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Index **Page**

REMOVAL OF HEAVY METALS FROM MINE WASTEWATER FROM MINES SASA AND BUCHIM, MACEDONIA USING ZEOLITE BEARING TUFF

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ABSTRACT

The adsorption of heavy metal ions (copper, manganese, zinc and lead) onto a zeolite bearing tuff (stilbite) from acid mine drainages taken from mines Sasa and Buchim, Macedonia is elaborated in this paper.

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 mine wastewater before and after treatment are obtained by AES - ICP.

The experiments were performed in a batch mode in a series of beakers equipped with magnetic stirrers by contacting 5 g of zeolite bearing tuff with a certain volume of 400 ml. Magnetic stirrer at 400 rpm was used for agitation up to 360 min, at temperature on 20ºC.

Zeolite bearing tuff successfully removes heavy metals (copper, manganese, zinc and lead) from studied mining wastewater. After treatment the concentration of heavy metals are reduced and the pH value are increased, so it can be released into natural waterways.

Key words: zeolite bearing tuff, adsorption, heavy metals, mine Sasa, mine Buchim.

1. 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 becomes 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, 2000). Pyrite is recognized as the major source of acid mine drainage, due to its abundance in the environment (Evangelou, 1998) but and 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).

Because 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. Their removal can be accomplished by a variety of techniques. Conventional methods typically involve such processes as coagulation, precipitation, ion-exchange, electrochemical methods, membrane processes, extraction, adsorption etc. Among these, adsorption is currently considered to be very suitable for wastewater treatment, with the high efficiency in heavy metal removal, because of its simplicity and cost effectiveness. Some widely used adsorbents for adsorption of heavy metals include activated carbon (M. Kobya, 2005), clay minerals (Ammann, 2003), biomaterials (Yesim Sag, 2000), industrial solid wastes and zeolites (E. Erdem, 2004) (Motsi, 2010) (Zendelska, 2015) (Silvio Roberto Taffarel, 2009) (Cabrera, 2005), characterized by a porous structure.

The respective and widely used adsorbent material in the adsorption processes is zeolite, because it has a high adsorption capacity, surface area and microporous structure.

Zeolites are crystalline microporous 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 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 occure 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.

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 (Sprynskyy, 2006), 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 easily can be regenerated. The zeolites have buffer effect, neutralization on the acidic solutions is achieved through the exchange of H+ ions from solution with the exchangeable cations in the zeolite structure (Leinonen, 2001).

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 heavy metal ions using zeolite bearing tuff from acid mine drainage from lead and zinc mine Sasa from Makedonska Kamenica, and copper mine Buchim, Radovish, both of Macedonia.

2. MATERIALS AND METHODS

2.1. 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 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.

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/cm3)			Dehydrated density(g/cm3)				Porosity (%)		
1.72			0.89				48.40		

The sample was analyzed 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.

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-lengt of CuKα=1.54178 Å. Operating voltage is U= 40.0 kV, current intensity I = 30.0 mA. 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 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 present minerals in the sample are stilbite, albite, anorthite, kaolinite and quartz.

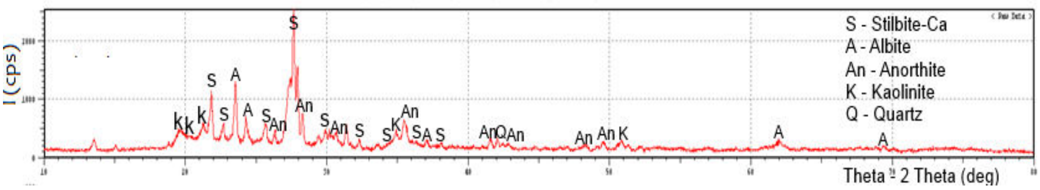


Figure 1. X–Ray diffraction of sample

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 Micrographs of 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.

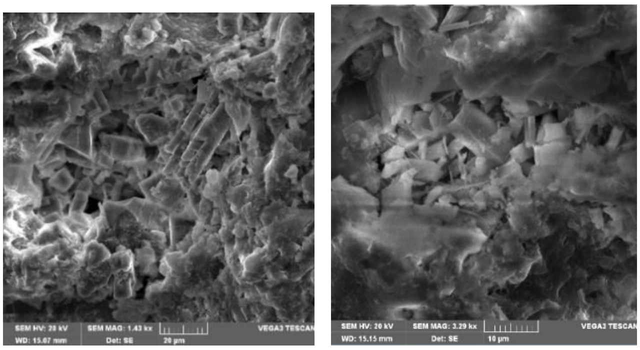


Figure 2. Micrographs of sample obtained from SEM analysis

2.2. Experimental procedure

Adsorption of heavy metals ions (Cu^{2+}, Zn^{2+} Mn^{2+} and Pb^{2+}) on zeolite bearing tuff was performed with acid mine drainages taken from mines SASA and Buchim from Macedonia. 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 (5g) with a volume of solution, 400ml. All experiments were performed at room temperature on 20±1°C. The pH was measured by 210 Microprocessor pH Meter. 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 analyzed. ICP-AES Agilent was used to analyze the concentration of metal ions in solution.

The adsorption capacity was calculated by using the following expression:

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

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).

3. RESULTS AND DISCUSSION

The acid mine drainages taken from mines SASA and Buchim, Macedonia are with high concentration of heavy metal ions. The initial concentration of heavy metal ions in both of mines are presented on Fig. 3 and 4. The initial pH value of drainage from mine SASA is 3.9 and from mine Buchim is 4.73.

From the initial concentrations and pH values can be seen that drainages from mines SASA and Buchim are acid mine drainages 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 2). For this reason, it is necessary to treat these drainages. On Fig. 3 and 4 also are given results, after treatment, for remained heavy metals concentration of acid mine drainages. Fig. 5 and 6 presents the results of adsorption of heavy metal ions from acid mine drainages onto zeolite bearing tuff and variation in pH values vs. contacting time.

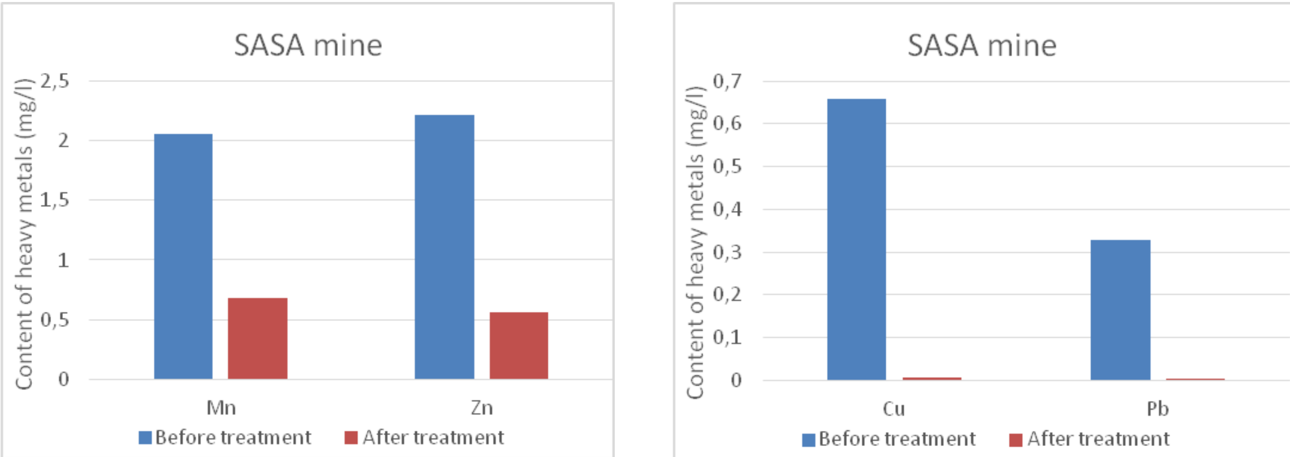


Figure 3. Initial and remained concentration of heavy metal ions in acid mine drainage from mine SASA

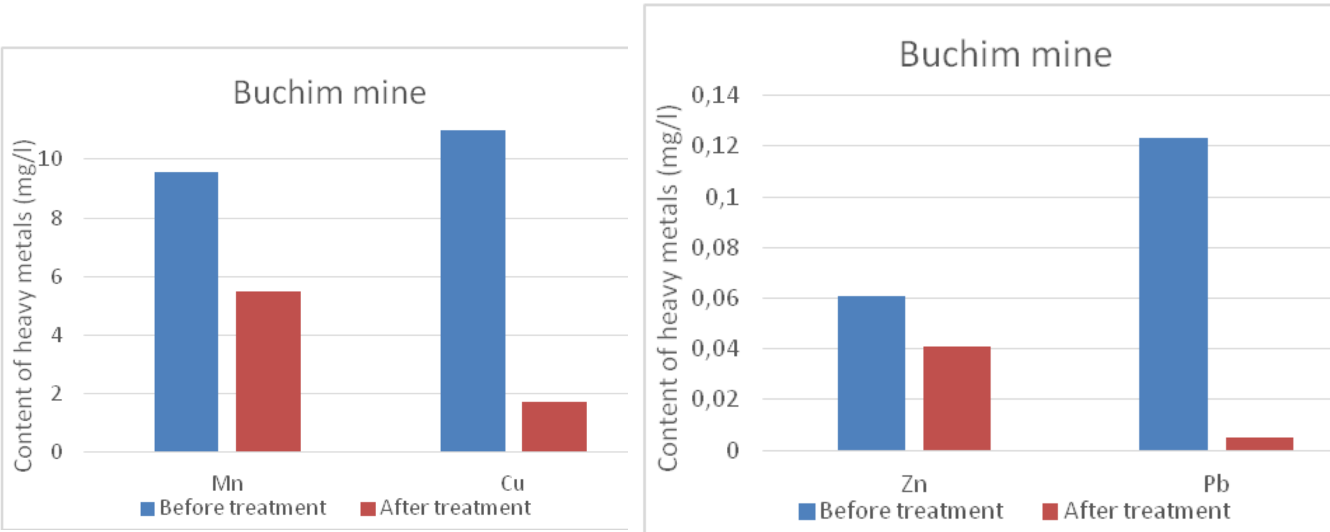
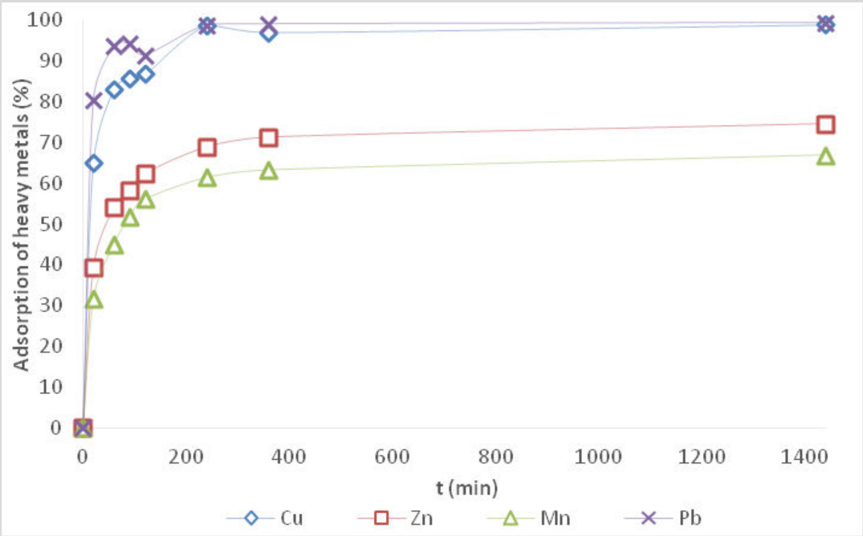
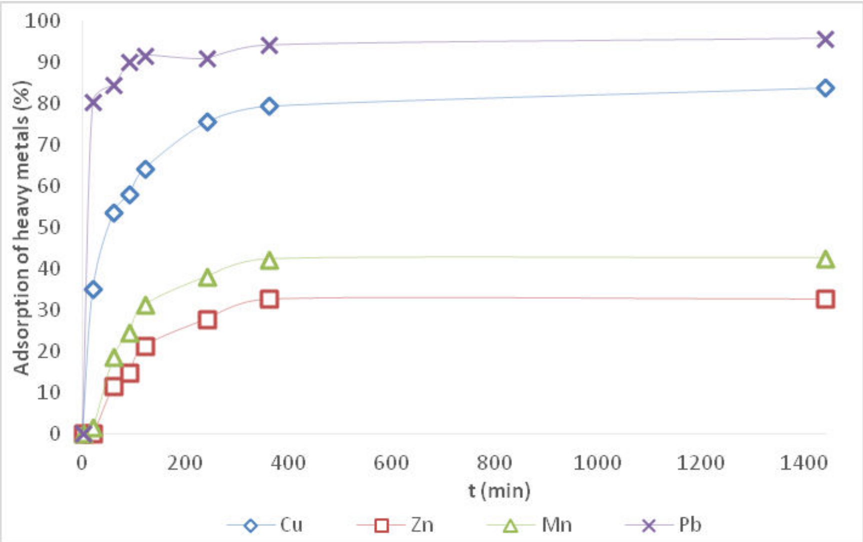


Figure 4. Initial and remained concentration of heavy metal ions in acid mine drainage from mine Buchim



a) mine SASA



b) mine Buchim

Figure 5. Kinetics of heavy metal adsorption

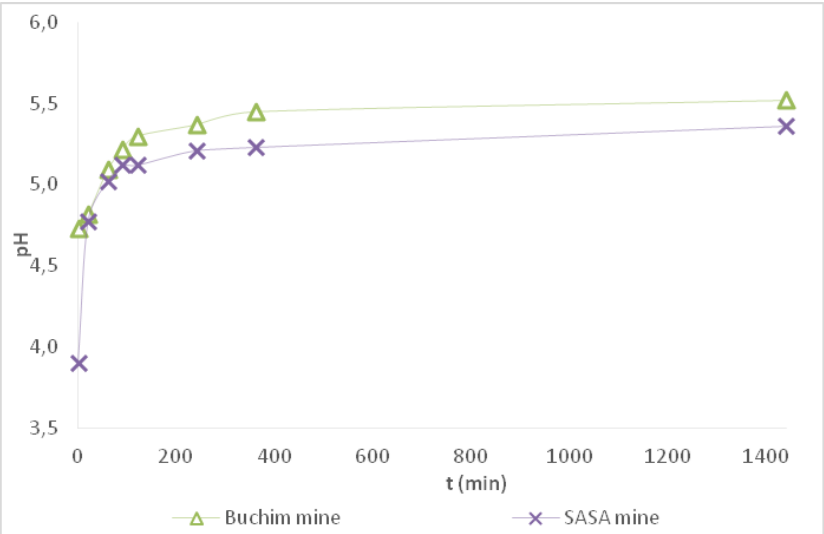


Figure 6. Variation in pH values vs. contacting time.

Table 2. Standards for Water Quality in the Republic of Macedonia: Maximum Permitted Concentration of Heavy Metal in Water

	Classification of water and concentration (mg/l)		
	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

As could be seen from presented results, adsorption of heavy metal ions from a both of acid mine drainages onto zeolite bearing tuff occurs efficiently. It means that more than 95% of lead ions and more than 85% of copper ions are removed from acid mine drainages. Approximate 70% of manganesse and zinc ions are removed from drainage from mine SASA and 40% of manganesse and zinc ions are removed from drainage from mine Buchim. Obtained water satisfy quality of III-IV class according to MPC (Table 2). According to zinc ion, the drainage from mine SASA after treatment is still with high concentration and belong in V class and according to copper and manganesse ions, the drainage from mine Buchim belong to V class. For this reason is necessary more detailed investigation. The obtained results for pH value can confirm the claim that zeolite bearing tuff has a buffering effect (E. Erdem, 2004), even in acid mine drainage.

4. CONCLUSION

The adsorption of heavy metal ions onto a zeolite bearing tuff from acid mine drainages taken from mines Sasa and Buchim, Macedonia occurs efficiently. Zeolite bearing tuff successfully removes heavy metals (copper, manganese, zinc and lead) from studied mining wastewater. After treatment the concentration of heavy metals are reduced and the pH value are increased, so it can be released into natural waterways.

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