

EFFECT OF COMPETING CATIONS (Cu, Zn, Mn, Pb) ADSORBED BY NATURAL ZEOLITE

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ABSTRACT

The aim of this work was to investigate the influence of the presence of competing cations on the individual adsorption of Cu^{2+} , Pb^{2+} , Zn^{2+} and Mn^{2+} from a solution containing a mixture of all these metal ions, by natural zeolite. In this work is shown compares the adsorption of each heavy metal ion from both single- and multi-component solutions. The amount adsorbed from multi-component solutions was affected significantly, except for Pb^{2+} where the difference between single and multi-component solution is minimal, almost insignificant. It was also determine the selectivity of natural zeolite, for the respective heavy metal ions. The selectivity series obtained for single component solution was: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$, and for multi-component solution was $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+} > \text{Zn}^{2+}$.

INDEX TERMS: copper, zinc, manganese, lead, zeolite, competing cation, selectivity series.

1. INTRODUCTION

Zeolite is a natural porous mineral in which the partial substitution of Si^{4+} by Al^{3+} results in an excess of negative charge. This is compensated by alkali and alkaline earth cations (Na^+ , K^+ , Ca^{2+} or Mg^{2+}). 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, nickel, zinc, manganese, cadmium, copper, chromium and/or cobalt), radionuclides as well as ammoniacal nitrogen (ammonia and ammonium) from municipal wastewater, industrial wastewater, acid mine drainage, mining operations, fertilizers, battery

manufacture, dyestuff, chemical pharmaceutical, electronic device manufactures and many others [1].

Most of 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.

Industrial wastewater and acid mine drainage typically contain many different metal ions as a mixture. These ions have the potential to affect the effectiveness of an adsorbent in treating the wastewater and that is based on their competition for exchange sites on and in the adsorbent. Therefore, it is important to investigate the impact of competing cations on the removal of each pollutant from solution.

The aim of this work was to investigate the influence of the presence of competing cations on the individual adsorption of Cu^{2+} , Pb^{2+} , Zn^{2+} and Mn^{2+} from a solution containing a mixture of all four metal ions, by natural zeolite. In this work is shown compares the adsorption of each heavy metal ion from both single- and multi-component solutions. Also, according to the maximum adsorption capacity (q_e) was

determine the selectivity of natural zeolite, for the respective heavy metal ions. There are a large number of selectivity series assigned to zeolites that contain clinoptilolite (Table 1).

Table -1: Examples of experimentally derived selectivity series of natural zeolite for different heavy metals from literature

Blanchard et al., 1984 [3]	$\text{Pb}^{2+} > \text{NH}_4^+ > \text{Ba}^{2+} > \text{Cu}^{2+} \approx \text{Zn}^{2+} > \text{Cd}^{2+} \approx \text{Sr}^{2+} > \text{Co}^{2+}$
Zamzow et al., 1990 [4]	$\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cs}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Cr}^{3+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Hg}^{2+}$
Moreno et al., 2001 [5]	$\text{Fe}^{3+} \approx \text{Al}^{3+} > \text{Cu}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+} > \text{Ca}^{2+} \approx \text{Sr}^{2+} > \text{Mg}^{2+}$
Inglezakis et al., 2002 [6]	$\text{Pb}^{2+} > \text{Cr}^{3+} > \text{Fe}^{3+} > \text{Cu}^{2+}$
Alvarez-Ayuso et al., 2003 [7]	$\text{Cu}^{2+} > \text{Cr}^{3+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$
Erdem et al., 2004 [8]	$\text{Co}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$
B. Calvo et al., 2009 [9]	$\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$
Sprynskyy, 2009 [10]	$\text{Cd}^{2+} > \text{Pb}^{2+} > \text{Cr}^{3+} > \text{Cu}^{2+} > \text{Ni}^{2+}$
Motsi, 2010 [11]	$\text{Fe}^{3+} > \text{Zn}^{2+} > \text{Cu}^{2+} > \text{Mn}^{2+}$
Sabry M. S. et al., 2012 [12]	$\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$

The selectivity of zeolite to adsorb various cations is the result of the complex combined effect of following parameters: 1.Parameters related to work conditions: the static or dynamic nature of the regime of adsorption, solid:liquid ratio, working temperature, initial concentration and pH of contact solutions, stirring intensity of the heterogeneous system as well as the nature of the cation and accompanying anion; 2.Parameters related to the characteristics of zeolite: the average diameter of particles, mineralogical and chemical composition, initial activation, internal structure of macropores and micropores and 3.Parameters related to the characteristics of adsorbed ions: hydrated radius of the ion, tendency to form hydrocomplexes in solutions, hydration energy and ionic mobility, as well as other factors [2].

2. MATERIALS AND METHODS

2.1 ADSORBENT

The natural zeolite- clinoptilolite was used in the recent study as an adsorbent for adsorption of heavy metals, such as Cu, Zn, Mn and Pb. The particle size range of the natural zeolite used in this study was 0.8 to 2.5 mm.

The chemical compositions of natural zeolite are presented in Table 2.

Table 2: Chemical composition of zeolite samples

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. This technique is based on observing the scattering intensity of an X – Ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. 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) shown that the natural zeolite contained clinoptilolite in the majority.

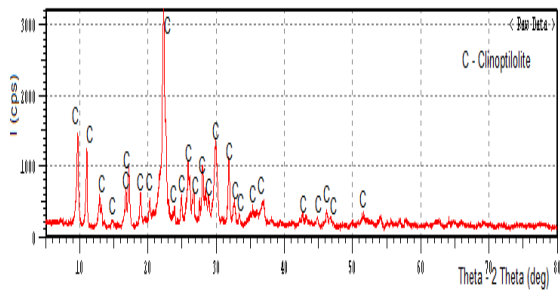


Figure 1: X-Ray diffraction of natural zeolite

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. EDS, stands for Energy Dispersive Spectroscopy, it is an analytical technique used for the elemental analysis of a sample based on the emission of characteristic X – Rays by the sample when subjected to a high energy beam of charged particles such as electrons or protons. Micrographs of natural zeolite samples obtained from SEM analysis are given in Fig. 2. The

micrographs clearly show a number of macro-pores in the zeolite structure. The micrographs also show well defined crystals of clinoptilolite.

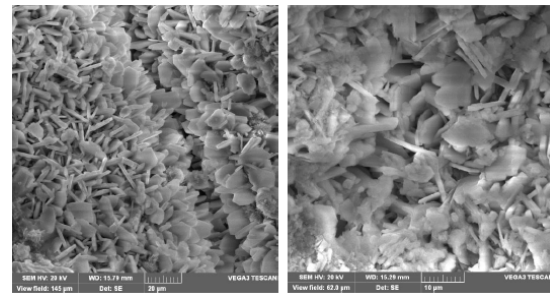


Figure 2: Micrographs of natural zeolite samples obtained from SEM analysis

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 3.

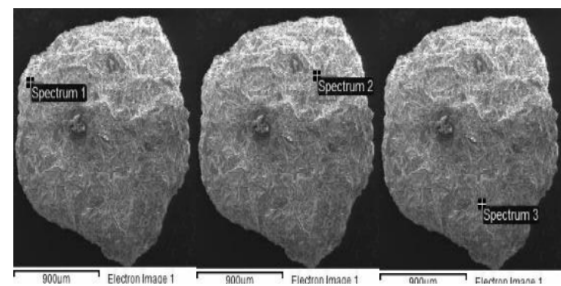


Figure 3: EDS analysis showing the scanning method for natural zeolite

Table -3: EDS analysis showing the elemental composition for natural zeolite

Element	Spect 1	Spect 2	Spect 3	Average	Standard deviation
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	

Results of EDS analysis showed that the predominant exchangeable cations in natural zeolite (clinoptilolite) structure were K^+ and Ca^{2+} .

2.2 ADSORBATE

The heavy metals, Cu, Zn, Mn and Pb were used as adsorbate in the recent investigations. Synthetic single and multi-component solutions of these metals were prepared by dissolving a weighed mass of the analytical grade salt $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$, $MnSO_4 \cdot H_2O$ and $Pb(NO_3)_2$, appropriately, in 1000ml distilled water.

2.3 EXPERIMENTAL PROCEDURE

Adsorption of heavy metals ions on zeolite was performed with synthetic single and multi-component ion solutions of Cu^{2+} , Zn^{2+} , Mn^{2+} and Pb^{2+} ions with initial concentration of 25 mg/l. Initial pH value 3.5 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 zeolite (5g) with a volume of solution, 400ml. Zeolite sample and aqueous phase were suspended by magnetic stirrer at 400 rpm. The agitation time was varied up to 360

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. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample.

The adsorption capacity was calculated by using the following expression:

$$q_s = \frac{V(C_0 - C_s)}{m}, \text{ (mg/g)} \quad (1)$$

where: q_s is the mass of adsorbed metal ions per unit mass of adsorbent (mg/g), C_0 and C_s 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).

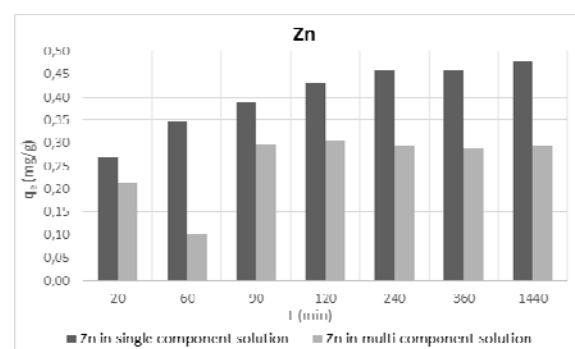
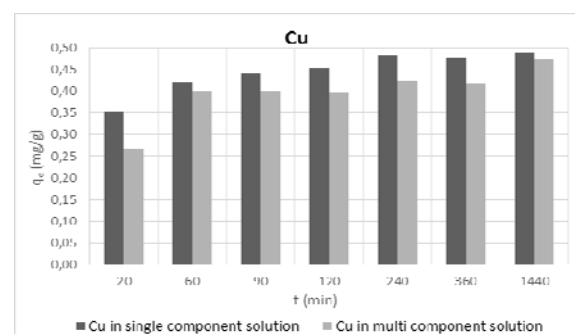
Degree of adsorption, in percentage, is calculated as:

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

3. RESULTS AND DISCUSSION

Experiments were carried out to investigate the influence of the presence of competing cations on the individual adsorption of Cu^{2+} , Zn^{2+} , Mn^{2+} and Pb^{2+} from a solution containing a mixture of all 4 metal ions, by natural zeolite.

On Chart 1 is made comparison of the adsorption of each heavy metal ion from both single- and multi-component solutions.



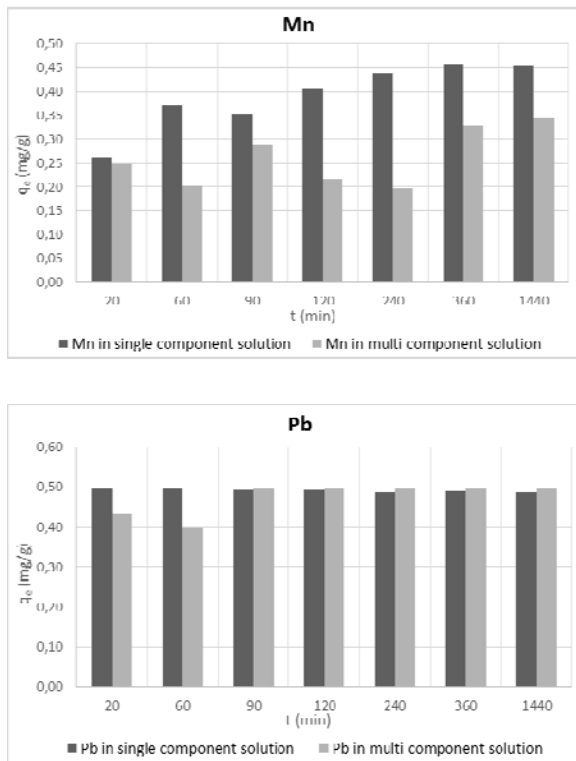


Chart -1: Comparison of the adsorption capacity of natural zeolite for Cu, Zn Mn and Pb from single and multi – component solutions

The amount adsorbed from multi-component solutions was affected significantly, except for Pb^{2+} where the difference between single and multi-component solution is minimal, almost insignificant. The results show that amount adsorbed Cu^{2+} from multi-component solution was decreased approximately 10%, and 25-50% for Zn^{2+} and Mn^{2+} compared to their single component solutions.

Moreover, the total amount of heavy metal ions adsorbed (all four cations) per unit mass of natural zeolite increased of multi-component solutions

compared to the amount of solute adsorbed from single component solutions.

According to the obtained results was determine the selectivity of used zeolite. This was done by comparing the maximum adsorption capacity (q_e) of natural zeolite for the respective heavy metal ion. The selectivity series obtained in single component solution was: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$, but in multi-component solution was $Pb^{2+} > Cu^{2+} > Mn^{2+} > Zn^{2+}$.

The difference in adsorption capacity of the natural zeolite for the heavy metal ions may be due to a number of factors which include hydration radii, hydration enthalpies and solubility of the cations. The hydration radii of the cations are: $r_{H}Zn^{2+} = 4.30\text{\AA}$, $r_{H}Cu^{2+} = 4.19\text{\AA}$, $r_{H}Pb^{2+} = 4.01\text{\AA}$ and $r_{H}Mn^{2+} = 4.38\text{\AA}$ [13] [14]. The smallest cations should ideally be adsorbed faster and in larger quantities compared to the larger cations, since the smaller cations can pass through the micropores and channels of the zeolite structure with ease [8]. Furthermore, adsorption should be described using hydration enthalpy, which is the energy that permits the detachment of water molecules from cations and thus reflects the ease with which the cation interacts

with the adsorbent. Therefore, the more a cation is hydrated the stronger its hydration enthalpy and the less it can interact with the adsorbent [11]. Because of its high Si:Al ratio, clinoptilolite has a low structural charge density. Therefore, divalent cations with low hydration energies are sorbed preferably compared to cations with high hydration energies [15]. The hydration energies of the cations are: -2010, -1955, -1760 and -1481 kJmol⁻¹ for Cu²⁺, Zn²⁺, Mn²⁺ and Pb²⁺ respectively [13] [14]. According to the hydration radii the order of adsorption should be Pb²⁺ > Cu²⁺ > Zn²⁺ > Mn²⁺, and according to the hydration enthalpies the order should be Pb²⁺>Mn²⁺>Zn²⁺>Cu²⁺.

According to the hydration energies and hydration radii, the zeolite will prefer Pb over Cu, Mn and Zn in multi-component solutions. Therefore, it is to be expected that high Pb concentrations will limit the uptake of Cu, Mn and Zn.

The above series according to the hydration radii is same with the experimentally obtained series for single component solution, which is Pb²⁺ > Cu²⁺ > Zn²⁺ > Mn²⁺. But the experimentally obtained series for multi-component solution is different

from above series according to the hydration radii and enthalpies.

4. CONCLUSIONS

The investigation for influence of the presence of competing cations on the individual adsorption of Cu²⁺, Zn²⁺, Mn²⁺ and Pb²⁺ from a solution containing a mixture of all this metal ions, by natural zeolite is done by comparing the adsorption of each heavy metal ion from both single- and multi-component solutions. From this is concluded that the amount adsorbed from multi-component solutions was affected significantly, except for Pb²⁺ where the difference between single and multi-component solution is minimal, almost insignificant. The amount adsorbed Cu²⁺ from multi-component solution was decreased approximately 10%, and 25-50% for Zn²⁺ and Mn²⁺ compared to their single component solutions.

The own unique selectivity series on investigated zeolite in single component solution was: Pb²⁺ > Cu²⁺ > Zn²⁺ > Mn²⁺, but in multi-component solution was Pb²⁺ > Cu²⁺ > Mn²⁺ > Zn²⁺. According to the hydration energies and hydration radii, the zeolite will prefer Pb over Cu, Mn and Zn in multi-component solutions. Therefore, it is to be expected

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