CADMIUM ADSORPTION FROM AQUEOUS SOLUTIONS BY MINE TAILINGS: BATCH EXPERIMENTAL STUDIES

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ABSTRACT

Heavy metals are considered as one of the important pollutants in the environment, particularly in the aquatic ecosystems. The presence of cadmium in food chain is toxic to human health. Different physical or chemical methods have been used for removing heavy metal ions in the water and wastewater treatments. The aim of this work was to assess the possibility of Cd⁡²⁺ removal from aqueous solutions by mine tailings, consisting mainly shale stones, from Irankouh lead and zinc mine, situated in Isfahan province, Iran. The adsorption experiments were carried out using batch technique, and the effects of pH, initial metal concentration and contact time on adsorption efficiency were studied. The results indicated that Cd adsorption increases with pH from 2 to 7 and maximum adsorption (%63) obtained at pH 6 and initial concentration of 10 mg/l. It is demonstrated that the mine tailings could be used as a low cost and effective adsorbent for cadmium.

Key Words: Heavy metal, Cadmium, Mine tailing, Adsorption, Batch experiment study

INTRODUCTION

The production and consumption of metals has increased rapidly since the industrial revolution. Heavy metals usually form compounds that can be toxic, carcinogenic or mutagenic, even in very low concentrations.¹¹ The contamination of water resources by toxic heavy metals through the discharge of industrial wastewater is a worldwide environmental problem.¹ The major toxic metal ions hazardous to humans as well as other forms of life are Cr, Se, V, Cu, Co, Ni, Cd, Hg, As, Pb, and Zn.¹⁸ Among these heavy metals, cadmium is one of the most potentially toxic. It is fairly mobile in soil and is primarily present as an organically bound, exchangeable, and watersoluble species.¹⁸ This metal is particularly toxic to higher animals, producing kidney and blood diseases among other health disorders. Industrial emissions, plating and mining activities contribute largely to the
presence of this metal ion in water either as direct discharge into water bodies or as atmospheric discharge. Various physicochemical methods including, adsorption, ion-exchange, reverse osmosis, electrochemical treatment and evaporative recovery have been employed to remove heavy metal ions from aqueous solutions. Adsorption process received considerable interest with the high efficiency for wastewater containing heavy metal ions. The design is simple, and it is sludge-free and requires low investment for installation and maintenance. However, the high value of some commercial sorbents such as activated carbon appears to be a limitation factor for extensively use of adsorption method in wastewater treatment. Many studies have been carried out in order to find effective and low cost adsorbents for the adsorption of heavy metals. Various inorganic and/or organic materials such as clay, zeolite, fly ash, coal, illite, shale and mine tailings have been reported as unconventional sorbent for heavy metals. The aim of this work was to assess the possibility of removing Cd$^{2+}$ from aqueous solutions by mine tailings, mainly consisting of shale stones, from Irankouh lead and zinc mine, situated in Isfahan province, Iran. These materials are generated in large quantities and valorized little for construction. Their disposal causes the environmental problems. Due to industrial development in this arid region, re-use of treated wastewater for irrigation or industrial uses could be partly compensating water shortage.

MATERIAL AND METHODS

Mine tailing characteristics

The mine tailing samples were obtained from Irankouh lead and zinc mine, situated in Isfahan province, Iran. The mine tailings were dried at 60 °C for 48 h, ground and sieved to a particle size of <2 mm. Chemical composition of the mine tailings was determined by XRF (X-ray fluorescence Spectroscopy) Table 1. Table1: The chemical composition of mine tailings

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Amount (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOI*</td>
<td>16.55</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>49.18</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>18.0</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>4.98</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>3.48</td>
</tr>
<tr>
<td>CaO</td>
<td>3.06</td>
</tr>
<tr>
<td>MgO</td>
<td>1.5</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.753</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.724</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.539</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.474</td>
</tr>
<tr>
<td>BaO</td>
<td>0.265</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.120</td>
</tr>
<tr>
<td>MnO</td>
<td>0.108</td>
</tr>
<tr>
<td>PbO</td>
<td>0.108</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>0.019</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>0.017</td>
</tr>
<tr>
<td>CuO</td>
<td>0.014</td>
</tr>
<tr>
<td>SrO</td>
<td>0.014</td>
</tr>
<tr>
<td>Total</td>
<td>99.9109</td>
</tr>
</tbody>
</table>

*Loss on ignition
SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, K$_2$O, CaO and MgO constitute about 80% of the mine tailings composition. Some physical and chemical properties of the sorbents such as pH (extracted water), EC (saturated), CEC (Cation exchange capacity) (acetate ammonium) and surface area (N2-BET) were determined Table 2.

### Table 2: Some of mine tailings properties

<table>
<thead>
<tr>
<th>pH</th>
<th>EC(ds/m)</th>
<th>CEC(cmol/kg)</th>
<th>BET surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.2</td>
<td>0.79</td>
<td>141.7</td>
<td>7</td>
</tr>
</tbody>
</table>

#### Adsorbate solutions

Synthetic stock solution of cadmium (1000 mg l$^{-1}$) was prepared by dissolving cadmium chloride {CdCl$_2$} in distilled water and then diluted to desired concentrations for adsorption experiments.

#### Batch experiment

The adsorption of Cd(II) on mine tailing was studied by batch technique. 1g of sorbent was mixed with 100mL solution of Cd, and then, the mixtures were shaken for 1 h (150 rpm). The effect of pH was studied with constant initial concentration of 10 mg/L. pH adjustments were carried out by pH-meter using 0.1N hydrochloric acid (HCl) and 0.1N sodium hydroxide (NaOH). For the kinetic investigation, the mine tailing was shaken for 5, 10, 15, 30, 60 and 120 min intervals with 10 mg/L Cd solution at pH=5.0. The effect of initial concentrations (10, 25, 50, 100, 200 and 500 mg/l) on adsorption was investigated at pH=5.0. After equilibration, the suspension of the adsorbent was separated from solution by filtration using Whatman no.42 filter paper. The concentrations of heavy metal ions were measured by AAS (Atomic Absorption Spectroscopy) model Perkin Elmer Analyst 700 using flame method. All experiments were duplicated. Adsorption amounts were calculated using the following equations

$$ q = \frac{(C_0 - C_e) V}{W} $$

(1)

where $q$ (mg/g) is adsorption amount; $C_0$ (mg/L) and $C_e$ (mg/L) are initial and equilibrated metal ion concentrations, respectively, $V$ (L) volume of added solution and $W$ (g) the mass of the adsorbent.

$$ E = \left(\frac{(C_0 - C_e)}{C_0}\right) \times 100 $$

(2)

where $E$ (%) represents removal efficiency.

#### RESULTS AND DISCUSSION

##### Effect of contact time

Fig. 1 shows the amount of metal ions adsorbed on the mine tailings as a function of contact time. The adsorption percentage of Cd (II) was increased with increase of contact time till equilibrium is attained. This finding is in agreement with recent work by Eloueai et al. who found the same behavior by studying the adsorption capacity of activated
phosphate rock for the removal of Cu, Cd, Pb and Zn from aqueous solutions. The optimal contact time to attain equilibrium with mine tailings was experimentally found to be about 30 min for Cd (II).

**Fig. 1**: Effect of contact time on Cd adsorption at pH= 5 and initial concentration of 10 mg/L.

**Effect of initial pH**

In general, the pH of solution is an important parameter affecting adsorption of heavy metals. Adsorption of Cd by mine tailings increased as the pH increased and reached about 60%

**Fig. 2**: The effects of pH on the adsorption percentage of Cd (II) at initial concentration of 10 mg/L Cd (II) and contact time 1h.

% at pH=5. At lower pH values, the adsorption efficiency was decreased. It is in agreement with findings of Garcia-Sanchez. The pH dependence of heavy metals adsorption is attributed to the competition for sorption surface sites between heavy metal and hydrogen ions. At higher pH, the precipitation could be the main mechanism for removal of heavy metal from solution. The effect of pH varies according to sorbent
Effect of initial metal ion concentration

The effect of Cd (II) concentrations ranging from 10 to 500 mg/L on the removal efficiency was determined at optimum conditions of pH with 1g adsorbent. Increasing the initial metal ion concentration in aqueous solution increased the amount of metal ion adsorbed but the percentage of metal ion adsorbed decreased. Similar results were observed for the adsorption of Pb$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, and Cd$^{2+}$ on clinoptilolite. This indicates a decrease in active sites on mine tailing as more metal ions are adsorbed. This behavior is well known as ‘loading effect’ which describes the extent to which the total number of sorption sites is occupied by the sorbate.

CONCLUSION

The preliminary investigation on adsorptive characteristics of the used mine tailings indicates that these available and low cost materials could be utilized as relatively effective adsorbent of solution cadmium. Further research is required to examine the adsorption of other heavy metals and improve the adsorption capacity of mine tailings by different chemical or physical treatments. The development of this process offers to small and medium industry producing wastewater containing heavy metal, the possibility of decrease their environmental pollution according to national and local standards.

REFERENCES


