

# Removal of lead ions from acid aqueous solutions and acid mine drainage using zeolite bearing tuff

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**Abstract:** The adsorption of lead ions onto a zeolite bearing tuff (stilbite) from synthetic acid aqueous solution and acid mine drainage taken from Sasa mine, Macedonia, is elaborated in this paper. The results present that adsorption occurs efficiently in both of cases.

The physical and chemical properties of the used natural material, zeolite bearing tuff, are characterized by X-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy. The concentration of metal ions in solution before and after treatment is obtained by AES-ICP.

The effectivity of zeolite bearing tuff is determined through a series of experiments under batch conditions from single ion solutions, whereby the main parameters are the effects of initial pH of solution, mass of adsorbent, initial metal concentration in solution, contacting time and competing cations. The maximum capacity of zeolite bearing tuff for removal of lead ions from solution is determined by equilibrium studies.

The experimental obtained data are fitted with Freundlich and Langmuir adsorption models. The experimental data are better fitted with Langmuir adsorption isotherm.

Zeolite bearing tuff is effective adsorbent for treating acid mine drainage. The results showed that 99% of lead ions are removed from acid mine drainage, i.e. the concentration of lead ions from 0.329 mg/dm<sup>3</sup> decrease to 0.002 mg/dm<sup>3</sup>. The pH value of acid mine drainage from 3.90 after treatment with zeolite bearing tuff increases to 5.36.

## Introduction

Mining activities expose a significant amount of mineral deposits containing pyrite, sphalerite, galena or other sulphide minerals deposited in the layers of rock beneath the earth's surface, where there is little or no oxygen. Mining activities bring these deposits to the surface where they are crushed to release valuable minerals like lead, copper, zinc, gold, nickel etc, whereas the tailings are left on the mine site. Thus large amounts of sulphide minerals become exposed to surface conditions, i.e. air and water, which will assist in the oxidation of the sulphide minerals to produce acid mine drainage (Jenkins et al. 2000). Pyrite is recognized as the major source of acid mine drainage due to its abundance in the environment (Evangelou 1998) but other metals commonly found in acid mine drainage, such as aluminum, copper, lead, nickel, zinc, etc, exist because they are present in the rocks with pyrite (Motsi 2010).

Acidic mine drainage is an environmental pollutant of major concern in mining regions throughout the world. The oxidative dissolution of sulphide minerals in the presence of water and oxygen gives rise to these acidic, metal laden waters. The high acidity of acid mine drainage and the large amounts of dissolved heavy metals generally make acid mine drainage extremely toxic to most living organisms (Penreath 1994).

When galena is present in the rock with pyrite, the lead is often found in acid mine drainage. People may be exposed

to lead by breathing air, drinking water, eating foods, or swallowing dust or dirt that contain lead. Once this lead gets into the lungs, it goes quickly to other parts of the body (such as the liver, kidneys, lungs, brain, spleen, muscles, and heart). After several weeks, most of lead moves into the bones and teeth and stay there for decades. The main target for lead toxicity is the nervous system. Long-term exposure results in decreased functions of the nervous system. The exposure to lead can cause weakness in fingers, wrists, or ankles, small increases in blood pressure, anemia and severely damage the brain and kidneys (U.S. Department of Health and Human Services 2007).

The Sasa mine, is one of the largest production facilities on the Balcan Peninsula for lead and zinc ore extraction, flotation separation and recovering of Pb and Zn concentrate. One of mine Sasa's negative effects on the environment, in direct consequence of mining activities, is production of mine drainages.

The mine drainages actually represent a transport medium to high concentrations of dissolved heavy metals.

The objective of this paper is to discuss the acid mine drainage problem, treatment and prevention using low cost materials like as zeolite bearing tuff, and present results of research on the removal of lead ions using zeolite bearing tuff from synthetic acid aqueous solution and acid mine drainage from lead and zinc mine Sasa from Makedonska Kamenica, Macedonia.

## Material and methods

### Analytical methods

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

The used adsorbent, zeolite bearing tuff, was studied using X-ray Diffractometer 6100 from Shimadzu 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 surface morphology of sample 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.

ICP-AES Agilent was used to analyze the concentration of metal ions in solution before and after treatment. 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.

Based on material balance, the adsorption capacity was calculated by using the following expression:

$$q_e = \frac{V(c_0 - c_e)}{m}, (mg/g) \quad (1)$$

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/dm<sup>3</sup>), respectively, V is the volume of the aqueous phase (dm<sup>3</sup>) and m is the mass of adsorbent used (g).

Degree of adsorption, in percentage, is calculated as:

$$AD\% = \left(1 - \frac{c_e}{c_0}\right) \cdot 100 \quad (2)$$

### Experimental procedure and conditions

The rate of adsorption is a complex function of several factors such as: initial solution pH and metal concentration, mass of adsorbent, adsorbent particle size, temperature, flow rate in columns and agitation speed in the case of batch experiments. Overall reaction rate may be influenced by the separate or combined effect of these factors. In these studies, some of these factors (initial solution pH, initial metal concentration, mass of adsorbent and competing cations) are investigated with regard to their effect on the efficiency of zeolite bearing tuff in removing lead from solution.

The contacting time is one of the most important parameters with influence on the adsorption process and is taken into

consideration in designing wastewater treatment system. For this reason, all experiments are performed according to certain time intervals.

For that purpose, adsorption of lead ions on zeolite bearing tuff was performed with synthetic single ion solutions of lead ions with different initial concentrations (5, 25, 50, 200 and 400 mg/dm<sup>3</sup>) and acid mine drainage from Sasa mine. Synthetic single component solutions of this metal were prepared by dissolving a weighed mass of the analytical grade salt Pb(NO<sub>3</sub>)<sub>2</sub> in 1 dm<sup>3</sup> distilled water.

Initial pH of prepared solutions was adjusted by adding 2% sulfuric acid and controlled by 210 Microprocessor pH Meter. Initial pH range of tested solution was 2.5, 3.5 and 4.5. The experiments were performed in a batch mode in a series of beakers equipped with magnetic stirrers by contacting a mass of adsorbent (2, 5 and 10 g) with a certain volume of 0.4 dm<sup>3</sup> of lead ions solution. Magnetic stirrer at 400 rpm was used for agitation up to 360 min, at temperature of 20°C. The final pH value was also measured. After predetermined time, the suspension was filtered and the filtrate was analyzed using ICP-AES Agilent to determine the concentration of metal ions in solution.

### Equilibrium studies

Equilibrium studies generally involve the determination of the adsorption capacity of a given material. This determination is important in accessing the potential of the material as an economic and commercially viable adsorbent.

Adsorption will be occurring upon contacting adsorbent with solutions containing an adsorbate. Until equilibrium will be established between the adsorbate in solution and adsorbed state, adsorption will continue. At equilibrium a relationship exists between the concentration of the adsorbate in solution and the "concentration" of the adsorbate in the adsorbed state (i.e., the amount of adsorbed per unit mass of adsorbent) (Armenante 1999).

Determination of the maximum capacity of used adsorbent for the removal of lead ions from solution was main objective of the equilibrium studies.

Experimental data were fitted to conventional adsorption mathematical models, namely the Freundlich and Langmuir models. These were used to predict the adsorption performance of zeolite bearing tuff.

### Langmuir model

The Langmuir isotherm model (Langmuir 1918), based on monolayer coverage of adsorbent surfaces by the adsorbate at specific homogeneous sites within the adsorbent, is represented as:

$$q_e = \frac{q_m K_l C_e}{1 + K_l C_e} \quad (3)$$

where  $q_e$ , mg/g, is the amount of solute adsorbed per unit mass of adsorbent at equilibrium;  $C_e$ , mg/dm<sup>3</sup>, is the residual adsorbate concentration in solution at equilibrium;  $q_m$ , mg/g, is the amount of solute adsorbed per unit mass of adsorbent corresponding to complete coverage of available sites,  $K_l$ , dm<sup>3</sup>/mg, is the Langmuir adsorption coefficient, this constant is related to the affinity between the adsorbent and solute, which is evaluated through linearization of Eq. 4:

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m} \quad (4)$$

The essential characteristics of Langmuir isotherm can be described by a dimensionless constant called equilibrium parameter,  $R_L$ , which is usually defined by:

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (5)$$

where  $K_L$  is the Langmuir constant that indicates the nature of adsorption and  $C_0$  is the highest initial metal concentration ( $\text{mg}/\text{dm}^3$ ). The value of  $R_L$  indicates the type of the adsorption isotherm to be either irreversible ( $R_L = 0$ ), favorable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavorable ( $R_L > 1$ ).

**Freundlich model**

The Freundlich isotherm model, based on monolayer adsorption on heterogeneous surfaces with a non-uniform distribution of adsorption heat, is represented as:

$$q_e = k_f C_e^{1/n} \quad (6)$$

where  $k_f$  and  $n$  are empirical Freundlich constants that are dependent on experimental conditions;  $k_f$  ( $\text{mg}/\text{g}$ ) is an indicator of adsorption capacity, while  $n$  ( $\text{g}/\text{dm}^3$ ) is related to the adsorption intensity or binding strength. Their values were determined from the linear form of the Freundlich equation, given by:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (7)$$

$1/n$  is the heterogeneity factor; values of  $1/n \ll 1$  indicate heterogeneous adsorbents, while values closer to or even 1 indicate a material with relatively homogeneous binding sites (Papageorgiou et al. 2006), (Ciobanu, et al. 2016). The zeolite should be a heterogeneous adsorbent due to its porous nature. Alvarez-Ayuso et al. (2003), Avila (2005) and Gunay et al. (2007) successfully used the Freundlich adsorption isotherm to model their results from equilibrium experiments.

**Results and Discussion**

**Characteristics of adsorbent**

In the recent study for adsorbent is used zeolite bearing tuff from Vetunica deposit, localized in northern marginal parts of the well-known Kratovo-Zletovo volcanic area in Republic of Macedonia. The particle size range of 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 analyzed on the content and type of exchangeable cations. The dominant ion, in the exchangeable position, is  $\text{K}^+$  (66.5 meq/100g), followed by  $\text{Ca}^{2+}$  (21.5 meq/100g),  $\text{Mg}^{2+}$  (8.5 meq/100g) and  $\text{Na}^+$  (3.5 meq/100g). The total cation exchange capacity is 0.94–1.07 meq/g.

The X-ray examination of the samples is performed by the X-ray powder diffractometer type Shimadzu XRD-6100 with Cu anode with radiation wave-length of  $\text{CuK}\alpha=1.54178 \text{ \AA}$ . Operating voltage is  $U=40.0 \text{ kV}$ , current intensity  $I=30.0 \text{ mA}$ . The samples are examined within 10.0–80.0 with 2.0 s on each step using control rotational mode with 60.0 rpm rotation speed.

The results of XRD (Fig. 1) show that minerals present in the sample are stilbite, albite, anorthite, kaolinite and quartz.

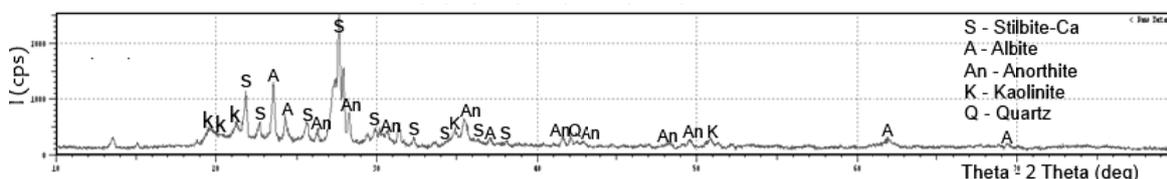
The surface morphology of the sample was studied using a scanning electron microscope, VEGA3 LMU. Micrographs of the sample obtained from SEM analysis are given in Fig. 2. The micrographs clearly show a number of macropores and well defined crystals of stilbite in the zeolite structure.

**Effect of initial metal concentration in solution**

The effect of initial metal concentration was investigated by contacting 5 g of zeolite bearing tuff, at pH 3.5, with different concentrations of single-component solutions, 5, 25, 50, 200, and 400  $\text{mg}/\text{dm}^3$ . An increase in concentration generally results in an increase in the amount of lead adsorbed. This may be due to an increase in the number of collisions between the reactants, leading to the observed increase in reaction rate and capacity, according to the collision theory (Connors 1990). Increasing the initial metal concentration in solution until the system reaches a saturation point will result in increase of adsorption

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

Chemical composition (%)									
$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	CaO	MgO	$\text{K}_2\text{O}$	$\text{TiO}_2$	$\text{Na}_2\text{O}$	MnO	$\text{P}_2\text{O}_5$	FeO
54.67	20.16	4.86	1.08	2.40	0.45	1.97	0.06	0.24	3.98
Hydrated density( $\text{g}/\text{cm}^3$ )			Dehydrated density( $\text{g}/\text{cm}^3$ )				Porosity (%)		
1.72			0.89				48.40		



**Fig. 1.** X-Ray diffraction of sample

capacity. After reaching a saturation point, increasing lead concentration will not result in any significant change in the amount adsorbed. Results of this investigation are presented on Table 2 and Fig. 3.

The results indicate that the amount of lead adsorbed by zeolite bearing tuff is dependent on the initial metal concentration in solution, especially when there is a higher difference between initial concentration, like as 50, 200 and 400 mg/dm<sup>3</sup> Pb.

As initial concentration increases, the adsorption of lead ions by zeolite bearing tuff also increases. This was expected because it 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 adsorbent (Barrer 1978).

Increase in initial metal concentration in solution not only results in an increase in the amount adsorbed ( $q_e$ ) but also in a decrease in the efficiency of adsorbents used for the removal of lead from solution. This conclusion can be seen from Table 2. Sprynskyy et al. (Sprynskyy 2006), Motsi (2010) and Golomeova and Zendelska (2016) also found a similar trend, that is, a decrease in efficiency, in their work, on the adsorption of some heavy metals from solution by zeolite.

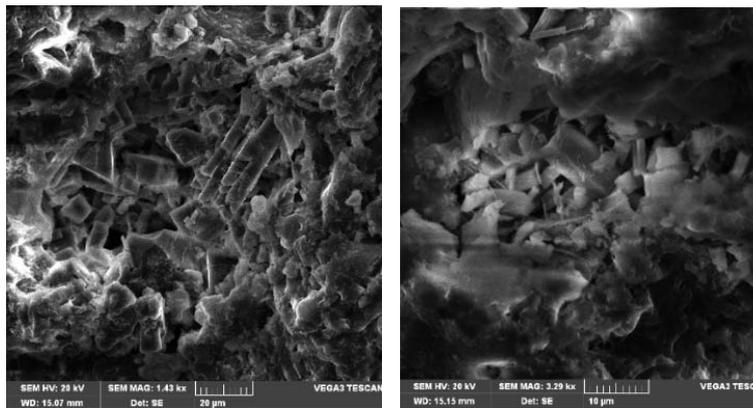


Fig. 2. Micrographs of sample obtained from SEM analysis

Table 2. Effect of initial ions concentration on the adsorption capacity of zeolite bearing tuff

Initial Concentration $C_0$ (mg/dm <sup>3</sup> )	Amount Adsorbed $q_e$ (mg/g)	Percentage Adsorbed (%)
5	0.4	100
25	0.2	100
50	4	100
200	15.5	96.9
400	27.224	85.1

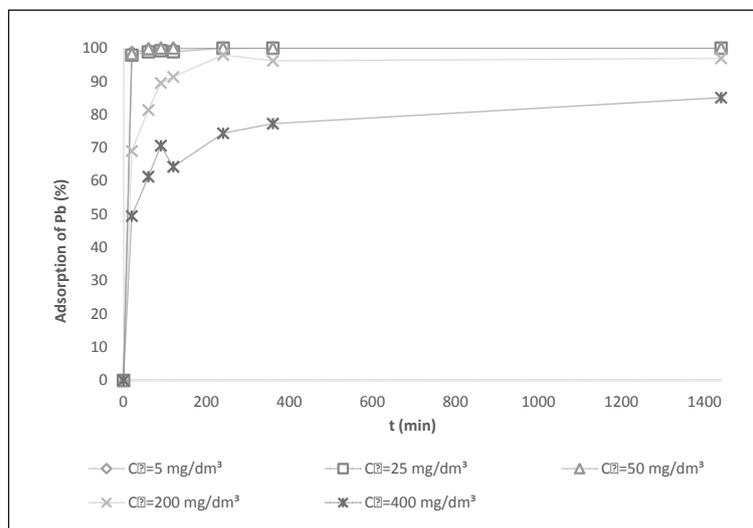


Fig. 3. Adsorption of lead ions according initial ions concentration (mg/dm<sup>3</sup>)

### Effect of mass of adsorbent

The effect of mass of adsorbent was investigated by contacting 2, 5, and 10 g of zeolite bearing tuff, at pH 3.5, with concentrations of single-component solutions of 5 mg/dm<sup>3</sup> Pb ions.

It is normal to be expected that an increase in the adsorbent mass should result in an increase in the adsorption of lead ions, because more adsorption sites are available per unit mass of adsorbent.

The results from this investigation are presented in Fig. 4 and they do not confirm previous assertion that an increase in the adsorbent mass resulted in an increase in the adsorption of lead ions. The adsorption of lead ions is without significant difference. From Fig. 4 it can be seen that percentage adsorbed is 99.6% with 2 g adsorbent and 99.9% using 5 g and 10 g adsorbent. This concentration of lead is almost completely adsorbed at the smallest mass of adsorbent.

### Effect of initial pH value of solution

The effect of initial pH of solution was investigated by contacting 5 g of zeolite bearing tuff, at three various pH values (2.5, 3.5, and 4.5), with concentrations of single-component solutions of 5 mg/dm<sup>3</sup> Pb ions.

According to Low et al., less adsorption at lower pH could be ascribed to hydrogen ions competing with the metal ions

for adsorption sites (Low et al. 2003). This means that the adsorbent surface becomes more positively charged at higher H<sup>+</sup> concentration, thus reducing the attraction between the adsorbent and metal ions. Contrary to this, with increasing pH value, the adsorbent surface becomes more negatively charged, thus facilitating greater metal uptake (Turan and Mesci 2011).

As expected, as pH of a solution decreases, lead removal efficiency also decreases.

This is because H<sup>+</sup> ions compete with lead cations for the same exchange sites (Alvarez-Ayuso 2003), and the electrostatic repulsion between the lead cations in solution and the protonated zeolite surface increases as more H<sup>+</sup> ions are adsorbed (Cabrera et al. 2005). Fig. 5 shows how the adsorption capacity of zeolite bearing tuff is affected by the solution's pH. Similar results on the efficiency of metal adsorption, dependent on the pH levels of solution, have been obtained by Moreno et al. (2001), Alvarez-Ayuso et al. (2003) and Motsi (2010).

### Effect of competing cations

The effect of competing cations was investigated to determine the influence of the presence of competing cations on the individual adsorption of Pb<sup>2+</sup> from a solution containing a mixture of four metal ions, such as Cu<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup> by zeolite bearing tuff. The experiments were done by contacting 5 g of zeolite bearing tuff, at pH 3.5 of solution and

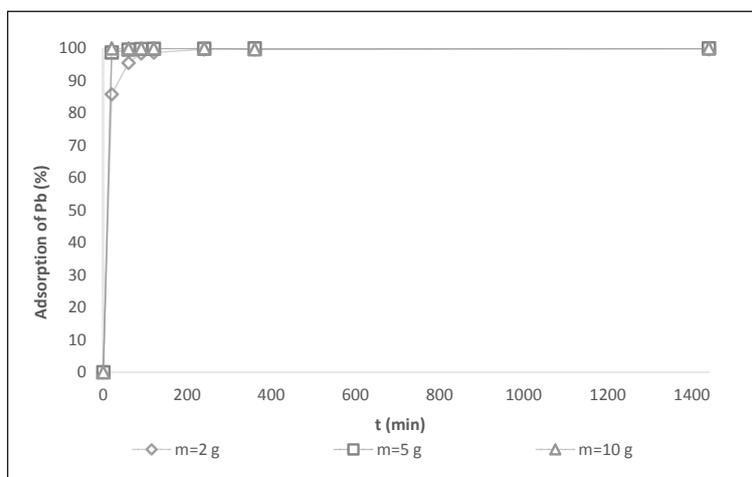


Fig. 4. Adsorption of lead ions according mass of adsorbent

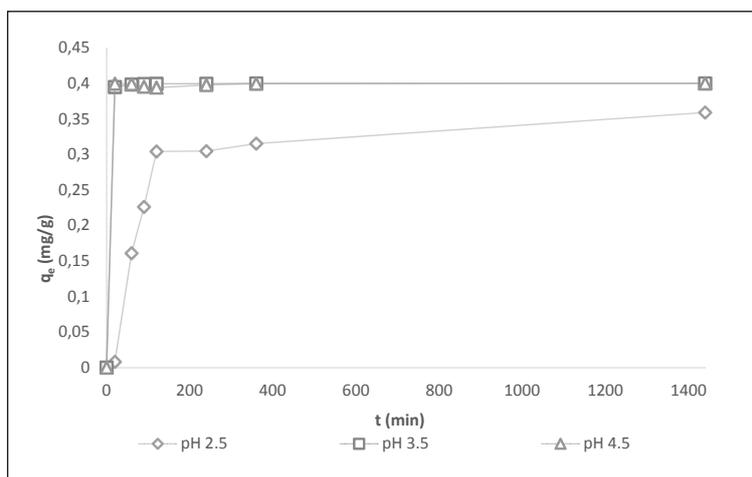


Fig. 5. Adsorption capacity according initial solution pH

temperature of 20°C with concentrations of single-component solutions of 25 mg/dm<sup>3</sup> Pb ions and concentrations of multi-component solutions of 25 mg/dm<sup>3</sup> Cu, 25 mg/dm<sup>3</sup> Zn, 25 mg/dm<sup>3</sup> Mn and 25 mg/dm<sup>3</sup> Pb. Synthetic multi-component solution of these metals was prepared by dissolving a weighed mass of the analytical grade salt CuSO<sub>4</sub>·5H<sub>2</sub>O, ZnSO<sub>4</sub>·7H<sub>2</sub>O, MnSO<sub>4</sub>·H<sub>2</sub>O and Pb(NO<sub>3</sub>)<sub>2</sub>, appropriately, in 1 dm<sup>3</sup> distilled water.

In Fig. 6 comparison is made of the adsorption of lead ion from both single- and multi-component solution.

The amount adsorbed from multi-component solutions was not affected significantly, because the difference between single and multi-component solution is minimal, almost insignificant, the amount adsorbed Pb<sup>2+</sup> from multi-component solution was decreased approximately by 1%, compared to their single component solutions.

Moreover, the total amount of adsorbed heavy metal ions per unit mass of zeolite bearing tuff increased from multi-component solutions compared to the amount of adsorbed ions from single component solutions.

The difference in adsorption capacity of the zeolite bearing tuff 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  $r_H Mn^{2+} = 4.38 \text{ \AA}$  (Jenkins 2000, Penreath 1994) The smallest cations should ideally be adsorbed faster and in larger quantities compared to larger cations, since the smaller cations can pass through the micropores and channels of the zeolite structure with ease (Calvo et al. 2009). 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, zeolite 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<sup>-1</sup> for Cu<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup> and Pb<sup>2+</sup> respectively (Jenkins 2000, Penreath 1994). According to the hydration radii the order of adsorption should be Pb<sup>2+</sup> > Cu<sup>2+</sup> > Zn<sup>2+</sup> > Mn<sup>2+</sup>, and according to the hydration enthalpies the order should be Pb<sup>2+</sup> > Mn<sup>2+</sup> > Zn<sup>2+</sup> > Cu<sup>2+</sup>.

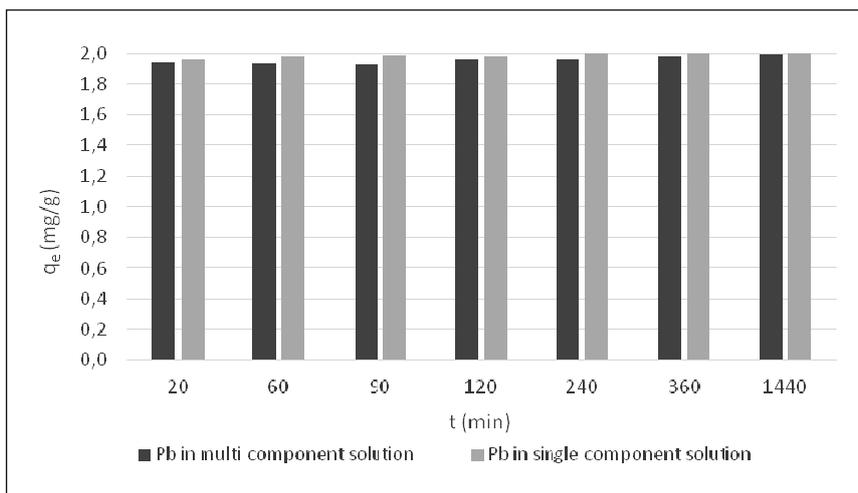
According to the hydration energies and hydration radii, lead has the smallest hydration energy and hydration radius of other studied cations and the zeolite bearing tuff will prefer Pb over Cu, Mn and Zn in multi-component solutions. Therefore, it is to be expected that the high Pb concentrations will limit the uptake of Cu, Mn and Zn.

**Equilibrium experiments**

Equilibrium experiments, whose main objective was to determine the maximum capacity of used adsorbent, zeolite bearing tuff, for removal of lead ions from solution were done by contacting 5 g adsorbent at pH 3.5 and temperature of 20±1°C with different concentrations of single component solutions 5, 25, 50, 200 and 400 mg/dm<sup>3</sup> of Pb<sup>2+</sup>.

Experimental data obtained from equilibrium experiments were fitted to the Langmuir and Freundlich adsorption isotherms. The values of the parameters for the two isotherms are presented in Table 3.

According to Freundlich model, values of the heterogeneity factor 1/n indicate that zeolite bearing tuff is heterogeneous adsorbent, because the value of heterogeneity



**Fig. 6.** Comparison of the adsorption capacity of zeolite bearing tuff for Pb from single and multi-component solutions

**Table 3.** Calculated equilibrium adsorption isotherm constants for the uptake of lead from solution by zeolite bearing tuff

Experimental		Langmuir				Freundlich			
q <sub>e</sub> (mg/g)	C <sub>e</sub> (mg/dm <sup>3</sup> )	q <sub>m</sub> (mg/g)	k <sub>l</sub> (dm <sup>3</sup> /mg)	R <sup>2</sup>	R <sub>L</sub>	k <sub>f</sub> (dm <sup>3</sup> /mg)	1/n	n (g/dm <sup>3</sup> )	R <sup>2</sup>
27.224	59.7	27.548	0.8875	0.9937	0.0028	9.3154	0.2667	3.7495	0.7525

factor is  $\ll 1$ . Based on the correlation coefficients ( $R^2$ ), the adsorption isotherms can be better described by the Langmuir model. The  $R_L$  values reported in Table 3, show that the behavior of  $Pb^{2+}$  adsorption onto used adsorbent was favorable ( $0 < R_L < 1$ ).

Adsorption isotherms obtained according to Langmuir and Freundlich models are compared with experimental data and are given in Figs 7 and 8.

The results in Fig. 8 also show that as the initial concentration of lead cations increases, the amount of metal adsorbed per gram of adsorbent ( $q_e$ ) increases. This is mainly due to the fact that at high metal concentrations, there is a higher solute concentration gradient, and this provides the necessary driving force for metal ions to displace exchangeable cations on the surface and from the internal micropores of natural zeolite (Papageorgiou et al. 2006, Evangelou 1998). However, this increasing trend is valid up to a point at which the maximum capacity of the adsorbent samples for the respective heavy metal cation is achieved, i.e., its saturation point.

The pH value was measured before and after treatment for each equilibrium study. Fig. 9 presents the variation in the equilibrium pH values with respect to initial lead concentration.

By measuring the pH value it can be concluded that pH values at equilibrium are greater than initial pH values. The difference between equilibrium pH and initial pH exhibits a descending trend with increasing initial lead concentration. The adsorption of  $H^+$  ions from solution will cause increase in pH value. As the initial concentration of lead increases, the concentration-driving force begins to favor the adsorption of lead ions in preference to  $H^+$  ions, and thus the descending trend of the equilibrium pH at higher initial lead concentrations. According to the results shown in Fig. 9, it can be confirmed that zeolite bearing tuff has a buffering effect.

### Acid mine drainage treatment

According to the results obtained for synthetic acid solutions it can be concluded that adsorption of lead ions onto zeolite bearing tuff at studied conditions occurs efficiently. Upon receipt of such a conclusion, the investigation continues with acid mine drainage taken from Sasa mine, Makedonska Kamenica, Macedonia.

The experiment was done by contacting 5 g of zeolite bearing tuff in  $0.4 \text{ dm}^3$  acid mine drainage. Magnetic stirrer at 400 rpm was used for agitation up to 360 min,

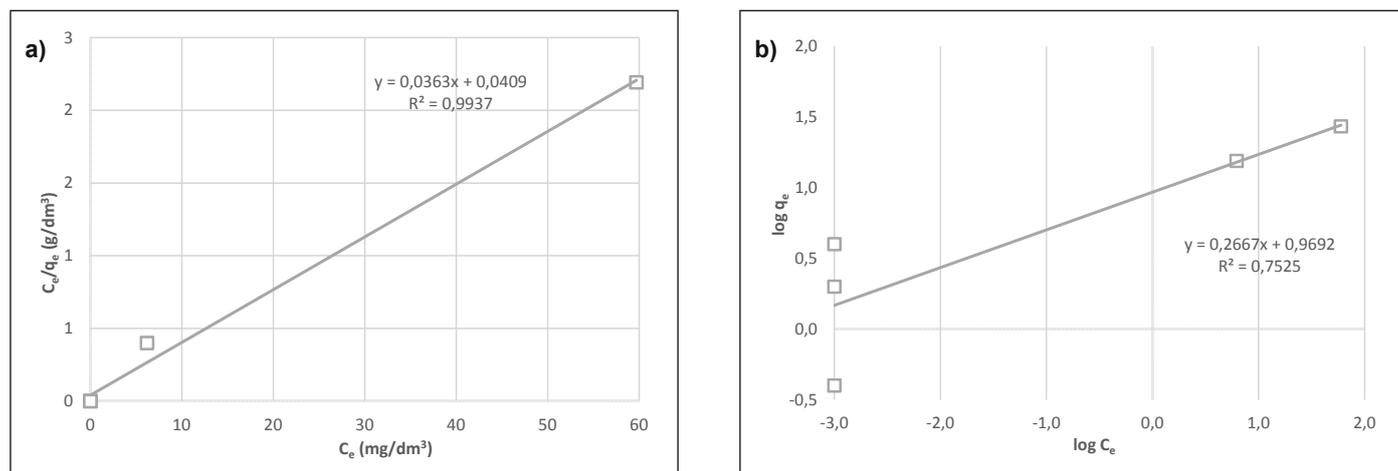


Fig. 7. Equilibrium isotherms  
a) Langmuir model b) Freundlich model

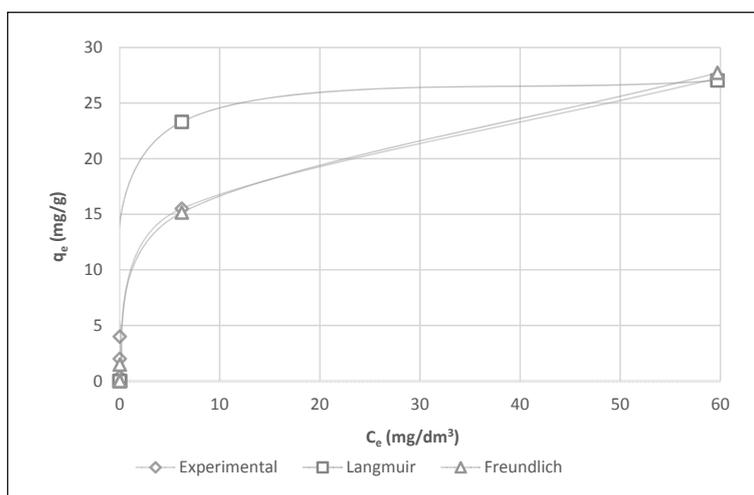


Fig. 8. Equilibrium isotherms for Pb adsorption onto zeolite bearing tuff-stilbite

at temperature of 20°C. The initial concentration of heavy metals and pH of acid mine drainage from Sasa mine are presented in Table 4.

From the initial concentration and pH value it can be seen that the drainage from Sasa mine is acid mine drainage with high concentration of lead ions and belongs in V class according to The Standards for Water Quality in the Republic of Macedonia: Maximum Permitted Concentration (MPC) of Heavy Metal in Water (Table 5).

In Table 4 also are given results for remained lead concentration and pH of acid mine drainage from Sasa mine after treatment. Figs 10 and 11 present the results of adsorption of lead ions from acid mine drainage onto zeolite bearing tuff and variation in pH values vs. contacting time.

As could be seen from presented results, adsorption of lead ions from acid mine drainage onto zeolite bearing tuff occurs efficiently. It means that more than 99% of lead ions is removed from acid mine drainage. Obtained water satisfies quality of I class according to MPC (Table 5).

Obtained selectivity series for acid mine drainage from Sasa mine is  $Pb^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$ . This confirms that the zeolite bearing tuff will prefer Pb over others present cations in the acid main drainage.

The obtained results for pH value can once again confirm the claim that zeolite bearing tuff has a buffering effect, even in acid mine drainage. According to E. Erdem et al. (2004) natural zeolite has a buffering effect.

### Conclusion

Adsorption of lead ions from synthetic acid solutions and acid mine drainage, taken from Sasa mine, using low cost materials like as zeolite bearing tuff (stilbite) was studied.

The adsorption of lead ions onto a zeolite bearing tuff from acid aqueous solution occurs efficiently. It is the most effective at lower concentration of lead ions and higher pH of the solution, and without significant impact of mass of adsorbent and competing ions. The maximum capacity of zeolite bearing tuff for removal of lead ions from solution was determined fitting the experimental data to the Freundlich and Langmuir adsorption models and can be concluded that Langmuir adsorption isotherm is better fitted with results obtained from the experiments.

According to the positive results obtained for synthetic acid solutions the investigation continues with acid mine drainage taken from Sasa mine. The adsorption of lead ions

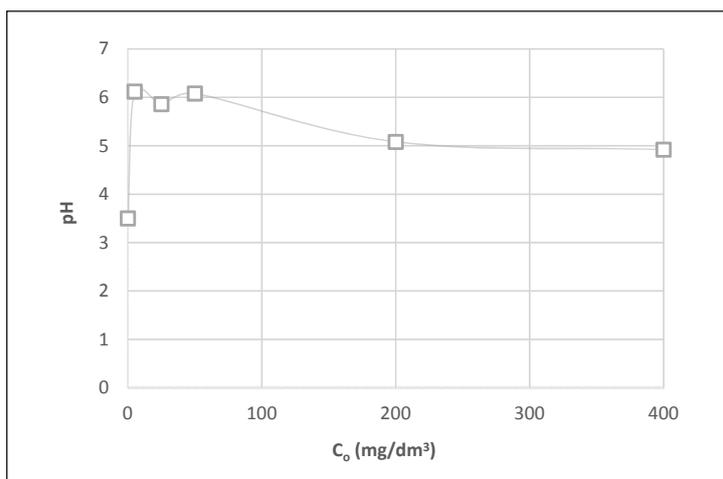


Fig. 9. Variation in pH values with respect to initial lead concentrations at equilibrium

Table 4. Initial and remain concentration and pH of acid mine drainage from Sasa mine

Acid mine drainage from SASA mine	Pb (mg/dm <sup>3</sup> )	Zn (mg/dm <sup>3</sup> )	Cu (mg/dm <sup>3</sup> )	Mn (mg/dm <sup>3</sup> )	pH
Initial concentration and pH	0.329	2.219	0.66	2.053	3,90
Remain concentration and pH	0.002	0.564	0.007	0.678	5,36

Table 5. Standards for Water Quality in Environmental Protection Agency, European Union, Japan and Macedonia

	Maximum Permitted Concentration of Heavy Metal in Water (mg/dm <sup>3</sup> )							
	Environmental Protection Agency	European Union	Japan			Macedonia		
			Environmental standard	Industrial effluent discharge limit	Drinking water	I-II class	III-IV class	V class
Pb	< 0.015	< 0.01	< 0.01	< 0.1	< 0.01	0.01	0.03	> 0.03
pH	6.5–8.5	6.5–9.5	6.5–8.6	5.8–8.6	5.8–8.6	6.3–8.5	5.3–6.3	< 5.3

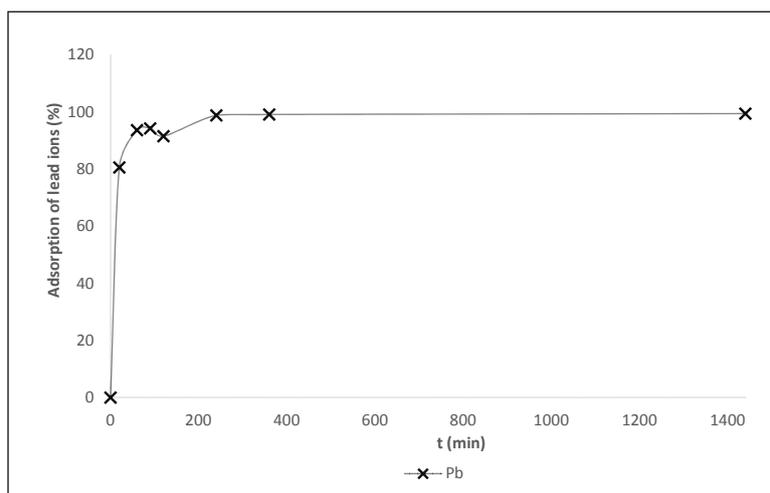


Fig. 10. Adsorption of lead ions from acid mine drainage onto zeolite bearing tuff

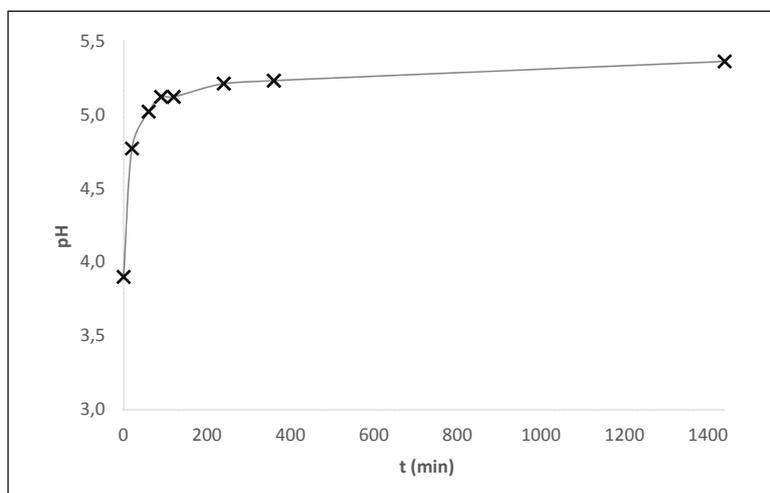


Fig. 11. Variation in pH values vs. contacting time

onto a zeolite bearing tuff from acid mine drainage also occurs efficiently. It means that zeolite bearing tuff is an effective adsorbent for treating acid mine drainage.

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