Equilibrium and kinetic studies for Cd(II) adsorption from aqueous solution on *Terminalia catappa* Linn leaf powder biosorbent

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*Terminalia catappa* Linn (TCL) leaf (almond leaf) powder was tested as a biosorbent in a batch adsorption system. The samples with and without Cd(II) adsorption were characterized using FTIR and SEM-EPMA techniques. Loading of Cd(II) onto TCL powder resulted in shift of various band positions (5 to 51 cm\(^{-1}\)) in the FTIR spectrum. The electron probe microanalyzer (EPMA) of Cd(II) loaded powder showed that Cd(II) was not uniformly distributed on the surface but only on specific sites. The experimental parameters chosen for adsorption studies were: pH (2.0 to 6.0), contact time (5 to 120 min), adsorbate concentration (50 to 500 mg L\(^{-1}\)), adsorbent concentration (0.25 to 5.0 g per 50 mL adsorbate), anions and Pb(II) concentration. With the increase in pH from 2.0 to 4.0, Cd(II) adsorption increased from 0.86 to 13.79 mg g\(^{-1}\) and with the further increase in pH to 5.5 only marginal increase to 14.12 mg g\(^{-1}\) was observed. Presence of chloride, sulphate or Pb(II) adversely affected Cd(II) adsorption onto TCL. The kinetics of adsorption could be best described by the pseudo-second-order equation. The three equilibrium models namely, Langmuir, Freundlich and Redlich-Peterson fitted well to the isothermic experimental data for TCL with regression coefficients of > 0.97. The maximum uptake capacity of the biosorbent was estimated to be 35.83 mg g\(^{-1}\).

**Keywords:** *Terminalia catappa* Linn leaf powder, Cadmium(II), Adsorption, Kinetics, Isotherms

The major toxic metal ions hazardous to humans as well as other forms of life are Cr, Fe, Se, V, Cu, Co, Ni, Cd, Hg, As, Pb, Zn etc. These heavy metals are of specific concern due to their toxicity, bio-accumulation tendency and persistency in nature. Major sources of heavy metal ion contamination in the environment are effluents from industries like batteries manufacture, metal extraction, surface finishing, paints, automotive, metal finishing, electroplating, electric cable manufacturing, tannery, steel and textile. Cd is highly toxic and its accumulation in human body causes erythrocyte destruction, nausea, salivation, diarrhea, muscular cramps, renal degradation, chronic pulmonary problems and skeletal deformation\(^1\). “Itai-Itai” disaster occurred due to cadmium contamination in Jintsu river of Japan\(^4\). The permissible limit of Cd in industrial discharges is set at 0.2 mg L\(^{-1}\) by the Ministry of Environment and Forests (MOEF), Government of India\(^4\). As per WHO’s recommendation, the maximum permissible limit of Cd in drinking water is 0.005 mg L\(^{-1}\). Therefore, the Cd in the effluents needs to be removed before discharge. Among the various water-treatment techniques described, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness\(^5\). The search for low-cost adsorbents that have metal binding capacities has intensified and materials locally available in large quantities such as natural materials\(^6-9\), agricultural\(^10-15\) and industrial wastes\(^16-24\) can be utilized as low-cost adsorbents. In recent years a number of studies have been carried out using leaves of various trees\(^25-29\). The biosorption on dried leaves is attributed to their protein, carbohydrates and phenolic compounds which have metal binding functional groups such as carboxyl, hydroxyl, sulfate, phosphate and amino groups. A scan of literature has indicated that no work has been reported on cadmium adsorption using *Terminalia catappa* Linn (TCL) leaf powder. In view of abundant availability of these leaves, it was thought worthwhile to carry out a systematic study to assess the potential use of
untreated *Terminalia catappa* Linn (TCL) leaf powder for removal of cadmium from aqueous solution.

**Experimental Procedure**

**Materials**

The green *Terminalia catappa* Linn (TCL) leaves were collected from trees available at the Institute of Minerals and Materials Technology, Bhubaneswar, India. The collected leaves were washed with tap water several times till the wash water contained no dirt particles followed by rinsing with distilled water. The washed leaves were then completely dried in sunlight for two weeks. The dried leaves were ground using domestic mixer blender. The powdered leaves of -75 µm particle size without any further pretreatment were used in the present studies.

Stock solution of cadmium concentration 1000 mg L\(^{-1}\) was prepared by dissolving 4.56 g of 100% 3CdSO\(_4\cdot8H_2O\) (Loba-chemie Indoaustranal Co.) in 2000 mL of distilled water. The pH of solutions for adsorption experiments was adjusted with 0.1 N HCl or NaOH.

**Biosorption procedure**

Biosorption experiments were performed at room temperature (30±1°C) in a water bath shaker (Remi make) at constant speed using 100 mL Borosil conical flasks containing 50 mL solution of different cadmium concentrations (50 to 500 mg L\(^{-1}\)). After 30 min of contact time (according to the preliminary sorption dynamics tests with 0.25 g *Terminalia catappa* Linn leaves biomass equilibrium was reached in 30 min) the reaction mixture was separated. The metal content in the solution was determined using Atomic Absorption Spectrometer (Perkin-Elmer Analyst 200, USA) at a wavelength of 228.80 nm. The amount of metal adsorbed by TCL leaves was calculated from the differences between initial Cd(II) concentration and metal content left in solution after adsorption using the following equation:

\[
q_t = (C_0 - C_f)V/m
\]

where \(q_t\) is the metal uptake (mg g\(^{-1}\)); \(C_0\) and \(C_f\) are the initial and final metal concentrations in the solution (mg L\(^{-1}\)), respectively; \(V\) the solution volume (L); \(m\) is the mass of biosorbent (g). For varying the experimental parameters, one parameter was changed at a time while keeping the rest constant.

**Instrumental analysis**

The adsorbent *Terminalia catappa* Linn (TCL) was characterized by FT-IR spectrometry both before and after Cd(II) adsorption using Spectrum GX of Perkin-Elmer, USA spectrophotometer in the range of 400 to 4000 cm\(^{-1}\) with a resolution of 1 cm\(^{-1}\) using 4 scans with background subtraction. For SEM-EPMA studies the powdered samples before and after cadmium adsorption were taken over a stud putting double adhesive carbon tape. The samples were then coated with gold through a gold sputter (JEOL, JFC-1100) and examined under Electron Microprobe (JEOL, JXA-8100) employing 20 kV and 10 nA current. The surface area measurement was carried out by BET method using CHEMBET 3000 (Quantachrome, USA) instrument by nitrogen adsorption-desorption measurements. Prior to analysis, samples were degassed at 110°C under nitrogen flow. Surface area of TCL obtained was 8.4 m\(^2\)g\(^{-1}\).

**Results and Discussion**

**Characterization of adsorbent with and without Cd(II) loading**

**FTIR studies**

FTIR spectra of virgin and cadmium loaded TCL is shown in Fig. 1. The peaks identified related to virgin TCL are as follows: the intense and broad absorption band around 3490 cm\(^{-1}\) can be assigned to OH stretching of hydroxyl group. As the frequency of free OH groups is sharp and is located around 3500 cm\(^{-1}\), these vibrations are associated with hydrogen bonds and thus the surface OH groups probably interact with water molecules adsorbed by the adsorbent, as suggested by Zawadzki\(^{31}\). The bands at 2970, 2930, 2849 cm\(^{-1}\) denote the presence of stretching C-H vibrations in CH\(_2\)\(^{32}\) or C=CH group. The band at 1739 cm\(^{-1}\) can be attributed to the...
presence of stretching C=O vibrations arising from groups such as lactone, quinone and carboxylic acids. The bands at 1664 and 1462 cm\(^{-1}\) may be due to the asymmetric and symmetric stretching COO\(^-\) vibrations or to skeletal C=C aromatic vibrations. The band at 1173 cm\(^{-1}\) is due to C=S stretching vibration. The bands at 1248 and 1080 cm\(^{-1}\) are compatible with absorptions due to S=O and S-O stretching in species such as HSO\(_4^-\) and SO\(_4^{2-}\). After Cd(II) adsorption, the bands shifted to lower values (5 to 41 cm\(^{-1}\)) as shown in Table 1. The significant changes in the wave numbers of various bands suggest that hydroxyl, C=O and C-O groups could be involved with adsorption.

**SEM studies**

The scanning electron micrograph (SEM) of the virgin TCL powder is shown in Fig. 2a. The surface seems to be complex and heterogeneous. After Cd(II) adsorption the surface morphology changed (Fig. 2b). Agglomeration of particles is observed. X-ray image map of the Cd(II) loaded powder (Fig. 2c) shows pixel concentration of Cd only on few of the powder grains, suggesting thereby adsorption of Cd(II) only by selective grains.

**Adsorption studies**

**Influence of solution pH**

It is well known that the pH of the medium affects the solubility of metal ions, thus pH is an important factor in metal adsorption. The effect of solution pH on adsorption of Cd(II) was studied in the range of 2.2 to 7.0. The pH of the medium affected the solubility of metal ions; therefore, pH is an important parameter to be considered.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q(_m) (mg g(^{-1}))</td>
<td>35.84</td>
</tr>
<tr>
<td>b (L mg(^{-1}))</td>
<td>0.03</td>
</tr>
<tr>
<td>R(^2)</td>
<td>0.99</td>
</tr>
<tr>
<td>K(_f) (mg(^{1-1/n})L(^{-1})g(^{-1}))</td>
<td>4.33</td>
</tr>
<tr>
<td>n</td>
<td>2.79</td>
</tr>
<tr>
<td>R(^2)</td>
<td>0.98</td>
</tr>
<tr>
<td>A (L mg(^{-1}))</td>
<td>1.0</td>
</tr>
<tr>
<td>B (L mg(^{-1}))</td>
<td>0.04</td>
</tr>
<tr>
<td>g</td>
<td>0.96</td>
</tr>
<tr>
<td>R(^2)</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Table 1.—Langmuir, Freundlich and Redlich-Peterson isotherm parameters

Fig. 2—Electron micrographs of TCL. (2a) original powder, (2b) and (2c) Cd(II) loaded powder.
parameter on adsorption of metal ions from aqueous solutions. As shown in Fig. 3 the uptake of Cd(II) depends on pH, increasing with the increase in pH from 2.0 to 5.5. With the increase in pH from 2.0 to 4.0, Cd(II) adsorption increased from 0.86 to 13.79 mg g$^{-1}$ and with the further increase in pH to 5.5 only marginal increase to 14.12 mg g$^{-1}$ was observed. Low adsorption at pH 2 could be due to the competition between hydrogen and Cd(II) ions on the adsorption sites. As the pH increased, the ligands such as carboxylate groups in Terminalia catappa L. would be exposed, increasing the negative charge density on the biomass surface, thereby increasing the attraction of metallic ions with positive charge and allowing the adsorption onto the cell surface. Similar trend was reported for the adsorption of Cd(II) onto coconut copra meal$^{36}$ and on husk of Lathyrus sativus$^{10}$.

**Effect of adsorbent dosage**

Figure 4 shows the effect of adsorbent dosage on the removal of cadmium from a solution containing 100 mg L$^{-1}$ of cadmium with different amounts of adsorbent at equilibrium conditions. The adsorption capacity decreased from 14.12 to 0.91 mg g$^{-1}$ with an increase in adsorbent dosage from 0.25 to 5 g per 50 mL of adsorbate solution at an initial Cd concentration of 100 mg L$^{-1}$. The decrease in the uptake capacity was due to availability of less amount of cadmium per unit mass of adsorbent$^{37}$.

**Effect of anions**

The amount of salt present in water varies depending on the source and quality of water. The presence of co-ions in solution affects the adsorption of metal ions. Effect of chloride and sulphate ions on adsorption of cadmium was studied by addition of required amounts of sodium chloride or sodium sulphate. The results are shown in Figs 5 and 6. Generally, the presence of chloride or sulphate ions inhibits cadmium uptake$^{37-40}$. In the present study, it is seen that an increase in the salt concentrations resulted in marginal decrease of cadmium uptake. This trend indicated that the Cd(II) uptake efficiency was affected when either NaCl or Na$_2$SO$_4$ concentration increased in the cadmium solution. Benaissa and Benguella$^{38}$ observed decrease in Cd(II) uptake capacity in the presence of chloride, sulphate or carbonate in the order CO$_3^{2-}$ > SO$_4^{2-}$ > Cl. The adverse effect could be due to (a) formation of soluble chloro$^{41}$/sulphato complexes, (b) competition between

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![Fig. 3](image1.png)

**Fig. 3**—Influence of solution pH on Cd(II) adsorption by TCL. Conditions: Cd, 100 mg L$^{-1}$; solution, 50 mL; adsorbent, 0.25 g of TCL of -75 µm; Temp., 30±1°C; time, 30 min.

![Fig. 4](image2.png)

**Fig. 4**—Effect of TCL dosage on adsorption of Cd(II). Conditions: Cd, 100 mgL$^{-1}$; pH, 5.5; solution, 50 mL; time, 30 min; Temp 30 ±1°C.

![Fig. 5](image3.png)

**Fig. 5**—Effect of NaCl concentration on Cd(II) adsorption by TCL. Conditions: Cd, 100 mg L$^{-1}$; pH, 5.5; solution, 50 mL; adsorbent, 0.25 g TCL of -75 µm; time, 30 min; Temp, 30±1°C.
Na\textsuperscript{+} and Cd\textsuperscript{2+} ions\textsuperscript{37} (Na\textsuperscript{+} entering the solution due to addition of sodium salt of chloride/sulphate) and (c) effect of supporting electrolyte\textsuperscript{40} when electrostatic attraction is the significant mechanism. Individual or combination of these reasons may be responsible for the observed results.

**Effect of lead**

Cadmium and lead are generally associated with each other, therefore, studies were undertaken to assess the extent of possible effect of lead on adsorption of cadmium with TCL. From the results given in Fig. 7, it indicates that lead is adsorbed in preference to cadmium. Cadmium adsorption decreased in the presence of Pb(II) ions and percentage decrease was more when concentration of Pb(II) increased. Adsorption of cations is dependant on many factors including ionic radii, hydration energy, ionic mobility and diffusion coefficient\textsuperscript{42}. Pb(II) has a higher ionic radii [Pb(II) 1.26Å, Cd(II) 0.60Å], and low hydration energy [Pb(II) 362 kcal/ion-g, Cd(II) 539 kcal/ion-g] when compared to Cd(II). Further Pb(II) has higher diffusion coefficient and higher ionic mobility\textsuperscript{42}. All these factors when combined may be responsible for preferred Pb(II) adsorption. Such preferential uptake of lead has also been observed for sugar beet pulp by Pehlivan et al.\textsuperscript{40} and on 6-line ferrihydrite by Mohapatra et al.\textsuperscript{39} Mata et al.\textsuperscript{43} observed in their studies with brown alga that the affinity of the metals followed the order Pb > Cu > Cd. They have explained the reason based on the ionic radii.

**Effect of contact time and adsorption kinetics**

The effect of contact time on Cd(II) uptake is shown in Fig. 8 (during these experiments 1 g adsorbent per 50 mL solution was taken). It is observed that the adsorption is governed by fast kinetics as the equilibrium is reached within a short period of 30 min. The high heterogeneity of the surface groups on TCL wall (carboxyl, phosphate, imidazole and amino groups) suggest that there are many types of bisorbent-metal ion interactions.

**Kinetic models**

The kinetics data was analyzed using two kinetic models, pseudo-first-order and pseudo-second-order kinetic model. These models correlate solute uptake, which is important in predicting the reactor volume. Linearised pseudo-first-order\textsuperscript{44} and pseudo-second-order\textsuperscript{45} kinetics equations are given in Eqs (2) and (3) respectively.

\[
\ln(q_e - q_t) = \ln q_e - k_1 t \\
t/q_t = 1/k_2 q_e^2 + t/q_e
\]

where \(t\) is the contact time (min), \(q_e\) (mg g\textsuperscript{-1}) and \(q_t\) (mg g\textsuperscript{-1}) are the amount of the solute adsorbed at equilibrium and at any time, \(k_1\) (min\textsuperscript{-1}) and \(k_2\) (g mg\textsuperscript{-1} min\textsuperscript{-1}) are the rate constants of pseudo-first-order and pseudo-second-order respectively.

Fig. 6—Effect of Na\textsubscript{2}SO\textsubscript{4} concentration on Cd(II) adsorption by TCL. Conditions: Cd, 100 mgL\textsuperscript{-1}; pH, 5.5; solution, 50 mL; adsorbent, 0.25 g TCL of -75 µm; time, 30 min; Temp, 30±1°C.

Fig. 7—Effect of Pb(II) on adsorption of cadmium by TCL. Conditions: Cd, 100 mgL\textsuperscript{-1}; pH, 5.5; solution, 50 mL; adsorbent, 0.25 g TCL of -75 µm; time, 30 min; Temp, 30±1°C.

Fig. 8—Effect of contact time on adsorption of cadmium by TCL. Conditions: Cd, 100 mgL\textsuperscript{-1}; solution, 50 mL; pH, 5.5; adsorbent, 0.25 g of TCL of -75 µm; Temp., 30±1°C.
Figure 9 shows the Lagergren pseudo-first-order kinetic plot for the adsorption of cadmium onto TCL. The calculated $k_1$ value and the corresponding linear regression correlation coefficient values were 0.595 min$^{-1}$ and 0.926 respectively. Though linear regression correlation coefficient $R^2$ was 0.926, but equilibrium uptake $q_e$ was 6.82 mg g$^{-1}$ which is higher than the experimental value (3.58 mg g$^{-1}$) indicating that kinetics is not governed by first order model.

To test the pseudo-second-order kinetic model, the plot of $t/q_t$ against $t$ of Eq. (3) was used (Fig. 10). The pseudo-second-order rate constant $k_2$, the calculated $q_e$ value and linear regression correlation coefficient value ($R^2$) were 0.475, 3.61 (experimental $q_e$ value 3.58 mg g$^{-1}$) and 0.998 respectively. Since the equilibrium uptake value predicted by the model is very close to that of experimental value along with high $R^2$ value indicate that this model fits the experimental data well.

**Equilibrium isotherms**

The results of cadmium adsorption on TCL by varying initial cadmium concentrations are shown in Fig. 11. The adsorption capacity increased from 8.42 to 32.36 mg g$^{-1}$ with the increase in initial Cd(II) concentration from 50 to 500 mgL$^{-1}$. The observed trend is due to the increase in driving force offered by the concentration gradient. At the same time % adsorption decreased from 84.24 to 32.36.

**Adsorption isotherm models**

The equilibrium data obtained were modeled with Freundlich$^{46}$, Langmuir$^{47}$ and Redlich-Peterson$^{48}$ adsorption equations as given by Eqs (4), (5) and (6) respectively.

\[
\frac{1}{q_e} = \frac{1}{q_m} + \frac{C_e}{bq_m} \quad \ldots (4) \\
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad \ldots (5) \\
q_e = A C_e^{1/(1+g)} \quad \ldots (6)
\]

where $q_m$ indicates the maximum monolayer adsorption capacity of adsorbent (mg g$^{-1}$) and the Langmuir constant $b$ (L mg$^{-1}$) is related to the energy of adsorption.

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \\
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \\
q_e = A C_e^{1/(1+g)}
\]

where $K_f$ (mg$^{1/(1/n)}$ L$^{1/n}$ g$^{-1}$) is the Freundlich constant related to adsorption capacity of adsorbent and $1/n$ is the Freundlich exponent related to adsorption intensity (dimensionless).

The fitted isotherm curves are given in Figs 12 to 14 and the parameters obtained for the present system along with $R^2$ values are given in Table 1. All the models fitted the data well as evidenced from the $R^2$ values obtained for these models. The monolayer adsorption capacity of Cd(II) on TCL was estimated to be 35.83 mg g$^{-1}$. Lower Cd(II) adsorption has been reported for several adsorbents such as grape stalk (27.88 mg g$^{-1}$)$^{41}$, sugar beet pulp (17.2 mg g$^{-1}$)$^{49}$, rice polish (9.72 mg g$^{-1}$)$^{50}$ and wheat bran (0.7 mg g$^{-1}$)$^{51}$.
when compared with the present study (35.83 mg g\(^{-1}\)). Due to fast kinetics and high adsorption capacity *Terminalia catappa* Linn leaf powder can be regarded as a potential biosorbent for Cd(II) removal from aqueous solutions.

**Conclusions**

The cadmium adsorption studies for *Terminalia catappa* Linn leaf powder showed that the adsorption is more dependent on parameters such as contact time, initial Cd(II) concentration, pH and adsorbent dosage. Presence of other cations and anions exhibited much less influence. The equilibrium uptake increased and percentage adsorption decreased with the increase in initial Cd(II) concentration. The plot of pH versus percentage adsorption showed steep increase in Cd(II) adsorption when the pH was increased from 2.0 to 4.0 (4.3 to 68.96) and thereafter stabilized (70.59). The percentage adsorption of Cd(II) increased from 71.63 to 90.80% by increasing the adsorbent dosage from 0.25 to 2g/50 mL solution. The isothermic data for TCL fitted well to the three equilibrium models namely, Langmuir, Freundlich and Redlich-Peterson with regression coefficients of > 0.97. The maximum uptake capacity of the adsorbent was estimated to be 35.83 mg g\(^{-1}\). The kinetics of the adsorption of Cd(II) on TCL has been described by the second-order kinetic model. The results obtained in these studies open perspectives with respect to the utilization of TCL for Cd(II) removal in the treatment of wastewater.

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