



REMOVAL OF LEAD IONS FROM ACID AQUEOUS SOLUTIONS USING ZEOLITE BEARING TUFF

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Abstract

Water pollution come from a number of different sources, and pollutants are divided up into various classes, such as organic pollutants, inorganic fertilizers, metals and radioactive isotopes. Organic pollutants are susceptible to biological degradation, unlike heavy metals which are not degrade into harmless products. Heavy metals are a common pollutant found in various industrial effluents. They are often encountered in mining operations and acid mine drainage. 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. For this reason, in this paper it is presented research of removal of lead ions from acid aqueous solution using zeolite bearing tuff.

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 and AES - ICP.

In order to determine the effectivity of zeolite bearing tuff a series of experiments were performed under batch conditions from single ion solutions. Experiments were carried out at different initial ions concentration, different initial pH values and different adsorbent mass. The adsorption kinetics is reasonably fast. It means that in the first 20 min approximately 90% of Pb²⁺ is adsorbed from single ion solutions.

Key words: zeolite bearing tuff, lead ions, adsorption

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 [1]. Pyrite is recognised as the major source of acid mine drainage, due to its abundance in the environment [2] but and other metals commonly found in acid mine drainage, such as aluminium, copper, lead, nickel, zinc etc, exist because they are present in the rocks with pyrite [3].

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, such as copper, zinc, manganese, iron, arsenic, lead etc., generally make acid mine drainage extremely toxic to most living organisms [4].

When galena is present in the rock with pyrite, the lead is often found in acid mine drainage. People can 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 in the blood and organs (such as the liver, kidneys, lungs, brain, spleen, muscles, and heart). After several weeks, most of the 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 result in decreased functions of the nervous system. Exposure of the lead can cause weakness in fingers, wrists, or ankles, small increases in blood pressure, anemia and severely damage the brain and kidneys. [5].

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

Experimental

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.

In the recent study for removal of lead ions from acid aqueous solutions 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 used material, such as chemical composition, physical characteristics and cation exchange capacity are presented in Table 1.

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

Chemical composition (%)										Hydrated density(g/cm ³)	Dehydrated density(g/cm ³)	Porosity (%)
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	1.72	0.89	48.40

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) shown that the sample is stilbite and the rest are: albite, anorthite, kaolinite and quartz.

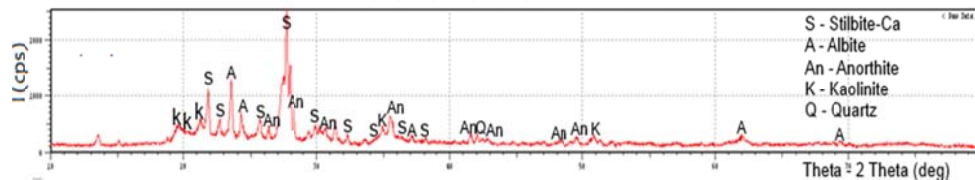


Fig 1. X–Ray diffraction of sample

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 Fig. 2. The micrographs clearly show a number of macro-pores and well defined crystals of stilbite in the zeolite structure.

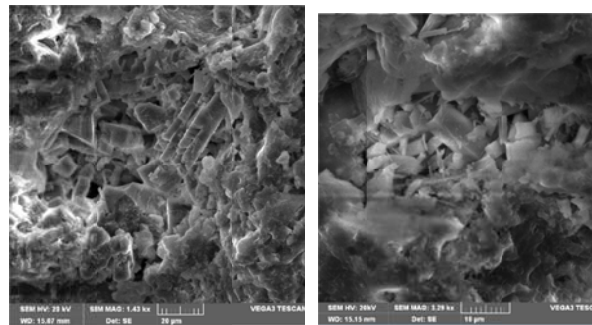


Fig. 2. Micrographs of sample obtained from SEM analysis

The rate of adsorption is a complex function of several factors such as: initial solution pH and 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 are investigated with regard to their effect on the efficiency of zeolite bearing tuff in removing lead from solution.

For that purpose, adsorption of lead ions on zeolite bearing tuff was performed with synthetic single ion solutions of lead ions with different initial concentration (5, 25, 50, 200 and 400 mg/l). Synthetic single component solutions of this metal were prepared by dissolving a weighed mass of the analytical grade salt $Pb(NO_3)_2$ in 1000 ml 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 400 ml of metal ions solution. Magnetic stirrer at 400 rpm was used for agitation up to 360 min, at room temperature on $20 \pm 1^\circ C$. The final pH value was also measured. After predetermined time, the suspension was filtered and the filtrate was analyzed. Liberty 110, ICP Emission Spectrometer, Varian and 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.

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

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

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/dm³), 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:

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

Results and Discussion

To determine the efficiency of zeolite bearing tuff in removing lead ions from acid aqueous solutions are investigated the factors which may be influenced the adsorption, such as: initial solution pH, initial ions concentration and mass of adsorbent. On the Figures 3-5 are presented obtained results for percentage of adsorbed lead ions depending of initial ions concentration and mass of adsorbent and initial solution pH.

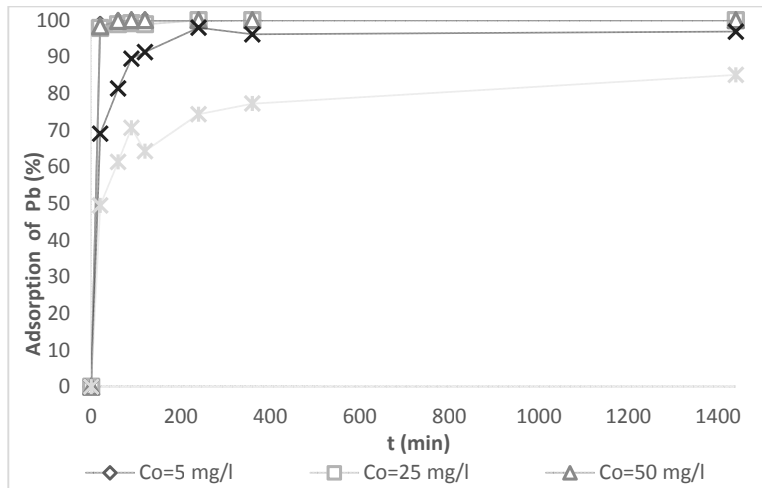


Fig. 3 Adsorption of lead ions according initial ions concentration

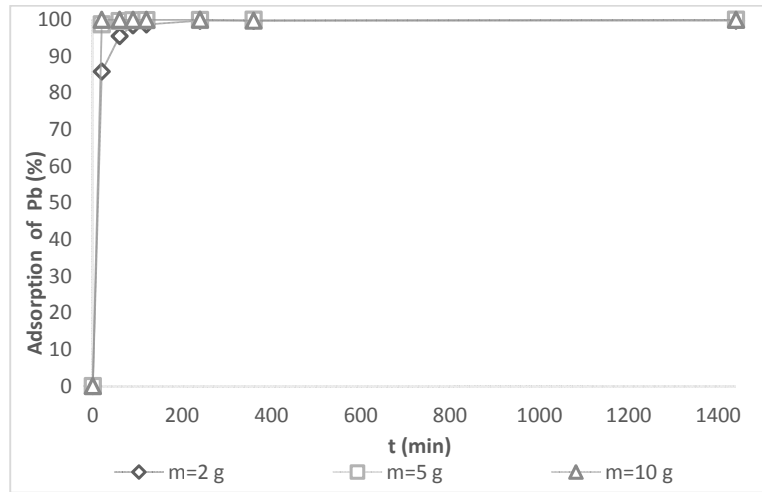


Fig. 4 Adsorption of lead ions according mass of adsorbent

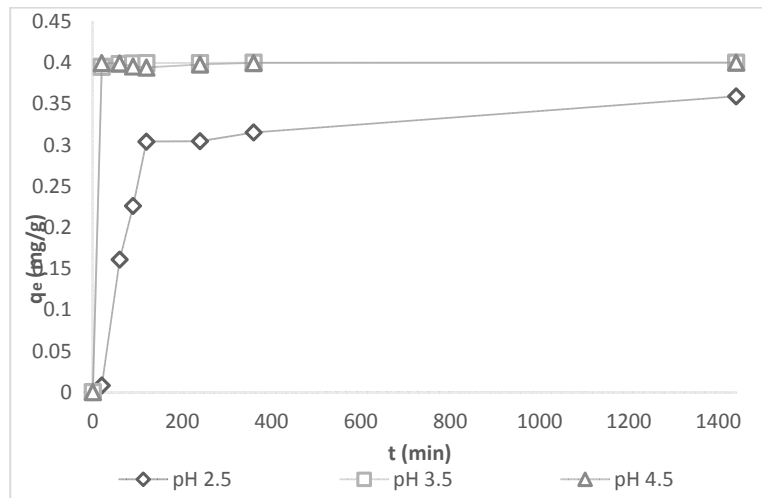


Fig. 5 Adsorption capacity according initial solution pH

The adsorption of lead ions from solution were efficiently onto zeolite bearing tuff.

Comparing the obtained experimental results for adsorption of lead ions according initial ions concentration can be concluded that zeolite bearing tuff has the highest degree of adsorption i.e. 100 % of Pb is adsorbed at 5, 25 and 50 mg/l Pb. As concentration of lead ions in solution increase (200 and 400 mg/l Pb), the adsorption of lead ions decrease from 96.9 % to 85 %.

The change in mass of adsorbent within the tested values showed no significant impact on adsorption. At all three studied values, percentage of adsorbed ions were 100 %. That means that high percentage of adsorbed ions can be achieved with less mass of used adsorbent.

Figure 5 shows that as solution pH decreases, lead removal efficiency also decreases. That is because H^+ ions compete with lead cations for the same exchange sites and electrostatic repulsion between the lead cations in solution and the protonated zeolite bearing tuff surface increases as more H^+ ions are adsorbed.

The adsorption kinetics is reasonably fast. It means that in the first 20 min high percentage of lead ions are adsorbed at all studied conditions.



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