

CLINOPTILOLITE VS. ACTIVATED CARBON AS A METHOD OF REMOVING HEAVY METALS FROM WATERS

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ABSTRACT. Acid mine drainage (AMD) is considered a major risk for groundwater and soil pollution if discharged in the environment without prior treatment, as it contains important quantities of heavy metals. The paper presents an experiment conducted using the batch technique, for the removal of six metals (Cd, Pb, Cu, Ni, Al, Zn) from AMD at the interaction with two filtering materials [zeolite (Z) and activated carbon (AC)], without chemical treatment. The results showed that the zeolite removed successfully Al and Pb in proportion of 96%, and the AC proved to be very effective in removing five (Al, Cd, Cu, Zn and Pb) out of the six metals studied, in proportion of 97%. Ni is the most difficult metal to be removed regardless the filtering material used. Although, better results are achieved for this metal at the interaction with AC - 20.11%, compared to zeolite - 18.97%. The efficiency of the two materials is given by the interaction time with AMD.

Key words: zeolite, activated carbon, acid mine drainage, water treatment

INTRODUCTION

Acid mine drainage or acid rock drainage refers to the outflow of acidic waters from ore or coal deposits, which is formed when materials containing sulphide are exposed to oxygen and water. It is usually characterised by low pH (due to the pyrite dissociation in water), high conductivity and high concentrations of heavy metals (Măicăneanu et al., 2013).

The *zeolites* are microporous crystalline alumina-silicates with a tetrahedral structure, containing Al in the form of $[AlO_4]^{5-}$ and Si in the form of $[SiO_4]^{4-}$, where every metallic atom is surrounded by four oxygen atoms. The pores and the cavities in their structure contain cations, such as sodium, potassium, calcium, magnesium

and water molecules as well (Payra and Dutta, 2003; Shoumkova, 2011). Due to their porous tri-dimensional structure, the zeolites have applications in many areas, among which water decontamination, soil remediation, agriculture, stock raising and health. One of the zeolites properties is their exceptional capacity to exchange ions with the liquid in contact without damaging their own structure (Shoumkova, 2011), therefore contributing to the water decontamination by retaining the heavy metals ions.

Unlike the zeolites which have a crystalline structure, the *activated carbon* is a filtration medium obtained from very different amorphous carbon-based materials (Çeçen and Özgür, 2011) (charcoal, coconut shell, walnut shell, watermelon shell, bamboo, used tires), subjected to pyrolysis (Chang et al., 2003). Its porous structure provides a large adsorption surface, being very efficient in removing both organic and inorganic pollutants.

The purpose of the present paper is a comparison between two methods used in the water decontamination process, the ion exchange and adsorption. In order to make a comparative study of the methods, two different filtering materials (in terms of their way of action) were used: zeolite volcanic tuff and AC. The aim is to show their capacity to reduce heavy metals concentration when used raw, even if the literature shows an improvement in adsorption capacity when chemically treated (Ismael et al., 2012; Chen et al., 2007).

EXPERIMENTAL SECTION

The experiments consisted in acid mine drainage interaction with zeolite $((\text{Na}_{3.35}\text{K}_{1.55}\text{Ca}_{0.93}\text{Ba}_{0.06}\text{Sr}_{0.01})(\text{Al}_{6.9}\text{Si}_{29.1}\text{O}_{72})(\text{H}_2\text{O})_4)$ and AC, at different time frames and different quantities of the two materials but at the same temperature of the water ($25\pm 1^\circ\text{C}$).

The AMD sample was collected from Ilba-Handal mine, in Maramureș County. The exchange ions method has been used in the AMD treatment, using volcanic zeolitic tuff, clinoptilolite type, of 1-3 mm granulation, exploited from Racos area, Brasov County, Romania. Granulated AC was used, being provided by Ecopur System SRL Bucharest,

The samples were measured using an inductively coupled plasma mass spectrometer (SCIEX Perkin Elmer Elan DRC II, Toronto, Canada). For calibration, matrix-matched MERCK standard solutions were used for preparation of calibration solution and control points. Samples were analyzed directly and when the concentration was too high, they were properly diluted to fit calibration interval. The DRC was used in rf-only mode. The pH and electric conductivity determination a Seven Multi pH-meter from Mettler Toledo Company was used. A drying oven was used for the drying of zeolite and the activation of activated carbon.

The experiments used dried zeolite and thermally activated AC only (through drying in a drying oven at 105°C). The two materials were sieved for the removal of the fine particles, on 0.8 mm sieve. The zeolite was repeatedly washed (8-10 times) with distilled water, dried at 105°C in an oven for 6 hours, and the AC was thermal activated at 105°C in a drying oven of the AC for 6 hours.

Four sets of experiments using batch technique were performed, for each filtering material at two different quantities. The method consists in static interaction between a solid and a liquid (aqueous) medium, in this case the zeolite/AC and the AMD. The zeolite and AC have been put in contact with AMD in Petri dishes for 1, 6, 24 and 48 hours. The quantities of the two filtration media were 10 g and 30 g and 100 ml for AMD.

The concentration, pH and conductivity of metals in AMD were measured both before and after the contact with zeolite and AC, in order to emphasize the reduction concentration level. The initial characteristics of AMD were: pH - 2.56, electrical conductivity - 3.75 [$\mu\text{S}/\text{cm}$], heavy metals concentrations: Al - 77,500 [$\mu\text{g}/\text{L}$], Cd - 597 [$\mu\text{g}/\text{L}$], Cu - 1000 [$\mu\text{g}/\text{L}$], Ni - 174 [$\mu\text{g}/\text{L}$], Pb - 83.5 [$\mu\text{g}/\text{L}$] and Zn 162,000 [$\mu\text{g}/\text{L}$].

RESULTS AND DISCUSSIONS

The concentration levels of the six subject metals, experimentally obtained before and after the interaction with zeolite and AC are graphically presented in Fig. 1. The graphical representation is made for four interaction time frames, for zeolite 10 g, 30 g and AC 10 g, 30 g.

The concentrations measurements show an efficient action of the AC on every metal studied, starting with the interaction time of 1 hour. The difference between the concentrations measured after 1 hour and after 6 hours is very large. The zeolites action is noticeable only for Pb, where the reduction of this metal concentration is highly reduced compared to the other five metals. It is noted that a three times larger amount of zeolite than AC is needed in order to achieve comparable or better results. For a short timeframe (1 hour), the zeolite action is more efficient than AC.

One can also notice that after the contact with AC, the concentrations fall below the maximum allowed level regulated by the current potability standard (Law 311/2004) for all six metals (Al = 200 $\mu\text{g}/\text{L}$, Cd = 5 $\mu\text{g}/\text{L}$, Cu = 100 $\mu\text{g}/\text{L}$, Ni = 20 $\mu\text{g}/\text{L}$, Pb = 10 $\mu\text{g}/\text{L}$, Zn = 5000 $\mu\text{g}/\text{L}$) at different timeframes. After the contact with zeolite the potability limit is reached for Al, Cu and Pb, after at least 6 hours of interaction between the volcanic tuff and AMD (Fig. 2). Table 1 presents the conditions necessary to achieve the potability limit for Al, Cd, Cu, Ni, Pb and Zn. Although, the AMD treated in these conditions does not become drinking water, as it needs further treatments in order to become drinkable.

The saturation of the filtering material occurs after 24 hours for Ni, Cu and Zn, followed by desorption which occurs after 48 hours. For Al and Pb the saturation occurs after 6 hours and desorption after 24 hours, followed by a new adsorption process after 48 hours. Cd is the only metal among the six metals studied, for which the saturation takes place after 48 hours.

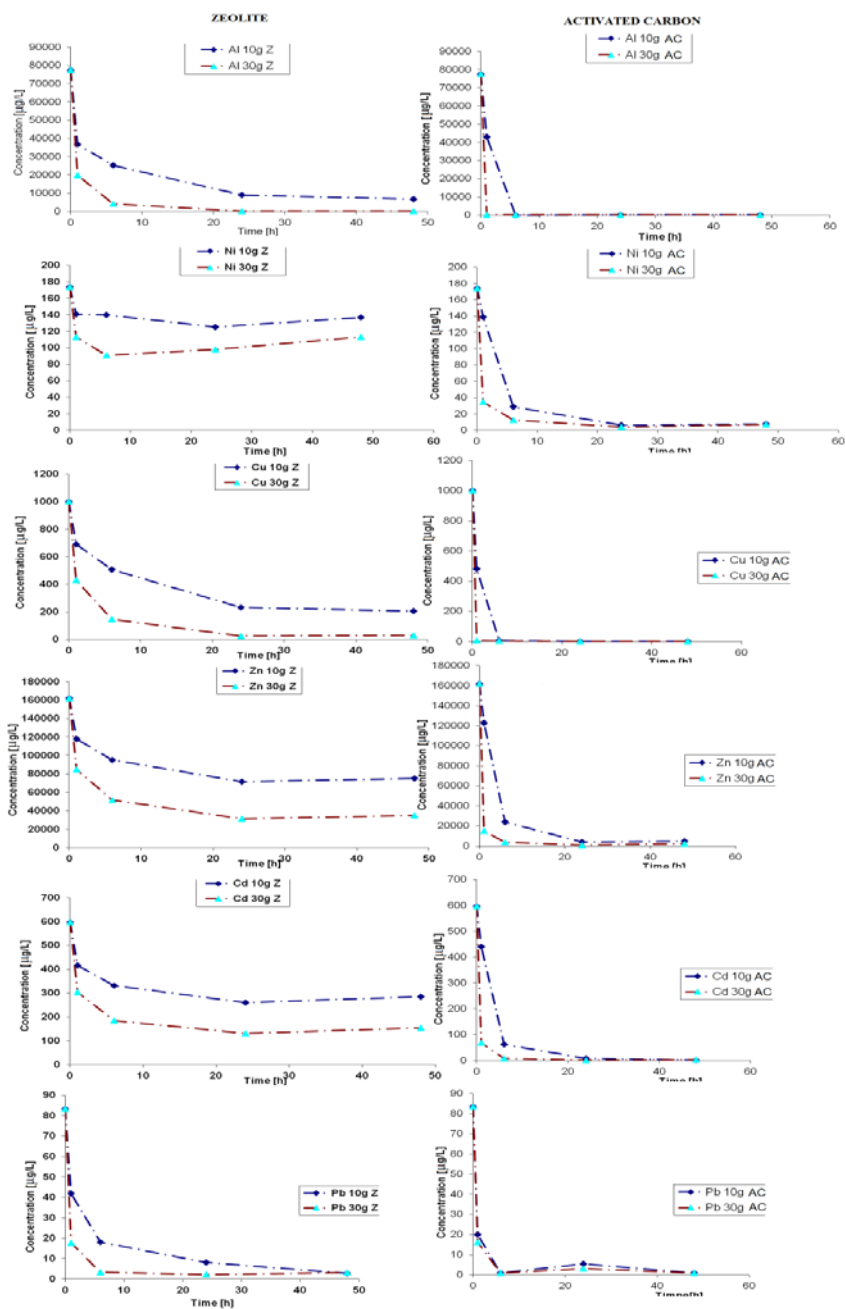


Fig. 1. Graphical representation of the six metals concentrations levels, experimentally obtained: (a) Al, (b) Cd, (c) Cu, (d) Ni, (e) Pb and (f) Zn

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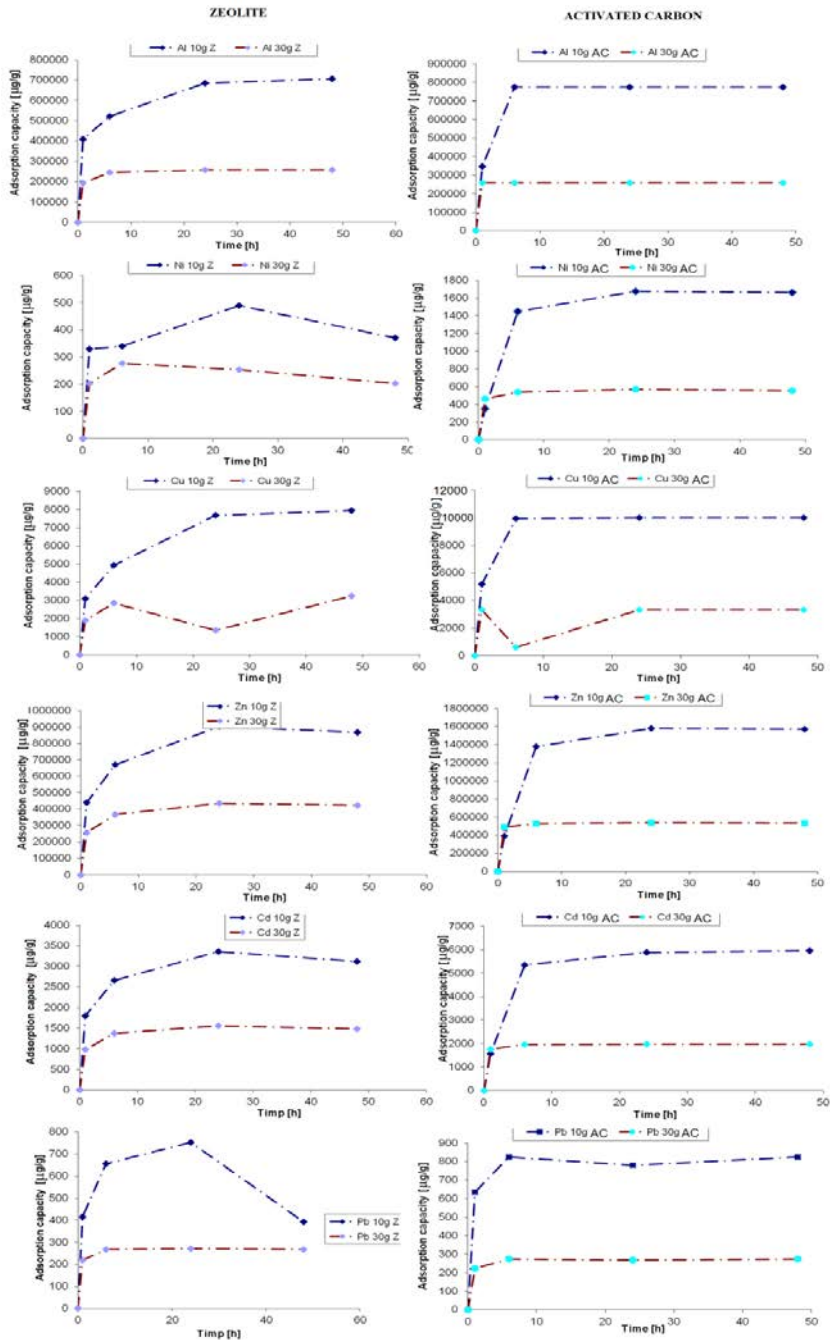


Fig. 2. Adsorption capacity of zeolite and activated carbon for Al, Ni, Cu, Zn, Cd and Pb

The interaction with AC (30 g) shows the best results obtained so far for the Ni concentration reduction, by 97.76% (Fig. 5) after 24 hours, this figure falling below the potability limit for Ni (20 µg/L). Although this metal remains the most difficult metal to remove at a short interaction time (1 hour with an efficiency of 79.94%). The maximum reduction of the Al concentration (99.98%) is reached after 24 hours, unlike the AC (10 g) (99.99%), where is reached after 6 hours. AC – 30 g is the best option in metal removal from AMD in this experiment, as all the six metals studied have very good results at a short interaction time (1 hour).

The adsorption capacity of the two materials was calculated with the formula:

$$q = \frac{(C_0 - C_t) \cdot V}{m_{AC}} [\mu\text{g}/\text{g}] \quad (1)$$

where: q – adsorption capacity [µg/g]; C_0 – initial concentration of the metals from the acid mine drainage [µg/L]; C_t – metal concentration at a certain time frame retained onto zeolite [µg/L]; V – acid mine drainage volume used in the adsorption experiments; $V=100$ ml, m_{AC} - zeolite/activated carbon quantity used in the experiment; $m_{AC} = 10$ and 30 g, respectively.

Fig. 2 represents the adsorption capacity of the zeolite compared to the one of the activated carbon used for the metals elimination from acid mine drainage.

The results show that the dynamic equilibrium is achieved for 10 g both for zeolite and activated carbon, for all the metals studied. Increasing the mass of adsorbent leads to a decrease in their adsorption capacity. This is probably due to the fact that as the adsorbent mass increases, the total area of interaction in the ion exchange process decreases, due to the particles overlapping and conglomeration (Lo et al., 2012; Huang et al., 2014; Nsami et al., 2013). However, for Ni, Zn and Cd after 1 hour interaction time, the dynamic equilibrium is reached at 30 g, for activated carbon.

From the studies on the adsorption of metals from acid mine drainage onto 10 g and 30 g of zeolite and activated carbon, it can be concluded that the optimum adsorbent mass required is 10 g.

The **efficiency** in percentage was calculated using the following equation (2) and is graphically represented in Fig. 3:

$$E = \frac{C_0 - C_t}{C_0} \cdot 100[\%] \quad (2)$$

where: E is the adsorption process efficiency [%], C_0 – is the initial metal concentration in AMD sample before treatment; [µg/L], C_t – the metal concentration at a certain time t [µg/L].

When the amount of zeolite is three times higher (30 g), the results are favourable for the Al concentration reduction, with a maximum of 99.78% reached after 48 hours. The lowest efficiency is noticed at Ni with 35.1%, which is almost two

times higher than the one reached for zeolite 10 g. The action of the zeolite for Cu and Pb is notable, with over 95% of concentration reduction. The desorption process can be observed for Cd, Cu, Ni, Pb and Zn, which occurs after 24 hours of interaction between the solid and liquid phase (Fig. 3).

After the interaction with AC (10 g), an important reduction of Al, Cu and Pb concentrations can be observed after 6, 24 and 48 hours, with an efficiency of almost 100% (Fig. 3). The lowest adsorption is for Ni, after 1 hour of interaction, with a concentration reduction of only 20.11 %.

In terms of *pH and electrical conductivity*, there is a growing trend after the contact with both materials (Table 1), with a higher efficiency of activated carbon over zeolite. Following the treatment of AMD with activated carbon, a change in pH is achieved, from acid to neutral (from 2.56 to 7.08 after 24 hours), pH values that correspond to drinking water. Both zeolite and AC influence positively the conductivity value, which increases to about the same level (above 4.20 $\mu\text{S}/\text{cm}$ after 48 hours). This phenomenon reflects the increase of the dissolved salts in the water, due to the ion exchange process that takes place in the interaction with zeolite and adsorption-desorption in contact with activated carbon.

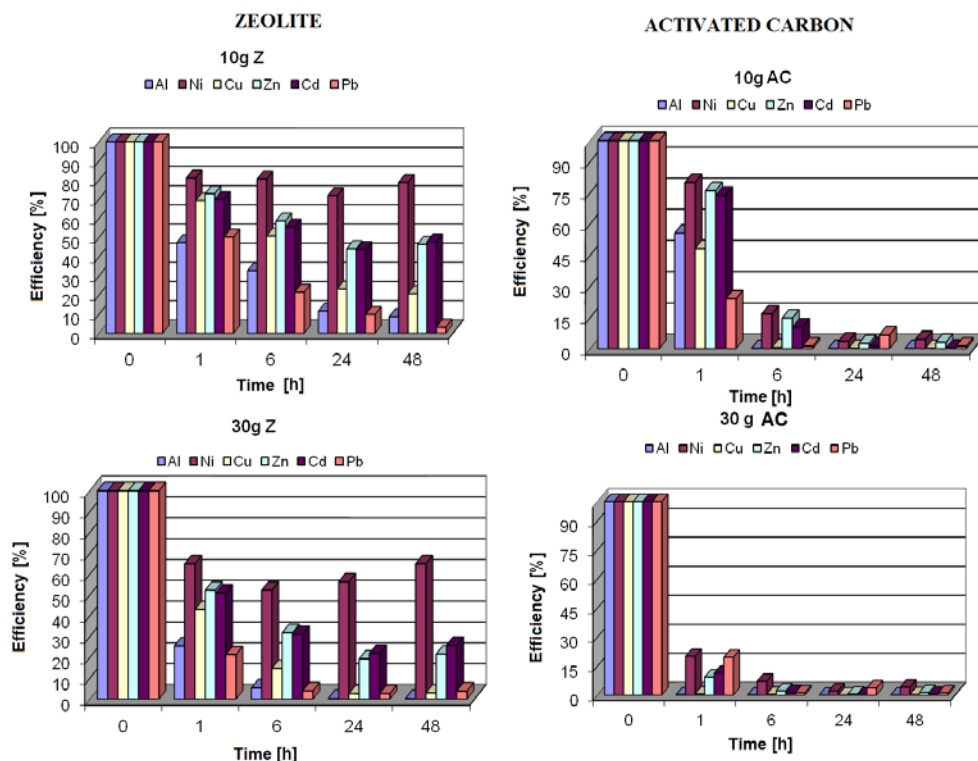


Fig. 3. The zeolite and activated carbon (10 and 30 g) efficiency in reducing the Al, Ni, Cu, Zn, Cd and Pb ions concentration, after the interaction with acid mine drainage

The adsorption/desorption equilibrium confers basic data for evaluating the physical and chemical applicability of the adsorption processes on an industrial scale. The equilibrium is often described by an isothermal process where the parameters express the surface properties and the affinity of the adsorbent (Ho et al., 2002). Based on these isotherms, equipment can be designed, estimations of the required adsorbent mass can be carried out or the calculation of the efficiency of pollutant purification degree can be made (Dechow, 1989). For this study, Freundlich and Langmuir isotherms have been calculated.

Linearized form of the Freundlich isotherm can be written as follows (Momčilović et al., 2011):

$$\log q = \frac{1}{n} \log C + \log K \tag{3}$$

where: q – adsorption capacity [$\mu\text{g/g}$]; C – pollutant concentration [$\mu\text{g/L}$]; K și n – constants that depend on the nature of the substance adsorbed and temperature, respectively Freundlich constants.

Also, the linearized form of Langmuir isotherm given by the following equation, has been calculated (Momčilović et al., 2011):

$$\frac{1}{q} = \left(\frac{1}{q_m \cdot K} \right) \cdot \frac{1}{C} + \frac{1}{q_m} \tag{4}$$

where: K - Langmuir equilibrium constant; q_m – adsorption capacity for monolayer formation; q – adsorption capacity [$\mu\text{g/g}$]; C – pollutant concentration [$\mu\text{g/L}$].

Table 1. Value of pH and electrical conductivity before and after the contact with zeolite and AC

Material	Contact time [h]	Material mass [g]	Before filtration		After filtration				
			pH	Conductivity [$\mu\text{S/cm}$]	pH	Conductivity [$\mu\text{S/cm}$]			
Zeolite	1	10	2.56	3.75	2.85	3.72			
	6				3.47	3.91			
	24				4.19	3.88			
	48				4.21	4.21			
Activated carbon	1				10	2.56	3.75	4.16	3.55
	6							6.81	4.20
	24							7.08	4.28
	48							7.21	4.49

The linearized forms of Freundlich and Langmuir isotherms for the metals adsorption onto zeolite and their linearization coefficients are presented in Fig. 4.

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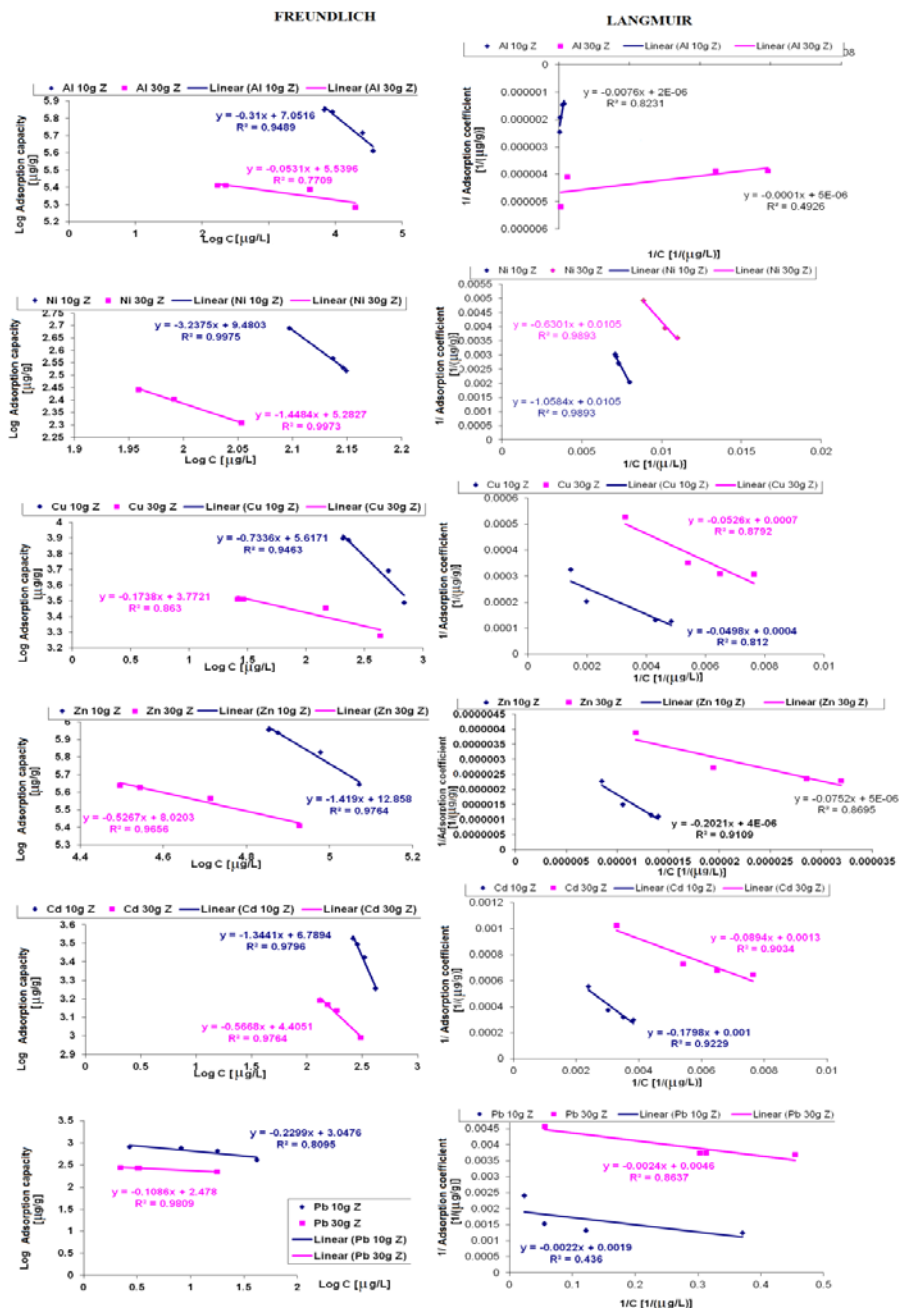


Fig. 4. Linearized Freundlich and Langmuir isotherms, for the adsorption of Al, Ni, Cu, Zn, Cd and Pb, onto 10 g and 30 g of zeolite

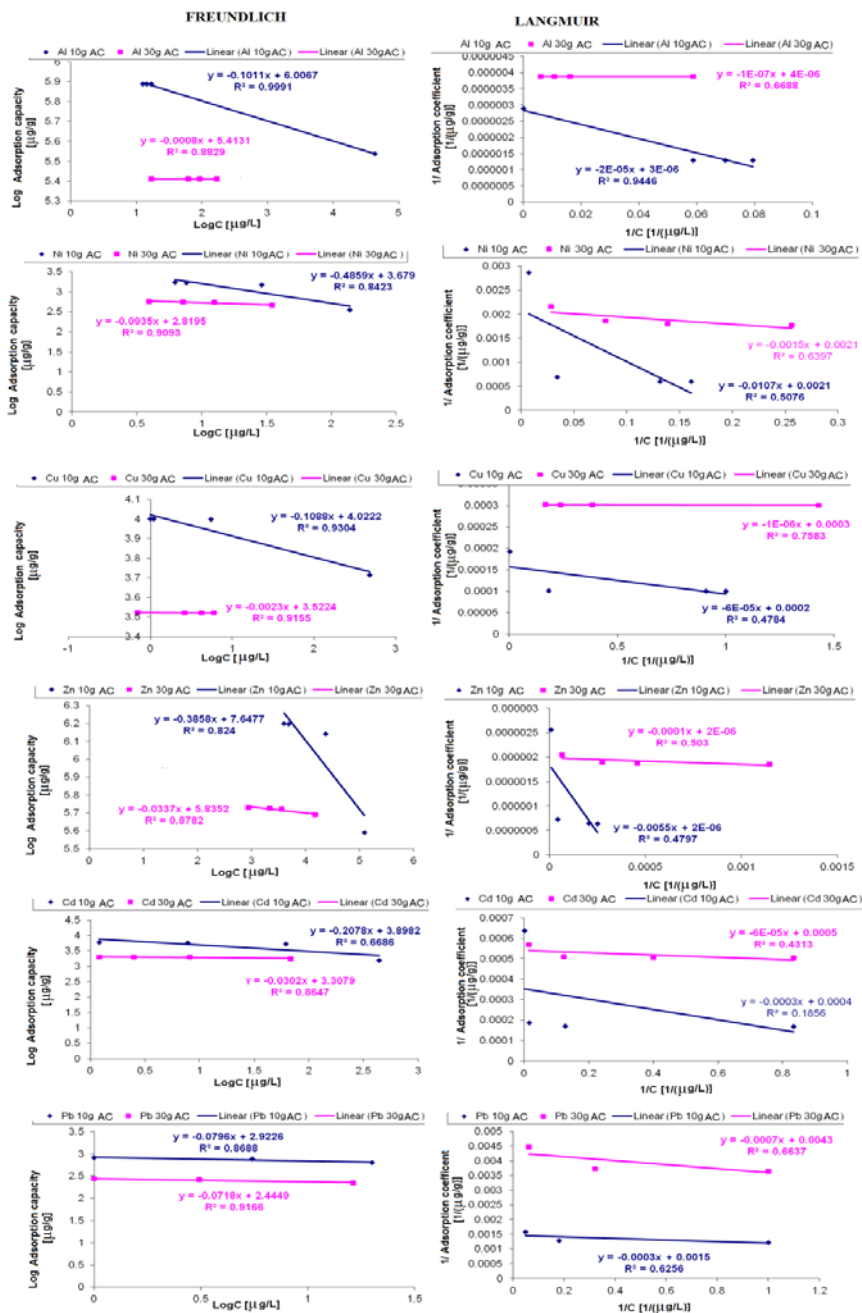


Fig. 5. Linearized Freundlich and Langmuir isotherms, for the adsorption of Al, Ni, Cu, Zn, Cd and Pb, onto 10 g and 30 g of activated carbon

Adsorption is considered favourable if $0 < R^2 < 1$, unfavourable if $R^2 > 1$, linear if $R^2 = 1$ and irreversible if $R^2 < 0$ [10]. From the data presented in Figure 4, it can be observed the fact that the mathematical model of the adsorption process for all the studied metals is Freundlich isotherm, where the correlation coefficient R^2 is closer to the value 1. For Ni and Cd, 10 g of zeolite is needed and 30 g in the case of Al, Cu, Zn and Pb.

The linearized forms of Freundlich and Langmuir isotherms are presented in Fig. 5 for the adsorption of Al, Ni, Cu, Zn, Cd and Pb onto 10 g and 30 g respectively of activated carbon.

From Fig. 5, it can be observed that considering the correlation coefficient R^2 , the adsorption process derives from Freundlich isotherm using 10 g of zeolite Al and Cu, and 30 g of activated carbon for Ni, Zn, Cd and Pb.

CONCLUSIONS

The data presented in this paper highlight the effectiveness of using dried zeolite and thermally activated AC only, emphasizing their ability to reduce the concentration of some heavy metals in waters, below the maximum level of contaminants accepted for drinking water, as regulated by law.

Increased efficiency of the AC in comparison with zeolite is evident when using the same amount of filtering material. Comparing the results for the Al, Cu and Pb after the contact with the two materials, one can observe that the use of AC involves a much lower interaction time than the use of zeolite, with better results in reducing the metals concentrations in the sample.

When the amount of zeolite increases, the results become comparable to or even better than those obtained after the contact with AC for two of the six metals studied (Ni after 6, 24 and 48 hours, and Pb after 24 hours). For certain metals (Al, Cd and Zn), the zeolite is more effective than AC in a short interaction timeframe (1 hour).

Aluminium as a metal is well removed from the waste waters probably due to the fact that the aluminium atom has the smallest atomic volume among the studied metals. This fact facilitates both ion exchange with the zeolite and adsorption on AC surface.

In the experiments carried out, both on zeolite and AC, the metal most easily to remove is aluminium and the most difficult one to remove is nickel.

Nickel is removed in small amounts from the wastewater due to the fact that the Ni^{2+} ion has the $[Ar]3d^8$ electronic structure, which facilitates the occurrence of the octahedral complexes in the water. The occurrence of these complexes is probably favoured, as compared to the ionic exchange with the zeolite or to the AC surface adsorption.

The use of AC for AMD treatment is more efficient than the zeolite in terms of pH, as it reaches a neutral level which corresponds to drinking water after 24 hours for the samples treated with AC.

The experiments made showed that in the retention process of metals from acid mine drainage onto zeolite and activated carbon, the adsorption capacity decreases with the increase of the adsorbent mass, the dynamic equilibrium being reached at 10 g of both zeolite and activated carbon. The mathematical model for the adsorption process on the two filtration materials is Freundlich isotherm.

As the two filtration materials act in different ways in the process of heavy metals retaining, and the results obtained for the same metal are different, the optimal choice for a water filtering would probably contain both zeolite and AC.

ACKNOWLEDGEMENTS

This paper was supported by the project "Improvement of the doctoral studies quality in engineering science for development of the knowledge based society-QDOC" contract no. POSDRU/107/1.5/S/78534, project co-funded by the European Social Fund through the Sectorial Operational Program Human Resources 2007-2013.

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