



Effect of Competing Cations (Cu, Zn, Mn, Pb) Adsorbed by Zeolite Bearing Tuff from Macedonia

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ABSTRACT

Zeolite bearing tuff (stilbite 27%) from Vetunica deposit, Republic of Macedonia was investigated as an adsorbent for removal of copper, zinc, manganese and lead ions from synthetic aqueous solutions. The aim of this study 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 zeolite bearing tuff. The obtained results show that the adsorption of studied ions in single and multi-component solution onto zeolite bearing tuff occurs efficiently. 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 selectivity of zeolite bearing tuff was also determined for the respective heavy metal ions. The selectivity series obtained for single and multi-component solution was: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$.

INTRODUCTION

Zeolites are crystalline microporous minerals, which are broadly distributed in nature. There are nearly 50 different types of zeolites, which are grouped according to the structure: Analcime group, Sodalite group, Chabazite group, Stilbite group, Natrolite group, Phillipsite group, Mordenite group, Bikitaite and zeolites with unknown structures (Smith 1963). Stilbite belong to stilbite series minerals. Stilbite-Ca is a common zeolite, while stilbite-Na, is rare. Stilbite-Ca occur in fractures and other cavities in basaltic rocks. Stilbite-Ca occur as a vein mineral in diagenetically altered or metamorphosed volcanic rocks. It also occurs as a vein mineral cutting non-volcanic rocks, such as pegmatite, gneiss, schist or granite.

Application of the zeolite in wastewater treatment is very important. The factors that make natural zeolite an attractive alternative for the treatment of wastewater are: cheap, since they are relatively abundant (Heping Cui 2006); zeolites have a high surface area due to their porous and rigid structure (Alvarez-Ayuso 2003); they also act as molecular sieves and this property can easily be modified to increase the performance of the zeolite (Sprynsky 2006); they have a favourable cation exchange capacity (CEC) (Yuan 1999); they have good selectivity for cations (Malliou 1994); in acidic conditions, the zeolites have good structural stability, and can be easily regenerated. The zeolites have buffer effect, neutralization of the acidic solutions is achieved through the exchange of H^+ ions from solution

with the exchangeable cations in the zeolite structure (Leinonen 2001).

The selectivity of zeolite to adsorb various cations is the result of the complex combined effect of the following parameters:

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 heterogenous system as well as the nature of the cation and accompanying anion.

Parameters related to the characteristics of zeolite: The average diameter of particles, mineralogical and chemical composition, initial activation, internal structure of macropores and micropores.

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 (L. Mihaly-Cozmuta 2014).

The aim of this study 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 the adsorbent zeolite bearing tuff that contains 27% stilbite from Macedonia. This paper compares the adsorption of each heavy metal ion from both single and multi-component solutions. In addition, according to the maximum adsorption capacity (q_c), the selectivity of zeolite bearing tuff was determined for the respective heavy metal ions.

MATERIALS AND METHODS

Adsorbent: Particle characterization reveals information on the physical and chemical nature of zeolite bearing tuff particles, which is related to its ability to remove heavy metal ions from solution.

In the present study zeolite bearing tuff from Vetunica deposit, localized in northern marginal parts of the well-known Kratovo-Zletovo volcanic area in Republic of Macedonia was used as an adsorbent. The particle size range of the used material was 0.8 to 2.5 mm.

The general characteristics of the zeolite bearing tuff, such as chemical composition and physical characteristics are presented in Table 1. The sample was analysed on the content and type of exchangeable cations. The dominant ion, in the exchangeable position, is K^+ (66.5 meq/100g), followed by Ca^{2+} (21.5 meq/100g), Mg^{2+} (8.5 meq/100g) and Na^+ (3.5 meq/100g). The total cation exchange capacity is 0.94-1.07 meq/g.

X-Ray Diffractometer 6100 from Shimadzu was used to investigate the mineralogical structure of the sample. 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) show that present minerals in the sample are stilbite, albite, anorthite, kaolinite and quartz. The surface morphology of sample was studied using a scanning electron microscope, VEGA3 LMU. This particular microscope is 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 the sample obtained from SEM analysis are shown in Fig. 2. The micrographs clearly show a number of macropores and well defined crystals of stilbite in the zeolite structure.

Adsorbate: The heavy metals, Cu, Zn, Mn and Pb were used

as adsorbate in the investigation. 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 1000 mL distilled water.

Experimental procedure: Adsorption of heavy metal ions on zeolite bearing tuff was performed with synthetic single and multi-component ion solutions of Cu^{2+} , Zn^{2+} , Mn^{2+} and Pb^{2+} with initial concentration of 25 mg/L. Initial pH value 3.5 of prepared solutions was adjusted by adding 2% sulphuric 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 bearing tuff (5 g) with a volume of solution, 400 mL. All experiments were performed at room temperature on $20 \pm 1^\circ C$. Adsorbent and aqueous phase were suspended by magnetic stirrer at 400 rpm. The agitation time was varied up to 360 minutes. The final pH value was measured and at the end of the predetermined time, the suspension was filtered and the filtrate was analysed. ICP-AES Agilent was used to analyse the concentration of metal ions in solution. 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:

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

Where, q_e is the mass of adsorbed metal ions per unit mass of adsorbent (mg/g), C_o 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).

RESULTS AND DISCUSSION

All experiments for different heavy metal ions were carried

Table 1: Chemical composition, density and porosity of zeolite bearing tuff.

Chemical composition (%)									
SiO ₂	Al ₂ O ₃	CaO	MgO	K ₂ O	TiO ₂	Na ₂ O	MnO	P ₂ O ₅	FeO
54.67	20.16	4.86	1.08	2.40	0.45	1.97	0.06	0.24	3.98
Hydrated density (g/cm ³)			Dehydrated density (g/cm ³)			Porosity (%)			
1.72			0.89			48.40			

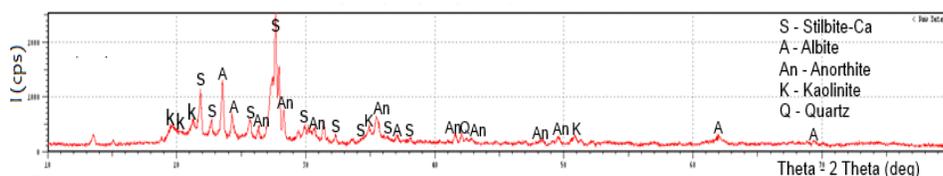


Fig. 1: X-Ray diffraction of sample.

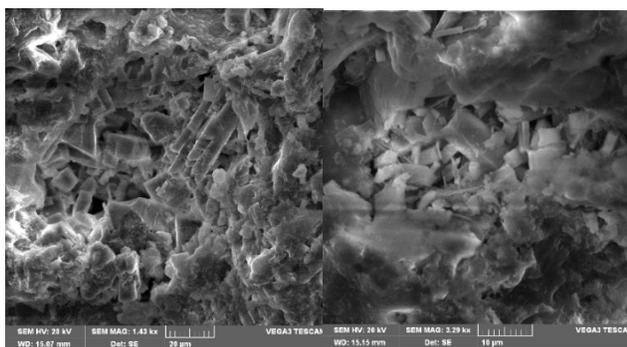


Fig. 2: Micrograph of the sample obtained from SEM analysis.

out at same conditions in order to follow the kinetics of adsorption of single component solutions and to investigate the influence of the presence of competing cations on the adsorption in multi component solution, by zeolite bearing tuff.

Fig. 3 shows comparison of the adsorption of each heavy metal ion from both single and multi-component solutions. From the obtained results shown in Fig. 3 it can be concluded that kinetics of lead adsorption is reasonably fast and after 20 min achieve equilibrium. Equilibrium for other ions is slower.

The amount adsorbed from multi-component solutions was affected significantly except for Pb^{2+} where the difference between single and multi-component solution was almost insignificant. The results show that amount of adsorbed Cu^{2+} from multi-component solution was decreased approximately 10%, and more than 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 zeolite bearing tuff increased with multi-component solutions compared to the amount of solute adsorbed from single component solutions.

According to the obtained results selectivity of the used adsorbent was determined. This was done by comparing the maximum adsorption capacity (q_c) of zeolite bearing tuff for the respective heavy metal ion. The own unique selectivity series on investigated zeolite bearing tuff in single component solution was the same as in the multi-component solution: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$.

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: $r_{\text{H}}\text{Zn}^{2+} = 4.30\text{\AA}$, $r_{\text{H}}\text{Cu}^{2+} = 4.19\text{\AA}$, $r_{\text{H}}\text{Pb}^{2+} = 4.01\text{\AA}$ and $r_{\text{H}}\text{Mn}^{2+} = 4.38\text{\AA}$ (Mobasherpour 2012, Nightingale 1959). 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 (Erdem 2004). 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 (Motsi 2010). 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 (Colella 1991). The hydration energies of the cations are: -2010, -1955, -1760 and -1481 kJmol^{-1} for Cu^{2+} , Zn^{2+} , Mn^{2+} and Pb^{2+} respectively (Mobasherpour 2012, (Nightingale 1959).

According to the hydration radii the order of adsorption should be $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$, and according to the hydration enthalpies the order should be $\text{Pb}^{2+} > \text{Mn}^{2+} > \text{Zn}^{2+} > \text{Cu}^{2+}$.

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.

CONCLUSION

The investigation for 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 these metal ions, by zeolite bearing tuff is done by comparing the adsorption of each heavy metal ion from both single and multi-component solutions.

The amount of adsorbed ions from multi-component solutions compared to their single component solutions was

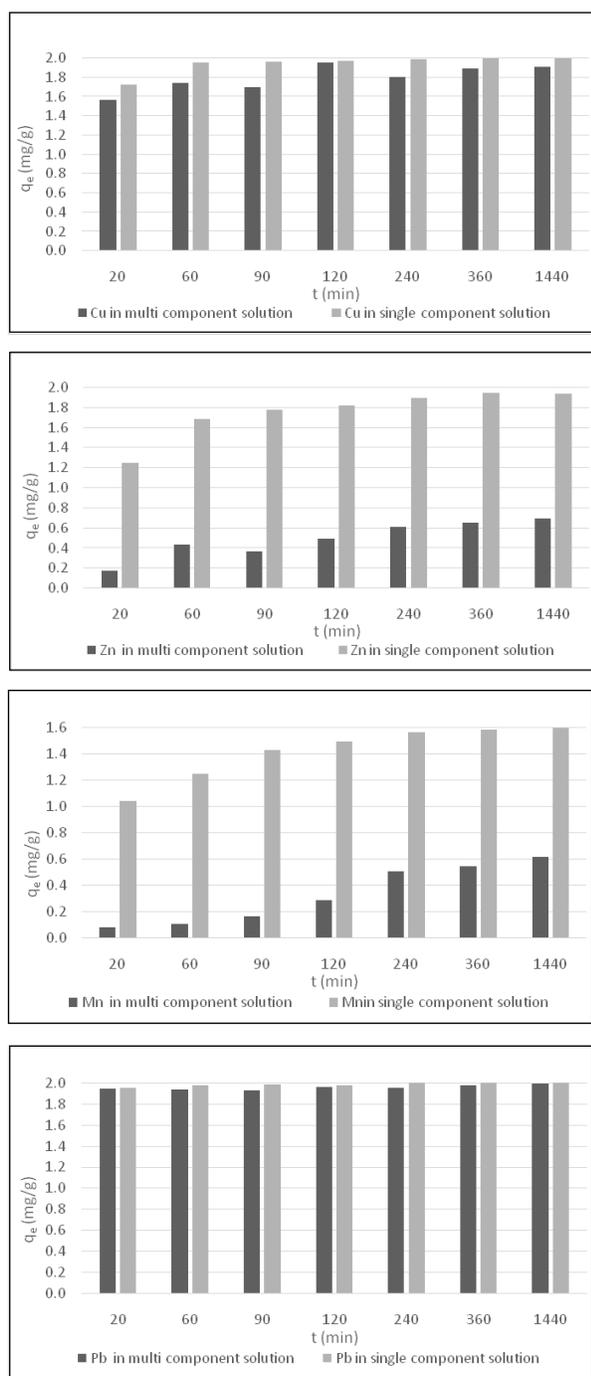


Fig. 3: Comparison of the adsorption capacity of natural zeolite for Cu, Zn, Mn and Pb from single and multi-component solutions.

decreased approximately 10% for Cu^{2+} , more than 50 % for Zn^{2+} and Mn^{2+} , but difference of amount adsorbed of Pb^{2+} is almost insignificant.

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 own unique selectivity series on the investigated zeolite bearing tuff in single and multi-component solution was the same as selectivity series according to the hydration radii: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$.

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