Batch Lead and Cadmium Ions Binding and Exchange Properties of Polymer-Coated Hydrous Iron(III) Oxide

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The possibility of Pb(II) and Cd(II) removal from the aqueous solutions by polymer-coated iron(III) oxide, having –COOH functional group, is studied. The effect of several operating variables such as duration of agitation, pH, initial concentration of adsorbate and temperature on metal removal by sorbent has been investigated in batch mode studies. The process of uptake is governed by the first-order kinetics. The adsorption kinetic data obtained from the experiments show that the process of Pb(II) and Cd(II) removal is mainly controlled by the internal diffusion. Sorption data have been correlated with both Langmuir and Freundlich adsorption models and indicate favourable adsorption with this new adsorbent material. The utility of the adsorbent has been tested using synthetic wastewaters. The spent absorbent can be regenerated using 0.2 M NaCl and can then be reused.

Introduction

The metal contamination is of environmental concern due to its effect on human health. The extensive use of metals and their widespread disposal to the environment have caused various types of acute and chronic disorders. It is important to develop suitable methods to remove metals from wastewater and to reduce aqueous metal concentrations to below threshold value. The conventional means of treating wastewaters containing metals include chemical precipitation, solvent extraction, and ion exchange. Recently, much interest has been exhibited in the use of adsorption technique for the removal of metals from wastewaters. Adsorption of metals onto activated carbon, starch xanthate, discarded tyre rubber, bituminous coal, flyash, hematite, waste Fe(III)/Cr(III) hydroxide, metallurgical slags and mixed oxide gels has already been reported. Recently, some research work also appeared connected with the study of the sorption characteristics of polymer-coated metal oxide gels. The main advantages of these materials are their high adsorption capacity and low cost in comparison with certain commercial polymeric ion exchangers. A number of materials such as silica gel, iron(III) oxide, tin(IV) oxide, titanium(IV) oxide have been used as polymer support for the preparation of adsorbents. The present work involves dynamic and equilibrium studies on sorption of Pb(II) and Cd(II) on polyacrylamide coated hydrous iron(III) oxide having carboxylate functional group.

Experimental Procedure

Hydrous Fe(III) oxide (HyFeO) was prepared by the method outlined by Hingston et al. The material was prepared by treating 0.5 M FeCl₃ solution (100 mL) with concentrated ammonia solution (14.0 M) at pH 7.0. The yield of HyFeO was found to be 53 g. Chemical modification of HyFeO was performed by its step-wise reaction with acrylamide/ N, N'-methylene bisacrylamide, ethylenediamine and succinic anhydride as follows (see also Figure 1). The air dried HyFeO was coated with polyacrylamide using the same procedure as described elsewhere. About 10 g HyFeO (1) was immersed in 300 mL of an aqueous solution containing 1.0 g N,N'-methylene bisacrylamide (2) and 1.0 g K₂S₂O₇. About 3 g of acrylamide (3) was added to the mixture and then stirred vigorously at 70°C. Polyacrylamide coated HyFeO (PCHyFeO) was then refluxed with ethylenediamine, (en)₂, in toluene for 8 h at 70°C. Finally, the product was converted into cation exchanger functionalised with carboxylic acid by treating one part (by weight) of the above material with (equal parts) by weight of succinic anhydride at pH 4.0 for 6 h. After reaction, the carboxylic acid bound PCHyFeO (PCHyFeO-COOH) was separated, washed with 1,4-dioxane, and ethanol and dried under reduced pressure. The dried material was then ground and sieved to separate parti-
cles of 0.508, 0.149, 0.106 and 0.074 mm size. After sieving the amount of material left was found to be 7.0%.

The specific surface area of the adsorbent was determined using N₂ gas adsorption and the BET equation was found to be 97.16 m²/g. The cation exchange capacity was evaluated using the method described by Huang et al. and was found to be 2.16 meq/g. The zero point charge pHₐ₀ is defined as the pH of the suspension at which the surface charge density σₛ = 0. A potentiometric titration method was used to determine the pH as a function of pH and ionic strength. Adsorbent (1g) was suspended in a 100 mL KNO₃ solution (0.001, 0.01 and 0.1 M) and titration was performed at 30°C by successive 20 to 100 μL increments of 0.1 M HNO₃ or KOH. The difference thus obtained between titration curves and those of the corresponding blank electrolyte solution yielded the net uptake Q₋ₐ and Q₋ₐ₋. The σₛ was calculated from the titration data using Eq. (1).

\[ \sigma_S = \frac{F}{S} \left[ (Q_0 - Q_{min}) \alpha_0 + (Q_{min} - Q_{min}^*) \alpha_e \right] \]  

where F is the Faraday constant, S is the specific surface area and (Q₀ - Q₋ₐ₋), the net uptake at pzc, the point of intersection of the σₛ vs pH curves (Figure 2) showed that the pH of the adsorbent occurred at 5.8.

Batch experiments were conducted by shaking 100 mg of the adsorbent with 50 mL of metal solution of desired concentration at constant temperature for the removal of metal having pH in the range 2-10, in 100 mL stoppered flasks in a shaking waterbath with a constant speed of 100 rpm. Initial pH of the solution was adjusted using either 0.1 M HNO₃ or 0.1 M NaOH. The volumes added for pH adjustment never exceeded 1.0% of the total volume. Samples were withdrawn at appropriate interval of time, filtered and analysed for Pb(II) and Cd(II) ions using atomic absorption spectrophotometer. Similar batch experiments were carried out for obtaining isotherm data for metal adsorption using the initial concentration ranging from 50 to 700 mg/L with constant liquid to solid mass ratio of 500. The amount of metal sorbed on the solid surface can be calculated by the difference of metal concentrations before and after equilibrium.

Results and Discussion

The percentage of metal removal for different contact time (0-300 min) and for initial concentration of 100 mg/L is depicted in Figure 3. Adsorption is an equilib-
A quasi-stationary state was obtained within 180 min of shaking with a concentration of absorbent 2 g/L. For practical consideration this was presumed to represent the equilibrium time for the adsorption of two metal ions under investigation. The maximum removal efficiency of 92.6% Pb and 80.1% Cd was achieved at an equilibrium period of 180 min.

The rate of adsorption which predict the contact period of adsorption can be determined using the Bhattacharya and Venkobachar equation:\[\text{ln} [1-U(t)] = -k_{ad} t\] \[\text{(2)}\]

where \(U(t) = \frac{(C_s - C_f)}{(C_s - C_i)}\)

Here, \(C_s\), \(C_f\), and \(C_i\) (mg/L) are the concentrations of the adsorbate initially, at any time \(t\), and at equilibrium, respectively. The plots of \(\text{ln}[1-U(t)]\) vs \(t\) (Figure 4) yielded straight lines, indicating the applicability of Bhattacharya and Venkobachar equation and explaining that the process followed first-order kinetics. The values of rate constants determined from the slope of the plots are \(2.721 \times 10^{-2}\) min\(^{-1}\) for Pb and \(2.346 \times 10^{-2}\) min\(^{-1}\) for Cd. The values of rate constants for the adsorption of Pb(II) and Cd(II) are comparable to those reported in the literature\(^{10}\).

Besides the adsorption at the outer surface of the adsorbent, there is also a possibility of intraparticle diffusion of metal ions from the bulk of the outer surface into the pores of the sorbent. This possibility was explored by plotting the amount of metal adsorbed vs \(t^{0.5}\) (Figure 5) which resulted an initial linear phase representing the film diffusion and subsequent curve, indicating intraparticle diffusion in the adsorption process. At an initial phase about 77.1% of Pb(II) and 63.5% of Cd(II) is adsorbed within a \(t^{0.5}\) value of 6 min and manifests an average uptake rate of about 6.93 and 6.42 mg/g min\(^{0.5}\), respectively. This is attributed to the instantaneous utilization of the most readily available adsorption sites on the adsorbent surface. The second phase may be attributed to a very slow diffusion of the adsorbed metals from the surface film into the micropores which are the least accessible sites of adsorption. This also stimulates a very slow rate of migration of metal ions from the liquid phase onto the adsorbent surface\(^{10}\).

The kinetic data were also tested for pore diffusion using Eq. (3)
\[ D_j = \frac{0.03}{r_{ad} \sigma^2} \]  

where \( r_{ad} \) is the time for half adsorption, \( r_c \) (cm) is the radius of the adsorbing particles and \( D_j \) is the diffusion coefficient. According to earlier workers, \( D_j \) value of the order of \( 10^{-13} \) \( m^2/s \) is indicative of pore diffusion and is the rate determining step. Since the values of \( D_j \) obtained for Pb(II) and Cd(II) were \( 6.582 \times 10^{-13} \) and \( 4.608 \times 10^{-13} \) \( m^2/s \), respectively; it was concluded that the process of adsorption of Pb(II) and Cd(II) on PCHY-FeO-COOH was pore-diffusion controlled. However, further experimental work is in progress to clarify this aspect.

The experimental data for the adsorption of metal ions at different sizes of adsorbent (0.508, 0.149, 0.106 and 0.074 mm) and at a fixed adsorbent dose (2 g/L) and initial metal concentration (100 mg/L) are shown in Figure 6. It can be observed that as the particle size decreased the adsorption of metal ion increased. As the particle size increased from 0.074 to 0.508 mm, the percentage of metal ion adsorbed decreased from 97.3 to 70.3 % in the case of Pb and 84.1 to 60.4 % in the case of Cd. The assumption that the smaller particle size offered comparatively large surface area results in a lower driving force per unit area remains very plausible.

The experiments with solution pH as a variable have also been carried out to determine the optimum pH range for maximum metal adsorption by the adsorbent material (Figure 7). The adsorption of metal increased with increase in pH up to a certain value and decreased with further increase in pH. The maximum adsorption took place in the pH range 5.0-8.0 for Pb(II) and 5.0-9.0 for Cd(II). The pHopt for the adsorbent was found to be 5.8 and below this pH, surface charge of the adsorbent is positive. When the initial pH of the reaction medium varied between 2.0 and 6.0, the final pH of the reaction medium remained between 1.2 and 4.8 for Pb and 1.6 and 5.2 for Cd. This indicates that as the metal ions are bound on the adsorbent, H+ ions from -COOH functional groups are released into the solution and it led to the conclusion that PCHyFeO-COOH probably acts as an acid form ion-exchanger. An increase in pH above \( pH_{opt} \) shows an increase in adsorption in which the surface of the sorbent is negatively charged and the sorbate species are still positively charged \( (\text{II}^+ \text{and MOH}^+) \). Above pH 6.0, where the adsorbent surface is negative and \( \text{II}^+ \) and MOH species are present in solution, the situation is electrostatically favourable for a higher uptake of metal ions. Decrease in adsorption at higher pH is due to the formation of soluble hydroxyl complexes. In the highly acidic medium, the adsorption of metal is hindered due to the electrical repulsion between \( \text{II}^+ \) species and protonated adsorbent surface.

In order to examine the effect of initial concentration on metal adsorption by PCHyFeO-COOH, experiments were conducted using concentrations varying from 50 to 700 mg/L at pH 6.0 and an adsorbent dose of 2 g/L. The results of the experiments are presented in Figure 8 as metal ion adsorbed \( (q_i) \) vs equilibrium metal ion concentration \( (C_e) \) at different temperatures. The adsorption isotherms are regular, positive and concave to the concentration axis. Initially the adsorption is quite rapid, which is followed by a slow approach to equilibrium at higher adsorbate concentrations. It is also observed that for the same equilibrium time, the adsorption is higher for greater values of initial metal ion concentration. Further, the uptake of Pb and Cd increased by increasing the temperature. This may be due to the dissolution of adsorbing species as well as changes in the size of pores of the adsorbent. The increased rate
of the intraparticle diffusion of metal ions into the pores of the adsorbent at higher temperature may also contribute to the increase in uptake because diffusion is an endothermic process\(^2\).

To evaluate the mechanistic parameters associated with the adsorption process, the adsorption data were analysed using the Langmuir and Freundlich isotherm models. The Langmuir model assumes uniform energies of adsorption into the surface and no transmigration of adsorbent in the plane of the surface. The Langmuir model is described by Eq. (4).

\[
\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad \ldots (4)
\]

where \(Q^0\) and \(b\) are Langmuir constants related to maximum adsorption capacity (monolayer capacity) and energy of adsorption, respectively. The plots of \(C_e/q_e\) vs. \(C_e\) give straight lines at each temperature (Figure 9) showing the applicability of Langmuir isotherm. Values of these constants are given in Table 1. The adsorption capacity \(Q^0\) is high for Pb-PCHyFeO-COOH system than for the Cd-PCHyFeO-COOH system. The values of \(Q^0\) increased with an increase in temperature, thereby indicating the process to be endothermic in nature. The thermodynamic parameters \(\Delta G^\circ\), \(\Delta H^\circ\) and \(\Delta S^\circ\) were computed using Eqs (5) and (6).

\[
\Delta G^\circ = RT \ln b \quad \ldots (5)
\]

\[
\ln b = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \ldots (6)
\]

The values of \(\ln b\) were plotted against \(1/T\) and found to be linear. Using the linear regression analysis, the \(\Delta H^\circ\) and \(\Delta S^\circ\) values were computed from the slope and intercept of the plots. Negative \(\Delta G^\circ\) values (Table 1) confirm the feasibility and spontaneous nature of the adsorption with a high preference of Pb and Cd for PCHyFeO-COOH. Positive \(\Delta H^\circ\) values indicate the en-

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**Figure 8** — The adsorption isotherms of Pb(II) and Cd(II) on PCHyFeO-COOH

**Figure 9** — The Langmuir plots for the adsorption of Pb(II) and Cd(II) on PCHyFeO-COOH
do thermic nature of the process while positive \( \Delta S^0 \) values reflect the affinity of the adsorbent material for the metal ions and suggest some structural changes in adsorbate and adsorbent.

The Freundlich isotherm is represented mathematically by Eq. (7)

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]

where \( K_f \) and \( 1/n \) are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. Linear plots of \( \log q_e \) vs \( \log C_e \) (Figure 10) show that adsorption of Pb(II) and Cd(II) onto PCHyFeO-COOH also follows Freundlich isotherm model. The values of \( K_f \) and \( 1/n \) for the two metals are given in Table 1. The values of \( 1/n \) between 0.1 and 1.0 represent good adsorption of metal ions onto PCHyFeO-COOH.

To find the competitiveness of metal adsorption on PCHyFeO-COOH, experiments were conducted using solutions containing Pb and Cd ions. The results of these experiments are given in Tables 2 and 3. The adsorption efficiency of the adsorbent material goes down by 8.5% for Pb in the presence of Cd (300 mg/L) and 19.5% for Cd in the presence of Pb (300 mg/L). The presence of Cd tended to reduce Pb adsorption, but the degree of suppression was less than that of Pb on Cd adsorption. Results of the present investigation are in good agreement with those of previous studies: the competitive effect of Pb on Cd adsorption are greater than those of Cd on Pb adsorption. It was observed that when solutions contain the same concentration of metal ions (50 mg/L), Pb exhibited the highest adsorption on PCHyFeO-COOH. For ions of the same valence, sorbent prefers the metal with higher atomic number.

The utility of the adsorbent material has been demonstrated by treating with synthetic wastewaters. The wastewaters from metallurgical industries may contain metals such as Zn, Cu, Al, Na, K, Ca and Mg along with
Pb and Cd. In order to examine the effect of these metal ions on Pb(II) and Cd(II) sorption by PCHyFeO-COOH, experiments were conducted with synthetic wastewaters containing metals like Zn, Cu, Al, Na, K, Ca, Mg, etc.

The composition of synthetic wastewaters is given in Table 4. The amount of adsorbent for the complete removal of Pb(II) and Cd(II) from 50 mL wastewater containing 25 mg/L metal (sample 1 of each metal) was found to be 150 and 250 mg, respectively; the corresponding amount of adsorbent for 50 mg/L metal was found to be 300 and 600 mg for sample 2 and 350 and 650 mg for sample 3. The results are in good agreement with those obtained from batch experiments mentioned above which indicate that the presence of other ions have no interference on the adsorption of metal ions by PCHyFeO-COOH.

Regeneration studies have been performed with (i) distilled water and (ii) 0.2 M NaCl solution. Only 11.7 % Pb(II) and 8.9 % Cd(II) desorption occurred in distilled water whereas 98.3 % Pb(II) and 90.1 % Cd(II) desorption were observed in 0.2 M NaCl. These results confirm the ion-exchange nature of adsorption process. After two cycles, the adsorption capacity of the adsorbent for Pb(II) and Cd(II) declined by 5 % and 6 % respectively. The recovery of Pb(II) in 0.2 M NaCl decreased from 98.3 % in the first cycle to 93.1 % in the third cycle whereas in the case of Cd(II) it decreased from 90.1 % to 84.2 %. The results show that the spent PCHyFeO-COOH can be effectively regenerated using 0.2 M NaCl. Column experiments to find out the effect of loading with various flow rates in removal process by the adsorbent are in progress.

Attempts have also been made to develop a model for predicting the adsorbent dose required to clean the wastewater and duration of replacement of adsorbent in

Table 2 — Competitive adsorption of lead in the presence of cadmium

<table>
<thead>
<tr>
<th>[Cd(II)] mg/L</th>
<th>Adsorption of Pb(II) in the absence of Cd(II)</th>
<th>Adsorption of Pb(II) in the presence of Cd(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/g %</td>
<td>mg/g %</td>
</tr>
<tr>
<td>50</td>
<td>46.33 92.66</td>
<td>42.0 84.16</td>
</tr>
<tr>
<td>100</td>
<td>46.33 92.66</td>
<td>45.85 91.70</td>
</tr>
<tr>
<td>200</td>
<td>46.33 92.66</td>
<td>44.5 89.14</td>
</tr>
<tr>
<td>300</td>
<td>46.33 92.66</td>
<td>42.0 84.16</td>
</tr>
</tbody>
</table>

Table 3 — Competitive adsorption of cadmium in the presence of lead

<table>
<thead>
<tr>
<th>[Pb(II)] mg/L</th>
<th>Adsorption of Cd(II) in the absence of Pb(II)</th>
<th>Adsorption of Cd(II) in the presence of Pb(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/g %</td>
<td>mg/g %</td>
</tr>
<tr>
<td>50</td>
<td>40.03 80.05</td>
<td>38.64 77.26</td>
</tr>
<tr>
<td>100</td>
<td>40.03 80.05</td>
<td>35.67 71.34</td>
</tr>
<tr>
<td>200</td>
<td>40.03 80.05</td>
<td>33.44 66.88</td>
</tr>
<tr>
<td>300</td>
<td>40.03 80.05</td>
<td>30.28 60.56</td>
</tr>
</tbody>
</table>

Table 4 — Composition of synthetic wastewater and the amount of adsorbent for complete removal of metals from 50 mL Solution

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>No. of samples</th>
<th>Composition (mg/L)</th>
<th>Amount of adsorbent (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
<td>1</td>
<td>Pb:25:Na4:10:Mg2:10:Ca2:10:NH4:1:10;</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Pb:50:Na4:10:Mg2:10:Ca2:10:NH4:1:10;</td>
<td>300</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>1</td>
<td>Cd:25:Na4:10:Mg2:10:Ca2:10:NH4:1:10;</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Cd:50:Na4:10:Mg2:10:Ca2:10:NH4:1:10;</td>
<td>600</td>
</tr>
</tbody>
</table>
Table 5 — Comparison between M/V values calculated and used

<table>
<thead>
<tr>
<th>Initial conc of metal, mg/L</th>
<th>Pb(II)</th>
<th>Cd(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>calculated</td>
<td>used</td>
</tr>
<tr>
<td>50</td>
<td>2.20</td>
<td>2.00</td>
</tr>
<tr>
<td>100</td>
<td>2.40</td>
<td>2.00</td>
</tr>
<tr>
<td>200</td>
<td>2.09</td>
<td>2.00</td>
</tr>
<tr>
<td>300</td>
<td>1.90</td>
<td>2.00</td>
</tr>
<tr>
<td>400</td>
<td>1.91</td>
<td>2.00</td>
</tr>
<tr>
<td>500</td>
<td>1.95</td>
<td>2.00</td>
</tr>
</tbody>
</table>

Table 6 — Regeneration data

<table>
<thead>
<tr>
<th>Cycles</th>
<th>Amount adsorbed mg/L</th>
<th>Amount adsorbed mg/L</th>
<th>Recovery %</th>
<th>Amount adsorbed mg/L</th>
<th>Amount adsorbed mg/L</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23.79</td>
<td>23.39</td>
<td>97.32</td>
<td>21.03</td>
<td>18.04</td>
<td>90.06</td>
</tr>
<tr>
<td>2</td>
<td>23.33</td>
<td>22.51</td>
<td>97.51</td>
<td>20.46</td>
<td>17.23</td>
<td>88.35</td>
</tr>
<tr>
<td>3</td>
<td>22.04</td>
<td>20.51</td>
<td>93.08</td>
<td>19.68</td>
<td>14.91</td>
<td>84.18</td>
</tr>
</tbody>
</table>

a batch reactor. When fresh adsorbent is used (q₀ = 0) and the mass balance equation the liquid phase to that adsorbed by the adsorbent:  

\[ V (C_e - C) = M (q - q₀) = M q \]  

At equilibrium  

\[ C_e = C \]

and  

\[ q = q_e \]

The Langmuir equation (Eq. 4) is applied to Eq. (8), gives Eq. (9).

\[ M = \frac{C_e - C}{V} = \frac{Q}{b C} \]

Equation (9) can help the engineers to determine the sorbent-solution ratio (g/L) for a given change in metal concentration from C_e to C. To test the robustness of the Eq. (9), the values of M/V for the selected sets of C_e and C values were calculated by using this equation. A comparison of the used and predicted values of M/V for sample values of C_e and C are shown in Table 5. Variation in calculated and used M/V values seems due to approximation in Q_e and b values in Eq. (4). Additional research is also warranted to test the applicability of the equation with respect to real industrial wastewaters.

Conclusions

The removal of Pb and Cd from aqueous solution seems feasible by adsorption onto polymer coated hydrous iron(III) oxide using a batch technique. Adsorption kinetic data indicate the applicability of first-order Bhattacharya and Venkobchar equation. Internal diffusion was found to be the rate limiting step. The surface charge on the adsorbent and the solution pH play a significant role in influencing the capacity of adsorbent towards metal ions. The optimum pH range for the removal of metal ions has been found to be 5-8 for Pb(II) and 5-9 for Cd(II). Thermodynamic parameters have been calculated and the adsorption data fits with both the Langmuir and Freundlich equations. Quantitative removal of Pb(II) and Cd(II) from synthetic wastewaters confirms the validity of the results obtained in batch-wise studies. Desorption studies reveal that the spent adsorbent can be regenerated using 0.2 M NaCl.

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