Kinetics of Pb(II) adsorption by polyacrylamide grafted sawdust

C Raji & T S Anirudhan*
Department of Chemistry, University of Kerala, Kariavattom, Trivandrum 695 581, India

Received 10 June 1996; accepted 4 December 1996

Lead(II) removal efficiency of polyacrylamide grafted sawdust has been investigated through laboratory experiments. Kinetic measurements have been made as a function of solution concentration of Pb(II) ions, pH and temperature. The slow step governing the rate of exchange is diffusion of ions through the exchanger particles. The equilibrium data fit well with the Langmuir isotherms. Thermodynamic parameters were also presented to predict the nature of adsorption. Adsorbent can be regenerated with acid and can then be reused.

Adsorption at solid-solution interface is an important means for controlling the extent of pollution due to metallic species of industrial effluents. The use of activated carbon and ion exchange resins is not suitable for developing countries due to their high capital and operational costs. Various low cost adsorbents such as onion skin, human hair, tea leaves and peat moss are known to adsorb Pb(II) ions from solutions in their native state and with suitable chemical treatment, the adsorption capacity can be significantly enhanced. Such adsorption characteristics have prompted many research workers to explore the possibility of using such chemically modified low cost materials as substrates for the more expensive ion exchange resins normally used for the removal of heavy metal pollutants from wastewaters.

Studies have been reported on the use of polymer grafted materials as an adsorbent for the removal of heavy metal ions from aqueous solutions. The use of polymer grafted materials for the removal of toxic heavy metals from wastewaters has been continued to attract considerable attention in recent years, particularly because they are capable of binding heavy metals by adsorption and ion exchange at higher temperatures. A limited study indicated the potential of surface modification of tree bark and tea leaves through polymerization in immobilizing the coloured water soluble polyphenols and improving physical characteristics of the adsorbents. Carboxylic functions substituted on the backbone of the polymer grafted materials increase the number and change the nature of sites capable of adsorbing metal ions in solution.

The huge deposit of sawdust around saw-mills has created problems in its disposal. Besides its utilisation in preparing packing materials it has also been recently used in water pollution control. In the present investigation, adsorption characteristics for the removal of Pb(II) ions from aqueous solutions onto polyacrylamide grafted sawdust have been studied.

Experimental Procedure

Sorbert—The starting material, sawdust (SD) of rubber wood (Hevea Brasiliensis) was used for the preparation of adsorbent. It was collected from a local timber industry, washed with distilled water and then dried. The product was grafted with polyacrylamide by using the procedure described by Shigetomi and Kojima. About 25 g SD was made to swell in 300 mL of an aqueous solution containing 2.5 g NN’ methylenebisacrylamide \([\text{CH}_2(\text{NHCOCH = CH}_2)]\) and 1.5 g potassium peroxy-disulphate. To the mixture then 7.5 g acrylamide \((\text{CH}_2 = \text{CH - CONHz})\) was added and the contents were stirred vigorously at 70°C. The polymerised product \([\text{SD - (CONHz)n - CONHz}]\) was then washed with water and dried at 80°C. The dried mass refluxed with ethylenediamine (25 mL) continuously for 8 h at 70°C. The product was then converted into the cation exchanger by treating one part by weight of the above material with equal parts by weight of succinic anhydride at pH 4 for 6 h. The excess succinic anhydride was washed out with 1, 4 dioxane and finally with ethanol, then dried. The dried polyacrylamide grafted sawdust, \(\text{SD - (CONHz)n - CONH(CH}_2)_2 - N\text{HCO(CH}_2)_2\text{COOH-(PGSD)}\) was sieved to get - 80 + 230 mesh size.
Characterization—The FTIR spectra of SD and PGSD were recorded on a Shimadzu FTIR-1801 spectrophotometer. The carboxyl stretching at 1710 cm⁻¹ and aromatic C–H stretching at 3035 cm⁻¹ are not affected in the SD and PGSD. However, the absence of methylene C–H stretching at 2970 cm⁻¹, hydroxyl stretching at 2615 cm⁻¹ and N–H stretching (amide) at 3430 cm⁻¹ in SD which is well pronounced in the PGSD is of significance. This observation clearly indicates the formation of polymeric chain (backbone) in the PGSD. The additional bands at 1658 cm⁻¹ (νC=O) and 1464 cm⁻¹ (νC–O) indicate the presence of COOH group in PGSD. Physical and surface properties of PGSD were carefully determined by standard methods. The characteristics of the adsorbent are: apparent density, 1.26 g/ml; moisture content, 2.1%; porosity, 0.49 mL/g; polymer content 19.3%; cation exchange capacity, 2.34 meq/g; surface area, 108 m²/g, and pH 5.9.

Adsorption experiments—Batch adsorption experiments were carried out by shaking 0.1 g PGSD with 50 mL aqueous solutions of lead nitrate of desired concentrations in different 100 mL stoppered conical flasks. Initial pH of the solution was adjusted with 0.05 M HNO₃ and 0.1 M NaOH using a pH meter. The samples were shaken at 125 rpm in a temperature controlled shaking machine. At the end of predetermined time intervals, the sorbate was centrifuged and supernatant was analysed for the remaining lead concentration using Perkin-Elmer 2380 Atomic Absorption Spectrophotometer.

Desorption experiments—To make the adsorption process more economical it was necessary to regenerate the spent adsorbent. After the attainment of equilibrium the supernatants were carefully decanted and desorption experiments were carried out by using (i) distilled water and (ii) aqueous medium of 0.5 M HCl. Experiments were performed by shaking 0.1 g spent adsorbent with 50 mL solutions. To regenerate, the same procedure was followed for three cycles. All the experiments were performed in duplicate and mean values were presented. Maximum deviation was ±5%.

Results and Discussion

Effect of adsorbent dosage—Adsorbent dosage is an important parameter because this determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The effect of adsorbent dosage (adsorbent prepared in different batches) was studied on Pb(II) removal keeping all other experimental conditions constant (Table 1). The results show that as the adsorbent concentration increases, percentage adsorption also increases, but the amount adsorbed per unit mass of the adsorbent decreases considerably. The decrease in unit adsorption with increase in the dose of adsorbent is basically due to adsorption sites remaining unsaturated during the adsorption reaction. It can be observed from the table that PGSD prepared in different batches produce the reproducible data with identical experimental conditions.

Effect of contact time and initial Pb(II) concentration—Fig. 1 shows that the removal of Pb(II) by PGSD increased from 24.3 mg/g (97.2%) to 84.3 mg/g (84.3%) by increasing concentration from 50 to 200 mg/L at pH 5. This shows that the removal of Pb(II) is highly concentration dependent. It is also clear that the equilibrium is achieved in 180 min and is independent of Pb(II) concentration. Initial portion of the curve is changed into a smooth curve and thereafter plateau region is reached. The removal curves

Table 1—Effect of adsorbent (prepared in different batches) dosage on Pb(II) removal (Pb(II) concn., 200 mg/L; pH, 5.0; agitation time, 3h; temperature, 30°C)

<table>
<thead>
<tr>
<th>Adsorbent dose, g/L</th>
<th>1st batch</th>
<th>2nd batch</th>
<th>3rd batch</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg/g</td>
<td>%</td>
<td>mg/g</td>
<td>%</td>
</tr>
<tr>
<td>2</td>
<td>88.40</td>
<td>88.4</td>
<td>87.90</td>
</tr>
<tr>
<td>4</td>
<td>47.60</td>
<td>95.2</td>
<td>47.90</td>
</tr>
<tr>
<td>10</td>
<td>19.52</td>
<td>97.6</td>
<td>19.38</td>
</tr>
<tr>
<td>15</td>
<td>13.21</td>
<td>99.1</td>
<td>13.16</td>
</tr>
</tbody>
</table>
are smooth and continuous indicating the formation of monolayer coverage of the adsorbate on the outer surface of the adsorbent17.

**Adsorption kinetics**—The effect of agitation time and temperature on Pb(II) removal by PGSD are shown in Fig. 2. The adsorption capacity increases from 84.3 to 95.2 mg/g with increase of solution temperature from 30 to 60°C indicating the process to be endothermic. The increase in uptake of metal ions with temperature may be due to the desolvation of the sorbing species and change in the size of the pores.

External mass transfer diffusion and intraparticle mass transfer diffusion models were used to evaluate the sorption kinetics. Intraparticle mass transfer diffusion model has been used successfully to describe the sorption of heavy metal ions by polymerised materials9. The possibility of intraparticle transport of adsorbate within the pores of polymerized material is expected because of the porous nature of the adsorbent18. In a rapidly stirred batch reactor, the adsorbate species are most probably transported from the solution to the solid phase through intraparticle transport which is often the rate limiting step in many adsorption processes19,20. In the present work, experimental conditions were set to study the particle diffusion mechanism only. Intraparticle diffusion was extensively studied: in this work the model chosen refers to the theories developed by Boyd et al21, and Reichenberg22. The adsorption kinetics are modelled according to the following equation:

\[ F = \frac{Q_t}{Q_e} = 1 - \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2Bt) \]  

(1)

where \( F \) is the fractional attainment of equilibrium at time \( t \), \( Q_t \) and \( Q_e \) are the amounts taken up at time \( t \) and equilibrium, respectively. \( B \) is the time co-ordinate of Boyd et al. equation and is expressed in terms of the effective diffusion coefficient \( D_e \) and particle radius \( r \) as

\[ B = \pi^2 \frac{D_e}{r^2} \]  

(2)

For the observed values of \( F \), corresponding \( Bt \) values as derived from Eq. (1) are obtained from Reichenberg's table22. The linearity test of \( Bt \) versus time plots is employed to distinguish between controlled rate of exchange. In the present system of investigation, the increase in the slope of the straight line plots (Fig. 3) and hence in the rate of exchange, with the increase in the temperature suggests that the rate of exchange is governed by the diffusion of exchanging ions within the exchanger particles. The values of the time co-ordinate \( B \) are determined as the slopes of the straight line plots using regression analysis. The values of effective diffusion coefficient \( D_e \) calculated from \( B \) and exchanger radius (Eq. 2) at 30, 40, 50 and 60°C are \( 8.23 \times 10^{-10}, 9.68 \times 10^{-10}, 10.29 \times 10^{-10} \) and \( 11.20 \times 10^{-10} \) cm²/s, respectively. The Arrhenius plot of \( \log D_e \) versus \( 1/T \) was found to be linear. The value of energy of activation, \( E_a \) as calculated from the slope of the plot is equal to 8.30 kJ/mol. The relatively low value of \( E_a \) suggests that Pb(II) adsorption is a diffusion controlled process23.

**Effect of pH**—Fig. 4 shows the effect of pH on the removal of Pb(II) from aqueous solution. At a pH of 2, only 40.5% of the total Pb(II) is ad-
sorbed and at a pH of 5 approximately 88.0% of the Pb(II) is removed. The extent of Pb(II) removal between a pH of 5 and 9 increased only marginally. Decreasing trend in adsorption is observed above pH 9. The effect of pH can be explained in terms of $pH_{zpc}$ of the sorbent. The $pH_{zpc}$ of PGSD was found to be 5.9, and below this pH surface charge of the sorbent is positive. On the other hand, at pH less than 5.9 the predominant lead species (Pb$^{2+}$ and Pb(OH)$^+$) are positively charged$^{24}$, and therefore, the uptake of metal in the pH range of 2-6 is a H$^+$-M$^{2+}$ exchange process. In PGSD, there is free -COOH group from which H$^+$ ions can be exchanged for cations in solutions.

Adsorption at a lower rate was observed at $pH > pH_{zpc}$ in which surface of the adsorbent is negatively charged and the sorbate species are still positively charged. As sorbent surface is negatively charged as well as the increasing electrostatic attraction between positively charged sorbate species and negative charged sorbent particles would lead to increase adsorption of metal ions$^{25}$. Decrease in removal of metal ions at lower pH is apparently due to the higher concentration of H$^+$ ions present in the reaction mixture which compete with Pb$^{2+}$ ions for the adsorption sites. Decrease in sorption beyond pH 9 is due to the formation of soluble hydroxy complexes.

Adsorption isotherm—Langmuir adsorption isotherm model was applied for adsorption equilibrium at all temperatures

$$\frac{C_e}{q_e} = \frac{1}{Q_0} + \frac{C_e}{Q_0 b}$$  \hspace{1cm} \ldots (3)

where $C_e$ is the equilibrium concentration (mg/L), $q_e$ is the amount adsorbed at equilibrium (mg/g) and $Q_0$ and $b$ are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The linear plots of $C_e/q_e$ versus $C_e$ suggest the applicability of Langmuir isotherms (Fig. 5). Table 2 contains the values of $Q_0$ and $b$ obtained by regression analysis. The equilibrium parameter $R_L$ has been calculated from the relationship

$$R_L = \frac{1}{1 + bC_0}$$  \hspace{1cm} \ldots (4)

where $C_0$ is the initial concentration (mg/L) and $b$ is the Langmuir constant (L/mg). The values of $R_L$ shown in Table 3, indicate that adsorption of Pb(II) on PGSD is a favourable process because $R_L$ values lies between 0 and 1.

Thermodynamic parameters were calculated from the variations of the thermodynamic distribution coefficient, $K_0$ with change in temperature. $K_0$ for the adsorption reaction was determined by the method of Biggar and Cheung$^{26}$ as applied by Varshney et al.$^{27}$, by plotting In $q_e/C_e$ versus $q_e$ and extrapolating to zero $q_e$ (Fig. 6). The standard free energy change, $\Delta G^0$ for the interaction of PGSD with Pb(II) was calculated as

$$\Delta G^0 = -RT \ln K_0.$$  \hspace{1cm} \ldots (5)

Table 2—Langmuir constants and thermodynamical parameters

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Langmuir constants</th>
<th>Thermodynamical parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>373.0</td>
<td>0.013</td>
</tr>
<tr>
<td>40</td>
<td>374.5</td>
<td>0.016</td>
</tr>
<tr>
<td>50</td>
<td>377.4</td>
<td>0.023</td>
</tr>
<tr>
<td>60</td>
<td>381.6</td>
<td>0.034</td>
</tr>
</tbody>
</table>

![Fig. 4—Effect of pH on the removal of Pb(II) by adsorption on PGSD](image1)

![Fig. 5—Langmuir plot for the adsorption of Pb(II) on PGSD](image2)
Table 3—Equilibrium parameters

<table>
<thead>
<tr>
<th>Initial concentration of Pb(II), mg/L</th>
<th>30°C</th>
<th>40°C</th>
<th>50°C</th>
<th>60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.609</td>
<td>0.555</td>
<td>0.468</td>
<td>0.374</td>
</tr>
<tr>
<td>100</td>
<td>0.439</td>
<td>0.384</td>
<td>0.306</td>
<td>0.230</td>
</tr>
<tr>
<td>200</td>
<td>0.281</td>
<td>0.237</td>
<td>0.181</td>
<td>0.129</td>
</tr>
<tr>
<td>250</td>
<td>0.238</td>
<td>0.199</td>
<td>0.149</td>
<td>0.107</td>
</tr>
</tbody>
</table>

Table 4—Desorption and regeneration data

<table>
<thead>
<tr>
<th>No. of cycles</th>
<th>Adsorption, mg/g</th>
<th>Desorption, mg/g</th>
<th>Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In distilled water</td>
<td>In 0.5M HCl water</td>
<td>In distilled water</td>
</tr>
<tr>
<td>1</td>
<td>24.8</td>
<td>2.01</td>
<td>2.01</td>
</tr>
<tr>
<td>2</td>
<td>23.9</td>
<td>1.83</td>
<td>1.83</td>
</tr>
<tr>
<td>3</td>
<td>22.7</td>
<td>1.36</td>
<td>1.36</td>
</tr>
</tbody>
</table>

After two cycles, the adsorption capacity of PGSD was reduced by 8.5% while recovery of Pb(II) decreased from 99.1% in the first cycle to 92.7% in the third cycle. A small fraction of sorbed Pb(II) not recoverable by regeneration presumably represents the Pb(II) which is bound through stronger interactions.

Conclusion

The present study shows that the adsorption capacity of PGSD can be effectively regenerated for further use by 0.5 M HCl.

References