Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2012.763048

51 (2013) 5559–5565
August

Taylor & Francis
Taylor & Francis Group

Adsorption filtration technology using iron-coated sand for the removal of lead and cadmium ions from aquatic solutions

Nada S. Ahmedzeki

Faculty of Engineering, Chemical Engineering Department, College of Engineering, University of Baghdad, Baghdad, Iraq
Email: dr_ahmedzeki@yahoo.com

Received 26 October 2012; Accepted 22 December 2012

ABSTRACT

The adsorptive removal of lead and cadmium ions from water using iron-coated sand (ICS) was investigated. Local natural sand (common constituent is SiO_2) was subjected to surface modification as impregnated with iron. The performance of ICS, as a low-cost filter media, was tested in the removal of lead and cadmium ions from water. Effects of pH, initial ion strength contact time, and adsorbent dosage were studied in a batch mode. High removal efficiency could be obtained for both ions as 99.99% for Pb and 90% for Cd. Results were manipulated to describe the adsorption process using different models for equilibrium isotherms and kinetics. Experimental data fitted Freundlich isotherm and second-order kinetics for both heavy metals.

Keywords: Heavy metal; Iron-coated sand; Adsorption; Low-cost adsorbent

1. Introduction

The development of innovative clean-up technologies remains a challenge as current procedures have many limitations such as being expensive, concentration or pollutant-specific, and many others.

Heavy metals are the major pollutants in wastewater such as lead, zinc, copper, cadmium, mercury, chromium, and arsenic. These metals accumulate in living tissues/organs and can cause accumulative poisoning and serious health problems such as cancer and brain damage. Among the top 20 hazardous substances elaborated by the Agency for Toxic Substances and Disease Registry (ATSDR) and the U.S. Environmental Protection Agency (USEPA), lead occupies the second place, just below arsenic. Manufacture of storage batteries, paints and pigments, oil, fertilizers, ammunition, solder, plumbing fixtures, ceramics, glass, cable coverings, radioactivity shields, lead smelting, and mining are the important industrial activities that contribute lead into the aqueous medium [1]. Concentration of lead ions in many industrial waters may be as high as 500 ppm. Hence, it is mandatory to reduce the lead levels in drinking water, wastewater, and water used for agriculture to the maximum permissible concentration of 0.1 ppm or less [2]. Cadmium is well known to produce toxic effects against humans. Long-term occupational exposure can cause adverse health effects against lungs, kidneys, and bones. The latter is a disease well known as “Itai-itai” [3]. Cadmium-polluted wastewater are generated by a number of industries that include mainly metal-finishing, electroplating, ceramics and inorganic pigments production, metallurgical alloying, zinc smelting, and acid mine drainage [4].

The major current methods for the removal of toxic metals from industrial effluents include chemical or electrochemical precipitation [5], ion exchange [6], adsorption on minerals, and reverse osmosis [7]. Compared with the other processes, adsorption is frequently used to remove pollutants in wastewater because the application of other techniques entails high costs. Adsorption is generally preferred due to its high efficiency, easy handling, and availability of different and especially low-cost adsorbents [8].

1.1. Metal-oxide coating sand

Metal oxides (such as iron oxides, aluminum oxides, or manganese oxides) have relatively high surface area and surface charge, and can be applied to the removal of heavy metals and organic matters from water and wastewater [9,10]. However, most of metal oxides are available only as fine powders or are generated in aqueous solutions as hydroxide floc or gel. Therefore, they are limited to reactor configurations incorporating with large sedimentation basins or filtration units because of the difficulty in solid/liquid separation. Besides, due to their low conductivity, the metal oxides alone are not suitable as filter media. Recently, some researchers have developed techniques for coating metal oxides onto sand surface in order to overcome the above problems of using metal oxide powders in water treatment process. The presence of external coatings using minerals and Fe, Mn, and Al-oxides on particle surfaces, which usually constitute only a minor fraction of the total solid mass of adsorbents, may change their sorptive properties. Removal of pollutants by coated adsorbents occurs by dissolution of the external which changes the reactive sites and/or specific surface area and prepare new adsorption sites [11]. The studies on metal-oxide-coated sand for removal of anions PO_4^{3-} and AsO_4^{3-} as well as cations Cu^{2+}, Pb^{2+}, and Mn^{2+}, from synthetic and real water had been reported by Jianbo et al. [12]. Ions of toxic metals can bind to the mineral surface in a number of ways, including absorption, adsorption, precipitation, and cation exchange. Investigation revealed that affinities of goethite surface for some heavy metals have the order given as; Cu > Pb > Zn > Cd > Co > Ni > Mn > Ca > Mg, which tends to follow the decrease in electronegativity and radii of the hydrated cations, with a slight variation [13].

Papini [11] concluded that the presence of small amounts of clays and (hydr)oxides can explain the difference in the adsorption capacity between natural and pure quartz sand even if different surface area has to be taken into account. Lee et al. [14] stated that by impregnation, a surface-modified sand is obtained and the specific surface area of sand increases.

The present investigation intends to exploit the use of coating of local sand with ferric ions. The removal efficiency of the prepared adsorbent was assessed for two important heavy ions, Pb(II) and Cd(II). The study was carried out for initial concentration dependence, pH, and adsorbent dosage effect. Equilibrium isotherms and the kinetic of the adsorption were also studied using different well-known models.

2. Materials and methods

2.1. ICS filter media

The impregnation method was used for coating sand in this study. Initially, local sand (<1.2 mm) was washed thoroughly with tap water until the run-off was clear. The wet sand was then dried at 110 ˚C and was soaked in 0.1 M HCl solution for 24 h. Then, the sand was rinsed to remove impurities, and dried at 110 ˚C.

Fe(III) stock solution having concentration of 2.5 M was prepared by dissolving $FeCl_3{\cdot}6H_2O$ in deionized water. Then, the mixture of 400 ml of this solution and 1 ml of 10 M NaOH was poured over 800 ml of dried sand placed in crucible dish with agitation. Then, the crucible was placed in an oven at 110 ˚C for 96 h and then at 200 ˚C for 24 h [12]. Washing with tap water and drying at 110 ˚C were the last step. The whole coating procedure was then repeated and the obtained coated sand was kept in a sealed container for further use.

2.2. Batch adsorption study

Different concentrations of Pb^{2+} and Cd^{2+} solutions were prepared from a stock of 400 mg/l solution prepared from analytical grade of $Pb(NO_3)_2$ and $Cd(NO_3)_2$, respectively.

The equilibrium isotherms were determined by mixing 1 g of ICS with 25 ml of each solution of heavy metal in conical flasks of different concentrations (10, 20, 30, 40, and 50 mg/l). Flasks were shaken at 200 rpm overnight to assure that equilibrium was reached. The residual concentration was analyzed using Atomic Absorption spectrophotometer. The adsorbed amount was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where q_e is the amount adsorbed at equilibrium, v volume of solution, C_o is the initial concentration, C_e is the concentration at equilibrium, and w is the amount of ICS.

The adsorption kinetics were investigated by adding 1 g ICS to 25 ml of 15 mg/l of heavy metal (Pb^{2+} or Cd^{2+}) solution. Samples were shaken and analyzed at different time intervals. All the samples were shaken at a constant speed of 200 rpm and analyzed by the same spectrophotometer aforementioned.

3. Results and discussion

3.1. Characterization of ICS filter media

The surface photographs of ICS is shown in Fig. 1. Magnification of 2000 and 25,000× by SEM is made to show the morphology of the surfaces. It can be seen that the deposition had changed the smooth surface of sand to a rough one due to the deposition of iron oxyhydroxide. By comparing Fig. 1(a) and (b), it appears that new cracks occurred on the surface with new micropores that appeared between the new crystals or cubes deposited of iron oxyhydroxide. It can be concluded that the coating step changed the morphology of natural sand. Fig. 1(d), shows that for the ICS, a particle size of less than 1 μm is obtained with many new pores of different sizes, ranging from 0.2 to 0.8 μm, while for the natural sand image, Fig. 1(c), with

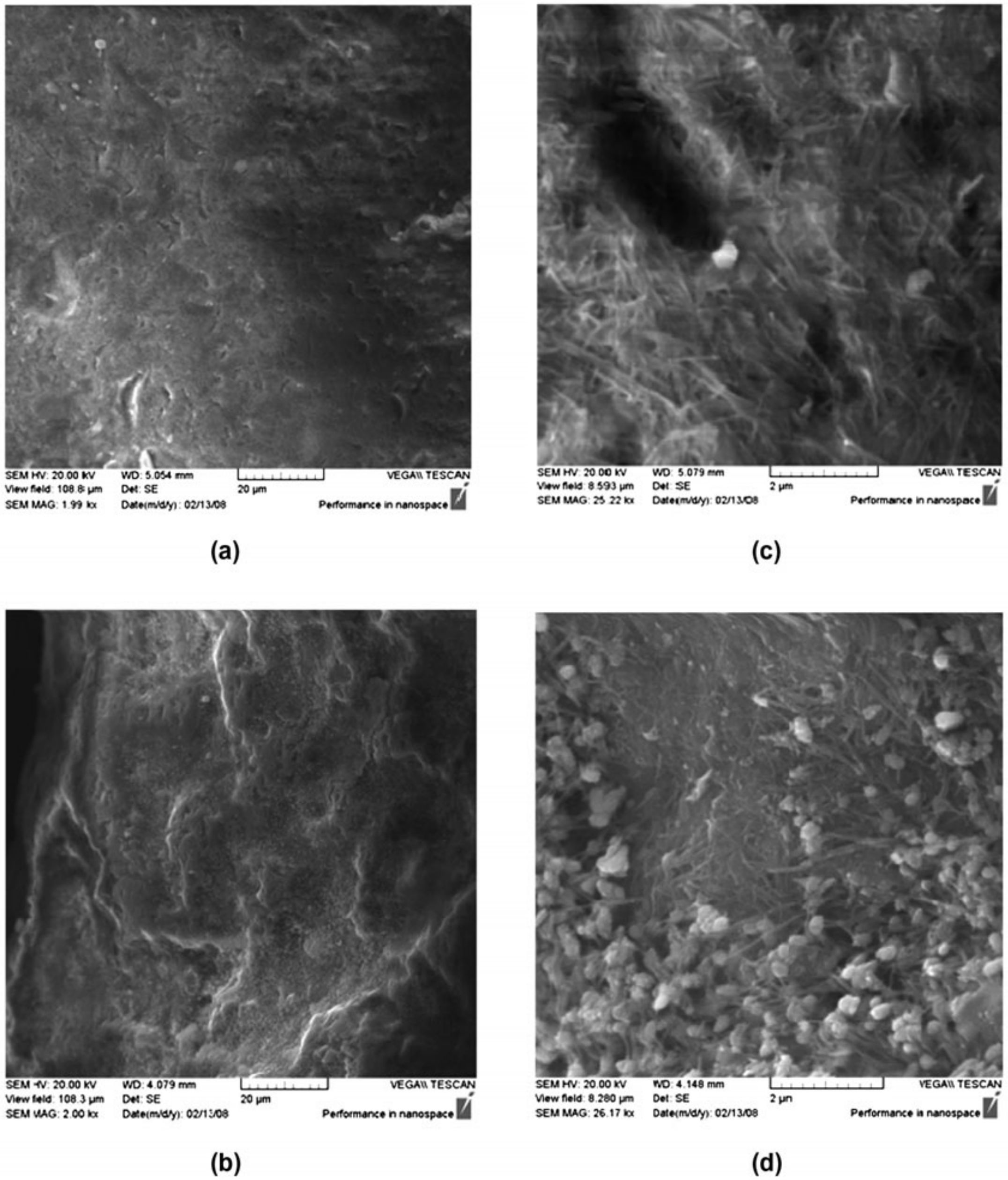

Fig. 1. SEM for natural sand, (a) and (c), and the prepared ICS (b) and (d). (a) and (b) at 2000 magnification. (c) and (d) at 25,000 magnification.

the same magnification, there appears a smooth surface with negligible surface containing pores. The amount of iron oxyhydroxide that deposits onto sand was determined to be about 30 mg of Fe/g of sand. Jianbo et al. [12] had used the same coating procedure and analyzed this amount to be 31.13 mg of Fe/g of sand.

3.2. Effect of time

The adsorption of lead ions on ICS is found to occur very fast reaching high levels. As it can be seen from Fig. 2 that only 12% of the lead initial concentration remained after 15 min from the start. The lead uptake increases until 10% of the initial concentration remained after 120 min. But cadmium ions, with larger radius size, had lower removal efficiency. Of the total initial concentration, 48.6% remained after 15 min reaching about 37% of the initial concentration that remained after 120 min. The important mechanism for this process is the Fe dissolution which prepares empty sites in the coated sand that will be available and ready for the uptake of heavy metals present in water. In other words, the process of ion exchange is controlling the adsorption process.

3.3. Effect of pH

The effect of pH on the adsorption of Pb^{2+} and Cd^{2+} on ICS was investigated by adding 1 g of ICS to 25 ml of solution of initial concentration of 15 mg/l, initial pH value of 4.5 and stirred at constant speed of 200 rpm for 120 min. The NaOH and HCl solutions of 0.1 M were used for pH adjustment. The results are shown in Fig. 3. The removal efficiency of cadmium ions is increased from 37 to 50% by increasing pH from 4 to 5 and then decreased sharply at pH 6 and the maximum value of 97% was obtained at pH 9. The pH affects the surface charge of the adsorbent as well as the degree of ionization of the adsorbate metal. At low pH values, the positive charge increases and H^+ ions will be acting as a competitor to the ions. So, the increase in the removal efficiency as pH increases may be attributed to the increasing of the available adsorption sites. Deliyanni et al. [4], found that the maximum adsorption capacity of Cd ions on akaganéite (iron-based nanoadsorbent) occurs at pH = 9 But the case with lead ions was not the same for it is clear that the adsorption of Pb ions is less sensitive to the variation of pH. Maliyekkal 2010 [2] had also concluded this fact when studied the adsorption of Pb on cellulose–nanoscale–manganese oxide composite.

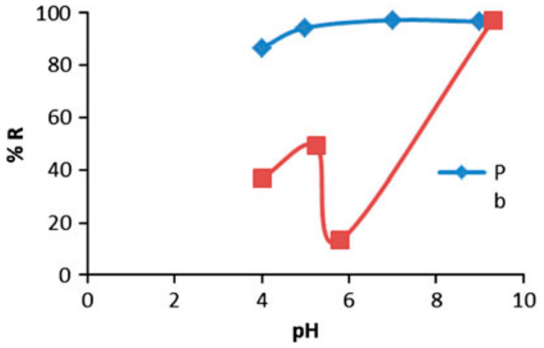

Fig. 3. Effect of initial pH on the removal efficiency of Pb and Cd ions on ICS.

3.4. Effect of ICS dosage

The ICS amount is studied using 25 ml of solution of initial concentration of 15 mg/l using 1,2, and 5 g of ICS, stirred at constant speed of 200 rpm for 120 min. It appears from Fig. 4 that increasing the amount of ICS increases the removal efficiency of both ions. The available adsorption sites and surface area are increased by increasing the amount of adsorbent. This is a common

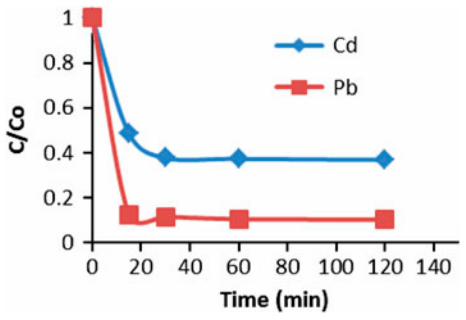

Fig. 2. Effect of time on the adsorption of lead and cadmium ions on ICS.

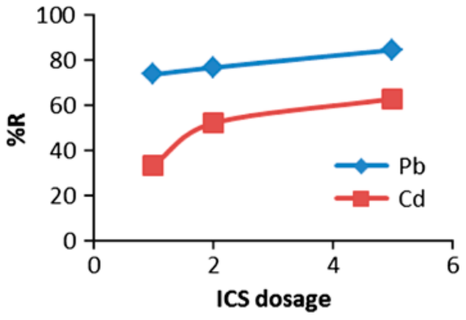

Fig. 4. Effect of ICS dosage on the removal Efficiency of Pb and Cd ions, 15 mg/l initial concentration, and 120 min.

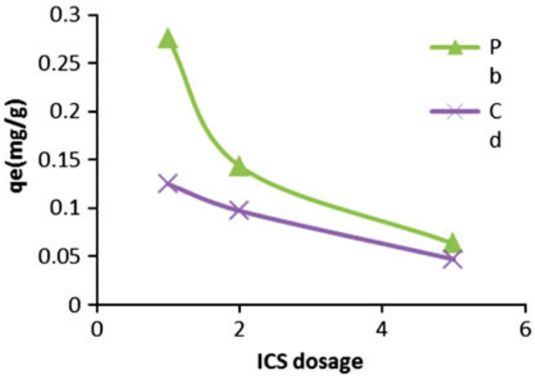

Fig. 5. Effect of ICS dosage on adsorption capacity of Pb and Cd ions, 15 mg/l initial concentration, and 120 min.

trend for adsorption techniques which indicates that more adsorbent means more uptake of pollutants at when other operating parameters remain constant. On the other hand, the amount of ions adsorbed per unit weight of adsorbent is decreased by increasing adsorbent dosage. This is regulated by Eq. (1) which shows that the amount adsorbed per gram is inversely proportional to amount of adsorbent. Fig. 5 shows this relationship.

3.5. Effect of Initial metal ion concentration

Different heavy metal initial concentrations of (10, 20, 30, 40, and 50 mg/l) were used with 1 g of each ICS, stirred at 200 rpm for two hours. The effect of initial concentration on the adsorption efficiency is drawn in Fig. 6. It can be seen that increasing initial concentration of ions decreases the removal efficiency, especially for Cd ions. This can be attributed to that there are no available adsorption sites for the extra ions at a constant amount of the adsorbent. The status for lead ions is slightly different. The adsorption of these ions, which have smaller radius, is high for all concentrations. Studies on these ions using other low-cost adsorbents had revealed the same trend [18].

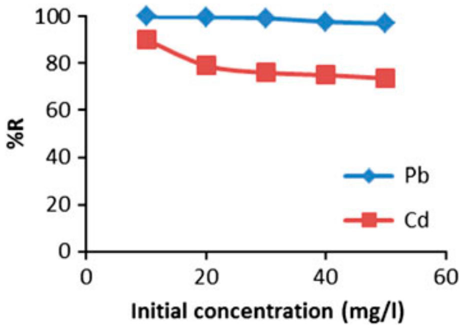

Fig. 6. Effect of initial concentration on the removal efficiency of heavy metals using 1 g ICS, 24 h.

3.6. Adsorption kinetics

The experimental results were tested using three kinetic models. The pseudo-first-order, pseudo-second-order, and intra-particle diffusion model, Table 1, contains the rate constants and correlation coefficient for each model. The linearized form of the three models, as given by Mbadcam et al. [15], is given below:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

$$q_t = k_i t^{0.5} \tag{4}$$

As it can be seen that the adsorption of lead and cadmium ions obey second-order model quite well. The calculated amount adsorbed at equilibrium (q_e) is 0.3375 and 0.2422 mg/g for lead and cadmium ions, respectively.

3.7. Adsorption isotherms

The most common adsorption models were used to study the type of equilibrium isotherms of lead and cadmium ions on ICS. Langmuir and Freundlich and Temkin models were used to fit the experimental data obtained in this study. Table 2 shows the parameters of each model along with their correlation coefficients as fitted to linear profiles. The three models described well the equilibrium status but the Freundlich model had approved that it is the best choice to fit the present adsorption. As it is known that that concept of Langmuir model assumes that adsorption occurs in a homogeneous monolayer with no interactions between molecules while Freundlich model assumes multilayer adsorption and the heterogeneity of the surface. The slope of (n) is a measure of the adsorption intensity or surface heterogeneity. It ranges between 0 and 1 and as the value gets closer to zero means that the surface is more heterogeneous [16].

For the values of (n) in Table 2, that is, 0.5382 for lead ions and 0.2985 for cadmium ions indicate good adsorption intensity and surface homogeneity of lead ions on ICS compared to cadmium ions. Experimental and theoretical adsorption isotherms as predicted by Freundlich model are shown in Fig. 7.

Table 1
Kinetic parameters

	Pseudo-first-order	Pseudo-second-order	Intra-particle diffusion
Pb	$k_1 = 0.0882$ (min^{-1}) $R^2 = 0.8103$	$k_2 = 6.614$ (mg/(mg min) $R^2 = 1$	$k_i = 0.0416$ ((mg/g)/$\mathrm{min}^{0.5}$) $R^2 = 0.3991$
Cd	$k_1 = 0.0846$ (min^{-1}) $R^2 = 0.8589$	$k_2 = 1.7163$ (mg/(mg min) $R^2 = 0.9993$	$k_i = 0.0286$ ((mg/g)/$\mathrm{min}^{0.5}$) $R^2 = 0.551$

Table 2
Adsorption isotherm models for lead and cadmium ions on ICS

Model	Parameter	Pb^{2+}	Cd^{2+}
Langmuir $q_e = \frac{q_m b C_e}{1+bC_e}$	q_m	0.184	0.168
	b	36.4	0.355
	R^2	0.9683	0.9347
Freundlich $q_e = k_f C_e^{\frac{1}{n}}$	K_f	0.218	0.042
	n	0.5382	0.2985
	R^2	0.9782	0.9698
Temkin $q_e = A + B \ln C$	A	0.2115	0.0308
	B	0.0364	0.0504
	R^2	0.978	0.869

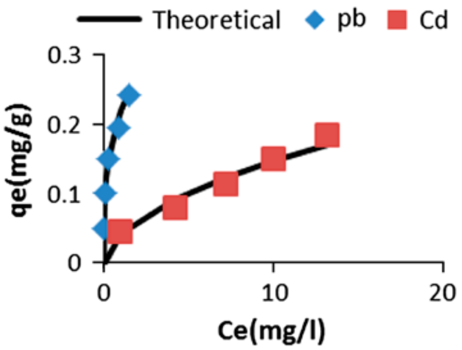

Fig. 7. Experimental and theoretical adsorption isotherms for adsorption Pb and Cd ions on ICS.

4. Conclusions

Adsorption filtration technology using iron-coated sand (ICS) was used for the removal of lead and cadmium ions from waste water. Sand which is an abundant material and considered as a low-cost adsorbent had proved to be efficient for solving water pollution problems after being subjected to coating with iron oxide by a careful impregnation method. Different operating conditions were investigated like pH, initial concentration, and adsorbent dosage. pH was found to be the most effective in the case of cadmium ions for high removal efficiency could be obtained at pH higher than 9. ICS was found quite suitable and efficient for lead ion removal at different ion concentrations and pH and it may be concluded that ICS has a good affinity for lead ion compared to cadmium ions. Freundlich model was found to fit the present experimental data with high correlation factor. The adsorption of both ions was found to obey second-order kinetics.

Nomenclature

q_e — amount adsorbed at equilibrium, mg/g ICS
C_e — concentration of heavy metal at equilibrium, ml/g
n — Freundlich constant
b — Langmuir constant
q_e — max. amount adsorbed, mg/g ICS
K_f — Freundlich constant
V — volume of solution, ml
W — mass of ICS, g

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