REMOVAL OF PB, CR, CU, AND ZN IONS THROUGH ADSORPTION USING LIBYAN SAND

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Abstract

Heavy metal pollution is an environmental problem of worldwide concern. Several industrial waste water streams may contain heavy metals such as, Pb, Cr, Cd, Ni, as well as Zn, As, Hg, Cu, and Ag. A wide range of low-cost adsorbents have been studied by many researchers for heavy metal removal. It is evident from our literature survey that inexpensive and locally available materials could be used instead of conventional expensive adsorbents. The sand is one of the effective and environmentally suitable, low cost materials for treatment of polluted water. The removal of four heavy metals, i. e. Pb. Cr. Cu. and Zn from aqueous solutions, using ordinary sand as an adsorbent, was studied at 20^o C. The amount of metal adsorbed to form monolayer on sand, obtained from Freundlich isotherm, exhibited the preference of metals for sand in the order Pb > Cr > Cu > Zn. The heavy metal-sand adsorption phenomena can be illustrated on the basis of the interaction between surface functional group of silicates (sand) and the metal ions. It is deduced that sand can be used as a low cost adsorbent for the removal of heavy metal from waste water (containing low concentration of metals) especially in the developing countries.

Keywords: Adsorption, Heavy metals, Sand.

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Introduction

The rapid growth of industrial activities during the last few decades is one of the major reasons for pollution of water, air and soil. Effluents from metallurgical, chemical, ceramics, electro-galvanization and textile industries are the main sources of water contamination. According to the World Health Organization (WHO, 1984), the metals of most immediate concern are lead, cadmium, copper, cobalt, aluminium, chromium, manganese, iron, nickel, zinc and mercury. Development of low cost adsorbents for mitigation of toxic ions is one of the most important areas of research and development. Various treatment techniques including adsorption, precipitation, ion exchange and reverse osmosis have been employed to eliminate or reduce the toxic ion concentrations in waste waters. Adsorption on solid surfaces is the most common one and efforts are being made continuously to develop new, low cost and efficient adsorbents for removal of heavy metals. Several low cost adsorbents such as agriculture wastes **[1]**, natural clay, soils, low grade ores **[2-9]** and industrial wastes **[10 – 14]** have been projected as potential adsorbents for mitigation of toxic cations from aqueous streams. 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^{2+} in water, these are biologically critical species [**15,16**] . Cr^{2+} 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 [**17**]. Lead [**18**] and zinc [**19 – 21**] have also been classified as water pollutants. Consequently, removal of heavy metals from waste water and industrial wastes has become a very important environmental issue. The process of adsorption is considered as one of the most suitable methods for 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 [**22**]. Peat moss was used for the removal of mercury, copper, cadmium [**23**] and nickel [**24**]. Claymperes delessertti(moss) was used for the adsorption of copper from aqueous solution [**25**]. Also lead, cadmium and zinc were adsorbed on waste tea leave [26]. The adsorbents discussed above show different adsorption efficiencies for different metals. In addition to the above adsorbents, soils and clays also showed remarkable potential towards the removal of heavy metals ions from water [**20, 27**]. Removal of heavy metals by slow sand filters has also been reported **[28-30].** 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 Freundlich adsorption isotherms and extracting the necessary parameters from them. Freundlich adsorption isotherm:

The Freundlich adsorption isotherm, applicable to solutions (adsorbate) can be expressed as

$$\log x/m = l/n \log C + \log K$$

Where x = the amount of heavy metal cation absorbed
m = weight of adsorbate
Thus x/m = amount absorbed per unit weight
l/n = constant
C = equilibrium concentration of metal cation
K = constant

Materials and methods

All heavy metal salts, i.e. chromium chloride, lead nitrate, copper sulphate, and zinc sulphate (Merck) were of analytical grade and were used without further purification. 500 g, ordinary sand was collected from Al-Briga City, Libya. It was washed several times with distilled water and left to dry in open air. Separate solutions, ranging in concentration from 200-1000 ppm, were prepared for each metal in distilled water. For each metal 150 ml of the solution was taken in 250 ml Erlenmeyer flask and 10 g sand was added (concentration of sand was thus 66.67 g/L). The pH of each mixture was adjusted to 5.7 by adding a few drops of 5 M KOH 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 20ºC. The solution, above the sand was filtered and its metal concentration, C in (mg/L) was determined using the Atomic Absorption Spectrophotometer.

Results and discussion

Freundlich adsorption isotherms Log c vs Log x / m gave a linear relation (straight lines) for all four metals as shown in fig. 1 to 4. The values of log x / m exhibit the preference of metal ions for sand in the order Pb> Cr> Cu> Zn. Among the four metals, Pb is most readily adsorbed on sand while Zn is the least readily adsorbed. In order to understand the above metal-trend of adsorption on sand, consideration of the types of associations among adsorbing metal ions, silica and feldspar (components of sand) may be helpful. Silica (SiO_2) has a structure composed of infinite three-dimensional frame work of tetrahedron [**31**]. 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. The relationship between the equilibrium concentrations(c) of the metal cations Pb^{2+}, Cr^{3+}, Cu^{2+} and Zn^{2+} and the amounts of cations adsorbed on sand surface (x/m) was studied at 20°C. The results are given in tables 1 to 4.

Table 1: Amounts of Pb^{2+} ions adsorbed onto sand at 20°C

Equilibrium Conc. of Pb^{2+}(C)			Amounts of Pb^{2+} adsorbed per 10 g sand (x/m)		
ppm	meq/L	log C	ppm	meq/g	log x/m
200	0.965	0.0154	124	0.598	-0.2229
400	1.931	0.2857	248	1.197	0.0781
600	2.896	0.4618	372	1.795	0.2542
800	3.861	0.5867	496	2.394	0.3791
1000	4.826	0.6836	620	2.992	0.4760

Table 2: Amounts of Cr^{3+} ions adsorbed onto sand at 20°C

Equilibrium Conc. of Cr^{3+} (C)			Amounts of Cr^{3+} adsorbed per 10 g sand (x/m)		
ppm	meq/L	log C	ppm	meq/g	log x/m
200	3.846	0.585	110	2.115	0.3254
400	7.692	0.886	229	4.404	0.6438
600	11.539	1.062	341	6.558	0.8168
800	15.386	1.187	456	8.769	0.9430
1000	19.232	1.284	569	10.942	1.0391

Each reading is the average of four measurements.

Table 3: Amounts of Cu^{2+} ions adsorbed onto sand at 20°C

Equilibrium Conc. of Cu^{2+}(C)			Amounts of Cu^{2+} adsorbed per 10 g sand (x/m)		
ppm	meq/L	log C	ppm	meq/g	log x/m
200	3.150	0.498	96	1.512	0.1795
400	6.300	0.799	196	3.087	0.4895
600	9.449	0.975	288	4.535	0.6566
800	12.589	1.100	392	6.173	0.7905
1000	15.748	1.197	470	7.402	0.8693

It is obvious that the amount of Pb^{2+}, Cr^{3+}, Cu^{2+} and Zn^{2+} ions adsorbed increase with increase in the equilibrium concentration of the cation in the bulk solution, but the increase becomes less for higher concentrations. However adsorption seems to reach a maximum value when all adsorption sites are occupied with ions.

Table 4: Amounts of Zn^{2+} ions adsorbed onto sand at 20°C

Equilibrium Conc. of Zn^{2+}(C)			Amounts of Zn^{2+} adsorbed per 10 g sand (x/m)		
ppm	meq/L	log C	ppm	meq/g	log x/m
200	3.059	0.4860	80	1.223	0.0876
400	6.117	0.7870	164	2.508	0.3993
600	9.176	0.9630	239	3.655	0.5629
800	12.234	1.0880	318	4.863	0.6869
1000	15.293	1.1840	375	5.735	0.7585

Applying the Freundlich adsorption isotherm equation to the experimental data, it satisfactorily fits and give a straight line relationship between log c and log x / m for Pb^{2+}, Cr^{3+}, Cu^{2+}, and Zn^{2+} (Figure 1 to 4).

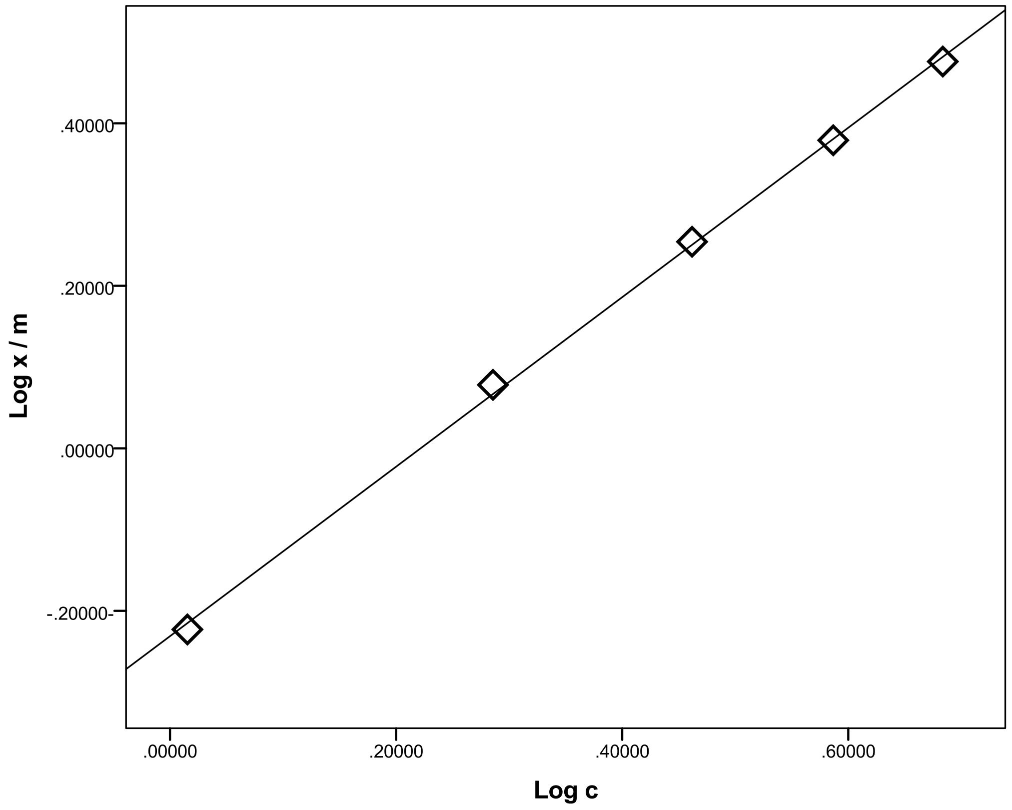


Fig. 1 Freundlich Adsorption Isotherms for Pb^{+2} at 20°C.

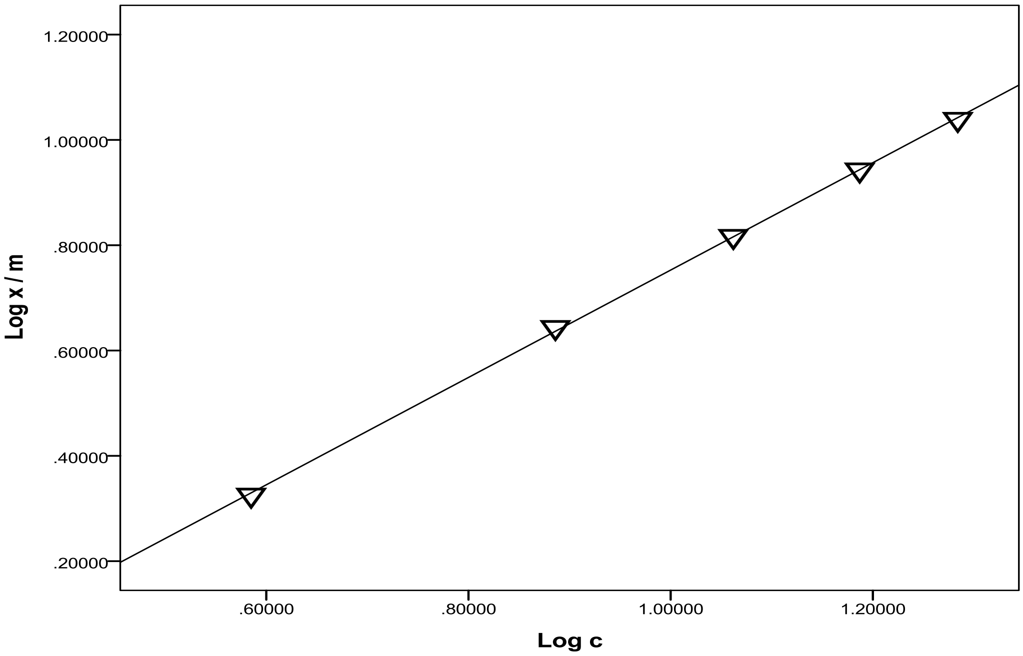


Fig. 2 Freundlich Adsorption Isotherms for Cr^{+3} at 20ºC.

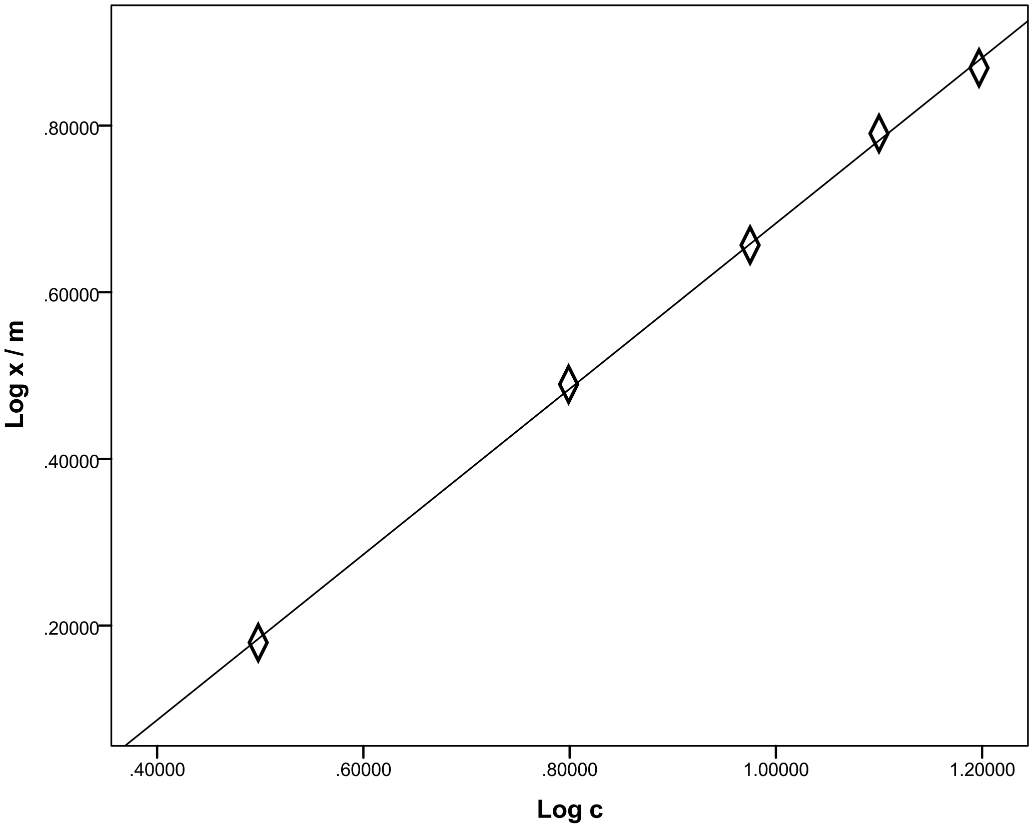


Fig. 3 Freundlich Adsorption Isotherms for Cu^{+2} at 20ºC.

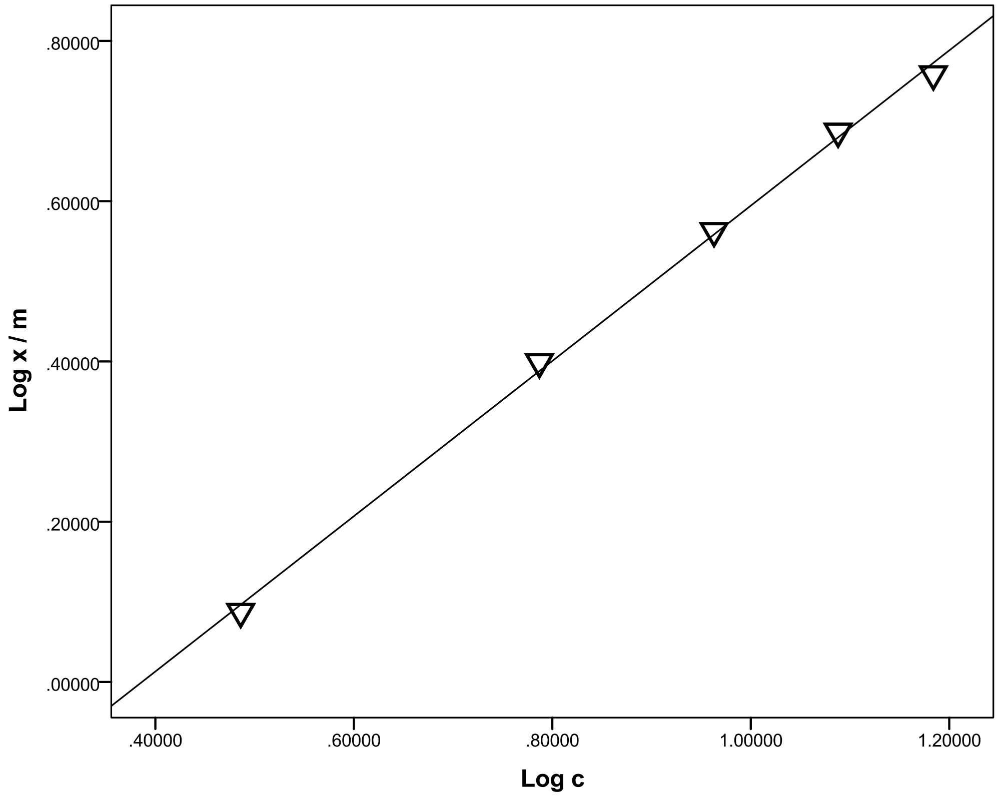


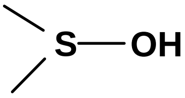
Fig. 4 Freundlich Adsorption Isotherms for Zn^{+2} at 20ºC

On the other hand the present data does not fit with Langmuir isotherms, however it has been reported that copper is adsorbed by clay minerals and by quartz according to Freundlich adsorption isotherm [**32**] Other researchers have reported that Cu^{2+} and Zn^{2+} cations are adsorbed both specifically and non-specifically by the soil [**33,34**]

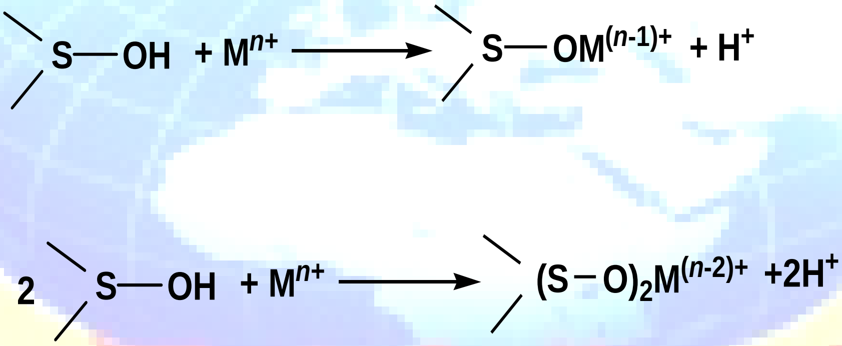
_Kuo and Mikkelson .[**35**] found that at extremely low concentrations (0.1 µg/g), zinc adsorption by soil could be described by Langmuir isotherm, whereas at higher concentrations only Freundlich equation could describe the adsorption. On the other hand, some other workers reported that copper adsorption could be described by Freundlich isotherm when its concentration was initially 200 µg or greater which agrees with the present results [**36**]

A surface functional group in silicates plays 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 [**37**](Donald. 1998). These functional groups provide surface sites for the chemisorption of transition and heavy metals [**31**] .

The surface functional groups can be represented as:

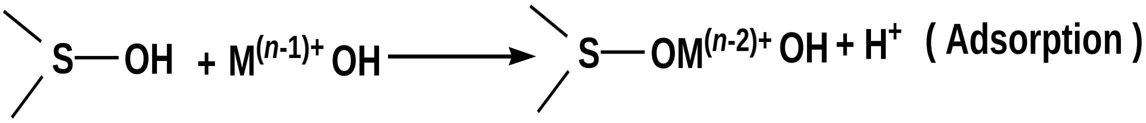


Where S is central atom (Si or Al) of adsorbing surface of silicates [**37**]. The surface hydroxyl groups dissociate in water and serve as Lewis bases towards metal cations (M^{n+}). Such deprotonated sites (one or possibly two) forms complex with the heavy metal ions as follows [**31**].



Heavy metal cations M^{n+} may also hydrolyze in aqueous solution and adsorb in a hydrolyzed form according to the following reaction.

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



The metal-surface bonding (adsorption) reaction is favoured by the metal's properties that favour its hydrolysis. Such properties include high charge, small radius and polarizability [**31**].

Though the values of adsorption 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 (Pb^{2+}) can easily be hydrolyzed in water[**31**] 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 [**38**].

Conclusion

The linear trend of the plots log c vs log x / m for Pb, Cr, Cu and Zn conform that their adsorption on sand also follows the Freundlich 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 heavy metals yet it can be used as a low cost adsorbent for their removal from waste waters especially in the developing countries.

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