Adsorption of Lead and Zinc Ions from Aqueous Solutions by Volcanic Ash Soil (VAS)

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Abstract

Adsorption of lead and zinc ions from aqueous solutions at 27 ± 1^0C by natural volcanic ash soil has been studied. The effect of pH, metals concentration, sorbent dosage and contact time were studied in batch experiments. The equilibrium data could be described well by the Langmuir and Freundlich isotherm equations and by the Gile's classification isotherm. The first method is quantitative and second is qualitative descriptive. Results show that the equilibrium is reached quickly (10 min), indicating that the adsorption sites are well exposed. The increased in initial metals ion concentration decreased the percent adsorption and increased the amount of metals uptake per unit weight of the sorbent (mg/g).

Result indicated that the adsorption capacity of the volcanic ash soil increased with an increase in the pH.

The uptake of lead was found to be greater than that zinc.

Key words: Adsorption, Volcanic ash soil, Lead, Zinc

INTRODUCTION

It has bees shown that the release of toxic substances and their dispersal in the environment may cause tragic effects on exposed populations (Benjamin et al. 1982). Over the past few decades the huge increase in the use of heavy metals has resulted in an increased flux of metallic substances in aquatic environment (Namasivayam et al., 1995). The most important characteristics of these metals are that they are non-degradable and therefore persistent (Namasivayam et al., 1995). Furthermore, most of the metals ions are toxic to living organisms (Budinova et al., 1994). Therefore, in order to have a pollution-free environment, the toxic materials should be removed from wastewater before its disposal (Benjamin et al. 1982).

There are several methods for removing those toxic metal ions from aqueous solutions, which include chemical precipitation, ion exchange, membrane processes, reverse osmosis, solvent extraction, evaporation, adsorption and … (Zouboulis et al., 1997; Strivastava et al., 1997). However, there are some specific disadvantages using most of these methods including costly equipment and operation, production of slugs or other toxic wastes, energy and space requirements. There are also several potential disadvantages to these traditional techniques. For instance, in order to remove complex agents that might inhibit precipitation, prior treatment maybe required. In time of precipitation the minimum solubility of various metals in a mixed waste stream generally occurs at different pH values. Consequently, maximum removal of one metal maybe occurs at pH value where the solubility of another is unacceptably high. Moreover, given more and more stringent treatment and disposal regulations, a successful precipitation process may not be the optimal solution to wastewater treatment problems (Zouboulis et al., 1997; Chen et al., 1991).

In the recent years the adsorption of heavy metals by a variety of substances has been the subject of many studies. Effort made to develop low-cost adsorbents (non-conventional adsorbents), for removal of metals from aqueous solutions including natural and industrial wastewater. Such efforts are well documented (Namasivayam et al., 1995; Johnson, 1990; Strivastava et al., 1997).

Ability of clay minerals has been thoroughly investigated by several researches. There are many factors that affect the adsorbability of dissolved element including the chemical form of metal, solution pH, time of contact, metal concentration, the presence of competing adsorbates, the amount of sorbent, organic matter, temperatures, particle size and others

(Orumwense, 1996; Johnson, 1990; Benjamin et al., 1982; Farrah et al., 1977).

EXPERIMENTAL

Materials

The material used, as adsorbent for this series of experiments was a natural volcanic ash soil from region Anar in Kerman province (Iran) (crushed to a particle size less than 50 mesh). This is identified by XRD and chemical analysis (Wet Methods) and chemical composition of soil sample is shown in table 1.

Table 1. Chemical analysis of dried volcanic ash soil

Composition	Wt%
SiO_2	58.00
Al_2O_3	10.00
Fe_2O_3	4.80
CaO	3.64
MgO	1.82
Na_2O	5.26
K_2O	1.44
LOI*	5.26

*LOI: Loss of Ignition

All divalent metal cation stock solutions (Pb, Zn) were prepared from the corresponding nitrate salts at a concentration of 1000 mg/lit (ppm). The metal nitrate salts and reagents for pH adjustment (HNO_3/NaOH) were from E.Merck, analytical reagent grade.

Methods

A batch technique was used to perform all adsorption experiments. All experiments were carried out in 300ml Erlenmyer flasks at a constant temperature of 27±1°C using a rotary shaker (150 rpm) A solution (50 ml) with known initial lead or zinc concentration (50 ppm) and pH value (3.0±0.1) was mixed with a definite amount of VAS. After that the sample was shaken for 300min in order to reach equilibrium the suspension was then filtered an metal concentration in filtrate as the amount of sorbent were determined.

The effect of various parameters such as pH (1.75-5.5), contact time (1-300min), metal concentration (10-100ppm) and amount of adsorbent (which in above was described) were studies unless otherwise specified most of the adsorption studies were carried out under the following condition: pH: 3.0±0.1, particle size<50 mesh, temp: 27±1°C, rate of shaking: 150rpm, contact time: 5h, solution volume: 50 ml, metal concentration: 50ppm.

RESULTS AND DISCUSSION

Adsorption Isotherms

Adsorption data for wide range of adsorbate concentrations are most conveniently described by adsorption isotherms, such as the Langmuir or Freundlich isotherms and Gile's classification isotherms, which relate adsorption density q_e (metal uptake per unit weight of adsorbent) to equilibrium adsorbate concentration in the bulk fluid phase, C_e.

Figure 1 shows the relationship between the different quantities of metal ion adsorbed per unit mass of volcanic ash soil and the equilibrium concentration of relevant ions. From the initial slope of the curves, the adsorption process of Pb^{2+} and Zn^{2+} on volcanic ash soil can be regarded as being of H (High affinity) and L (Medium affinity) type according to the classification of Gile, respectively.

The Langmuir isotherm is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_0}{Q_0}$$

Where C_e is the equilibrium concentration (mg/l), q_e is the amount adsorbed at equilibrium time (mg/g) and Q_0 and b are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The plot of C_e/q_e vs. C_e is linear which show that the adsorption of metals follows Langmuir isotherm model (Fig.2). Q_0, b and R^2 are presented in table 2. The Freundlich adsorption isotherm was also applied for the adsorption of metal ions and is represented by the following equation:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e$$

Where C_e is the equilibrium concentration (mg/l), q_e is the amount adsorbed at equilibrium time (mg/g) and k_f and n are Freundlich constants. n gives an indication of

the favourability and k_f (mg/g) the capacity of the adsorbent. Linear plots of $\log C_e$ vs. $\log q_e$ show that the adsorption of metals on to volcanic ash soil also follows Freundlich isotherm model (Fig.3). Values of n, k_f and R^2 are presented in table 2.

Table 2. Freundlich and Langmuir constants VAS

Metals	Freundlich adsorption			Langmuir adsorption		
	k_f	n	R^2	Q_0	b	R^2
Pb^{2+}	3.62	3.62	0.99	7.98	1.16	0.99
Zn^{2+}	1.19	2.80	0.97	5.50	0.11	0.90

Generally, experimental data were better fitted to the Freundlich equation than to the Langmuir equation. However satisfactory correlation coefficient were obtain using the later equation for Pb^{2+} and Zn^{2+} (R^2>0.99, R^2>o.97 respectively). From the k_f, it can be concluded that adsorption of relevant metals are in the order $Pb^{2+} > Zn^{2+}$. Jia-Jun Ke (1992) reported that the adsorption of several heavy metals by bentonite are in the order $Cu^{2+}>Zn^{2+}>Ni^{2+}>Cd^{2+}$.

Effect of metal concentration

The increase in initial metal ions concentration decreased the percent adsorption and increase the amount of metal uptake per unit weight of the adsorbent (mg/g) (Fig.4).

Effect of sorbent concentration

The effect of the volcanic ash soil concentration illustrates quite interesting dependence is on one hand, as was to be expected, the percentage of lead and zinc sorption increases with the increasing volcanic ash soil concentration (Fig.5).

Effect of initial pH

The percent adsorption or lead and zinc with pH, which is typical of metal cation adsorption by metal oxides (Fig.6), at low pH the adsorption percentages are negligible. In between pH values 2.5 and 3.5 these percentages increase sharply, attaining values that stay almost constant for higher pH values the dependence on the sorption effect on pH has almost a S-like course observed by other authors as well (Smith et al., 1996; Benjamin et al., 1982) in metal cations sorption with non-organic sorbents.

Effect of agitation time

Figure 7 shows that increasing agitation time increased the lead and zinc uptake and it remained constant after 10 minutes; which indicating the adsorption sites are well exposed.

CONCLUSIONS

It has been observed from the experiments that volcanic ash soil is a good material, which can adsorb heavy metals at lower concentration. The order of adsorption of metals on volcanic ash soil under same conditions is $Pb^{2+}>Zn^{2+}$. The adsorption isotherms are obtained and they are well describes by the Freundlich equation. The adsorption capacity depends on the sorbent concentration, initial pH, metal concentration and contact time. With increase in the volcanic ash soil concentration and pH, adsorption of metals on the volcanic ash soil increased.

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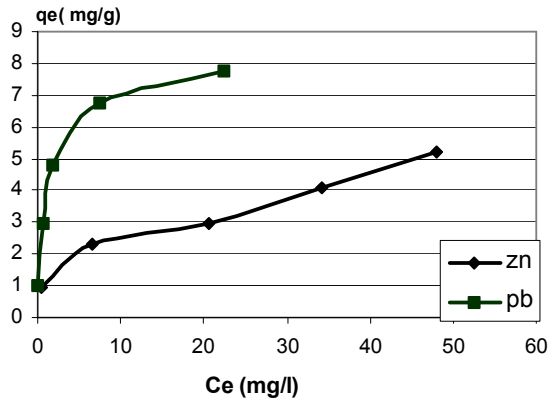


Fig.1. Sorption iothrems of Pb and Zn ions by VAS

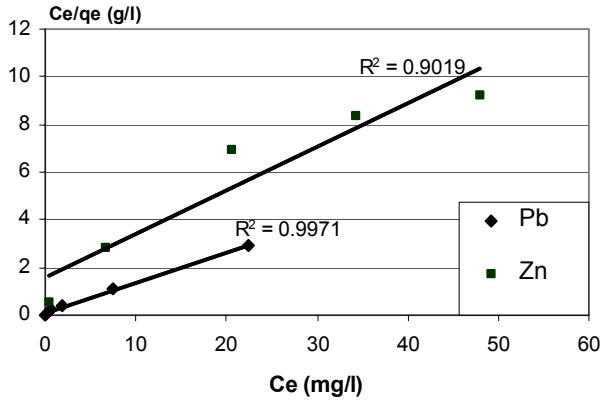
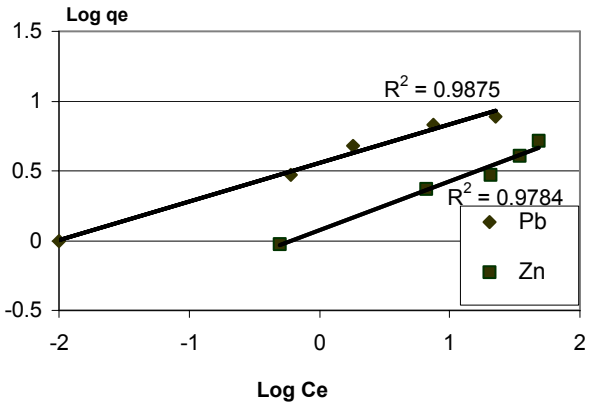


Fig2. Langmuir Isotherms



Fif.3. Freunlich Isothers

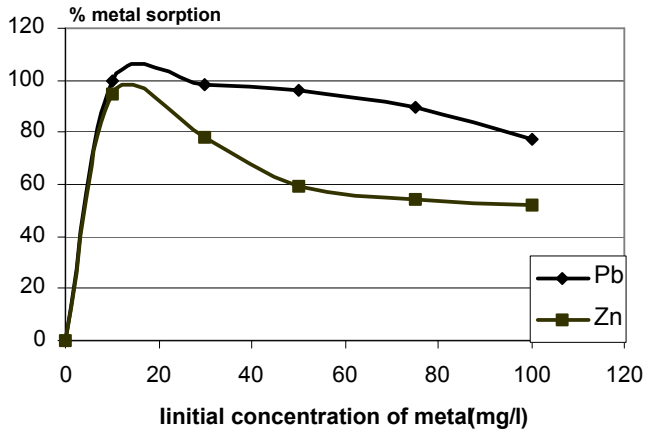


Fig.4. Effect of initial concentration of Pb and Zn ions on the sorption by VAS

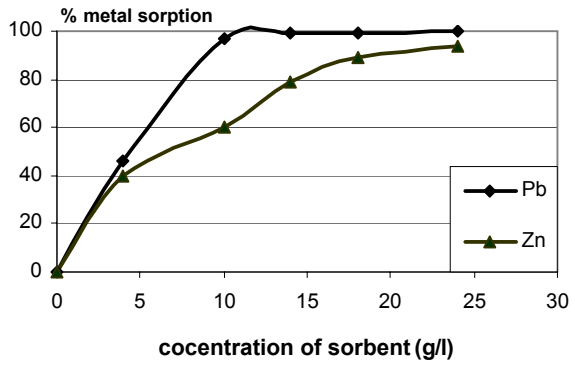


Fig.5.Effect of sorbent concentration on sorption of Pb and Zn ions by VAS.

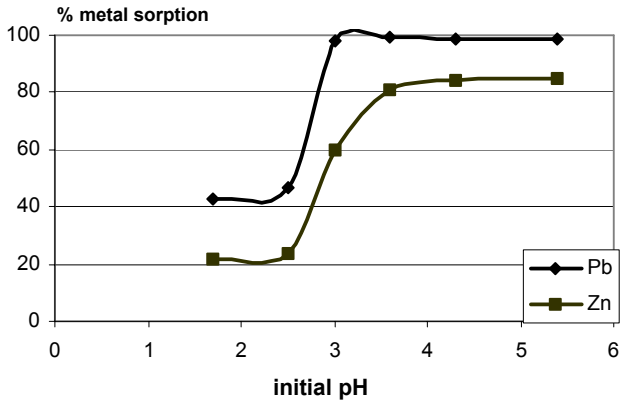


Fig.6. Effect of initial pH on the sorption of Pb and Zn ions by VAS.

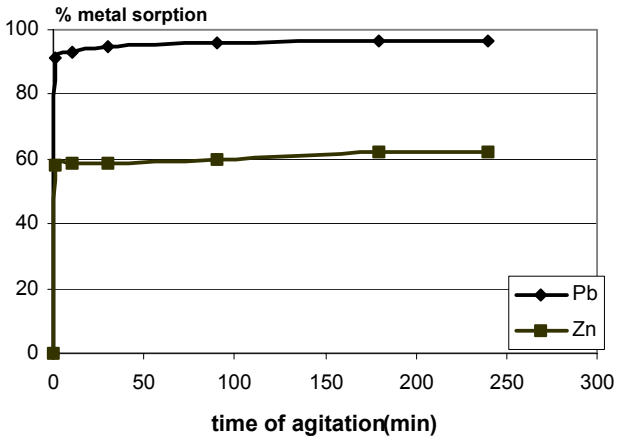


Fig.7. Effect of agitation time on sorption of Pb and Zn ions by VAS.