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Removal Behavior of Surface Modified Sand for Cd(II) and Cr(VI) from Aqueous Solutions

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Sand which is a good filter medium and widely used in wastewater treatments possesses a very insignificant sorption capacity for several heavy metal toxic ions. However, surface-modified sand as impregnated with manganese is supposed to possess fair removal capacity at least for the low level removal of several heavy metal toxic ions from aqueous solutions since manganese is likely to be aggregated onto the sand surface as manganese dioxide which is a good adsorbing material. The present investigation intends to exploit the use of sand obtained from the river Tlawng, Sairang site, Aizawl, Mizoram, India. The sand sample was impregnated with Mn(II) by a wet method. Further, the surface morphology of this manganese-impregnated sand (MIS) was obtained using scanning electron microscopy, which showed that the manganese oxide occupied the surface of the sand and clustered on it. The particle size of coated manganese oxide was found to be in the nanoscale range. Moreover, the specific surface area of the sand was also increased with this impregnation. Further, the removal efficiency of MIS was assessed for two important heavy metal toxic ions, that is, Cr(VI) and Cd(II). The study was carried out for the pH and concentration dependence of sorptive solutions. Results obtained for the concentration dependence were further analyzed by the Freundlich and Langmuir adsorption isotherms.

Introduction

The contamination of surface or ground waters by toxic heavy metals is one of environmental and public concern because of the fact that these ions are virtually nonbiodegradable and tend to accumulate in living organisms, causing various biological disorders.[1] Although several heavy metals are reported to be essential trace ions, enhanced intake causes several adverse effects toward humans. Further, the increased level of industrialization and urbanization is one of the major sources of contamination of water bodies. The removal of toxic heavy metal ions from wastewaters has received increased attention recently for global awareness of the underlying detriment of heavy metals in the environment. Applications of traditional treatment techniques have enormous cost and continuous input of chemicals, which becomes impracticable and also causes further environmental damage.[2] Chemical precipitation has been traditionally employed to remove toxic heavy metal ions from aqueous solutions. However, metal removal via coagulation or flocculation is, in many cases, insufficient to meet strict regulatory requirements.[3] Hence, interest lies toward more effective, economic, and eco-friendly techniques to be developed for the fine-tuning of effluent and wastewater treatment.[4,5] In this regard inorganic ion-exchangers play a predominant role for the removal or speciation of several cationic and anionic species from wastewaters, and if the adsorbent is chosen so carefully and the solution chemistry adjusted accordingly, it can provide an effective waste treatment technique even over a wide range of solution pH.[6−10]

Heavy metals such as cadmium (Cd) and chromium (Cr) often are present in industrial wastewaters, are known to be hazardous to the aquatic ecosystem, and pose serious health hazards toward human beings. Cadmium is one of the dangerous pollutants, originating from metal plating, metallurgical alloying, mining, ceramics, and other industrial operations.[11] Cadmium toxicity may be observed by a variety of syndromes and effects including renal dysfunction, hypertension, hepatic injury, lung damage, and tetragenic effects.[12] Similarly, Cr(VI) is poisonous to most living organisms and has many applications including in-wood preservation.[13] Humans are exposed to excessive amounts of Cr(VI) through food, drinking water, and inhaling air that contains chromium. The average daily intake from air, water, and food is estimated to be (0.01 to 0.03) μg, 2.0 μg$\cdot$L^{-1}, and 60.0 μg, respectively.[14] Cr(VI) is known to be toxic to both plants and animals, as a strong oxidizing agent and potential carcinogen.[15] Cr(VI) is considered by the IARC (International, Agency for Research on Cancer) as a powerful carcinogenic agent that modifies the DNA transcription process, causing important chromosomic aberrations.[16] Therefore, the presence of Cr(VI) in water causes several environmental problems, and as mentioned by Muir,[17] the NIOSH (National Institute for Occupational Safety and Health) recommends that the levels of Cr(VI) in water should be reduced to 0.1 mg$\cdot$L^{-1}.

Sand is widely used as a filter medium for the treatment of wastewaters, and it was found that during the treatment, manganese and iron, if present in wastewater, are to be deposited on the surface of the sand in the form of their oxides. Moreover, either naturally or laboratory coated sand with manganese has been found to be fairly effective for the removal of several toxic heavy metal ions due to its high exchange capacity and selectivity toward these toxic ions.[18,19] Moreover, it may also provide removal efficiency even down to the trace level. Hence,

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keeping this in view, the present study is conducted as to impregnate sand with Mn(II) and to characterize the impregnated sand. The suitability and selectivity of this manganese-impregnated sand (MIS) is then assessed for the low level removal of two important toxic heavy metal ions, namely, Cd(II) and Cr(VI), from aqueous solutions.

Experimental Section

Preparation of Manganese-Impregnated Sand (MIS) Samples. Manganese-coated sand was prepared by taking 120 g of sand ((30 to 60) BS in size) obtained from the local river Tlawng at the Sairang site, Aizawl, Mizoram, India and 100 mL of 0.05 M manganese chloride solution at pH = 9.0 in a beaker. The mixture was constantly stirred at (60 to 70) °C until the volume was reduced to about 10 mL. The solution was then kept in a drying oven at (90 to 100) °C for the complete evaporation of water. The sample was then kept at 160 °C for about 3 h for complete drying and better coating stability of the manganese. It was cooled to room temperature and again washed with distilled water several times. Finally the MIS sample was dried in a drying oven at 70 °C overnight. This dried MIS sample was used for the present investigation.

Batch Experiments. The pH_{PZC} is defined as the pH value where the net surface charge is zero. Hence, to evaluate the pH_{PZC}, the usual acid and base titrations were carried out by taking 5 g of a MIS sample in 500 mL of distilled water and titrated against the 0.1 $mol \cdot L^{-1}$ HNO_3 or NaOH solutions, and the corresponding pH was recorded using a pH meter. The titration data were further utilized to evaluate the pH_{PZC}. The pH_{PZC} for MIS was found to be 6.28.

Batch experiments were carried out to study the effect of pH on Cr(VI) and Cd(II) sorption by taking potassium dichromate solutions and cadmium nitrate solutions of (20 and 10) $mg \cdot L^{-1}$ concentrations, respectively, at different pH values of 2 to 10. The pH of the sorptive solutions was adjusted by adding drops of concentrated HNO_3/NaOH solutions. To 100 mL of each of these sorptive solutions, 0.5 g of the MIS sample was added. The solutions were constantly shaken for about 24 h in a rotary shaker at (25 ± 1) °C. The solutions were filtered with a 0.45 μm syringe filter, and the filtrates were then subjected to UV−visible spectrophotometry (Thermo Electron Corporation, England; model: UV1) analysis for Cr(VI) determination and AAS (Varian Spectra AA-300) for total cadmium determinations.

Similarly, the concentration dependence study was carried out varying the sorptive concentrations from (5 to 100) $mg \cdot L^{-1}$ (for Cr(VI)) and (1 to 20) $mg \cdot L^{-1}$ (for Cd(II)), keeping the solution pH constant (3.0 for Cr(VI) and 6.0 for Cd(II)). The 100 mL sorptive solutions were equilibrated with 0.5 g of MIS at (25 ± 1) °C for 24 h in a rotary shaker. The solutions were filtered with a 0.45 μm syringe filter, and the filtrates were then analyzed to measure the bulk sorptive concentrations.

Results and Discussion

Characterization of MIS. The effective coating of manganese onto the surface of sand was determined by using the US EPA method 3050B and was found to be 1446 $mg \cdot kg^{-1}$. Further, scanning electron microscopy (SEM) images (using FE-SEM model: SU-70, Hitachi, Japan) showed that the bare sand possessed a very compact and disordered surface structure with few pores on its surface (see Figure 1). Moreover, it contained several aggregated particles of silica. On the other hand MIS samples showed distinct micropores on its surface and a higher specific surface area, owing to the aggregation of manganese likely in the form of manganese dioxide on the sand surface. They were very orderly clusters onto the sand surface, and the particle size of manganese seems to be of the order of nanometers.

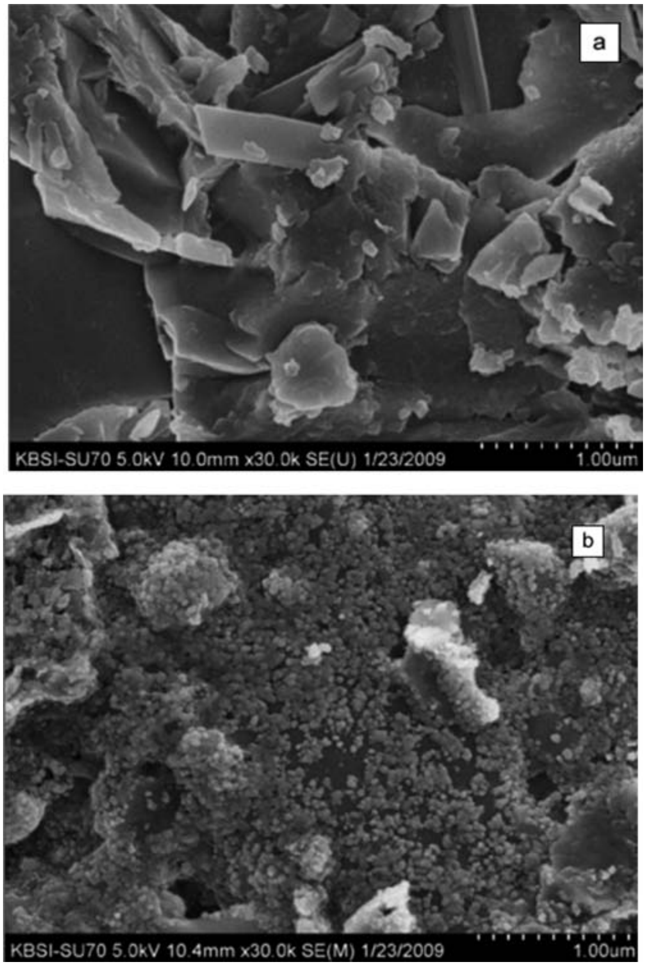

Figure 1. SEM images of (a) bare sand and (b) MIS.

Table 1. Physical Parameters Obtained with the Brunauer−Emmett−Teller (BET) Analyzer

	BET surface area	pore volume	pore size
	$m^2 \cdot g^{-1}$	$cm^3 \cdot g^{-1}$	nm
sand	8.51	$3.54 \cdot 10^{-3}$	1.96
MIS	9.21	$2.02 \cdot 10^{-3}$	2.14

Further, the physical properties of bare sand and MIS were obtained with a surface area and porosimetry system (model ASAP 2020, Micromeritics, USA) and are returned in Table 1. The MIS apparently possessed a relatively higher specific surface area.

Speciation Study of Cr(VI) and Cd(II). The speciation of Cr(VI) (20 $mg \cdot L^{-1}$) and Cd(II) (10 $mg \cdot L^{-1}$) were obtained using the MINEQL geochemical simulation program keeping the ionic strength (0.01 $mol \cdot L^{-1}$) and temperature (25 °C) constant as a function of solution pH. The equilibrium constants used are given in Table 2. The outcome of the results are shown in Figures 2 parts a and b respectively for Cr(VI) and Cd(II). Figure 2a clearly indicates that Cr(VI) exists as the soluble anionic species of CrO_4^{2-}, $HCrO_4^-$, or $Cr_2O_7^{2-}$ throughout the pH region, that is, 2 to 10. However, up to a pH of about 5.5, the major species of Cr(VI) is $HCrO_4^-$, and beyond pH 5.5 the predominant species is the CrO_4^{2-}. On the other hand the Cd(II) speciation showed (*cf* Figure 2b) that even up to pH 9.0 cadmium exists predominantly as the Cd^{2+} soluble cationic

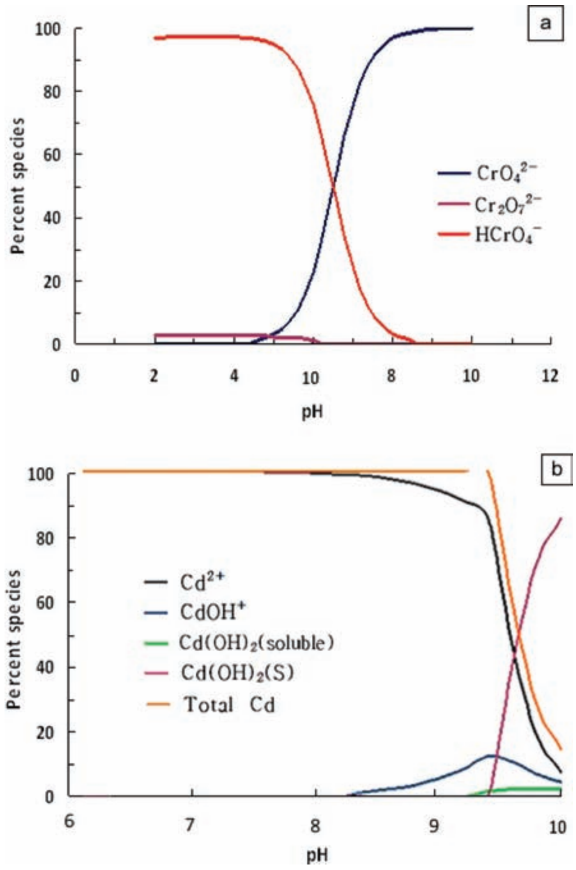

Figure 2. Speciation of (a) Cr(VI): 20 mg·L and (b) Cd (II): 10 mg·L^{-1} as a function of pH.

Table 2. Various Equilibrium Constants Used for the Speciation of Cr(VI) and Cd(II) in Aqueous Solutions at 25 °C and 0.01 mol·L^{-1} KNO_3 Ionic Strength

equilibrium	log *K*
$2CrO_4^{2-} + 2H^+ \leftrightarrow Cr_2O_7^{2-} + H_2O$	14.560
$CrO_4^{2-} + H^+ \leftrightarrow HCrO_4^-$	6.510
$CrO_4^{2-} + 2H^+ \leftrightarrow H_2CrO_4$ (aq)	6.419
$Cd^{2+} + 3H_2O \leftrightarrow Cd(OH)_3^- + 3H^+$	−32.505
$Cd^{2+} + 4H_2O \leftrightarrow Cd(OH)_4^{2-} + 4H^+$	−47.288
$Cd^{2+} + H_2O \leftrightarrow Cd(OH)^+ + H^+$	−10.097
$Cd^{2+} + 2H_2O \leftrightarrow Cd(OH)_2$ (aq) $+ 2H^+$	−20.294
$2Cd^{2+} + H_2O \leftrightarrow Cd_2(OH)^{3+} + H^+$	−9.397

species. Beyond pH 9.0 cadmium turns into the insoluble $Cd(OH)_2$ species. In between, a maximum of about 12 % of the $Cd(OH)^+$ species occurred at pH 9.4.

Removal Behavior of MIS for Cr(VI) and Cd(II). Effect of pH. The pH dependence data for the removal behavior of Cr(VI) and Cd(II) by MIS are obtained and presented graphically in Figure 3. Figure 3 clearly demonstrates the percent removal of these two ions as a function of pH. It is to be noted that in increasing the pH from 2.0 to 11.0 the removal percentage of Cd(II) increased from 14 % to 99 %, respectively, whereas the percent removal of Cr(VI) for a similar increase in pH, that is, from 2 to 10, decreased from 85 % to 72 %. The pH dependence data obtained by MIS may be explained with the help of the surface properties of MIS as well as the properties of the adsorbing species present in solution. Since MIS is likely to possess a manganese dioxide layer on its surface, the pH_{PZC} for manganese dioxide[20] is reported to be 5.5 against the experimentally obtained value of 6.28. The different values of pH_{PZC} may be because of the mineralogical species of manganese oxide; also possibly this value is due to the combination of the bare sand surface and the manganese-coated surface. Hence, the surface is supposed to be positively charged below pH 6.2, and beyond that it becomes negatively charged (see eq 1).

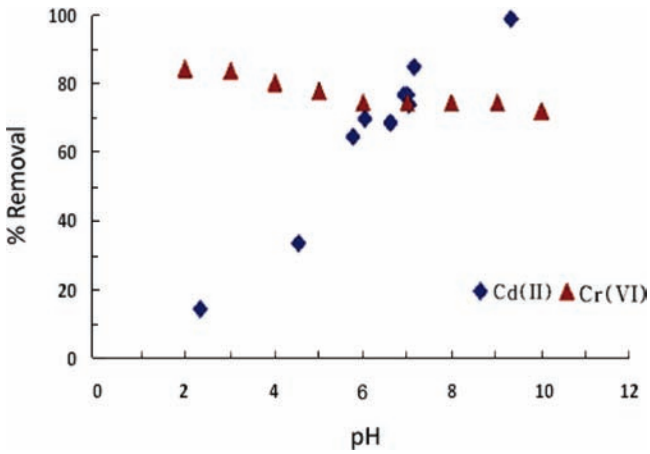

Figure 3. Effect of pH on the sorption of Cr(VI) and Cd(II) onto the surface of MIS [initial concentration of Cr(VI): 20 mg·L^{-1} and Cd(II): 10 mg·L^{-1}].

$$\equiv SH_2^+ \leftrightarrow \equiv SH^0(pH_{PZC}) \leftrightarrow \equiv S^- \qquad (1)$$

The higher uptake of Cr(VI) at very low pH may be explained because of the anionic species of Cr(VI) present ($HCrO_4^-$, CrO_4^{2-}, $Cr_2O_7^{2-}$; see Figure 2a), which preferred the positively charged solid surface. However, the decrease in adsorption at higher pH values may be due to the competitiveness of the oxyanions of chromium and OH^- ions in the bulk solutions. In this region perhaps the repulsion of negatively charged surface to Cr(VI) anion also reduced the adsorption of Cr(VI) at higher pH. Moreover, the processes of oxo group protonation and Cr(VI) reduction are lowered because both of these reactions require protons.[21,22] Similar pH dependent results have also been reported for Cr(VI) on various sorbents previously.[23−25]

On the other hand, cadmium mostly exists in the cationic form in the pH range 2 to 9.0; hence, a sharp increase in adsorption occurred after pH 5.5, since the surface apparently becomes negatively charged and a further increase in pH beyond pH 9.0 leads to almost 100 % Cd(II) removal perhaps due to the mixed effect of adsorption and formation of insoluble species of cadmium, that is, $Cd(OH)_2$ (see Figure 2b). Moreover, below the pH 5.5 the removal of Cd(II) was greatly hindered, since the surface itself possesses a positive charge and the cadmium occurs in its cationic form, that is, Cd^{2+} in this pH region. In general the specific surface reactions may occur as follows.[18,26]

$$\equiv MnOH + Cd^{2+} \rightarrow \equiv MnO^-Cd^{2+} + H^+ \qquad (2)$$

$$\equiv MnO^- + Cd^{2+} \rightarrow \equiv MnO^-Cd^{2+} \qquad (3)$$

$$2(\equiv MnOH) + Cd^{2+} \rightarrow (\equiv MnO^-)_2Cd^{2+} + 2H^+ \qquad (4)$$

$$2(\equiv MnO^-) + Cd^{2+} \rightarrow (\equiv MnO^-)_2Cd^{2+} \qquad (5)$$

Further, it is interesting to note that at neutral pH conditions, that is, usual water pH, the employed solid MIS caused the removal of almost 80 % of these two pollutants, present in the aqueous solutions (see Figure 3). Hence, the material showed potential applicability to effectively decontaminate water polluted with Cr(VI) or Cd(II) at neutral pH conditions.

Effect of Sorptive Concentration. It has been mentioned that the initial concentration of a metal ion provides an important driving force to overcome all mass transfer resistances of the

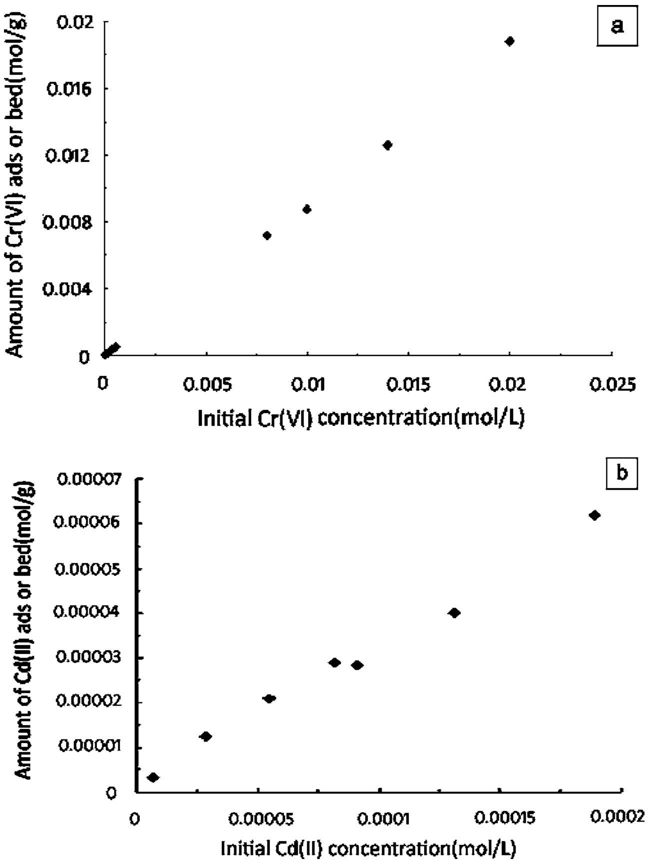

Figure 4. Effect of concentration on the sorption of (a) Cr(VI) pH: 3.0 and (b) Cd(II) pH: 6.0 onto the surface of MIS.

metal ion between aqueous and solid phases.[27] The effect of sorptive concentration on the removal behavior of MIS for Cr(VI) and Cd(II) was obtained by varying the sorptive concentration from ($9.63 \cdot 10^{-5}$ to $2.00 \cdot 10^{-2}$) $\text{mol} \cdot \text{L}^{-1}$ for Cr(VI) at pH 3.0 and ($7.30 \cdot 10^{-6}$ to $1.89 \cdot 10^{-4}$) $\text{mol} \cdot \text{L}^{-1}$ for Cd(II) at pH 6.0. The results obtained are shown in Figure 4 parts a and b respectively for Cr(VI) and Cd(II). It is to be noted that increasing the initial concentration apparently caused an increase in uptake of these two metal cations by the MIS. Further, by quantitatively increasing the concentration of Cr(VI) from ($9.63 \cdot 10^{-5}$ to $2.00 \cdot 10^{-2}$) $\text{mol} \cdot \text{L}^{-1}$, the amount of Cr(VI) removed was increased from ($8.44 \cdot 10^{-5}$ to $1.88 \cdot 10^{-2}$) $\text{mol} \cdot \text{g}^{-1}$. Similarly, the Cd(II) was increased from ($8.54 \cdot 10^{-7}$ to $6.47 \cdot 10^{-5}$) $\text{mol} \cdot \text{g}^{-1}$ for an increase in initial sorptive concentration from ($7.30 \cdot 10^{-6}$ to $1.89 \cdot 10^{-4}$) $\text{mol} \cdot \text{L}^{-1}$. Similar observations are reported by several authors along with our report as well.[2,23,28,29]

The concentration dependence data obtained at equilibrium between solid and solution interfaces were further utilized to build the adsorption isotherms, and it was found that these were fitted well by the Freundlich adsorption isotherm (eq 6), rather than the Langmuir isotherm. A reasonably good linearity was obtained while plotting the values of log a_e versus log C_e (see Figure 5.).

$$\log a_{\mathrm{e}} = \frac{1}{n} \log C_{\mathrm{e}} + \log K_{\mathrm{f}} \qquad (6)$$

where a_e and C_e are the amount adsorbed ($\text{mol} \cdot \text{g}^{-1}$) and bulk sorptive concentration ($\text{mol} \cdot \text{L}^{-1}$) at equilibrium, respectively, and K_f and $1/n$ are the Freundlich constants referring to adsorption capacity and adsorption intensity or surface heterogeneity, respectively.[30] Further, in the case of $1/n = 1$, the partition between the two phases is independent of the concentration, and the case of $1/n < 1$ (the most common) corresponds to a normal L-type Freundlich isotherm,[31] while $1/n > 1$ is indicative of a cooperative sorption, which involves strong interactions between the molecules of the adsorbate.[32,33] These constants, that is, K_f and $1/n$, are estimated respectively by intercepts and slopes of the straight lines obtained while plotting log a_e versus log C_e (Figure 5a,b). The Freundlich constants along with the coefficient of determination (R^2) values obtained for these two systems are given in Table 3. The estimated adsorption capacities (i.e., K_f) for Cr(VI) and Cd(II) toward the MIS were found to be (0.326 and 0.111) $\text{mol} \cdot \text{g}^{-1}$, respectively. These results suggest that MIS possesses a relatively higher removal capacity for Cr(VI) compared to Cd(II). Further, the values obtained for the $1/n$ are less than one for Cd(II), whereas it is more than one for Cr(VI). As indicated previously, that is, $1/n > 1$, the Cr(VI) may have strong interactions within the sorbate molecules accompanied with cooperative sorption. Similar results are also reported for the Cr(VI) removal using the green alga *Ulva lactuca* and its activated carbon.[34] On the other hand Cd(II) possesses $1/n < 1$, which indicates that the MIS solid contains a heterogeneous nature and also points it toward the exponential distribution of adsorption sites.[35] On the other hand, the nonapplicability of the Langmuir adsorption isotherm is indicative of chemisorption, or perhaps an ion-exchange type uptake process took place at the surface. Moreover, the multilayer coverage along with the lateral interaction of sorbed ions could take place at the solid surface.

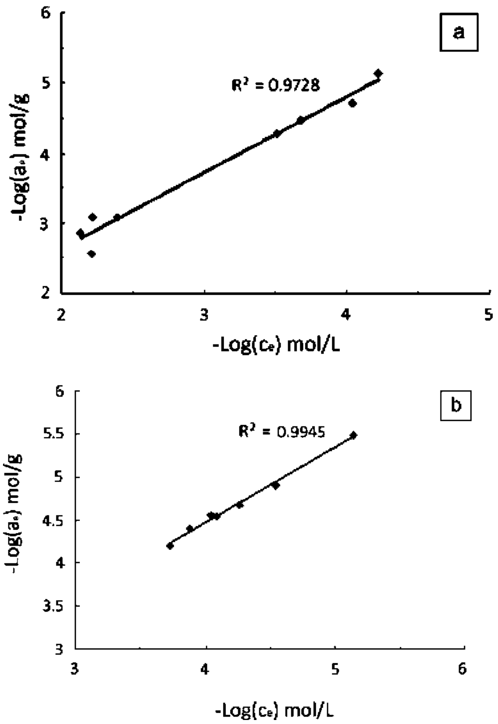

Figure 5. Freundlich adsorption isotherm for the sorption of (a) Cr(VI) and (b) Cd(II).

Further, the sorption capacity of MIS for these two pollutants, that is, Cr(VI) and Cd(II), obtained using the Freundlich fitting method are compared to the sorption capacities of different materials employed for these two pollutants in Table 4. Table 4 clearly demonstrates that MIS possesses very comparable sorption capacities for these two pollutants and, hence, is likely to be a possible alternative material for the treatment of waste waters contaminated with these pollutants.

Table 3. Freundlich Constants Obtained for the Cr(VI) and Cd(II) Sorption onto the Surface of MIS

Cr(VI)			Cd(II)		
$1/n$	K_f ($\text{mol}\cdot\text{g}^{-1}$)	R^2	$1/n$	K_f ($\text{mol}\cdot\text{g}^{-1}$)	R^2
1.076	0.326	0.973	0.879	0.111	0.994

Table 4. Adsorption Capacities Obtained for Cr(VI) and Cd(II) Using Different Materials

sorbents	sorption capacity of Cr(VI) $\text{mg}\cdot\text{g}^{-1}$	sorption capacity of Cd(II) $\text{mg}\cdot\text{g}^{-1}$	refs
Afsin-Elbistan fly ash		0.2306^a	36
Seyitomer fly ash		0.0925^a	36
food waste (areca)		1.086^b	37
MnO_2 loaded D301 resin		77.88^a	38
palygorskite clay	58.5^a		39
maghemite nanoparticles	1.9^b		40
bauxite	0.5^a		41
Escherichia coli biofilm supported on kaolin	1.5^c	1.1^c	42
aniline formaldehyde condensate coated silica gel	0.89^b		43
moss (*Hylocomium splendens*)		32.5^a	44
MIS	6.27^b	0.99^b	present study

[a] Langmuir. [b] Freundlich. [c] Kinetic.

Conclusions

Manganese-coated sand (MIS) was prepared by the wet coating method, and SEM images of MIS showed that the manganese oxide occupied the surface and pores of the sand and clustered on it. The particle and pore size of coated manganese oxide was found to be in the nanoscale range. The amount of manganese coated was found to be 1446 $\text{mg}\cdot\text{kg}^{-1}$. Further, the MIS sample was exploited for the low level removal of Cr(VI) and Cd(II) from aqueous solutions. Results obtained showed that the lower pH values favored the uptake of Cr(VI), whereas the moderate-to-higher pH region favored Cd(II) removal. Moreover, relatively high uptake of these two pollutants at neutral pH conditions enhances the applicability of MIS to decontaminate water contaminated with Cr(VI) or Cd(II) at this pH. Similarly, the concentration dependence data fitted well the Freundlich adsorption isotherm rather than the Langmuir isotherm. The sorption capacity was obtained to be (0.326 and 0.111) $\text{mol}\cdot\text{g}^{-1}$, respectively, for Cr(VI) and Cd(II) ions. This work was partly supported by a Korea Science and Engineering Foundation (KOSEF) grant funded by the Korean Government (MEST) (No. 2009-0078010).

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