



Proceedings of
XVI BALKAN MINERAL PROCESSING CONGRESS
Belgrade, Serbia, June 17-19, 2015



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Edited by

Nadežda Čalić, Ljubiša Andrić,
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REMOVAL OF HEAVY METAL IONS FROM AQUEOUS SOLUTIONS USING CLINOPTILOLITE

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Abstract: Heavy metals are a common pollutant found in various industrial effluents. They are often encountered in mining operations and acid mine drainage. The heavy metals are highly toxic and are non-biodegradable, therefore they must be removed from the polluted streams in order to meet increasingly stringent environmental quality standards.

Removal of heavy metals can be accomplished by a variety of techniques. Conventional methods typically involve the use of processes such as coagulation, precipitation, ion-exchange, electrochemical methods, membrane processes, extraction, biosorption, adsorption, etc. Among these methods, adsorption is currently considered to be very suitable for removal of heavy metals because of its simplicity and cost effectiveness. Some widely used adsorbents for adsorption of heavy metals include activated carbon, clay minerals, biomaterials, industrial solid wastes and zeolites.

The removal of copper, zinc, manganese and lead ions from synthetic aqueous solutions was performed using clinoptilolite. In order to determine the effectivity of clinoptilolite a series of experiments were performed under batch conditions from single ion solutions. Experiments were carried out at different initial ions concentration, different initial pH values and different adsorbent mass.

The adsorption of copper, zinc, manganese and lead ions from single ion solution onto natural zeolite occurs efficiently. It is the most effective at lower ions concentration, higher mass of zeolite and higher pH value of the solution.

Keywords: clinoptilolite, lead, zinc, copper, manganese.

INTRODUCTION

Zeolite is a natural porous mineral in which the partial substitution of Si⁴⁺ by Al³⁺ results in an excess of negative charge. This is compensated by alkali and alkaline earth cations (Na⁺, K⁺, Ca²⁺ or Mg²⁺). Zeolites have been used as adsorbents, molecular sieves, membranes, ion-exchangers and catalysts, mainly because zeolite exchangeable ions are relatively innocuous. Thus, zeolites are particularly suitable for removing undesirable heavy metal ions (e.g. lead (Golomeova, 2014), nickel (Jakupi, 2014), zinc (Zendelska, 2014, Zendelska, 2014), manganese, cadmium, copper, chromium and/or cobalt), radionuclides as well as ammoniacal nitrogen (ammonia and ammonium) from municipal wastewaters, metal plating facilities, electroplating, mining operations, fertilizers, battery manufacture, dyestuffs, chemical pharmaceutical, electronic device manufactures and many others (Silvio Roberto Taffarel, 2009).

The aim of this work was to investigate the removal of copper, zinc, manganese and lead ions from synthetic aqueous solutions using natural zeolite, clinoptilolite. In order to determine the effectivity of clinoptilolite a series

of experiments were performed under batch conditions from single ion solutions. Experiments were carried out at different initial ions concentration, different initial pH values and different adsorbent mass.

MATERIALS AND METHODS

Adsorbent

The natural zeolite - clinoptilolite was used in the recent study as an adsorbent for adsorption of heavy metals, such as copper, zinc, manganese and lead. The particle size range of the clinoptilolite used in this study was 0.8 to 2.5 mm.

The chemical composition of clinoptilolite is presented in Table 1.

Table 1, Chemical composition of clinoptilolite

Typical chemical composition in % wt			
SiO ₂	69.68	CaO	2.01
Al ₂ O ₃	11.40	Na ₂ O	0.62
TiO ₂	0.15	K ₂ O	2.90
Fe ₂ O ₃	0.93	H ₂ O	13.24
MgO	0.87	P ₂ O ₅	0.02
MnO	0.08	ratio Si/Al	4.0-5.2
Cation exchange per cation		K ⁺	41 meq/100g
		Na ⁺	16.10 meq/100g
		Ca ²⁺	67.14 meq/100g
		Mg ²⁺	3.88 meq/100g
Total cation exchange capacity		1.8-2.2 meq/g	

X-Ray Diffractometer 6100 from Shimadzu was used to investigate the mineralogical structure of natural zeolite samples. The diffraction data obtained are compared to the database maintained by the *International Centre for Diffraction Data*, in order to identify the material in the solid samples. The results of XRD (Fig. 1) showed that the natural zeolite contained clinoptilolite in the majority.

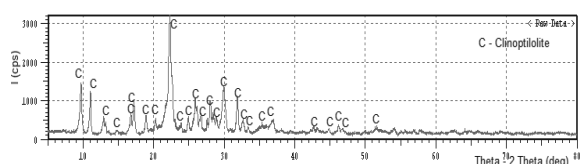


Figure 1, X-Ray diffraction of natural zeolite

The surface morphology of natural zeolite was studied using a scanning electron microscope, VEGA3 LMU. This particular microscope is also fitted with an Inca 250 EDS system. Micrographs of natural zeolite samples obtained from SEM analysis are given in Fig. 2. The micrographs clearly show a number of macropores in the zeolite structure. The micrographs also show well defined crystals of clinoptilolite.

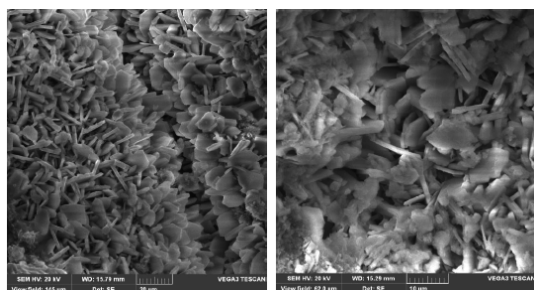


Figure 2, Micrographs of natural zeolite samples obtained from SEM analysis

An electron beam was directed onto different parts of the samples in order to get a more accurate analysis (Fig. 3) and the elemental composition of natural zeolite (clinoptilolite) are presented in Table 2.



Figure 3, EDS analysis showing the scanning method for natural zeolite

Table 2, EDS analysis showing the elemental composition for natural zeolite

Element	Spect 1	Spect 2	Spect 3	Aver.	Std. devia.
O	58.46	55.4	58.83	57.56	1.882
Na	0.27	0.15	0.3	0.24	0.079
Mg	0.72	0.66	0.77	0.72	0.055
Al	5.28	5.52	5.03	5.28	0.245
Si	29.55	31.36	29.47	30.13	1.068
K	2.73	2.96	2.44	2.71	0.26
Ca	1.9	2.42	1.66	1.99	0.388
Fe	1.1	1.53	1.5	1.38	0.24
Total	100	100	100	100	

The results of EDS analysis showed that the predominant exchangeable cations in natural zeolite (clinoptilolite) structure were K⁺ and Ca²⁺.

Adsorbate

The heavy metals, Cu, Zn, Mn and Pb were used as adsorbate in the recent investigations. Synthetic single component solutions of these metals were prepared by dissolving a weighed mass of the analytical grade salt CuSO₄.5H₂O, ZnSO₄.7H₂O, MnSO₄.H₂O and Pb(NO₃)₂, appropriately, in 1000ml distilled water.

Experimental procedure

Adsorption of heavy metals ions on clinoptilolite were performed with synthetic single component ion solutions of Cu²⁺, Zn²⁺, Mn²⁺ and Pb²⁺ ions with different initial concentration (5, 25, 50, 200 and 400mg/l). Initial pH value (2.5, 3.5 and 4.5) of prepared solutions was adjusted by adding 2% sulfuric acid and controlled by 210 Microprocessor pH Meter. The experiments were performed in a batch mode in a series of beakers equipped with magnetic stirrers by contacting a mass of 2, 5 and 10g adsorbent with a volume of solution, 400ml. Adsorbent and aqueous phase were suspended by magnetic stirrer at 400 rpm. The agitation time was up to 120 minutes. At the end of the predetermined time, the suspension was filtered and the filtrate was analyzed. The final pH value was also measured. All experiments were performed at

room temperature on $20\pm 1^\circ\text{C}$. The initial and remaining concentrations of metal ions were determined by Liberty 110, ICP Emission Spectrometer, Varian.

The adsorption capacity was calculated by using the following expression:

$$q_e = \frac{V(C_0 - C_e)}{m}, \text{ (mg/g)} \quad [1]$$

where: q_e is the mass of adsorbed metal ions per unit mass of adsorbent (mg/g), C_0 and C_e are the initial and final metal ion concentrations (mg/l), respectively, V is the volume of the aqueous phase (l) and m is the mass of adsorbent used (g).

Degree of adsorption, in percentage, is calculated as:

$$AD\% = \left(1 - \frac{C_e}{C_0}\right) \cdot 100 \quad [2]$$

RESULTS AND DISCUSSION

Effect of adsorbent mass

A series of experiments at different adsorbent masses, that is, 2, 5 and 10 g, were performed at the temperature $20\pm 1^\circ\text{C}$ and pH value 3.5 in 400ml solution agitated for 120 minutes. The concentration of the single component solution was 400, 25, 200 and 5mg/l of Cu^{2+} , Zn^{2+} , Mn^{2+} and Pb^{2+} , appropriately.

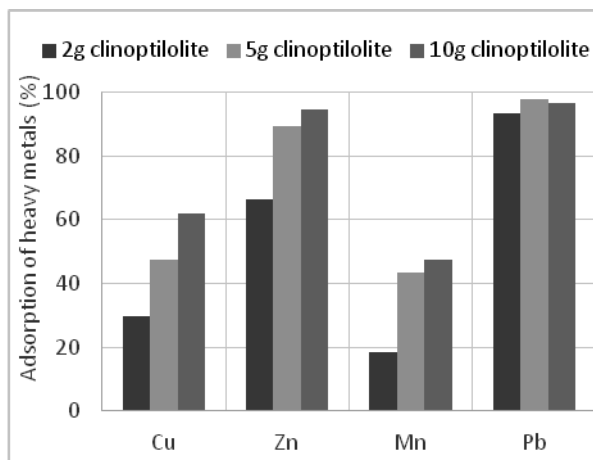


Figure 4, Effect of adsorbent mass

The plots of the amount of metal adsorbed versus mass of adsorbent for each used heavy metals are shown in Fig. 4. According to the percentage of metal adsorbed from solution, we can see that an increase in adsorbent mass resulted in an increase in the adsorption of the heavy metals. This is because as adsorbent mass increases more adsorption sites are

available per unit mass of adsorbent added. Except Pb ions, there are no significant difference with increasing of adsorbent mass.

Effect of initial solution concentration

The results of the experiments to measure the adsorption of cations from aqueous solutions onto the clinoptilolite according to initial concentration of heavy metals in solution are shown in Fig. 5. Single component solutions 400ml were mixed with 5 g clinoptilolite and agitated for 120 minutes at the temperature $20\pm 1^\circ\text{C}$ and pH value 3.5. The concentration of the single component solution was 5, 25, 50, 200 and 400mg/l of Cu^{2+} , Zn^{2+} , Mn^{2+} and Pb^{2+} .

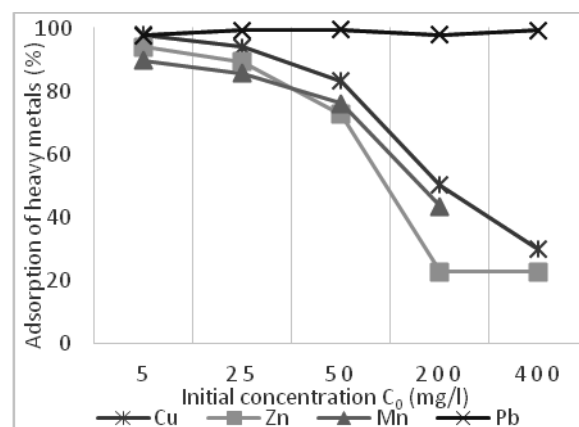


Figure 5, Effect of initial solution concentration

An increase in concentration generally results in an increase in the amount of metal adsorbed and the rate of adsorption. This may be a result of an increase in collisions between the reactants, leading to the observed increase in reaction rate and capacity according to the *Collision Theory* (Connors, 1990). The adsorption capacity will increase with an increase in initial concentration until the system reaches a saturation point, at which point further increase of the adsorbate concentration will not result in any significant change in the amount adsorbed, q_e .

Table 3, Effect of initial solution concentration on the adsorption capacity of clinoptilolite

Heavy Metals	Initial Concentration C_0 (mg/l)	Amount Adsorbed q_e (mg/g)	Percentage Adsorbed (%)
Cu	5	0.391	97.840
	25	1.880	94.000
	50	3.328	83.200
	200	8.008	50.050
	400	9.544	29.825
Zn	5	0.376	94
	25	1.786	89.32
	50	2.901	72.52
	200	3.619	22.62
	400	7.263	22.69
Mn	5	0.358	89.6
	25	1.713	85.64
	50	3.039	75.98
	200	6.960	43.45
Pb	5	0.390	97.60
	25	1.984	99.20
	50	3.982	99.54
	200	15.642	97.76
	400	30.143	94.19

The results (Table 3) indicate that the amount of metal adsorbed by clinoptilolite at equilibrium is dependent on the initial metal concentration. The increase in the amount of metal adsorbed as initial concentration increases is a consequence of an increase in the concentration driving force. The concentration driving force is important because it is responsible for overcoming the mass transfer resistance associated with the adsorption of metals from solution by the zeolite (Barrer, 1978). Therefore, as initial concentration increases, the driving force also increases resulting in an increase in metals uptake by the clinoptilolite.

Table 3 also reveals that an increase in initial concentration not only results in an increase in the amount adsorbed (q_e) but a decrease in the efficiency of clinoptilolite for the removal of heavy metal from solution. According to initial lead concentration in solution, there are no significant difference with increasing of lead concentration in solution, again. It means that removal of lead ions from solution is not depends on both the adsorbent mass and initial lead concentration in solution.

Motsi (Motsi, 2010) also found a similar trend, that is, a decrease in efficiency, in his work on

the adsorption of Cu, Mn, Zn and Fe from solution by clinoptilolite.

Effect of initial solution pH

A series of experiments at different initial pH values (2.5, 3.5 and 4.5) were performed at the temperature $20 \pm 1^\circ\text{C}$ and mass of adsorbent 5g in 400ml solution agitated for 120 minutes. The concentration of the single component solution was 400, 25, 200 and 5mg/l of Cu^{2+} , Zn^{2+} , Mn^{2+} and Pb^{2+} , appropriately.

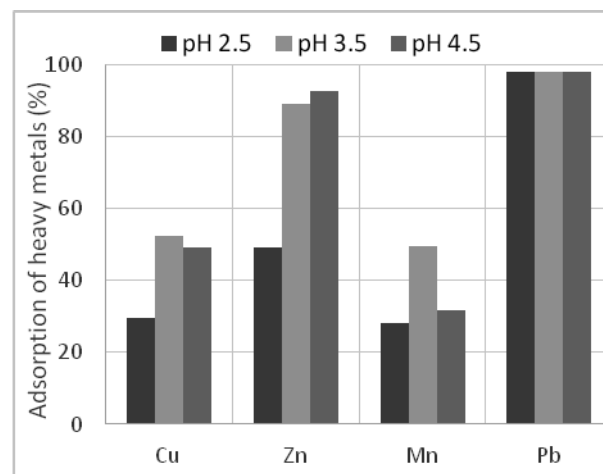


Figure 6, Effect of initial solution pH

The pH of the solution in contact with clinoptilolite has an obvious impact on its ability to remove metals since the acidic solution can influence both the character of the exchanging ions and the character (structure) of the clinoptilolite itself. Fig. 6 shows that as solution pH decreases, metal removal efficiency also decreases, but only at copper and zinc ions. The adsorption of lead ions using clinoptilolite is not depends of pH values, again.

That is because H^+ ions compete with metal cations for the same exchange sites (Alvarez-Ayuso, 2003) and electrostatic repulsion between the metal cations in solution and the protonated clinoptilolite surface increases as more H^+ ions are adsorbed (Cabrera, 2005).

CONCLUSION

The adsorption of copper, zinc, manganese and lead ions from single ion solution onto clinoptilolite occurs efficiently. It is the most effective at lower ions concentration, higher mass of zeolite and higher pH value of the solution, except lead. Adsorption of lead ions from solution using clinoptilolite is not depends

of adsorbent mass, initial lead concentration and pH values on solution.

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