ADSORPTION OF CADMIUM(II) IONS FROM AQUEOUS SOLUTION BY *TECTONA GRANDIS* L.F. (TEAK LEAVES POWDER)

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Batch adsorption studies were undertaken with the abundantly available waste biosorbent *Tectona grandis* L.f. leaf powder for removal of cadmium(II) from aqueous solutions. The adsorption experiments were performed under various conditions such as time, temperature, different initial Cd(II) concentrations, pH, adsorbent dosage, and adsorbent particle size. The data showed that in 30 minutes, 1 g of *Tectona grandis* L.f. could remove 86.73% of cadmium(II) from 50 mL aqueous solution containing 100 mg L^{-1} of Cd. The isothermal data fitted well to both Langmuir and Freundlich models for Cd(II) adsorption on *Tectona grandis* L.f. Using the Langmuir model equation, the monolayer sorption capacity of *Tectona grandis* L.f. was evaluated to be 29.94 mg g^{-1}. The optimum pH value was found to be 5.5. The pseudo-first-order and pseudo-second-order kinetic models were used to describe the kinetic data. The dynamic data fitted well to the pseudo-second-order kinetic model. Cd(II) adsorption was only marginally affected in the temperature range of 30 to 50°C. An SEM of Cd(II) loaded powder showed formation of agglomerates. The FTIR of Cd(II) loaded powder showed negative shift in the wave numbers.

Keywords: Cadmium (II); Tectona grandis L.f.; Adsorption; Isotherms; Kinetics

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INTRODUCTION

Water and soil are contaminated due to indiscriminate discharge of hazardous solid wastes and liquid effluents. These wastes need to be treated to meet the stringent legislative standards before discharge. Cadmium is one of the toxic metals found in wastewater discharges of the electro-plating, battery, photovoltaic cell, metallurgical, and textile industries (Salim 1992; Cheung 2001). 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 (Patterson and Passino 1987; Lehoczky et al. 1998). Due to its toxicity, the permissible limit of Cd(II) in industrial discharges is set at 0.2 mg L^{-1} by the Ministry of Environment and Forests (MOEF), Government of India (MINAS 2001). The maximum permissible limit of Cd(II) in drinking water is 0.005 mg L^{-1}, as recommended by the WHO. Therefore, the Cd(II) in the effluents needs to be removed before discharge. A number of techniques are reported in the literature to treat Cd(II) contaminated water, namely chemical precipitation (Esalah et al. 2000), adsorption (Kaikake et al. 2007; Mohan and Singh 2002; Matheickal et al. 1999; Ozer and Pirincci 2006; Singh et al. 2005, 2006;

Mohapatra and Anand 2007), ion exchange (Koivula et al. 2000; Kocaoba 2007; Wang and Fthenakis 2005; Demirbas et al. 2005; Pehlivan and Altun 2006; Ayuso and Sanchez 2007), and membrane separation processes (Canet et al. 2002). Adsorption has been shown to be an economically feasible alternative method for removing heavy metals from wastewater. Activated carbon is generally used as the adsorbent; however, it is relatively expensive. There are some reports on the removal of cadmium using cheaply available agricultural waste materials (Ho 2004; Nouri et al. 2007; Ghodbane et al. 2007; Mohan et al. 2006; Ajmal et al. 2003; Martinez et al. 2006; Low et al. 2000; Zacaria et al. 2002; Cay et al. 2004; Iqbal et al. 2002; Taty-Costodes et al. 2003; Upendra and Manas 2006; Bailey et al. 1999; Shen and Duvnjak 2005; Brown et al. 2000; Cimino et al. 2000; Levya-Ramos et al. 2005; Ho and Ofomaja 2006; Orhan and Buyukgungor 1993).

With a view to develop an abundantly available waste material as a potential adsorbent, the present study was taken up. The adsorbent used in this study is teak leaves (*Tectona grandis* L.f.) powder, in which the adsorption takes place on surface of insoluble cell walls. Though *Tectona grandis L.f* has been used to adsorb copper (King et al. 2006; Kumar et al. 2006a) and zinc (Kumar et al. 2006b), kinetic and equilibrium studies of cadmium removal have not been reported. The insoluble cell walls of teak leaves are largely made up of cellulose and hemicelluloses, lignin, condensed tannins, and structural proteins. In other words, one-third of the total dry matter in teak leaves should have good potential as metal scavengers from solutions and waste waters, since the above constituents contain functional groups. The responsible groups in lignin, tannin, or other phenolic compounds are mainly carboxylate, aromatic carboxylate, phenolic hydroxyl, and oxyl groups (Crist et al. 1981). The wood of the teak tree is used for furniture, flooring, joinery, trim, doors, paneling, carving, musical instruments, turnery, vats, boat masts and decks, railway sleepers, mine props, fuel, fence posts, etc. The leaves, which are usually not used, are taken in the present study for cadmium removal from aqueous solution to investigate the possibility of utilizing them for treatment of waste water.

EXPERIMENTAL

Materials

Preparation of biosorbent

Green *Tectona grandis L.f (TLP)* leaves were collected from trees abundantly available at the Institute of Minerals and Materials Technology, Orissa, India. The collected leaves were washed with tap water several times until 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 a domestic mixer. The dried leaves of 75–212μm particle size were used as biosorbent without any pretreatment for cadmium adsorption.

Chemicals

A stock solution of cadmium concentration 1000 mg L^{-1} was prepared by dissolving 4.5637 g of 100% $3CdSO_4 \cdot 8H_2O$ (Loba-chemie Indoaustranal Co.) in 2000mL

of double-distilled water. All other chemicals used were of Analar Grade. The pH of solutions was adjusted with 0.1N HCl and NaOH solutions.

Biosorption experiments

Biosorption experiments were performed at room temperature (30±1 ^{0}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. After 30 min of contact (according to the preliminary sorption dynamics tests with 1 g *Tectona grandis L.f* biomass), equilibrium was reached. The contents were filtered, and the filtrate was analyzed after proper dilutions using an Atomic Absorption Spectrometer (Perkin Elmer AAnalyst 200, USA) at a wavelength of 228.80 nm. The amount of metal adsorbed by *TLP* leaves powder was calculated from the differences between metal quantity added to the biomass and metal content left in solution using the following equation:

$$q_t = (C_0 - C_f)V/M \qquad (1)$$

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); and M is the mass of biosorbent (g).

Various experimental parameters changed were: time (0 to 120 min), pH (2.0 to 5.5.), adsorbate concentration (50 to 500 mg L^{-1}), adsorbent concentration (1 to 5 g per 50 mL of adsorbate), average particle size (-75 to -212 μm), temperature (30 to 50 ^{o}C), NaCl and Na$_2$SO$_4$ concentrations (0 to 100 mg L^{-1}), and Pb(II) concentration (0 to 100 mg L^{-1}). The standard experimental conditions were: pH 5.5, time 30 minutes, adsorbate solution 50 mL, initial Cd(II) concentration 100 mg L^{-1}, temperature 30 ^{o}C, and adsorbent dose 1 g of TLP. For varying the experimental parameters, one parameter was changed at a time while keeping the rest constant.

Instrumental analysis

The adsorbent *Tectona grandis L.f* (before and after Cd(II) adsorption) was characterized by FT-IR spectrometry using a 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 studies the original powdered samples before and after cadmium adsorption were taken over a stud, by application of double adhesive carbon tape. The samples were then coated with gold through a gold sputter (JEOL, JFC-1100). They were then examined under the Electron Microprobe (JEOL, JXA-8100) employing 20kV and 10 nA current.

The crystalline phases in the TLP powder were characterized with an X-ray diffractometer (XRD; PW1830 XRD with CoKa radiation with λ = 1.79A^o) at a scan speed of 1.2^o min^{-1}.

The surface area measurement was carried out by the BET method using a CHEMBET 3000 (Quantachrome, USA) instrument by nitrogen adsorption-desorption measurements. Prior to analysis, samples were degassed at 110 ^{o}C under nitrogen flow. The surface area of TLP obtained was 6.35 m^2 g^{-1}.

RESULTS AND DISCUSSION

Characterization

SEM studies

In order to know the surface structure of *Tectona grandis* L.f.(TLP), morphological analysis of the TLP was performed by scanning electron microscopy (SEM), and results are shown in Fig. 1. From the figure, it can be seen that TLP has an amorphous and granular surface. The SEM observation revealed its complex and porous surface texture.
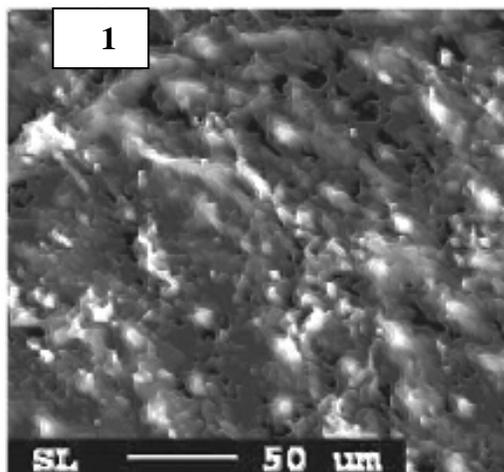

Fig.1. Electron micrographs of *Tectona grandis* L.f. leaf

FTIR studies

The FT-IR spectrum of TLP is given in Fig. 2. FTIR measurements showed the presence of the following functional groups: a broad band at 3404 cm^{-1} which is due to stretching absorptions of –OH. The bands at 2923 and 2852 cm^{-1} indicate the presence of stretching C-H vibrations in CH_2 or C=C-H group. The band at 1738 cm^{-1} suggests the presence of stretching C=O vibrations arising from groups such as lactones, quinine (Gomez-Serrano et al. 1994), and carboxylic acids (George and McIntyre 1987). The band at 1645 cm^{-1} may be due to the asymmetric and symmetric stretching COO$^-$ vibrations or the skeletal C=C aromatic vibrations (Gomez-Serrano et al. 1994; Van der Mass 1969).

XRD studies

The XRD pattern of TLP (Fig. 3) does not show very sharp peaks and more or less looks amorphous. The peaks at 2θ values of 17.48, 28.275, 34.82, 41.86, 44.55 and 52.34 corroborate the presence of γ$CaSO_4$, $CaCl_2$, γCaSO4/iron oxide, Fe_3O_4, $MgFeSiO_4$, and $CaCl_2$/iron oxide, respectively.
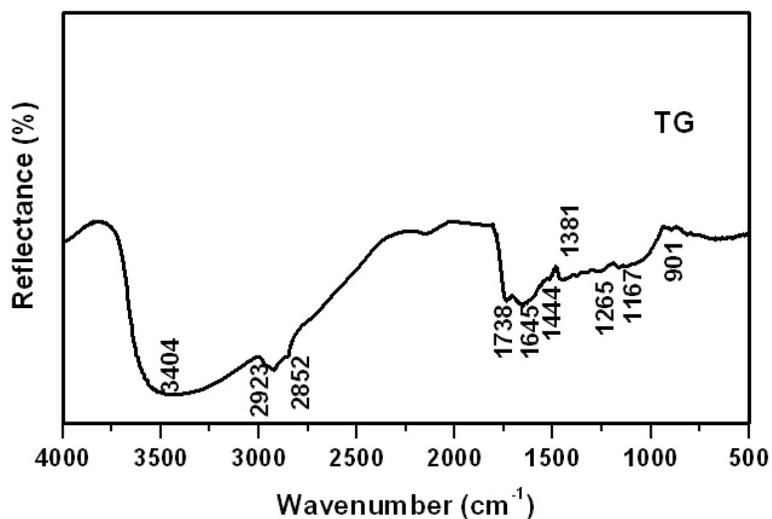
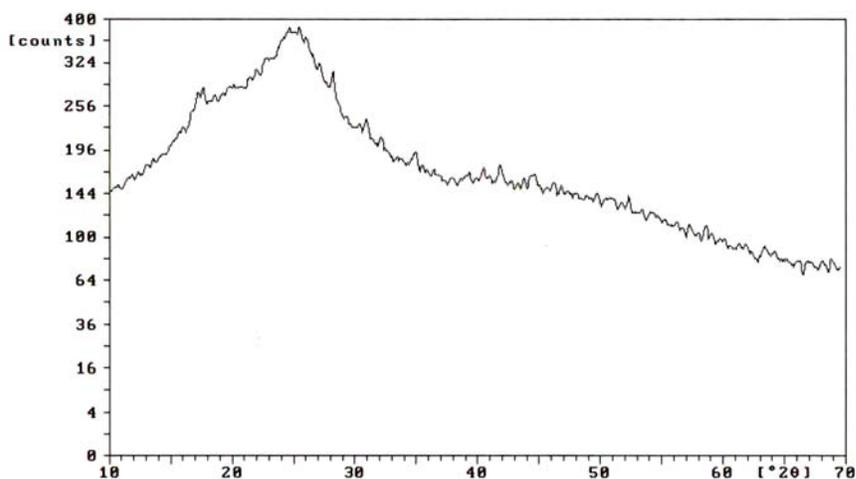**Fig. 2.** FT-IR Spectrum for the adsorbent *Tectona grandis L.f. powder (TLP)*

Fig. 3. XRD pattern of *Tectona grandis* L.f. leaf

Batch Adsorption Studies

Effect of contact time

Time course profiles for the adsorption of cadmium (II) from a solution of 100 mg L^{-1} of cadmium are shown in Fig. 4. The data obtained from the adsorption of cadmium(II) ions on the *Tectona grandis* L.f. showed that a contact time of 30 min was sufficient to achieve equilibrium and the adsorption did not change with further increase in contact time. The uptake and unadsorbed cadmium(II) concentrations at the end of 120 min, defined as the equilibrium values, q_e (mg g^{-1}) and C_e (mg L^{-1}), were estimated to be 4.34 and 13.27, respectively.
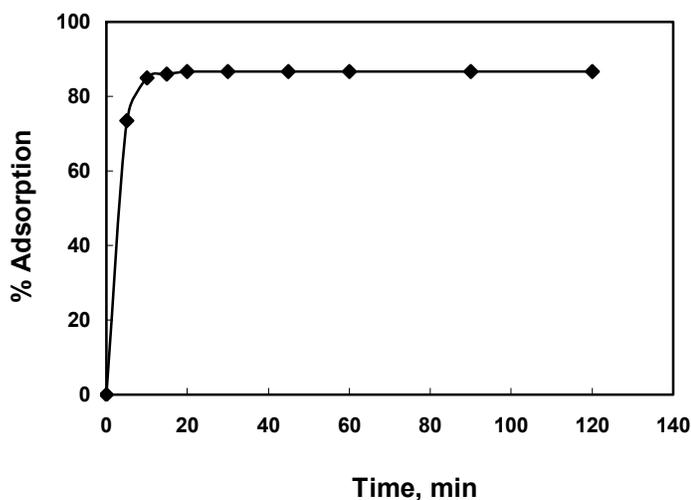
Fig. 4. Effect of contact time on adsorption of cadmium by *Tectona grandis* L.f. leaf. Conditions: Initial Cd 100 mgL^{-1}, pH 5.5, solution 50mL, TLP 1g of -75µm, temp. 30±1°C, time 30 min.

Effect of initial metal ion concentration

　　　　Several experiments were undertaken to study the effect of initial adsorbate concentration on cadmium(II) removal from the solution. The results given in Fig. 5 show that the metal uptake (loading capacity) increased and percentage adsorption of cadmium(II) decreased with the increase in initial metal ion concentration. This increase (2.23–25.64 mg g^{-1}) is a result of the increase in the driving force, i.e. the concentration gradient. However, the percentage adsorption of cadmium(II) ions on TLP decreased from 89.04 to 51.28%. Though an increase in metal uptake was observed, the decrease in percentage adsorption is expected as it is attributed to lack of sufficient active sites so as to accommodate much more metal available in the solution. At lower concentrations, all cadmium(II) ions present in solution could interact with the binding sites, and thus the percentage adsorption was higher than those at higher initial cadmium(II) ion concentrations.

Influence of pH

　　　　Previous studies have reported that for adsorption of metals by biological materials, pH is an important factor (Kapoor et al. 1999; Ho 2005). There is an observed relationship between the amount of metal adsorbed and the magnitude of negative charge on the surface of the biosorbent, which is related to the surface functional groups (Selatnia et al. 2004). Availability of negatively charged groups at the biosorbent surface is necessary for the biosorption of metals to proceed (Luef et al. 1991). The ionic form of the metal in solution and the electrical charge on the biological material depends on the solution pH. Ionization of the polar functional groups available with most agricultural by-products is therefore pH-dependent. For pH values greater than the pK_a of these groups, the sites are mainly in dissociated form and can exchange H$^+$ with metal ions in solution. At pH values lower than pK_a of these groups, complexation phenomena can occur, especially in the case of carboxylic groups (Fourest and Volesky 1996). pH is an environmental factor that affects not only site dissociation, but also the solution

chemistry of the heavy metal ions: hydrolysis, complexation, by organic/or inorganic ligand, redox reactions, and precipitation. On the other hand, it strongly influences the speciation and biosorption availability of the metal ions in solution (Warren and Ferris 1998; Corapcioglu and Huang 1987).
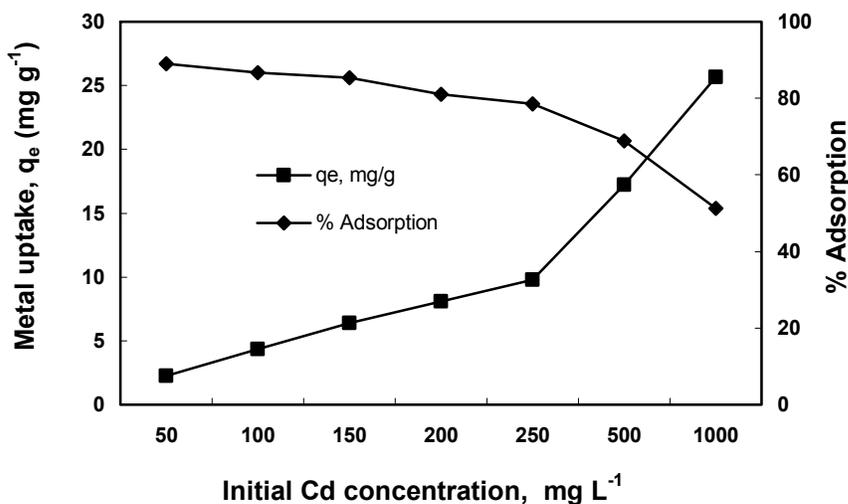

Fig. 5. Effect of initial metal ion concentration on the adsorption of cadmium by *Tectona grandis* L.f. leaf. Conditions: Solution 50mL, pH 5.5, TLP 1g of -75μm, temp 30±1°C, time 30 min.

As shown in Fig. 2, *Tectona grandis* L.f. has a high content of ionizable groups (carboxyl groups) that make it very liable to the influence of pH. The uptake of free ionic cadmium(II) depends on pH, increasing with the increase in pH from 2.0 to 5.5 (Fig. 6). The less sorption amount at low pH is due to competition between hydrogen and cadmium(II) ions for the sorption sites. As the pH increased, the ligands such as carboxylate groups in *Tectona grandis* L.f. 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. The optimum pH for cadmium(II) adsorption was found to be 5.5, and other adsorption experiments were performed at this pH value. The pH_{PZC} of the sample was found to be 7.85 without cadmium adsorption and 7.02 with cadmium. The shift of 0.83 units is attributable to cadmium adsorption, as shown in Fig. 7.

Effect of adsorbent dosage

The other variable chosen for studying cadmium(II) adsorption was the amount of adsorbent, which was varied from 20 to 100 g L^{-1} while keeping the cadmium concentration as 100 mg L^{-1} (Fig. 8.). The increase in adsorbent dosage from 20 to100 mg L^{-1} resulted in an increase from 86.73 to 97.79% in adsorption of cadmium(II). This is because of the availability of more binding sites for complexation of cadmium(II) ions.
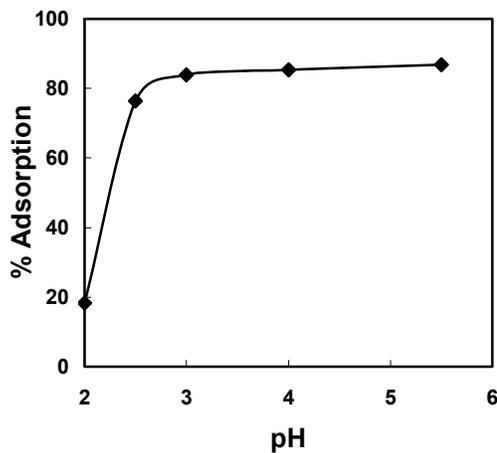
Fig.6. Effect of pH on cadmium adsorption by *Tectona grandis* L.f. Conditions: Initial Cd 100 mgL^{-1}, solution 50 mL, TLP 1g of -75μm, temp30±1°C, time 30 min
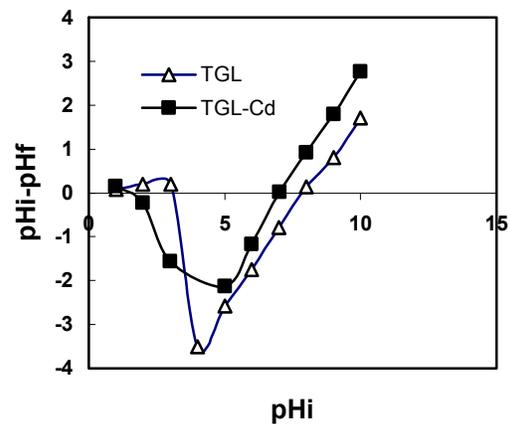

Fig.7. pH$_{PZC}$ of *Tectona grandis* L.f. pH$_i$ is the initial pH and pH$_f$ is the equilibrium pH obtained after 72 hours
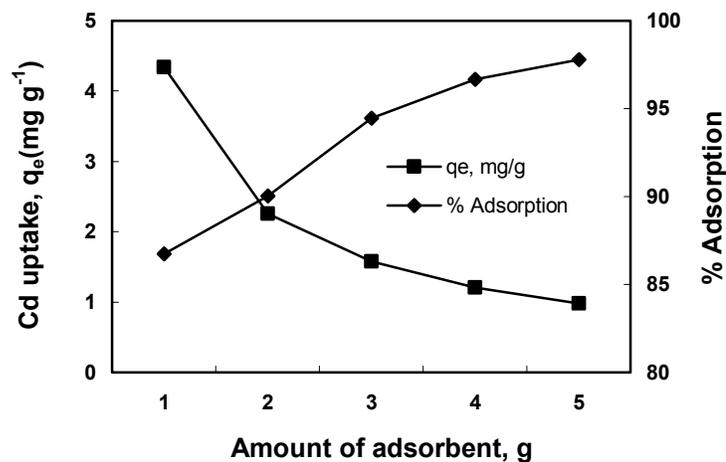

Fig.8. Effect of *Tectona grandis* L.f. dosage on adsorption of cadmium. Conditions: Initial Cd 100 mgL^{-1}, solution 50mL, pH 5.5, sorbent-75μm, temp. 30±1°C, time 30 min.

Effect of adsorbent particle size

The percentage of cadmium(II) adsorption on *Tectona grandis* L.f. increased marginally from 81.19 to 86.73 with decreasing particle size from 212 to 75 μm (Fig. 9). The adsorption was increased due to an increase in the surface area of the particle.
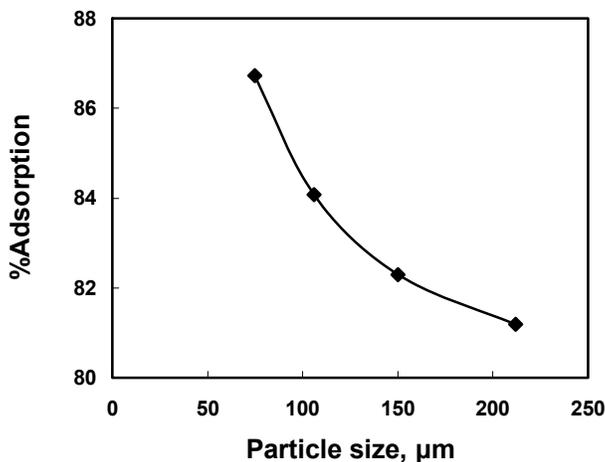
Fig. 9. Effect of *Tectona grandis* L.f. particle size on adsorption of cadmium. Conditions: Initial Cd 100 mg L^{-1}, solution 50mL, pH 5.5, TLP 1g, temp.30±1^{0}C, time 30 min.

Effect of temperature

Effect of temperature was studied in the range of 30 to 50 ^{o}C by keeping the rest of the parameters such as adsorbate concentration at 100 mg L^{-1}, the pH at 5.5, and the adsorbent concentration at 1g in 50 mL. Figure 10 shows a very marginal increase in percent adsorption with increase of temperature in the studied range.
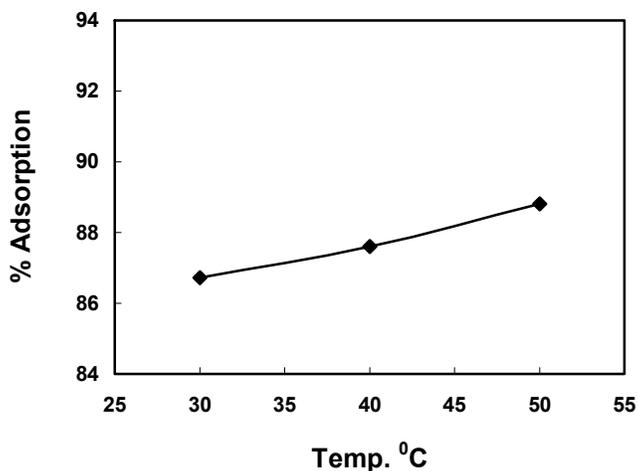

Fig. 10. Effect of temperature on adsorption of cadmium. Conditions: Initial Cd 100 mg L^{-1}, solution 50mL, pH 5.5, TLP 1g, time 30 min.

Effect of presence of anions

Generally the effluents and contaminated water contain many anions and cations, chloride and sulphate being the most prevalent ones. Hence the effect of these anions was studied. The required amount of sodium chloride or sulphate was added to obtain the desired concentrations. The results are shown in Fig. 11.
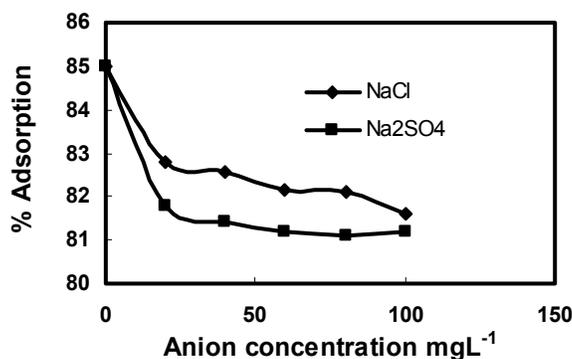
Fig. 11. Effect of NaCl/Na$_2$SO$_4$ on adsorption of cadmium. Conditions: Initial Cd 100 mgL^{-1}, solution 50mL, pH 5.5, TLP 1g, temp.30±1°C, time 30 min.

From the above figure, it is clear that both chloride and sulphate ions had a marginal adverse effect on the adsorption of cadmium. As the sodium chloride concentration increased from 0 to 100 mg L^{-1}, cadmium adsorption decreased from 85 to 81.62%. Similarly, when the sodium sulphate concentration increased from 0 to 100 mg L^{-1}, cadmium adsorption decreased from 85 to 81.2%. A similar observation was made by Benaissa and Benguella (2004) during the study of effect of anions on Cd(II) sorption on chitin. Recently Mohapatra et al. (2009) have made similar observations during their study on cadmium(II) adsorption on 6-line ferrihydrite.

Effect of lead

Cadmium and lead are generally associated with each other. Effluent waters emanating from the battery industry contain these two metal ions. Hence studies were under taken to assess the extent of possible effect of lead on the adsorption of cadmium with TLP. Results are shown in Fig. 12.
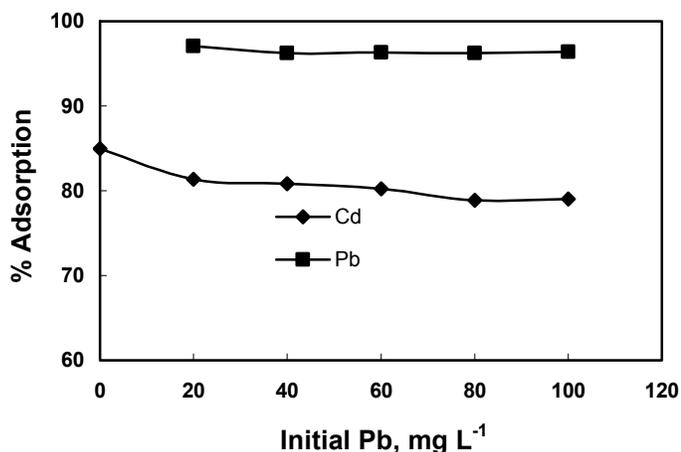

Fig. 12. Effect of lead on adsorption of cadmium. Conditions: Initial Cd 100 mgL^{-1}, solution 50mL, pH 5.5, TLP 1g, temp.30±1°C, time 30 min.

It was found that more than 96% of lead got adsorbed. In the presence of lead, cadmium adsorption was slightly lowered from 85% to 79%. Preferential sorption of Pb(II) from Pb(II)-Cd(II) solution has been observed by Mahapatra et al. (2009) too.

Equilibrium Studies

Langmuir and Freundlich isotherms

Linear forms of the Langmuir (1918) and Freundlich (1906) equations are given by Eqs.(2) and (3) respectively,

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{2}$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{3}$$

where C_e(mg L^{-1}) and q_e(mg g^{-1}) are equilibrium concentrations in solution and solid, respectively. q_m is the maximum loading capacity of adsorbent in mg g^{-1}, b is the Langmuir constant related to free energy of adsorption (L mg^{-1}), K_f is the Freundlich constant indicative of relative adsorption capacity of adsorbent(mg$^{1-1/n}$L$^{1/n}$ g^{-1}), and n is the Freundlich constant indicative of the intensity of adsorption.

The linearised Langmuir and Freundlich adsorption isotherms obtained at room temperature (30±1°C) are shown in Figs. 13 and 14, respectively, and adsorption coefficients computed from these are given in Table 1. Both curves had good linearity (correlation coefficient), indicating strong binding of cadmium(II) ions to the surface of *Tectona grandis* L.f. particles. From the Langmuir isotherm, the adsorption affinity constant (b) and maximum capacity (q_m) of the cadmium(II) to form a complete monolayer on to the surface of the *Tectona grandis* L.f. biomass were estimated as 0.011(L mg^{-1}) and 29.94mg g^{-1}, respectively.

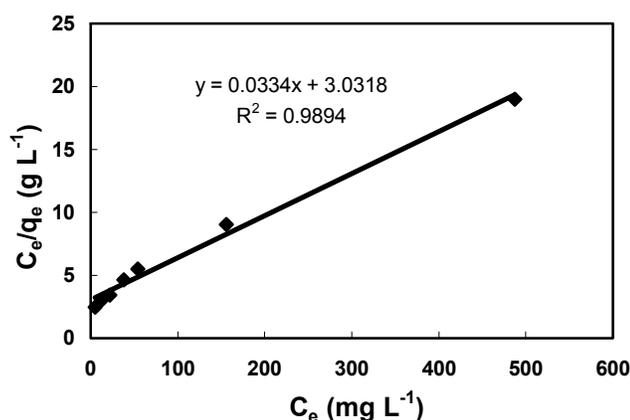**Fig. 13.** Langmuir adsorption isotherm for cadmium. Conditions: Solution 50mL, pH 5.5, TLP 1g, -75µm, temp.30±1°C, time 30 min.
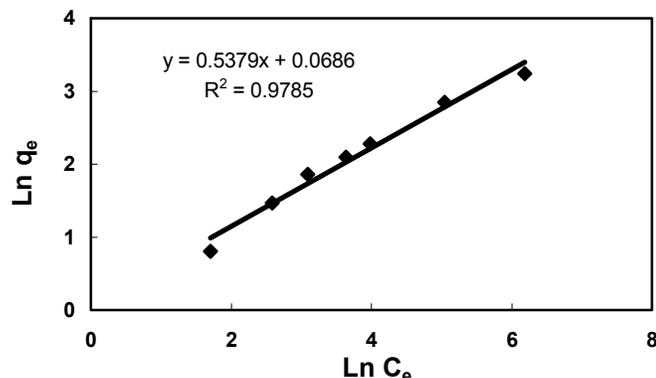.

Fig.14. Freundlich adsorption isotherm for cadmium. Conditions: Solution 50mL, pH 5.5, TLP 1g, -75μm, temp.30±1°C, 30 min.

Table 1. Langmuir and Freundlich Model Parameters

Temp. °C	Langmuir model			Freundlich model		
	q_m (mgg^{-1})	b (Lmg^{-1})	R^2	K_f (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	n	R^2
30	29.94	0.011	0.9894	1.071	1.859	0.9785

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter (Hall et al. 1966), as given in Eq. (4),

$$R_L = 1/(1 + bC_0) \tag{4}$$

where b is the Langmuir constant and C_0 is the initial metal concentration (mg L^{-1}). The value of R_L indicates the shape of isotherm to be either unfavorable ($R_L > 1$) or linear ($R_L = 1$) or favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L value obtained was 0.476, which indicates a favorable isotherm shape ($0 < R_L < 1$) for adsorption of Cd(II) on TLP in the concentration range studied.

For Freundlich isotherm, the constants related to the adsorption coefficients (K_F) and intensity (n) were 1.071 and 1.86, respectively. A favorable adsorption tends to have a Freundlich constant 'n' between 1 and 10 (Febrianto et al. 2009). The correlation coefficients obtained from the Langmuir model and Freundlich model were 0.9894 and 0.9785, respectively (Figs. 13 and 14).

Kinetic Studies

Information on the kinetics of solute uptake is required for selecting optimum operating conditions for a full-scale batch process. Figure15 gives the plot between metal uptake, q_t (mgg^{-1}) versus time, t (min) for an initial solute concentration of 100 mgL^{-1}. From the figure it was observed that q_t value increased with increase in contact time. The kinetics of the adsorption data was analyzed using two kinetic models, pseudo-first-order and pseudo-second-order which are described below.
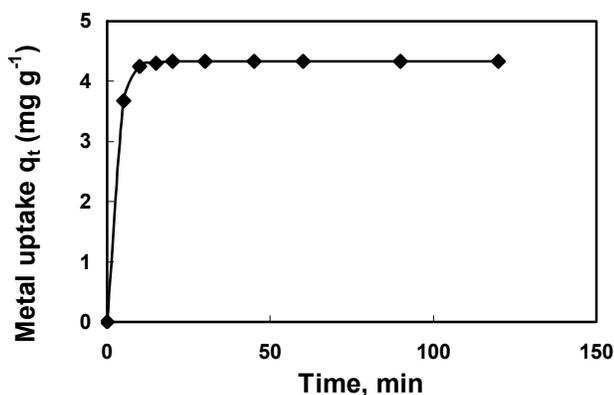
Fig. 15. Effect of contact time on Cd uptake by TLP. Conditions: Initial Cd 100 mgL^{-1}, solution 50mL, pH 5.5, TLP 1g of -75μm, temp.30±1°C, time 30 min.

Pseudo-first-order model

The possibility of adsorption data following Lagergren pseudo-first-order kinetics is given by the linearized eq. (5).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{5}$$

In order to obtain the rate constant, a straight-line plot (Fig. 16) of $\ln(q_e - q_t)$ versus time was made for *Tectona grandis* L.f. for initial cadmium(II) concentration, 100 mg L^{-1}. The intercept of the above plot should equal $\ln(q_e)$. However, if q_e from intercept does not equal the equilibrium cadmium (II) uptake, then the reaction is not likely to be first-order, even if this plot has high correlation coefficient with the experimental data. The correlation coefficient was found to be 0.9768, and the calculated equilibrium uptake, q_e (3.32) was not equal to experimental value of q_e (4.34), suggesting the insufficiency of the pseudo-first-order model to fit the present kinetic data.

Pseudo-second-order model

The pseudo-second-order model, Eq.(6), as proposed by Ho (1995) and Ho and MacKay (2000), was tried to explain the sorption kinetics.
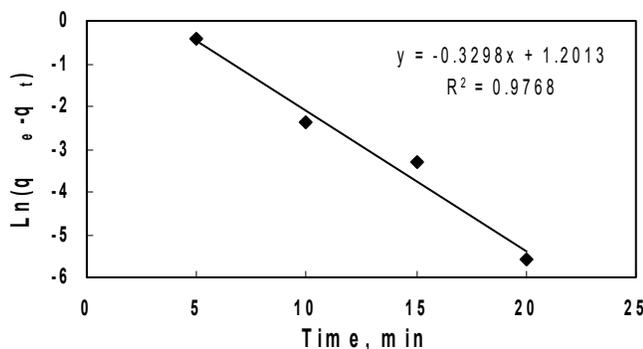

Fig. 16. Pseudo-first-order adsorption of cadmium by TLP. Condition: Initial Cd 100 mgL^{-1}, Solution 50mL, pH 5.5, TLP 1g of -75μm, temp.30±1°C, time 30 min.

The linear form of pseudo-second-order model can be expressed as,

$$t/q_t = 1/k_2 q_e{}^2 + 1/q_e\, t \tag{6}$$

where t is the contact time (min), q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts of metal adsorbed at equilibrium and at any time, t. If second-order kinetics is applicable, the plot (Fig. 17) of t/q_t versus t of Eq. (6) should give a linear relationship from which the constants q_e and k_2 can be determined. The rate constants and the correlation coefficients for both tested models have been calculated and are summarized in Table.2. It was seen that the pseudo-second order model fit very well, giving a very high correlation co-efficient of 1 with a q_e value of 4.348 mg L^{-1}.
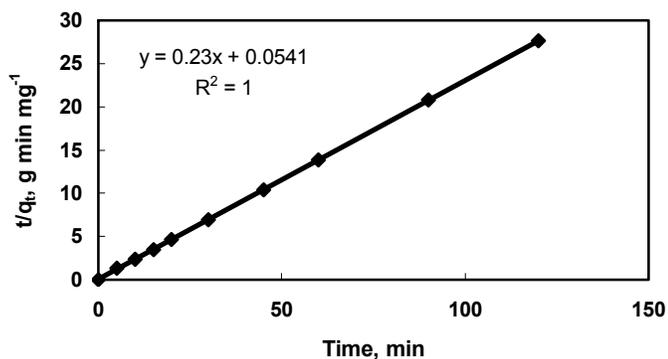

Fig. 17. Pseudo-second-order adsorption of cadmium by TLP. Conditions: Initial Cd 100 mgL^{-1}, solution 50mL, pH 5.5, adorbent 1g of -75μm, temp.30±1°C, time 30 min.

Table 2. Kinetic Constants for Cadmium(II) on *Tectona Grandis* L.f.

Pseudo-first-order constants				Pseudo-second-order constants			
$k_1\,min^{-1}$	R^2	$q_{e,}$ mgg^{-1}		$k_2\,gmg^{-1}min^{-1}$	$q_{e,}$ mgg^{-1}		R^2
		Cal	Expt.		Cal	Expt.	
0.3298	0.9768	3.32	4.34	0.9778	4.348	4.34	1

Characterization of Cadmium Loaded TLP

SEM and FTIR studies

SEM can characterize metal accumulation of adsorbed metal ion on the biosorbent surface. Figure 18 shows that the *Tectona grandis* L.f. has an amorphous and granular surface, which indicates micro-precipitation of cadmium after its adsorption, indicating cadmium-granular interaction. The original *Tectona grandis* L.f. leaf was devoid of any Cd. Around 30% of the powdered grains (doped with Cd) showed pixel concentration of Cd, suggesting thereby adsorption of cadmium by selective grains.
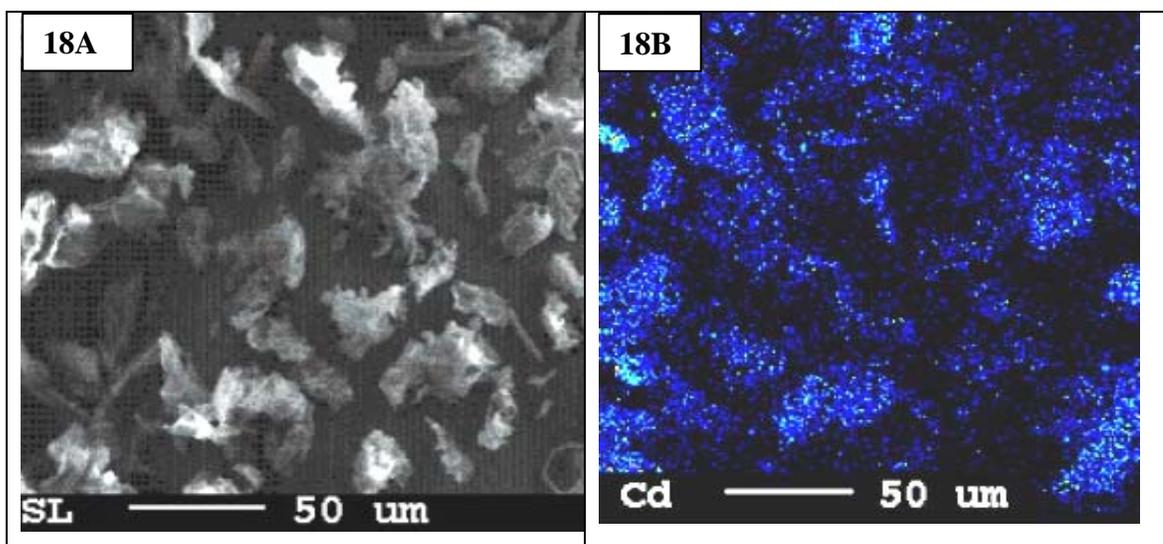
Fig. 18. Electron micrographs of cadmium-loaded *Tectona grandis* L.f. leaf powder

The TLP loaded with Cd(II) showed similar FTIR spectra as obtained for Cd(II) loading, except that the bands had shifted to lower values (3 to 17 cm^{-1} in TG-Cd sample (Fig.19). The comparisons of various band positions and shifts in wave number for TLP with or without Cd(II) adsorption are given in Table 3. These shifts may be attributed to the changes in counter ions associated with carboxylate and hydroxylate anions, suggesting that acidic groups, carboxyls, and hydroxyls, are predominant contributors in the metal uptake (Ashkenazy et al. 1997).
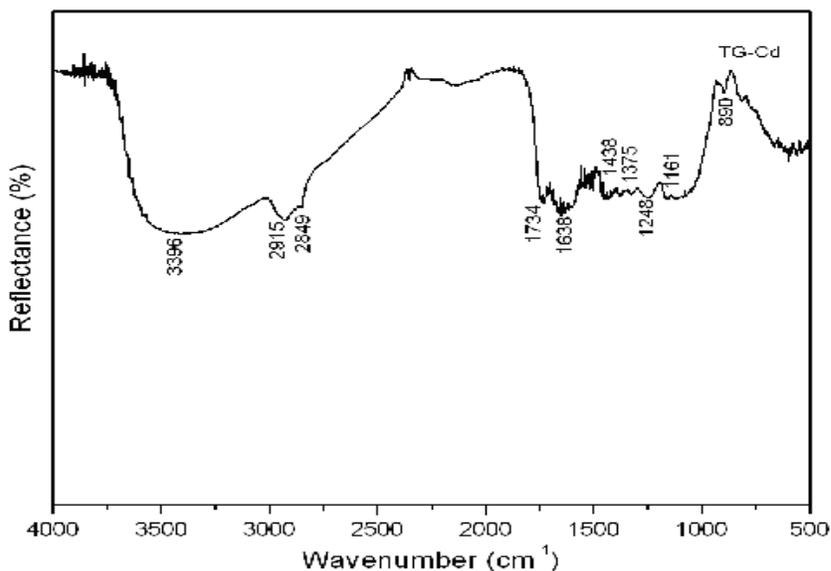

Fig. 19. FT-IR spectra for *Tectona grandis L.f.* after cadmium adsorption

Table. 3. Wave Numbers Shift after Cadmium Adsorption

Wave number cm⁻¹		
Before cadmium loading	After cadmium loading	Shift in wave number
3404	3396	8
2923	2915	8
2852	2849	3
1738	1734	4
1645	1638	7
1444	1438	6
1381	1375	6
1265	1248	17
1167	1161	6
901	890	11

CONCLUSIONS

Based on the present study, the following conclusions can be drawn.

1. The cadmium adsorption for *Tectona grandis L.f.* powder is strongly affected by parameters such as initial concentration, pH, adsorbent dosage, and adsorbent particle size. The equilibrium uptake increased and percentage adsorption decreased with increasing of the initial concentration. The present work helped in identifying a new source of adsorbent for removal of Cd(II) from effluent wastes containing low concentrations of metals.
2. Both Langmuir and Freundlich equilibrium models proved to be good fits for the experimental data for *Tectona grandis* L.f.
3. The uptake capacity of the adsorbent 29.94 mgg⁻¹ is more than many other adsorbents.
4. The kinetics of the adsorption of cadmium (II) on *Tectona grandis* L.f. could be described by a second-order kinetic model.
5. The presence of chloride or sulphate have an adverse effect on percent adsorption of cadmium.
6. The presence of lead as a competing cation shows that lead is preferentially adsorbed when compared to cadmium.
7. The SEM studies indicated that the cadmium-loaded leaf powder has a tendency to form agglomerates.
8. The FTIR spectrum of a cadmium-loaded sample showed a negative shift in the wave numbers for almost all peaks

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