Removal Of Heavy Metals Through Adsorption Using Sand

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INTRODUCTION

Water contaminants include a large number of chemicals ranging from aromatic hydrocarbons, organic solvents, pesticides and metals. Heavy metal contamination is commonly found in areas where industrial effluents are discharged into natural waters. The harmful effects of such metals on living being are well known. Chromium exists in as Cr^{3+} and Cr^{6+} in water. These are biologically critical species (Sawyer, 1994; Dara, 1997); Cr^{6+} is carcinogenic in nature whereas long-term exposure to Cr^{3+} can cause allergic skin reactions leading to cancer. Similarly, copper is extremely toxic to aquatic biota (U. S. EPA, 1985). Lead (Manahan, 1991) and zinc (Diamond, 1993; Murray, 1994; Evangelou, 1998) have also been classified as water pollutants. Consequently, removal of heavy metals from wastewater and industrial wastes has become a very important environmental issue. The process of adsorption is considered one of the most suitable methods of the removal of contaminants from water and a number of low cost adsorbents have been reported for the removal of heavy metals (ions) from aqueous solutions.

Activated charcoal is very efficient in removal of metal ions, but is readily soluble under very low and high pH conditions (Huang, 1989).

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Peat moss was used for the removal of mercury, copper, cadmium (Coupal, 1976) and nickel (Ho, 1995). Claymperes delessertti (moss) was used for the adsorption of copper from aqueous solution (Lee, 1989). Also lead, cadmium and zinc were adsorbed on waste tea leaves (Tec, 1988). The adsorbents discussed above show different adsorption efficiencies for different metals.

In addition to the above adsorbents, soils and clays also show remarkable potential towards the removal of heavy metals ions from water (Murray, 1994; Evangelou, 1998). Removal of heavy metals by slow and filters has also been reported (Sehmidt, 1997; Muhammad, 1997; 1998).

In the present work adsorption potential of ordinary sand towards selected heavy metal ions i.e. Cr^{3+}, Cu^{2+}, Pb^{2+} and Zn^{2+} has been examined by plotting the Langmuir adsorption isotherms and extracting the necessary parameters from theme.

Langmuir adsorption isotherm: The Langmuir adsorption isotherm, applicable to solutions (adsorbate) can be expressed as (Jaffer, 1983):

$$\frac{m}{x} = \frac{1}{a_x K} \cdot \frac{1}{C_1} + \frac{1}{a_m}$$

where: C_i is the concentrated (mg/L) of adsorbate (metal) at equilibrium; X is the concentration (mg/L) of adsorbate (metal) adsorbed at equilibrium; m is the concentration (g/L) of adsorbent); a_x is the amount (mg/g) adsorbate adsorbed to form a monolayer; and K is the Langmuir constant. A plot of $\frac{m}{x}$ against $\frac{1}{C_i}$ gives a straight line from the intercept and slope of which a_m and K can be calculated. Here the units of the ratio $\frac{m}{x}$ is g/mg.

1. MATERIAL AND METHOD

All heavy metal salts i.e., chromium chloride, copper sulfate, lead acetate and zinc sulphate (Merk) were analytical grade and

were used without further purification. 500 g ordinary sand was collected from a riverbed near Rawalpindi, Pakistan. It is washed several times with distilled water and left to dry in open air.

Separate solutions, ranging in concentration from 1-5 mg/L, were prepared for each metal in distilled water. For each metal 225 ml of solution was taken in 250 ml Erlenmeyer flask and 10 g sand was added (concentration of sand was thus 44.45 g/L). The pH of each solution was adjusted to around 6.0 by adding a few drops of NaOH solution. At this slightly acidic pH a metal precipitation does not occur. The flasks in triplicate were capped and shaken on the flask shaker at 50 r/min for 24 hours at 20^0C. The solution, above the sand was filtered and its metal concentration, C_i (mg/L)

was determined using the Atomic Absorption Spectrophotometer, Varian, model: AA-375.

2. RESULTS AND DISCUSSION

Langmuir isotherm $\dfrac{m}{x}$ vs. $\dfrac{1}{C_i}$ gave a linear relation (straight lines) for all four metals as shown in Fig. 1 to 4 respectively. Whereas Fig. 5 i.e. x/m vs. C_i (initial conc. of metal) for Cr^{3+} exhibits an increasing trend. Table 1 illustrates the data calculated from the isotherms for all the four metals.

The value of a_x exhibit the preference of metal ions for sand in the order $Pb > Cr > Cu > Zn$. Among the four metals Pb is most readily absorbed on sand while Zn is the least readily adsorbed.

Table – 1

Adsorption data obtained from Langmuir isotherms

Metal	a_x mg/g	K L/mg
Pb^{2+}	0.169	0.71

Cr^{3+}	0.148	1.68
Cu^{2+}	0.144	2.45
Zn^{2+}	0.131	2.51

In order to understand the above metal-trend of adsorption on sand, consideration of the types of associations among adsorbing metal ions and silica and feldspar (components of sand) may be helpful. Silica $\left(SiO_2\right)$ has a structure composed of infinite three-dimensional framework of tetrahedron (Murray, 1994). Each silicon atom forms four single bonds with four oxygen atoms located at the four corners of a tetrahedron. Like silica, feldspars are also framework of silicates.
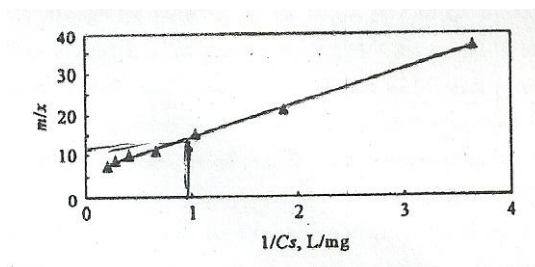

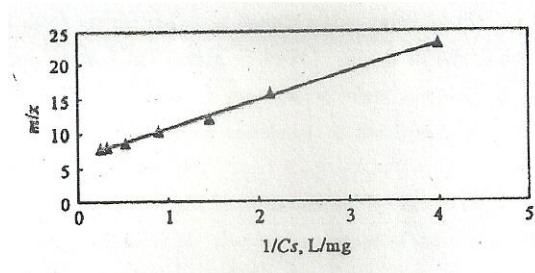Fig. 1 Langmuir adsorption isotherm for Pb^{2+} onto sand at 20^0C

Fig. 2 Langmuir adsorption isotherm for Cr^{3+} onto sand at 20^0C

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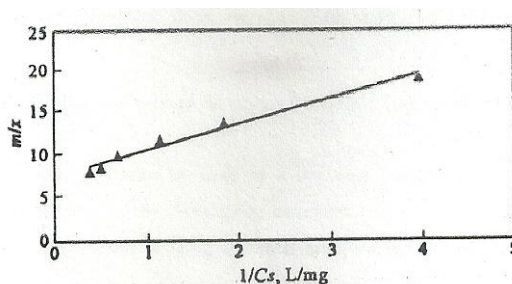e-ISSN: 2348-6848
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Fig. 3 Langmuir adsorption isotherm for Zn^{2+} onto sand at 20^0C

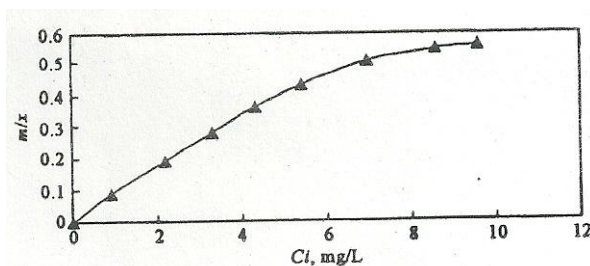Fig. 4 x/m (amount of Cr^{3+} adsorbed per gram of sand) increases with the initial conc. C_i of Cr^{3+}
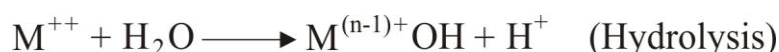
A surface functional group in silicates plays a significant role in the adsorption process. It is a plane of oxygen atoms bound to the silica Tetrahedral layer and hydroxyl groups that are associated with the edges of the silicate structural units. (Donald, 1998). These functional groups provide surface sites for the chemisorption of transition and heavy metals (Murray, 1994). The surface functional groups can be represented as:

$$\diagup\!\!\!\diagdown S\!-\!OH$$
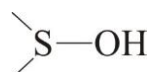
Where S is central atom (Si or Al) of adsorbing surface of silicates (Donald, 1998). The surface hydroxyl groups dissociate in water and serve as Lewis bases towards metal cations $\left(M^{++}\right)$. Such deprotonated sites (one or possibly two) forms complex with the heavy metal ions as follows. (Murray, 1994)

$$S\!-\!OH + M^{++} \longrightarrow S\!-\!OM^{(n-1)+} + H^{+},$$

$$2\ S\!-\!OH + M^{++} \longrightarrow (S\!-\!O)_2 M^{(n-2)+} + 2H^{+}.$$
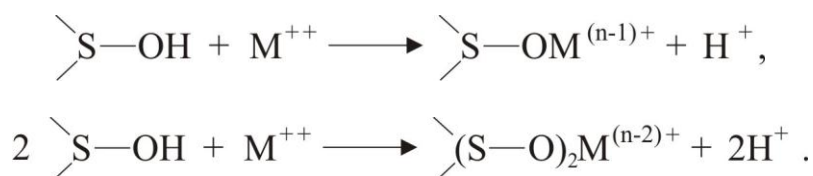
Heavy metal cations M^{++} may also hydrolyse in aqueous solution and adsorb in a hydrolyzed form according to the following reaction.

$$M^{++} + H_2O \longrightarrow M^{(n-1)+}OH + H^{+} \quad \text{(Hydrolysis)}$$

$$\text{S—OH} + \text{M}^{(n-1)+}\text{OH} \longrightarrow \text{S—OM}^{(n-2)+}\text{OH} + \text{H}^+ \text{ (Adsorption)}.$$

The metal-surface bonding (adsorption) reaction is favoured by the metal's properties that favor its hydrolysis. Such properties include high charge, small radius and polarizable (Murray, 1994)

Though the values of a_x for all the four metals do not differ much yet the reason of slightly higher value for Pb^{2+} is that silica adsorbs it a bit strongly as it $\left(Pb^{2+}\right)$ can easily be hydrolyzed in water (Murry, 1994), which in turn favors its chemisorptions on silicates. Cr^{3+}, due to its trivalent nature adsorbs bit more than the two other divalent metals (Cu^{+2} and Zn^{2+}). It is, therefore, can be deduced that adsorption and hydrolysis are somewhat correlated; if the heavy metal ion is easily hydrolysable, its adsorption on silicates is relatively higher as in the case of Pb^{2+}.

The sand after adsorption becomes saturated with the adsorbed metals. It can be disposed off by employing it as a component of concrete used in various construction purposes. In a study Vallejo et. al. proposed a method of immobilization of industrial residues containing zinc and chromium using two types of cements (Vallejo, 1999).

3. CONCLUSION

The linear trend of the plots $\dfrac{m}{x}$ vs. $\dfrac{1}{C_i}$ for Pb, Cr, Cu and Zn confirm that their adsorption on sand also follows the Langmuir adsorption model.

The removal capacity of sand for heavy metals in aqueous solutions is related to their (metals) potential towards hydrolysis.

Though ordinary sand adsorbs only a small amount of heavy metals yet it can be used as a low cost adsorbent for their removal from wastewaters (containing low conc. of such metals), especially in the developing countries.

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