Adsorption behaviour of Pb(II), Cd(II) and Zn(II) on NALCO plant sand

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Present investigation evaluates the adsorption of Pb(II), Cd(II) and Zn(II) ions on plant sand of National Aluminum Company, Orissa, India. The XRD pattern and FTIR spectra showed goethite, alumina and silica as the major phases in the sand. Effects of various parameters such as time, pH, temperature, metal ions and adsorbent concentrations were studied. The adsorption followed pseudo second order kinetics for all the three cations. The proton stoichiometry was dependent on the nature of the metal ion showing the order Zn(II)>Cd(II)>Pb(II). The adsorption was found to be in the order Zn(II)>Cd(II)> Pb(II) with loading capacities of 47.79, 42.2 and 22.8 mg g\(^{-1}\) of plant sand sample. The adsorption data was fitted to various models. The thermodynamic parameters (\(\Delta G^0\), (\(\Delta H^0\)) and (\(\Delta S^0\)) have been evaluated. The XRD patterns of Pb(II) adsorbed plant sand sample showed that the crystallinity of silica phase was affected with the appearance of (110) plane and disappearance of (011) plane. It also disturbed the (110) plane of goethite. Cd(II) adsorbed sample showed disappearance of (011) plane of silica phase and transformation of alumina phase Al\(_2\)O\(_3\) to \(\sigma\)-Al\(_2\)O\(_3\). The adsorption of Zn(II) showed prominence of (110) plane of goethite with disappearance of \(\sigma\)-Al\(_2\)O\(_3\) phase.

**Keywords:** Plant sand, Adsorption, Isotherms, Kinetics, Heavy metal ions, XRD

Heavy metals are generally considered as a threat toward human’s health and ecosystems because of their potentially high toxicity. Unlike organic pollutants, heavy metals do not undergo biological degradation and tend to accumulate in the organisms, thereby eventually entering the food chains. Lead and cadmium belong to the group of serious hazardous heavy metals. Due to their high toxicity various government agencies have imposed strict and more stringent environmental legislations on wastewater discharges. Removal of heavy metals from wastewater has been a subject of major concern to scientists for many years. Among various methods applied for the removal of colloidal and dissolved heavy metals from aqueous solutions, adsorption onto various materials including, natural, commercial and bioadsorbents are widely used. Some of the low-cost adsorbents for the removal of heavy metals like waste tea leaves\(^1\), agricultural by-products such as almond shells, olive stones, and peach stones\(^2\), biomass\(^3\), sediments of rivers\(^4\), bed sediments of river Ganga\(^5\) were used for removing various heavy metals. Recently, interest in low-cost, high-surface-area materials, especially metal oxides such as iron oxides, aluminum oxides and silica, with their unique applications, in adsorption and chemical catalysis, has been growing. Numerous researchers have used iron oxide as an adsorbent to treat heavy metals and organic compounds from wastewater\(^6-8\). Janssen et al.\(^9\) found that clay–Al hydroxide polymers (CAIHO) can bind heavy metals effectively, and may play an important role in the adsorption behaviour and metal binding capacity of soils. Esmaili et al.\(^10\) studied Zn adsorption on natural volcanic ash soil containing iron and aluminum. A low-cost adsorbent, iron oxide on activated alumina was developed by Huang et al.\(^11\) for removing heavy metals from wastewater. During treatment of bauxite by Bayer’s process, the coarse material from alkali digested ore is separated and mixed with red mud for disposal. This coarse material termed as Plant Sand generated in aluminum refineries comprising mainly of iron, aluminum and silica can be a good adsorbent. In this study the utility of NALCO Plant Sand of National Aluminum Company (NALCO), India, in removing Pb(II), Cd(II) and Zn(II) ions from aqueous solutions was examined. Though zinc is not toxic but its removal in some of hydrometallurgical solutions is essential especially before nickel elecro-winning.
Experimental Procedure

Plant sand sample was collected from NALCO, Orissa, India. The sample was ground and sieved to obtain -150 Mesh B.S.S (100% <100 μm). The sample was washed till a pH of 7.0 was obtained, filtered and dried in an air oven at 100ºC for 24 h. A weighed amount of the dried sample which is coded as NA, was subjected to tri-acid digestion for wet chemical analysis. Iron was analyzed volumetrically and other metal ions were analysed after proper dilutions by Atomic Absorption Spectrophotometer (Perkin-Elmer Model 2380). Nitrate salt of Pb, Cd and Zn (E-MERCK) were used as the heavy metal sources. Stock solutions of metal ions, prepared by dissolving their nitrate salt in distilled water, were taken as the adsorptive solution. All other chemicals were of analytical grade and used as received. In all experiments distilled water was used.

The X-ray diffraction (XRD) measurements were done over a range of 20 to 70º using Phillips Powder Diffractometer Model PW3710 with CoKα radiation at a scan speed of 8º min⁻¹. Surface area was measured with Quantasorb 1750 instrument. IR spectra of the plant sand sample was obtained using the instrument Model No. FTS-800.

The adsorption experiments were carried out in a horizontal shaker having provisions for temperature and agitation control. For each experiment 50 mL of metal ion solution of desired concentration and pH was taken in 100 mL stoppered conical flask and a weighed amount of adsorbent was added to it. The contents were stirred at 160 RPM for desired period of time at constant temperature. For fitting adsorption isotherm the data was generated at different initial concentrations of metal ions (50-500 mg L⁻¹) while keeping the adsorbent dose fixed (2 g L⁻¹). In order to test the reproducibility, some of the experiments were carried in duplicate and the reproducibility was found to be within ±2%. The pHₚₑₙ of prepared sample was determined following Balistrieri and Murray method. The chemicals used were of BDH and Merck grade.

Results and Discussion

Chemical analysis and characterization

The chemical analysis of a typical NALCO plant sand sample (coded as NA) showed it to contain iron (20%) and acid insolubles as major fractions. The other metal ions such as Ni, Cu and Co were less than 5 ppm with Cr as 0.45%. The major constituents present in the sample were iron, alumina and silica. The specific surface area of the sample was 73 m²g⁻¹.

The IR pattern of NA sample given in Fig. 1 shows bands at 710, 630, 450, 380 and 270 cm⁻¹. Since this material is a complex mixture of iron, aluminium and silicon oxides, peaks were assigned to the multiple phases. The band at 710 cm⁻¹ may be assigned to OH torsional mode overlapping with Al–O stretching vibrations. The bands observed at 630 and 450 cm⁻¹ are attributable to stretching and bending modes of AlO₆. Besides corresponding to AlO₆, the peak at 450 cm⁻¹ also corresponds to Si–O–Si bending mode. The IR bands at 380 and 270 cm⁻¹ correspond to Fe–O stretching vibrations of goethite.

Comparative study of adsorption behaviour of Pb(II), Cd(II) and Zn(II) on NA

Effect of contact time

The time data at 35ºC given in Fig. 2 shows that % adsorption of Pb(II), Cd(II) and Zn(II) increased up to 30 min and further increase in contact time did not change % adsorption indicating attainment of quasi equilibrium state. In all subsequent experiments, the equilibrium time was maintained at 30 min. The results show that the order of adsorption was Zn(II)>Cd(II)>Pb(II), 44.8, 43.07 and 32.21% of Zn(II), Cd(II) and Pb(II) ions at 30 min were adsorbed from the solutions. The ionic radii of Pb, Cd and Zn are 0.118, 0.097 and 0.074 nm, respectively. Normally, cations with larger ionic radii preferentially displace cations with smaller ionic radii. Based on ionic radii, the predicted order of bonding preference should have been: Pb(II) > Cd(II) > Zn(II). The adsorption pattern of Zn(II)>Cd(II)>Pb(II) for NA may be due to different types of adsorption sites (hydrophobic or nonionic versus ionic) that depend on the nature of the adsorbate and the adsorbent.
less on cation electro negativity. A trend for higher Zn(II) adsorption in a similar environment of Pb(II) and Zn(II) has also been reported for iron and aluminum oxides systems.

The time data upto 240 min was tested for four kinetic models given below:

Pseudo-first-order rate equation of Lagergren
\[ \log (q_e - q_t) = \log q_e - k_1 t / 2.303 \times t \] ... (1)

Pseudo-second-order rate equation
\[ t / q_t = 1 / k_2 q_e^2 + 1 / q_e t \] ... (2)

The intraparticle diffusion model
\[ q_t = k_d t^{1/2} + C \] ... (3)

The Elovich equation
\[ q_t = \alpha + \beta \ln t \] ... (4)

where \( q_e \) and \( q_t \) are the amounts of the metal ions adsorbed (mg g\(^{-1}\)) at equilibrium and at time \( t \) (min), respectively. \( k_1 \) is the adsorption rate constant (L min\(^{-1}\)) for 1st order kinetic, \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) is the rate constant of pseudo-second-order adsorption reaction. \( k_d \) is the intra particle diffusion rate constant (mgg\(^{-1}\)min\(^{-1/2}\)). \( \beta \) is the initial adsorption rate of Elovich equation (mg g\(^{-1}\)min\(^{-1}\)), and the parameter \( \alpha \) is related to the extent of surface coverage (mg g\(^{-1}\)) and activation energy for chemisorption.

The plots of (i) \( t / q_t \) versus \( t \), (ii) \( \log (q_e - q_t) \) versus \( t \), (iii) \( q_t \) versus \( \ln t \), and (iv) \( q_t \) versus \( t^{1/2} \) for adsorption of Pb(II), Cd(II) and Zn(II) onto NA were used to get the rate parameters according to Eqs (1-4). The plots for pseudo second order kinetics and Elovich kinetics are given in Figs 3 and 4 (for other two models the plots are not given). The kinetic parameters for four kinetic models and correlation coefficients of Pb(II), Cd(II) and Zn(II) under similar conditions were calculated from these plots and are listed in Table 1. From this data it is observed (i) pseudo second order reaction plots show straight lines with \( r^2 \) values of 0.99 for Pb(II), Cd(II) and Zn(II) (ii) the calculated \( q_e \) values obtained from pseudo second order kinetics were close to the experimentally obtained \( q_e \) values for the three metal ions supporting the pseudo second order reaction kinetics. The \( r^2 \) values for Elovich plots show \( r^2 \geq 0.9 \). In general the adsorption kinetics following the pseudo second order reaction kinetics agree with chemisorption as the rate-limiting mechanism through sharing or exchange of electron between sorbent and sorbate and Elovich equation shows both the chemisorption nature of adsorption as well as the heterogeneous surface of adsorbent. These results point towards chemisorption of all the metal ions on NA as well as the heterogeneous surface of NA.
Effect of pH

Solution pH has been identified as the most important variable governing metal adsorption. To study whether the sorption on NA depended on solution pH, metal uptake was studied at pH ranging from 2.0 to 6.0 (where chemical precipitation is avoided, so that metal removal could be related to the adsorption process) at a temperature of 35ºC. Metal ion uptake was strongly affected by pH of the metal ions solutions (Fig. 5). Metal ions uptake by NA increased as the pH increased. At a pH of 2.0, the percentage adsorption on NA is low for all three metal ions, as large quantities of protons compete with metal cations for the adsorption sites. In this case adsorption occurs by the electrostatic attraction. The increase in adsorption with increase of pH may also be explained on the basis of aqua complex formation of the oxides present in the NA and its subsequent acid–base dissociation at the solid–solution interface. The pH effect is also dependent on the surface morphology of the adsorbents. The major constituents of NA are SiO₂, FeOOH and Al₂O₃. The silica (SiO₂) in NA could adsorb either positive or negative contaminants depending on the pH of the solution. The central ion of silicates has an electron affinity, giving the oxygen atoms bound to it low basicity. This allows the silica surface to act as a weak acid, which can react with water, forming surface silanol (SiOH) groups. As a result, at low pH the silica surface is positively charged and at high pH values it is negatively charged. The zero point charge (pH_pzc) of silica is generally 2.0. Other solid materials such as, iron and alumina, also show this phenomenon of developing positive or negative charges depending on pH. Iron as FeOOH has a zero point charge at pH 7-7.8, while that of alumina (Al₂O₃) is at pH_pzc 8. This indicates that the maximum metal ions adsorption capacity of NA can be attributed to the electrostatic interaction of the adsorbate with surface silica, aluminum and iron sites. Pb(II) adsorption increases with increasing pH, with a sharp rise occurring between pH 3 and 5 whereas in case of Cd(II) and Zn(II) % adsorption sharply increases between pH of 3 and 4. To have an insight into the chemical adsorption process the PZC of the material was calculated in presence of the three cations. The PZC of the NALCO plant sand samples was found to be 4.99 which is shifted slightly to higher pH (Fig. 6) in presence of Pb(II), Cd(II) and Zn (II) with the values as 5.2, 5.75 and 5.95 respectively. This confirms the electrostatic attraction between the surface and the metal ions.

Effect of initial metal ion concentration

50 mL of metal ion solutions of different concentrations ranging from 50 to 500 mg L⁻¹ were contacted with 2 g L⁻¹ of adsorbent at a pH of 4.0, at 35ºC for a period of 30 min. The % adsorption was in the order Zn(II)>Cd(II)>Pb(II) within the wide range of initial metal ion concentrations. To quantitatively estimate amount of metal ion adsorbed, the loading capacities were calculated at all initial metal ion

| Table 1—Kinetic parameters for adsorption of Pb(II), Cd(II) and Zn(II) on NA |
|-----------------|-----------------|-----------------|
|                 | Pb(II) | Cd(II) | Zn(II) |
| q<sub>exp</sub> | 17.55  | 26.9   | 26.15  |
| Pseudo 1<sup>st</sup> order |
| k₁ (min⁻¹)    | 1.93   | 1.33   | 3.86   |
| q<sub>e</sub>  | 3.39   | 9.5    | 9.89   |
| r²             | 0.84   | 0.86   | 0.95   |
| Pseudo 2<sup>nd</sup> order |
| k₂ (g mg⁻¹ min⁻¹) | 1.54  | 0.38   | 1.05   |
| q<sub>e</sub>  | 17.69  | 27.17  | 26.31  |
| r²             | 0.99   | 0.99   | 0.99   |
| Intraparticle diffusion |
| kₖ (g mg⁻¹ min⁻¹/²) | 24.38 | 67.81  | 54.45  |
| C               | 14.17  | 16.69  | 19.16  |
| r²             | 0.86   | 0.94   | 0.69   |
| Elovich model |
| α (mg g⁻¹)   | 12.59  | 12.75  | 15.05  |
| β (mg g⁻¹ min⁻¹) | 0.91 | 2.435  | 2.193  |
| r²             | 0.97   | 0.97   | 0.90   |
concentrations and are given in Fig. 7. It shows that the amount of Pb(II) adsorbed per gram of material was \(~22.8\) mg when the initial Pb(II) concentration was \(300\) mg \(L^{-1}\) and with further increase in its concentration to \(500\) mg \(L^{-1}\), no change in loading capacity was observed. However, for Cd(II) and Zn(II) the maximum loading capacities of \(42.2\) and \(47.79\) mg g\(^{-1}\) of NA were obtained with the initial metal ion concentration of \(450\) mg \(L^{-1}\).

**Proton stoichiometry (\(\chi\))**

Quantitative information on the relation between the adsorption of metal ions and the release of protons can be obtained by linearization of a general overall mass action equation for sorption, including hydrolysis, adsorption, and exchange reactions \(27\).

\[
\log[q_e]/[S] [C_e] = (\chi) p\mathbf{H} + \log K_p \quad \ldots (5)
\]

where \(q_e\) defined as earlier, \([S]\) is the concentration of vacant sites, \(C_e\) is the equilibrium concentration of adsorbate in mgL\(^{-1}\), \(\chi\) is the proton stoichiometry, and

\(K_p\) is an overall equilibrium constant. If \(K_p\) is independent of \(p\mathbf{H}\), then the value of \(\chi\), obtained from a graph of \(\log([q_e]/[C_e])\) against \(p\mathbf{H}\) (Kurbatov plot), indicates the overall proton stoichiometry of the adsorption equilibrium \(28\).

The data corresponding to effect of initial concentration except at low concentration (50 mg \(L^{-1}\)) of adsorbate was taken into consideration for calculating proton stoichiometry. The \(\log([q_e]/[C_e])\) values were plotted against the final \(p\mathbf{H}\) values obtained at 30 min with varying initial metal ion concentrations. From the slope of plots given in Fig. 8, the values of \(\chi\) were estimated to be 0.63, 0.77 and 1.03 for Pb(II) Cd(II) and Zn(II) respectively. A higher proton stoichiometry for Zn(II) as compared to Pb(II) has been reported for goethite \(28\).

**Effect of temperature**

A series of experiments were conducted at different temperatures (35, 45, 55 and \(65^\circ\)C) and at various \(p\mathbf{H}\) values (Figs 9-11) while keeping rest of parameters as: adsorbent concentration 2 g \(L^{-1}\), adsorbate concentration 100 mg \(L^{-1}\) and time 30 min. Increase of temperature from 35 to \(65^\circ\)C increased the sorption of all the three metal ions, indicating the process to be endothermic \(29\). This effect is characteristic of a chemical reaction or bond being involved in the adsorption process \(30\). However from Fig. 11, it is observed that the adsorption of Zn(II) on NA is more affected by higher temperature at higher \(p\mathbf{H}\) as compared to Pb(II) and Cd(II) adsorptions.

**Thermodynamic parameters**

The mechanism of sorption may be determined through the thermodynamic quantities such as change in free energy \((\Delta)G^0\), change in enthalpy of adsorption
Fig. 9—Effect of temperature at various pH on Pb(II) adsorption on NA sample. Conditions: Adsorbent conc. 2 g L\(^{-1}\), adsorbate conc. 100 mg L\(^{-1}\) and time 30 min.

Fig. 10—Effect of temperature at various pH on Cd(II) adsorption on NA sample. Conditions: Adsorbent conc. 2 g L\(^{-1}\), adsorbate conc. 100 mg L\(^{-1}\) and time 30 min.

Fig. 11—Effect of temperature at various pH on Zn(II) adsorption on NA sample. Conditions: Adsorbent conc. 2 g L\(^{-1}\), adsorbate conc. 100 mg L\(^{-1}\) and time 30 min.

Fig. 12—Vant’ Hoff plots for Pb(II), Cd(II) and Zn(II) adsorption on plant sand. Conditions: Adsorbent conc. 2 g L\(^{-1}\), adsorbate conc. 100 mg L\(^{-1}\), time 30 min and pH 5.23.

\((\Delta)H^0\) and change in entropy \((\Delta)S^0\). Thermodynamic parameters were calculated at pH 5.23 at various temperatures and initial metal ion concentrations of 100 mg L\(^{-1}\).

The free energy of adsorption reaction is given by the following equation:

\[(\Delta)G^0 = -RT \ln K_c \quad \ldots \ (6)\]

where \(R\) is the gas constant, \(T\) is the temperature (in Kelvin) and \(K_c\) is distribution coefficient which is determined as:

\[K_c = q_e/C_e \quad \ldots \ (7)\]

The values of \((\Delta)H^0\) and \((\Delta)S^0\) were determined from the Van’t Hoff equation as given below.

\[
\log K_c = (\Delta)S^0 / 2.303R - (\Delta)H^0 / 2.303RT \quad \ldots \ (8)
\]

From the slopes and intercepts of the plots between Log \(K_c\) and \(1/T\), \((\Delta)H^0\) and \((\Delta)S^0\) were calculated and are given in Table 2. Typical Vant’ Hoff plots at a pH of 5.23 for the three metal ions are shown in Fig. 12. The positive value of \((\Delta)H^0\) confirms the endothermic\(^{31}\) adsorption of all the three metal ions. The positive \((\Delta)S^0\) values reflect that significant change occurs in the internal structure of adsorbent during adsorption of metal ions in both the samples. Heat of adsorption and entropy values of some adsorbents\(^{32-34}\) are also compared in Table 2.

**Isotherm models**

The adsorption data obtained for variation of metal ion concentrations were treated using Langmuir, Freundlich and Temkin isotherm models as given by Eqs (9) to (11).

Langmuir \(C_e/q_e = 1/(bq_m) + (1/q_m)C_e \quad \ldots \ (9)\)
Freundlich \( q_e = K_F C_e^n \) \hspace{1cm} \ldots (10)

Temkin isotherm \( q_e = RT/b \ln A + RT/b \ln C_e \) \hspace{1cm} \ldots (11)

According to Hall et al.\(^{35}\), the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter \( R_L \), expressed by Eq. (12).

\[
R_L = 1/(1 + bC_e) \hspace{1cm} \ldots (12)
\]

where \( q_e \) and \( C_e \) have been defined earlier and \( K_F \) and \( 1/n \) are constants indicating the sorption capacity and the sorption intensity, respectively. The Freundlich constant, ‘\( n \)’ indicates the degree of favourability of adsorption. \( RT/b = B \) related to the heat of adsorption and \( A \) to the equilibrium binding constant \( (L \text{ mg}^{-1}) \) corresponding to the maximum binding energy are Temkin isotherm constants. \( R \) is the universal gas constant \( (8.314 \text{ J mol}^{-1} \text{ deg}^{-1}) \). The validity of the Temkin theory, based on chemisorption on energetically heterogeneous surfaces, introduces the possibility of adsorbate/adsorbate interactions.

The experimental data of Fig. 9 was fitted to Eqs (9) to (11). All the three model equations showed goodness-of-fit for Cd(II) and Zn(II) (Table 3).

![Graph](image-url)

**Table 2—Thermodynamic parameters:** Conditions: Adsorbent conc. 2 g L\(^{-1}\), adsorbate concentration 100 mg L\(^{-1}\), pH 5.23 and time 30 min.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>( (\Delta) H^0 ) (kJ mol(^{-1}))</th>
<th>( (\Delta) S^0 ) (J mol(^{-1}) deg(^{-1}))</th>
<th>( (\Delta) G^0 ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35(^{\circ})C</td>
<td>45(^{\circ})C</td>
<td>55(^{\circ})C</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>6.376</td>
<td>18.14</td>
<td>-0.76</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>9.34</td>
<td>29.82</td>
<td>-0.18</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>23.76</td>
<td>75.48</td>
<td>-0.53</td>
</tr>
</tbody>
</table>

**Table 2**—Thermodynamic parameters: Conditions: Adsorbent conc. 2 g L\(^{-1}\), adsorbate concentration 100 mg L\(^{-1}\), pH 5.23 and time 30 min.

<table>
<thead>
<tr>
<th>Present study</th>
<th>At pH 5.23</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
<td>11.58</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>11.71</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>20.44</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>At pH 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
</tr>
<tr>
<td>Cd(II)</td>
</tr>
<tr>
<td>Zn(II)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>At pH 3.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(II)</td>
</tr>
<tr>
<td>Cd(II)</td>
</tr>
<tr>
<td>Zn(II)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Red mud(^{32})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(II)</td>
</tr>
<tr>
<td>Zn(II)</td>
</tr>
</tbody>
</table>

Table 2—Thermodynamic parameters: Conditions: Adsorbent conc. 2 g L\(^{-1}\), adsorbate concentration 100 mg L\(^{-1}\), pH 5.23 and time 30 min.

However, the adsorption data for Pb(II) fitted to Langmuir isotherms (Fig. 13) only. The parameters calculated from the three isotherms are given in Table 3.

The values of Langmuir equilibrium coefficient, \( b \), were found to be of same magnitude \((0.01 \text{ Lg}^{-1})\) for Cd(II) and Zn(II) whereas it differed for Pb(II) adsorption \((0.11 \text{ Lg}^{-1})\) indicating that lead adsorption process involves more heat of adsorption. The
Langmuir monolayer capacity, $q_m$, values were found to be 21.78, 51.28 and 58.13 mg g$^{-1}$ for Pb(II), Cd(II) and Zn(II) respectively. The separation factor $R_L < 1$ for all the metal ions, indicate that all the metal ions prefer to be in the bound state with surfaces. The loading capacities for other natural occurring adsorbent$^{32,34,36,37}$ along with the adsorbent used in the present study are compared in Table 4. The Freundlich plot does yield a linear curve for Cd(II) and Zn(II), the curve seems to bend slightly upwards at higher values of $C_e$, because adsorption is approaching a maximum value, indicating almost complete monolayer coverage of the adsorbent particles.

**XRD studies of the metal ions adsorbed NA sample**

With a view to study the effect of metal ions adsorption on the crystalline phases of NA sample, Table 4—Comparative table for Langmuir monolayer capacity of different natural occurring materials

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Pb(II)</th>
<th>Zn(II)</th>
<th>Cd(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sericitic pyrophyllite$^{36}$ (SP)</td>
<td>32.5</td>
<td>—</td>
<td>13.03</td>
</tr>
<tr>
<td>Red mud$^{32}$</td>
<td>—</td>
<td>14.51</td>
<td>13.03</td>
</tr>
<tr>
<td>Rice husk$^{37}$</td>
<td>11.0</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Chromite mine overburden$^{33,34}$</td>
<td>27.54</td>
<td>22.47</td>
<td>—</td>
</tr>
<tr>
<td>Nalco plant sand (present work)</td>
<td>21.78</td>
<td>51.28</td>
<td>58.13</td>
</tr>
</tbody>
</table>

Fig. 14—XRD patterns of (a) NALCO plant sand sample (NA) and metal ions adsorbed NALCO plant sand samples (NA) (b) Pb(II), (c) Cd(II) and (d) Zn(II).
the Pb(II), Cd(II) and Zn(II) adsorbed NA surfaces were obtained under the experimental conditions for maximum loading capacities. The solids were separated after filtration, washed with distilled water till free of soluble metal ions and dried in an air oven at 100°C for 24 h. The XRD patterns of these samples along with original NA sample are shown in Fig. 14. The XRD pattern of NA shows the presence of goethite, Al₂O₃, σ-Al₂O₃ and silica (JCPDS, 1980, File No 29-713, 2000: 71-1684; 47-1292; 81-0067). The goethite seems to be disordered because of the weak reflection at d-value of 4.18 Å (110) plane which should have a RI (relative intensity) of 100% in pure well-crystallized goethite. It may be due to occlusion of other metal ions in goethite matrix. The Al₂O₃ reflections at d-values of 2.61, 2.37 and 1.66 Å (JCPDS 2000: 71-1684) are all strong indicating that Al₂O₃ is also the dominant component of the sample. The reflections at 3.97 and 3.18 Å are characteristic peaks for SiO₂ (JCPDS, 2000; 81-0067).

From the XRD patterns of the metal ion loaded samples, it is observed that the major peaks at d-values of 3.97, 3.52, 2.61, 2.44, 2.15, 1.80 and 1.66 Å remain more or less undisturbed. For Pb(II) adsorbed sample, the peaks corresponding to goethite at 4.16 Å (110 plane) and to silica at d-value of 3.16 (011 plane) disappeared. For Cd(II) adsorbed NA sample, the intensity of the peak corresponding to σ-Al₂O₃ phase at d-value of 4.59 Å (111 plane) increased to five times, one new peak at d-value of 2.85 Å (220 plane) corresponding to σ-Al₂O₃ appeared and the peak at d-value of 3.16 Å corresponding to silica phase disappeared. For Cd(II) adsorbed NA sample, the intensity of the peak corresponding to σ-Al₂O₃ phase at d-value of 4.59 Å (111 plane) increased to five times, one new peak at d-value of 2.85 Å (220 plane) corresponding to σ-Al₂O₃ appeared and the peak at d-value of 3.16 Å corresponding to silica phase disappeared. In case of Zn(II) adsorbed sample peak at d-value of 4.59 Å corresponding to σ-Al₂O₃ phase disappeared and the peak corresponding to goethite at 4.16 Å became prominent.

Conclusions
The plant sand sample obtained from National Aluminum Company comprised of goethite, alumina and silica phases. The adsorption data for Pb(II), Cd(II) and Zn(II) was generated under different experimental conditions by varying time, pH, temperature, concentration of metal ions and adsorbent. The time data of three metal ions fitted to pseudo second order kinetics. With the increase of pH from 2 to 5.23 and adsorbent concentration from 1 to 2.5 g L⁻¹, the % adsorption increased for all the three metal ions. From the variation in initial concentration the maximum loading capacities of 47.79, 42.2 and 22.8 mg g⁻¹ were estimated for Zn(II), Cd(II) and Pb(II) respectively. The proton stoichiometry was found to be dependent on nature of the metal ion showing the order Zn(II)>Cd(II)>Pb(II) with the values of proton stoichiometry constant χ as 0.63, 0.77 and 1.03 for Pb(II) Cd(II) and Zn(II) respectively. The positive values of (Δ)H° confirmed the endothermic sorption of all the three metal ions while the positive (Δ)S° values reflected that significant changes occurred in the internal structure of adsorbent during adsorption of metal ions. For Pb(II) adsorbed sample, the peaks corresponding to goethite at 4.16 Å (110 plane) and to silica at d-value of 3.16 (011 plane) disappeared. For Cd(II) adsorbed NA sample, the intensity of the peak corresponding to σ-Al₂O₃ phase at d-value of 4.59 Å (111 plane) increased to five times, one new peak at d-value of 2.85 Å (220 plane) corresponding to σ-Al₂O₃ appeared and the peak at d-value of 3.16 Å corresponding to silica phase disappeared. In case of Zn(II) adsorbed sample peak at d-value of 4.59 Å corresponding to σ-Al₂O₃ phase disappeared and the peak corresponding to goethite at 4.16 Å became prominent.

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