ECOTERRA

JOURNAL OF ENVIRONMENTAL RESEARCH AND PROTECTION

Printed ISSN: 1584-7071
Online ISSN: 2248-3128

2018, Volume 15, Issue 1

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Online ISSN: 2248-3128

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ECOTERRA Journal of Environmental Research and Protection was developed with the aim of responding to the growing needs of environmental specialists, now widely recognized in the scientific media. It is a quarterly journal, edited since 2004, with the clearly stated mission of fostering the communication and dissemination of interesting results among researchers and practitioners from a wide range of scientific areas, such as earth sciences, environmental protection, risk assessment, disaster management and so on.

ECOTERRA Journal of Environmental Research and Protection includes high-quality researches in the fields of engineering sciences, earth sciences, biotechnologies, environmental protection, notes on national and international scientific events, books or articles reviews and synthesis papers in the specific fields of the journal.

This issue of ECOTERRA journal is published under the aegis of The National Society of Environmental Science and Engineering (SNSIM), together with S.C. I.C.P.E. BISTRIŢA S.A. (Institute for Research and Development in Technologies and Equipments for Environmental Protection Bistriţa), and the Faculty of Environmental Sciences and Engineering, University „Babeş-Bolyai" of Cluj-Napoca. SNSIM is a professional association of experts from academic and research institutes having specific activities in the field of environmental science and engineering. Its mission is to develop and promote the professional interests of their members, within a national and international context and to contribute to the development of the environmental science and engineering field in science and research.

Given the high interest of scientists and the variety of submissions, ECOTERRA has taken an initiative to become a peer-reviewed journal, having the articles published on its webpage. Thus, the research results will be accessible via the Internet for immediate worldwide, serving the best interests of the scientific community.

This new issue comprises diverse and original research from a broad spectrum of areas as varied as best available technology, natural gas extraction, atmospheric risks, waste management, energy efficiency, water purification, integrated environmental marketing, risk communication and equipments for environmental protection.

We are very thankful to the scientists and institutions that have contributed to the past history and, we hope, to the future development of this journal. This issue would not have been possible without the support of the editorial board members and the authors. We continue to welcome article submission in all fields of environmental science and engineering that will further stimulate research in these areas.

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Zeolite bearing tuff as an adsorbent for heavy metals removal from aqueous solutions and acid mine drainage

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Abstract. Zeolite bearing tuff (stilbite 27%) from Vetunica deposit, localized in northern marginal parts of the Kratovo-Zletovo volcanic area in Republic of Macedonia was investigated as an adsorbent for removal of copper, zinc, manganese and lead ions from synthetic aqueous solutions and acid mine drainage from Sasa lead - zinc mine in Republic of Macedonia. In order to determine the metals uptake at equilibrium a series of experiments were performed under batch conditions from single ion solutions. Experiments were carried out at different initial concentration of metal ions, at initial pH = 3.5, temperature of 20±1°C and agitation time up to 360 min. The adsorption isotherm of the metal ions on the adsorbent was determined and correlated with the Langmuir and the Freundlich adsorption isotherm models. The Langmuir isotherm exhibited a better fit for the adsorption data for copper, lead and manganese ions, but adsorption of zinc ions is fitting by the Freundlich isotherm. According to the maximum adsorption capacity (q_e) it was determined the selectivity of zeolite bearing tuff for the respective heavy metal ions. The selectivity series was $Pb^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$. The adsorption of copper, zinc, manganese and lead ions from diluted solution and acid mine drainage on to zeolite bearing tuff occurs efficiently.
Key Words: copper, zinc, manganese, lead, zeolite bearing tuff, stilbite, equilibrium isotherm, Sasa mine.

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., the tailings are left on the mine site. Thus large amounts of sulphide minerals become exposed to surface conditions, that is, 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 also 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 (Pentreath 2007).

The Sasa mine, as one of the largest production facilities on the Balcan Penisula for lead and zinc ore extraction, flotation separation and recovering of Pb and Zn concentrate is a potential environmental aspect. One of the environmental impacts with negative effect, which is a 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 of removal of copper, zinc, manganese and 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 Method

Adsorbent. Zeolites are natural porous minerals, which are broadly distributed in nature. There are nearly 50 different types of zeolites that 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 belongs to stilbite series minerals. Stilbite-Ca is a common zeolite, while stilbite-Na, is rare. Stilbite-Ca occurs in fractures and other cavities in basaltic rocks. Stilbite-Ca occures as a vein mineral in diagenetically altered or metamorphosed volcaniclastic rocks. It also occurs as a vein mineral cutting non-volcanic rocks, such as pegmatite, gneiss, schist, or granite (Golomeova et al 2016).

In the recent study for adsorbent is used zeolite bearing tuff that contains stilbite 27% from Vetunica deposit, localized in northern marginal parts of the well-known Kratovo-Zletovo volcanic area in Republic of Macedonia (Blazev et al 2014).

The general characteristics of the zeolite bearing tuff, such as chemical composition and physical characteristics are presented in Table 1 (Zendelska 2015; Zendelska et al 2018).

Table 1

Chemical composition, density and porosity of zeolite bearing tuff

Chemical composition (%)									
SiO_2	Al_2O_3	CaO	MgO	K_2O	TiO_2	Na_2O	MnO	P_2O_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		

The particle size range of used material was 0.8 to 2.5 mm. The sample was analyzed on the content and type of exchangeable cations. The dominant ion, in the exchangeable position, is K^+ (66.5 meq/100 g), followed by Ca^{2+} (21.5 meq/100 g), Mg^{2+} (8.5 meq/100 g) and Na^+ (3.5 meq/100 g). The total cation exchange capacity is 0.94-1.07 meq/g.

X-Ray Diffractometer (XRD) 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 (Figure 1) shown that present minerals in the sample are stilbite, albite, anorthite, kaolinite and quartz.

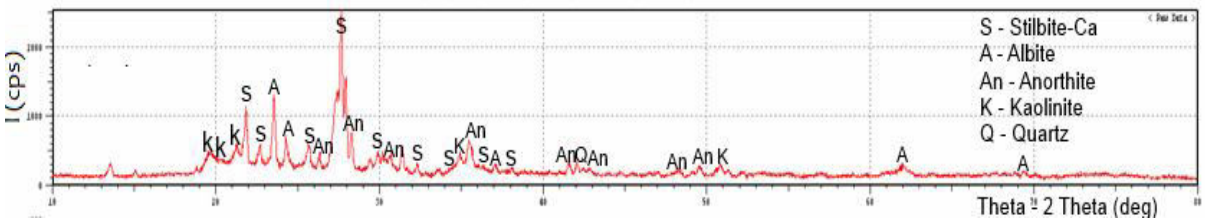

Figure 1. X–Ray diffraction of sample.

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. Micrographs of sample obtained from SEM analysis are given in Figure 2. The micrographs clearly show a number of macropores and well defined crystals of stilbite in the zeolite structure.

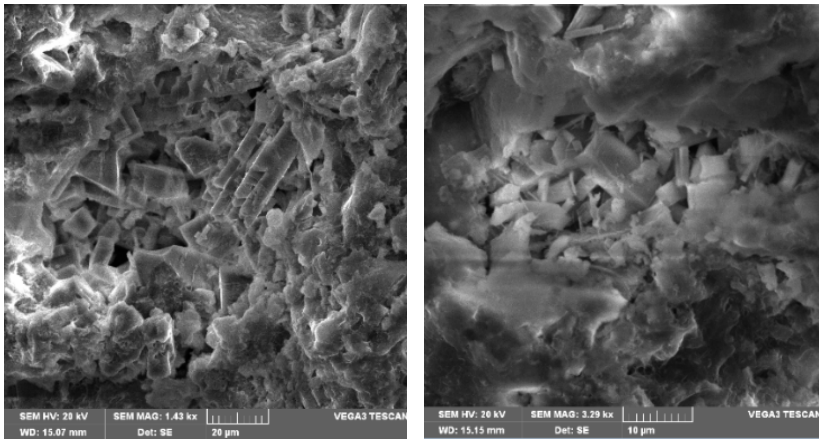

Figure 2. Micrographs of sample obtained from SEM analysis.

Adsorbate. The heavy metals, Cu, Zn, Mn and Pb were used as adsorbate in the recent investigations. For equilibrium experiments, synthetic single component solutions of these metals were prepared by dissolving a weighed mass of the analytical grade salt $CuSO_4.5H_2O$, $ZnSO_4.7H_2O$, $MnSO_4.H_2O$ and $Pb(NO_3)_2$, appropriately, in 1000 mL distilled water. For study acid mine drainage treatment was used drainage water from lead and zinc mine Sasa from Makedonska Kamenica, Macedonia.

Experimental procedure. Adsorption of heavy metals ions on zeolite bearing tuff was performed with synthetic single component ion solutions of Cu^{2+}, Zn^{2+}, Mn^{2+} and Pb^{2+} ions with different initial concentration of (5, 25, 50, 200 and 400 mg L^{-1}) and acid mine drainage from Sasa mine. Initial pH value 3.5 of prepared solutions was adjusted by adding 2% sulfuric acid and controlled by 210 Microprocessor pH Meter. All 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. The experiments were performed at room temperature on 20±1°C. Adsorbent and aqueous phase were suspended by magnetic stirrer at 400 rpm. The agitation time was up to 360 minutes, after that time suspensions were leave to 24 hours. The final pH value was measured and at the end of the predetermined time, the suspension was filtered and the filtrate was analyzed. ICP-AES Agilent was used to analyze 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.

All experiments and studies were performed in the laboratories of the University Goce Delcev in Stip, Macedonia in period of January to May 2015.

The adsorption capacity was calculated by using the following expression:

$$q_e = \frac{V(C_0 - C_e)}{m}, \ (mg\ g^{-1}) \quad (1)$$

where: q_e is the mass of adsorbed metal ions per unit mass of adsorbent (mg g^{-1}), C_0 and C_e are the initial and final metal ion concentrations (mg L^{-1}), 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:

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

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 adsorber. At equilibrium

a relationship exists between the concentration of the species in solution and the "concentration" of the same species in the adsorbed state (i.e., the amount of species adsorbed per unit mass of adsorbent).

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

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^{-1}, is the amount of solute adsorbed per unit mass of adsorbent at equilibrium; C_e, mg L^{-1}, is the residual adsorbate concentration in solution at equilibrium; q_m, mg g^{-1}, is the amount of solute adsorbed per unit mass of adsorbent corresponding to complete coverage of available sites, K_l, l mg^{-1}, is the Langmuir adsorption coefficient, this constant is related to the affinity between the adsorbent and solute, which is evaluated through linearization of Eq. 3:

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

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: C_0 is the highest initial metal concentration (mg L^{-1}) and K_l is the Langmuir constant that indicates the nature of adsorption. The value of R_L indicates the type of the adsorption isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

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 (mg g^{-1}) is an indicator of adsorption capacity, while n (g L^{-1}) is related to the adsorption intensity or binding strength. Their values were determined from the linear form of the Freundlich equation, given by:

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

where: 1/n is the heterogeneity factor; values of 1/n << 1 indicate heterogeneous adsorbents, while values closer to or even 1 indicate a material with relatively homogeneous binding sites (Papageorgiou et al 2006).

Results and Discussion. The main objective of the equilibrium studies was to determine the maximum capacity of zeolite bearing tuff towards copper, zinc, manganese and lead removal under the studied conditions. The results of equilibrium studies are presented in Table 2 and Figure 3.

It is concluded that as the initial concentration of metal cations increases, the amount of metal adsorbed per gram of zeolite bearing tuff (q_e) increases (Figure 3). 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 micro-pores of natural zeolite (Motsi 2010). However, this increasing trend is valid up to a point at which the maximum capacity of the natural zeolite samples for the respective heavy metal cation is achieved, that is, its saturation point.

Table 2

Calculated equilibrium adsorption isotherm constants for the uptake of metals from solution by zeolite bearing tuff

Heavy metal	*Experimental*		*Langmuir*				*Freundlich*			
	q_e (mg g^{-1})	C_e (mg L^{-1})	q_m (mg g^{-1})	k_L (L mg^{-1})	R^2	R_L	k_f (L mg^{-1})	1/n	n (g L^{-1})	R^2
Cu	25.656	79.3	25.0627	0.2065	0.9155	0.0119	4.7808	0.3646	2.7427	0.7786
Zn	25.408	82.4	29.0698	0.0464	0.845	0,0511	1.6118	0.6128	1.6319	0.9849
Mn	5.416	132.3	6.0386	0.0640	0.998	0.0376	0.4992	0.5349	1.8695	0.9378
Pb	27.224	59.7	27.548	0.8875	0.9937	0.0028	9.3154	0.2667	3.7495	0.7525

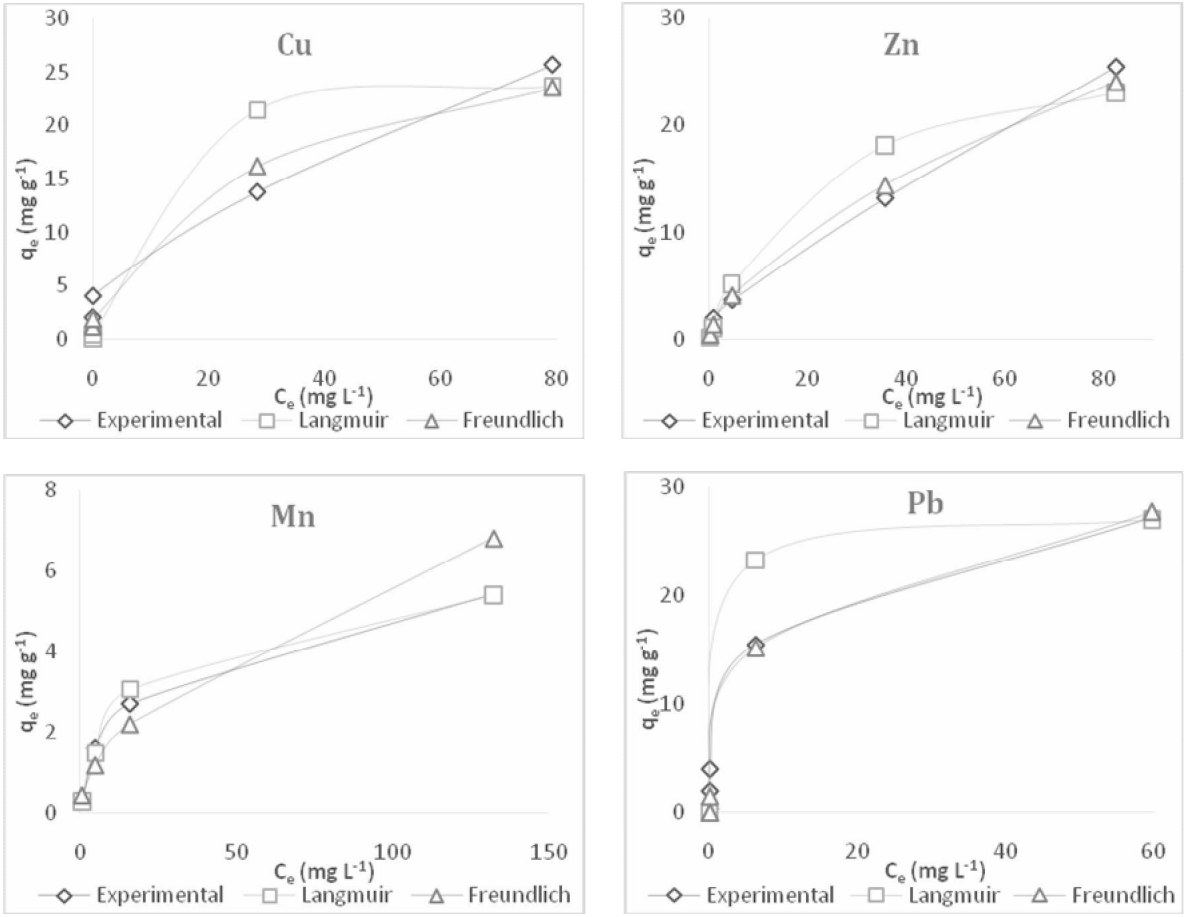

Figure 3. Equilibrium isotherms for the removal of heavy metals from solution.

Experimental data obtained from equilibrium experiments were fitted to the Langmuir and Freundlich adsorption isotherms. The values of the constants in the models and correlation coefficients obtained are summarized in Table 2 and the data calculated by theoretical models (lines) are shown in Figure 3. According to the Freundlich model, values of the heterogeneity factor 1/n, for all these metals, indicate that zeolite bearing tuff is heterogeneou adsorbent. Used adsorbent is 27% stilbit and should be a heterogeneous adsorbent due to its porous nature. Based on the correlation coefficients (R^2), the adsorption isotherms for Cu, Mn and Pb can be better described by the Langmuir model, but for Zn is better described by Freundlich model. The applicability of the Langmuir isotherm suggests monolayer coverage of the metal ions at the surface of

the zeolite bearing tuff or that a similar exchangeable ions with equivalent concentration was exchanged by metal ions.

The R_L values reported in Table 2, show that the behaviour of metal ions adsorption for all studied metals was favourable ($0 < R_L < 1$).

The selectivity of used adsorbent was done by comparing the maximum adsorption capacity (q_e) of zeolite bearing tuff for the respective heavy metal ion. The own unique selectivity series in single component solution was: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$.

The equilibrium pH value was measured and the variation in the pH with respect to initial metal concentration in each equilibrium study are given on Figure 4. The equilibrium pH values are greater than the initially adjusted pH values and the difference between equilibrium pH and initial pH exhibits a descending trend with increasing initial metal concentration. The increase in pH is a result of the adsorption of H^+ ions from solution, and as the initial concentration of metal increases, the concentration driving force begins to favour the adsorption of metal ions in preference to H^+ ions, and thus the descending trend of the equilibrium pH at higher initial metal concentrations.

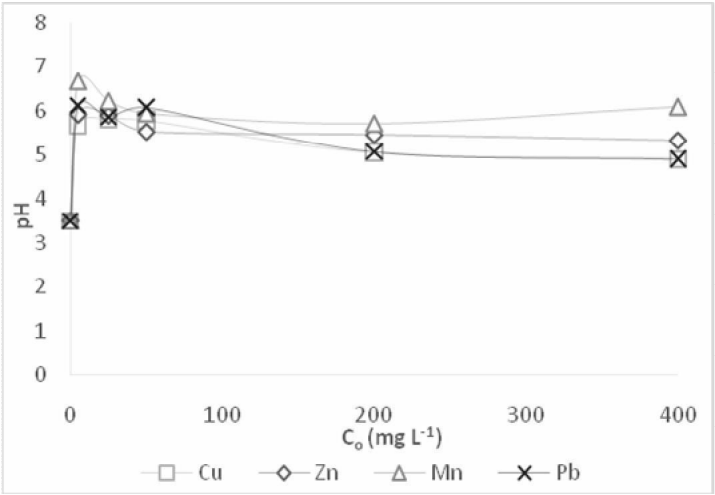

Figure 4. Equilibrium pH change with respect to various initial metal concentrations.

According to Erdem et al (2004), natural zeolite has buffer effect and with this results can confirms that zeolite bearing tuff has buffer effect.

According to the results obtained for synthetic acid solutions can be concluded that adsorption of used heavy metal 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 400 mL acid mine drainage. Magnetic stirrer at 400 rpm was used for agitation up to 360 min, after that time suspensions were leave to 24 hours, at temperature on 20°C. The initial and remained metal concentration and pH of acid mine drainage from Sasa mine are presented in Table 3.

Table 3

Initial and remain concentration and pH of acid mine drainage from Sasa mine

Acid mine drainage from SASA mine	*Cu (mg L^{-1})*	*Zn (mg L^{-1})*	*Mn (mg L^{-1})*	*Pb (mg L^{-1})*	*pH*
Initial concentration and pH	0.66	2.219	2.053	0.329	3.90
Remain concentration and pH	0.007	0.564	0.678	0.002	5.36

From the initial concentration and pH value can be seen that drainage from Sasa mine is acid mine drainage with high concentration of heavy metal 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 4).

Table 4

Standards for water quality in the Republic of Macedonia: maximum permitted concentration of heavy metal in water

	Classification of water and concentration (mg L^{-1})		
	I-II class	III-IV class	V class
Cu	0.01	0.05	> 0.05
Zn	0.1	0.2	> 0.2
Mn	0.05	1	> 1
Pb	0.01	0.03	> 0.03
pH	6.3-8.5	5.3-6.3	< 5.3

Figures 5 and 6 present the results of adsorption of studied metal ions from acid mine drainage onto zeolite bearing tuff and variation in pH values vs. contacting time.

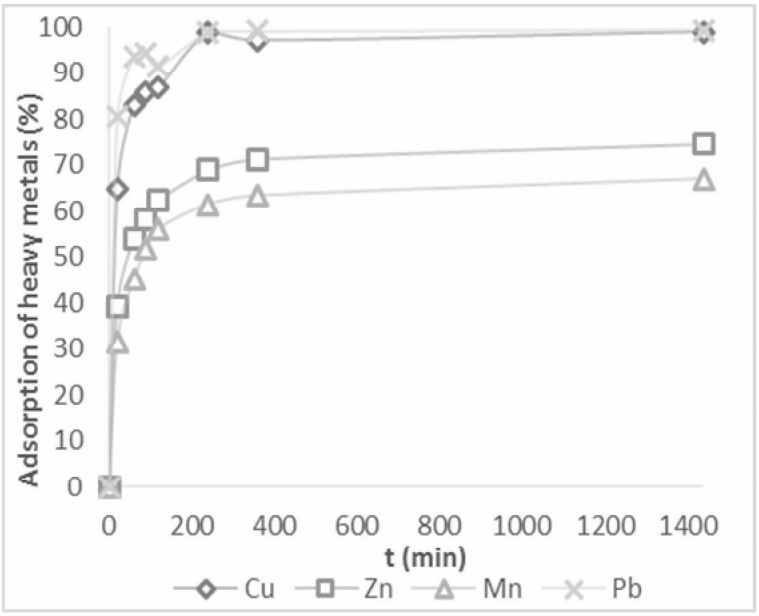

Figure 5. Adsorption of heavy metals from acid mine drainage onto zeolite bearing tuff.

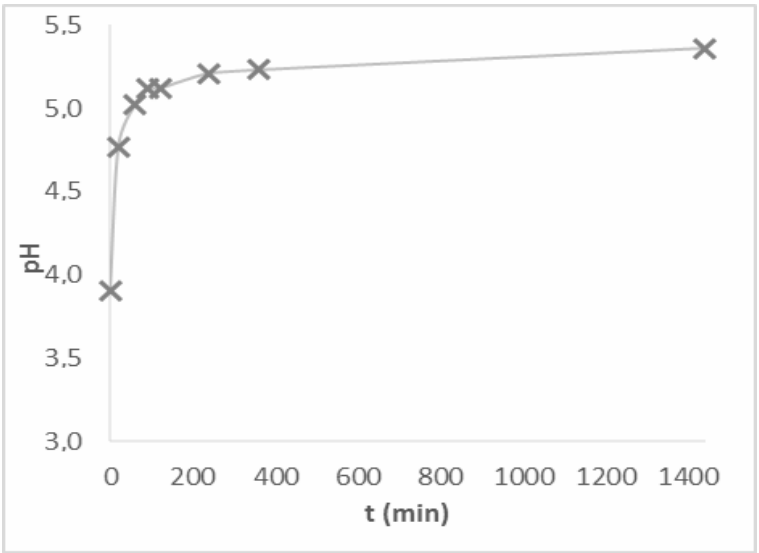

Figure 6. Variation in pH values vs. contacting time.

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 are removing from acid mine drainage. It can be concluded that kinetics of lead adsorption is reasonably fast and after 20 min more than 80% lead ions were adsorbed. Equilibrium for others studied ions are achieve slowlier. Adsorption of copper, zinc and manganese ions at equilibrium are 98.9, 74.5 and 66.9% respectively.

The difference in adsorption capacity of the natural zeolite for the heavy metal ions may be due to a number of factors that include hydration radii, hydration enthalpies and solubility of the cations. The hydration radii of the cations are: $r_H Zn^{2+}$ = 4.30Å, $r_H Cu^{2+}$ = 4.19Å, $r_H Pb^{2+}$ = 4.01Å and $r_H Mn^{2+}$ = 4.38Å; and hydration energies of the cations are: -2010, -1955, -1760 and -1481 kJmol^{-1} for Cu^{2+}, Zn^{2+}, Mn^{2+} and Pb^{2+} respectively (Nightingale Jr. 1959; Mobasherpour et al 2012). According to the hydration radii the order of adsorption should be $Pb^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$, and according to the hydration enthalpies the order should be $Pb^{2+} > Mn^{2+} > Zn^{2+} > Cu^{2+}$.

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.

As mentioned above, zeolite bearing tuff has buffer effect. It is confirmed again on Figure 6 and pH from 3.90 increase to 5.36. According to pH value, acid mine drainage after treatment belong to III-IV class. The quality of acid mine drainage after treatment for lead and copper concentration satisfy quality of I-II class, for manganese III-IV class and for zinc the concentration is still high and belongs to V class according to MPC (Table 4).

Conclusions. The adsorption of copper, zinc, manganese and lead ions from diluted solution and acid mine drainage from Sasa mine onto zeolite bearing tuff occurs efficiently.

Equilibrium studies for single component solutions show that adsorption of these metal ions strongly depends on the initial concentration. As the initial concentration of metal cations increases, the amount of metal adsorbed per gram of zeolite bearing tuff (q_e) increases. This study shows that selectivity series of zeolite bearing tuff for studied ions was: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$.

Upon that conclusion, the study continues with acid mine drainage from Sasa mine, Makedonska Kamenica, Macedonia that is with high concentration of heavy metal ions and belongs in V class according to The Standards for Water Quality in the Republic of Macedonia. The results from this study shows that at equilibrium more than 99, 98, 74 and 66% of lead, copper, zinc and manganese, respectively, were removed from the acid mine drainage. The selectivity series of zeolite bearing tuff for the acid mine drainage was same as selectivity series obtained for single component solutions.

The quality of acid mine drainage after treatment for lead and copper satisfies the quality of I-II class, for manganese III-IV class and for zinc the concentration is still high and belongs to V class according to MPC.

The obtained information will be basis for further research for acid mine drainage treatment with zeolite bearing tuff from Vetunica deposit, Republic of Macedonia.

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Received: 05 March 2018. Accepted: 24 March 2018. Published online: 30 March 2018.
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How to cite this article:
Zendelska A., Golomeova M., Golomeov B., Krstev B., 2018 Zeolite bearing tuff as an adsorbent for heavy metals removal from aqueous solutions and acid mine drainage. Ecoterra 15(1):35-43.