard chemical requirements of ASTM C 618 for the sum of the SiO_2, Al_2O_3 and Fe_2O_3 content ($\geq$ 70% for Class F and between 50 % and 70 % for Class C) [9]. The surface morphology of the fly ash and fly ash/chitosan composite are shown in Figure 1a and b.
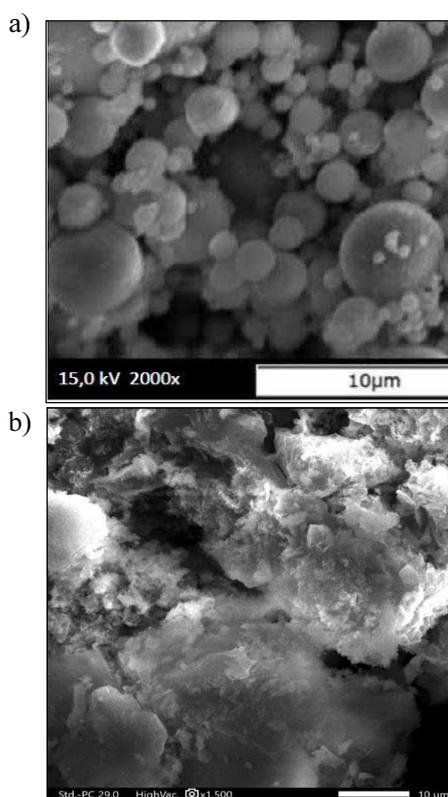

Fig. 1. SEM microphotographs of: a) fly ash and b) fly ash/chitosan composite

The SEM micrographs revealed amorphous surface morphology for the fly ash and a semicrystalline

surface morphology for the irregularly shaped fly ash/chitosan composites. Following modification of the fly ash with chitosan, a reduction of the inter molecular distances of the fly ash was observed, thereby increasing the contact area, which facilitates metal ion adsorption onto the composite [18]. The elemental composition for the fly ash and the chitosan was determined by means of an XRF analyzer, which are shown in Figure 2a and b. The XRF spectra was recorded and compared between the fly ash and chitosan for elemental analysis. As can be seen, the Fe peaks are the most intensive for fly ash. In addition to Fe peaks, other peaks for fly ash were observed. The Ni, Zn, As contents are quite small and the corresponding peak is at 5.61 keV. The peak at 4.47 keV indicates the presence of K and Ti. The Mn peaks on the line at 5.60 keV is totally masked by the Fe peaks. The peak at 15.60 keV indicates the presence of Sr. The XRF spectrum of the chitosan contain Rh, which corresponds to the line at 17.10 keV, and the Ca peak corresponds to line 4.51 keV. The amounts of Fe, Pb, Sr also were recorded.
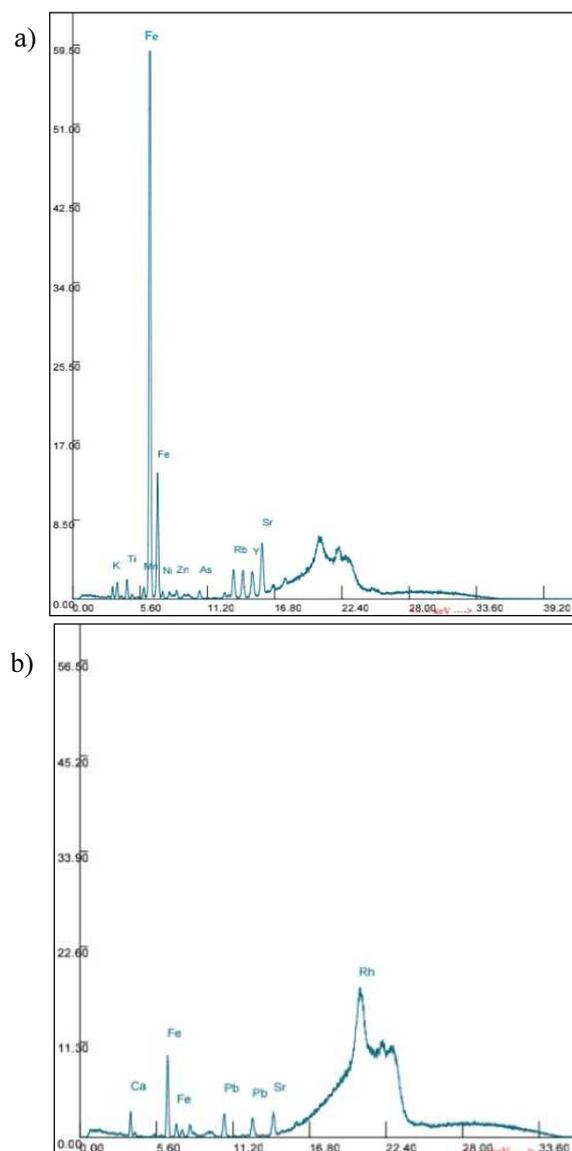

Fig. 2. Elemental composition of: a) fly ash and b) chitosan

Characteristic bands of the composition oxides were obtained by FTIR spectroscopy, and are presented in Figure 3. The broad band in the region 3400-3000 cm^{-1} resulted from the stretching vibrations of surface OH groups of -Si-OH groups and surface adsorbed water molecules, which indicates the presence of strong hydrogen bonding [19, 20].

The band at 1607 cm^{-1} was attributed to δO-H bending vibrations of the water molecule [19]. The broad band with strong intensity centered at around 1000 cm^{-1} was assigned to the Si(Al)-O-Si valent asymmetric stretch. The broadening of the band around 1000 cm^{-1} in the FA/chitosan composites was a result of bond vibration overlapping. The bands at 1066 and 1028 cm^{-1} that correspond to C-O stretching and originate from chitosan were located in this region [21]. The origin of the fly ash contributes to small shifting of the band towards lower frequencies. This phenomenon may indicate the formation of a new product (amorphous alumino silicate gel phase) due to the dissolution of the fly ash amorphous phase in the strong alkaline activator − NaOH [22]. For chitosan, the characteristic bands were assigned to O-H stretching and amine N-H at 3300 cm^{-1}. The additional peak at 2800 cm^{-1} corresponds to the aldehyde C-H stretching of glutaraldehyde. The peaks at 1030 and 1050 cm^{-1} were C–OH stretching.
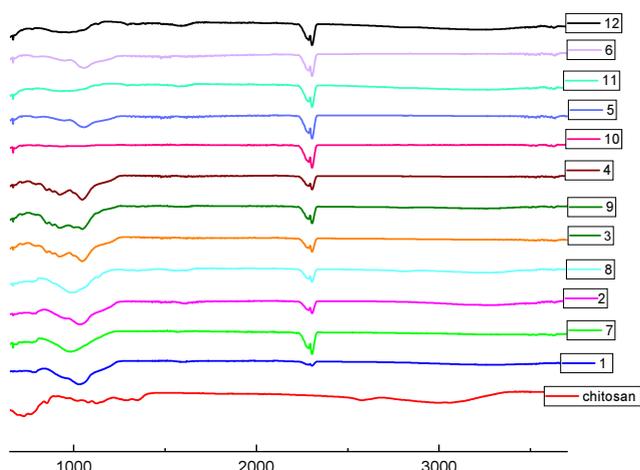

Fig. 3. FTIR spectra of chitosan and of fly ash/chitosan composites

Adsorption analysis

The efficiency of the adsorption of metal ions is expressed by the removal percentage, which is determined by the equation:

$$\%R = \frac{C_0 - C_e}{C_0} \cdot 100 \qquad (1)$$

where C_0 [mg/L] is the initial concentration of metal ions and C_e [mg/L] is the equilibrium concentration of metal ions.

Equation (2) is used to calculate the amount of metal ions adsorbed at equilibrium time q_e [mg/g]:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \qquad (2)$$

where V is the solution volume [m^3] and m is the amount of glass adsorbent [g].

Adsorption isotherms are important because they describe the interaction between the adsorbent and adsorbate and in describing the adsorption equilibrium of the process. In this study, the Langmuir isotherm was employed to determine the maximum adsorption capacities of the fly ash samples. For this purpose the linear form of the Langmuir isotherm was utilized, equation (3):

$$\frac{C_e}{q_e} = \frac{1}{q_m \cdot b} + \frac{C_e}{q_m} \qquad (3)$$

where q_m [mg/g] is the maximum adsorption capacity and b [l/mg] is the Langmuir equilibrium constant.

The Langmuir parameters were computed from the slopes and intercepts of the linear plot of C_e as the abscissa and C_e/q_e as the ordinate as displayed in the following figures. Figure 4a, b and c shows the plots of the linear form of the Langmuir adsorption isotherm for the Cu(II) systems: sample 8, sample 9, sample 10, sample 11 and sample 12, respectively.

Figure 5a, b and c shows the plots of the linear form of the Langmuir isotherm for the Pb(II) systems – sample 8, sample 9, sample 10, sample 11, and sample 12, respectively.
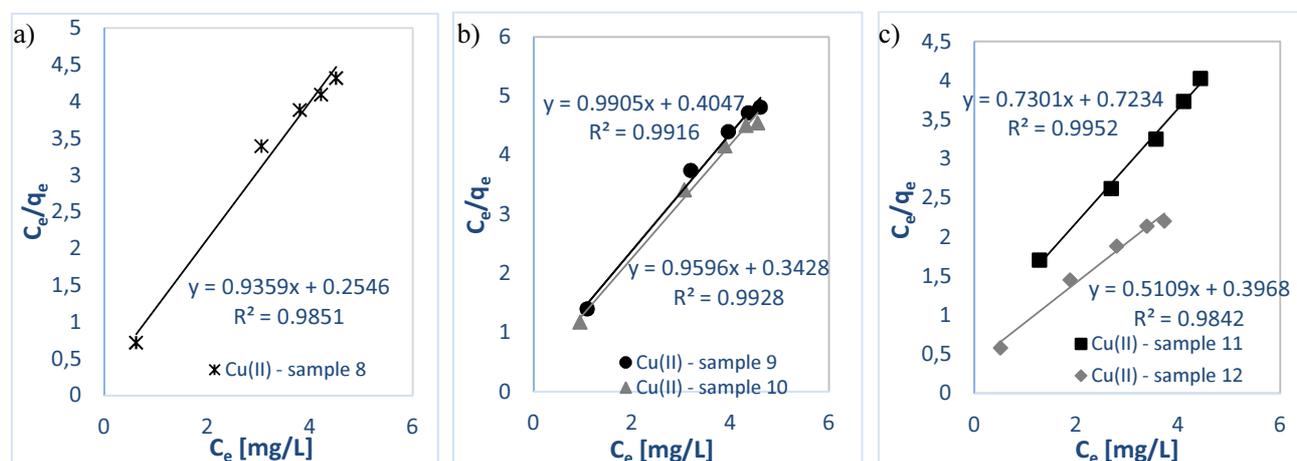

Fig. 4. Langmuir isotherms for Cu(II) system: a) sample 8, b) samples 9 and 10, c) samples 10 and 11
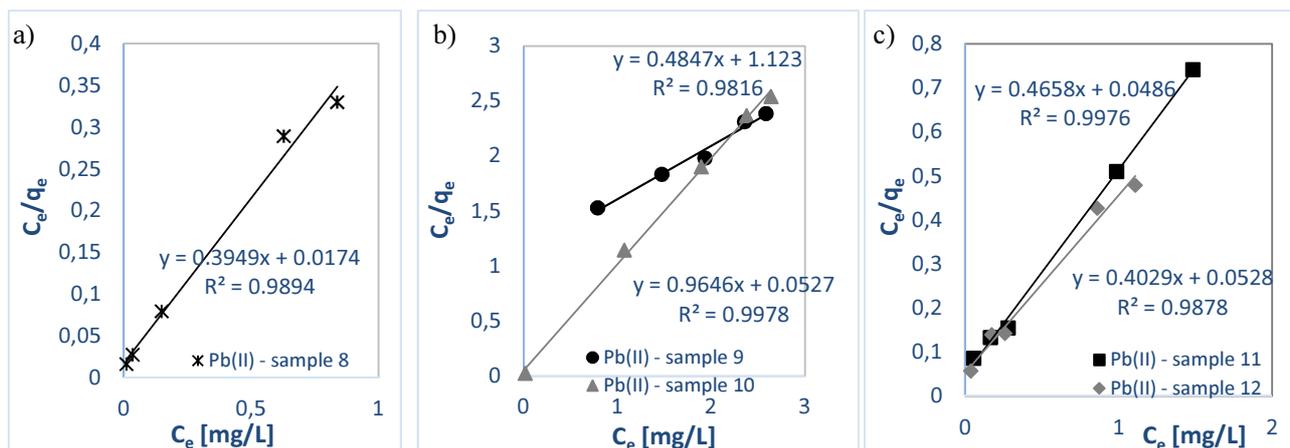
Fig. 5. Langmuir isotherms for Pb(II) system: a) sample 8, b) samples 9 and 10, c) samples 11 and 12

The Freundlich isotherm model is applied to model the adsorption on heterogeneous surfaces. The linear form of this empirical equation is:

$$log q_e = \frac{1}{n} log C_e + log K_F \qquad (4)$$

where n is an empirical parameter related to the intensity of adsorption and K_F [mg/g] is the Freundlich constant.

Figure 6 refers to the plots of the linear form of the Freundlich isotherm for the Cu(II) systems – sample 8, Cu(II) – sample 9 and Cu(II) – sample 10 and Cu(II) – sample 11 and Cu(II) – sample 12, respectively.

The plots of the linear form of the Freundlich isotherm for the Pb(II) systems – sample 8, Pb(II) – sample 9 and Pb(II) – sample 10 and Pb(II) – sample 11 and Pb(II) – sample 12, are given in Figure 7.
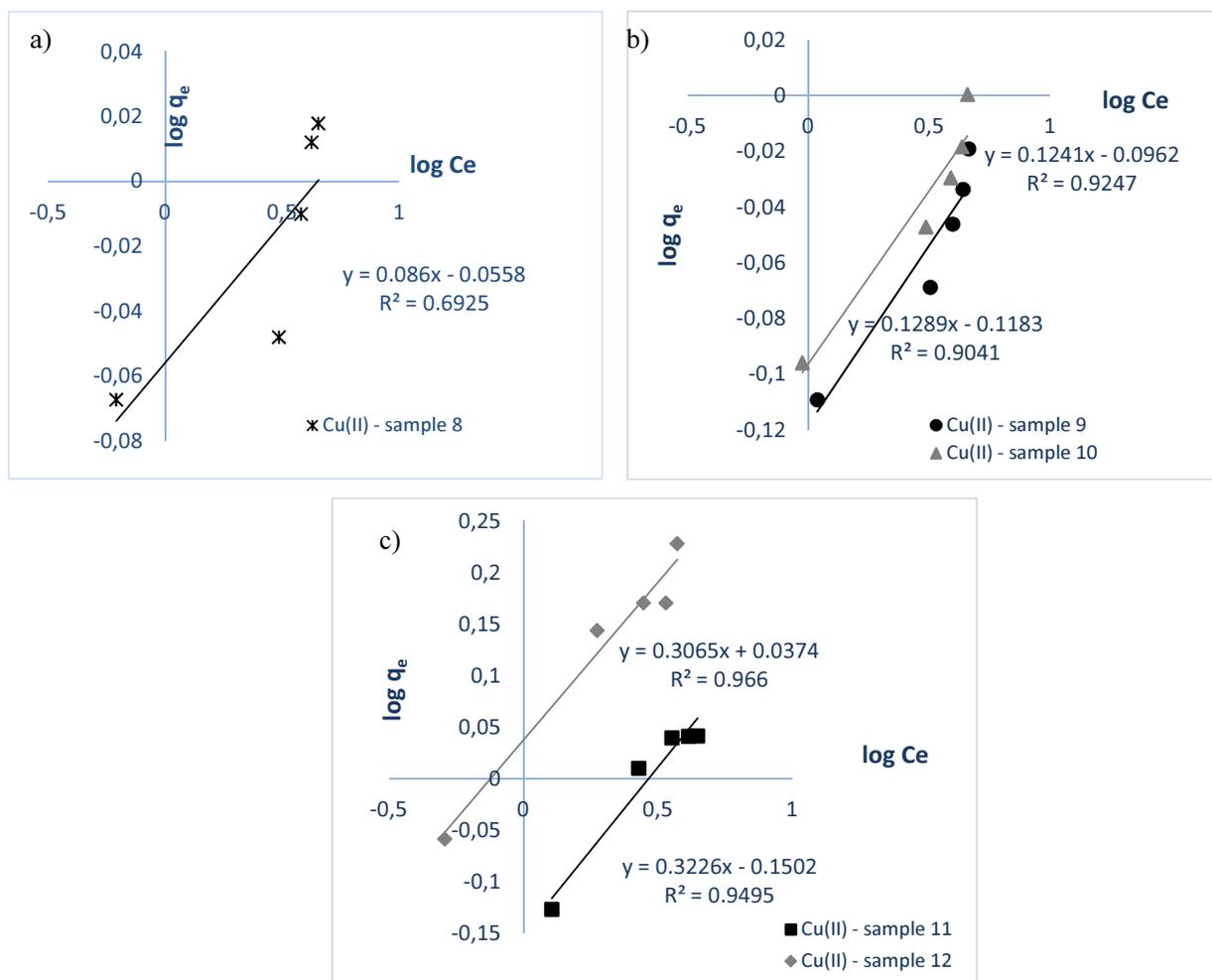

Fig. 6. Freundlich isotherm for Cu(II) systems: a) sample 8, b) samples 9 and 10, c) samples 11 and 12
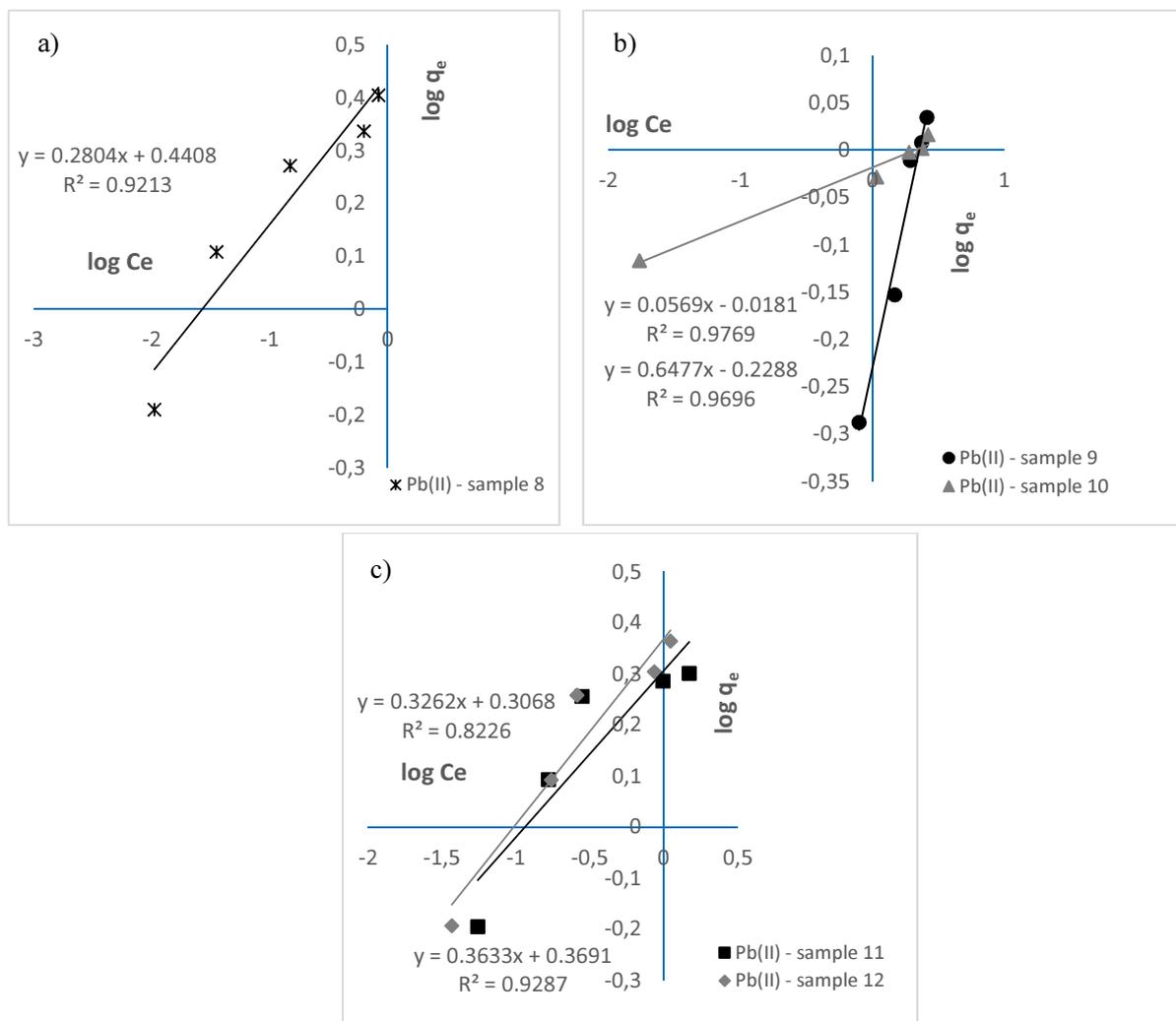
Fig. 7. Freundlich isotherm for Pb(II) systems: a) sample 8, b) samples 9 and 10, c) samples 11 and 12

TABLE 1. **Langmuir and Freundlich isotherm parameters and removal percentages**

SAMPLE	Isotherm models		Metal			
	Langmuir	Freundlich	Cu(II)	Pb(II)	Cu(II)	Pb(II)
8	q_m [mg/g]	K_F [mg/g]	1.0685	2.5326	0.8794	2.7593
	b	n	3.68	22.70	11.63	3.57
	R^2	R^2	0.9851	0.9894	0.6925	0.9213
	%R	%R	89.3 %	99.7 %	89.3 %	99.7 %
9	q_m [mg/g]	K_F [mg/g]	1.0096	2.0631	0.7616	0.5905
	b	n	2.45	0.43	7.76	1.54
	R^2	R^2	0.9916	0.9816	0.9041	0.9696
	%R	%R	81.1 %	79.7 %	81.1 %	79.7 %
10	q_m [mg/g]	K_F [mg/g]	1.0421	1.0367	0.8013	0.9591
	b	n	2.80	18.30	8.06	17.57
	R^2	R^2	0.9928	0.9978	0.9247	0.9769
	%R	%R	83.6 %	99.6 %	83.6 %	99.6 %
11	q_m [mg/g]	K_F [mg/g]	1.3697	2.1468	0.7076	2.0267
	b	n	1.01	9.58	3.10	3.07
	R^2	R^2	0.9952	0.9976	0.495	0.8226
	%R	%R	77.8 %	98.6 %	77.8 %	98.6 %
12	q_m [mg/g]	K_F [mg/g]	1.9573	2.4820	1.1000	2.3394
	b	n	1.29	7.63	3.26	2.75
	R^2	R^2	0.9842	0.9878	0.966	0.9287
	%R	%R	91.1 %	99.1 %	99.1 %	99.1 %

Using the obtained equations of the Langmuir and Freundlich plots, the adsorption capacities for Cu(II) and Pb(II) ions of all the investigated materials were determined, and the other isotherms parameters. These values and the values of the correlation coefficients are listed in Table 1. The linearity of the plots, as well as the values for the correlation coefficients ($R^2 > 0.98$) for all the systems, given in Table 1, show that the Langmuir isotherm model matches the experimental data well and indicate that the Langmuir isotherm fits better than the Freundlich isotherm for all the investigated systems.

Comparing the data obtained for the efficiency of the adsorbents in the removal of copper and lead ions, (Table 1), it can be concluded that the FA-based adsorbents exhibit greater efficiency in the removal of lead ions. All the treated samples – 8, 10, 11 and 12 – have shown outstanding results with percentages of removal of Pb (II) above 99 %, namely 99.7 %, 99.6 %, 99.1 % and 98.6 %, respectively.

The results presented above demonstrate that fly ash from different sources, untreated as well as modified with NaOH, possess good adsorption characteristics that allow them to be successfully exploited as materials for heavy metal ion removal from aqueous solutions.

Equation (1) was used to calculate the removal percentages of Cu(II) and Pb(II). Figure 8 presents the histogram that shows the efficiency of fly ash/chitosan composites in removing Cu(II) and Pb(II).
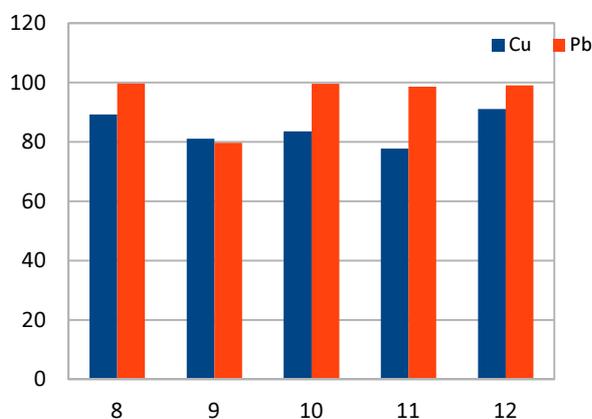

Fig. 8. Removal efficiency of Cu(II) and Pb(II) from fly ash/chitosan composites

As can be seen from Figure 4b) and c, as well as from the values presented in Table 1 for removal percentages, the treated materials have improved efficiency in the elimination of Cu(II) and Pb(II) ions. This was expected because the modification of the starting materials leads to the formation of new pores, thereby increasing the surface area. As a result, the adsorption capacities of the treated samples are improved and higher values of the metal ion removal percentages are obtained. Similar conclusions were reached by other researchers who investigated the adsorption characteristics of untreated and treated fly ash [23-25].

CONCLUSIONS

In this study, fly ash modified with chitosan for the adsorption of Cu^{2+} and Pb^{2+} was investigated. The following conclusions were drawn:
- From the SEM analysis we can see that the intermolecular distances of the fly ash are reduced after modification of the fly ash with chitosan.
- From the XRF analysis it can be observed that the most dominant element in the structure of fly ash is iron.
- The maximum metal sorption was found to occur at pH 6.0.
- The efficiency trend was Pb(II) > Cu(II). The results indicate that the removal efficiency for Cu(II) and Pb(II) ions was 91.1 % and 99.7 % respectively.
- The Langmuir model agreed well with the experimental data for the adsorption of Cu^{2+} and Pb^{2+} based on the R^2.

Based on of the above results, it can be concluded that the FA/chitosan composite is a suitable adsorbent for the removal of Cu(II) and Pb(II) ions from an aqueous solution in terms of its high adsorption capacity, natural and abundant availability and low cost.

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