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Kinetic, Equilibrium and thermodynamic studies on the biosorption of Cd(II) from aqueous solutions by the leaf biomass of C*alotropis procera* – 'Sodom apple'

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ABSTRACT: The kinetics, equilibrium and thermodynamics of the biosorption of Cd (II) from aqueous solution by the leaf biomass of *Calotropis procera* popularly known in western Nigeria as '*bom bom*'and genrally known as Sodom apple were investigated at different experimental conditions. Optimum conditions of pH, contact time, biomass dosage, initial metal ion concentration and temperature were determined to be 5, 60 minutes, 110 mg, 0.3 mM and 27°C respectively. The maximum biosorption capacity was found to be 8.91 mg/g. The kinetic studies indicated that the biosorption process of the metal ion followed the pseudo-second-order and intraparticle diffusion models with an R^2 value of 0.998 and 0.985 respectively. Equilibrium studies showed that the biosorption of Cd (II) is well represented by both Freundlich and Langmuir isotherms but the Langmuir model gave a better fit with an R^2 value of 0.979, Langmuir constant b_m of 0.0080 and monolayer adsorption capacity, Γ_m of 123.46. The calculated thermodynamic parameters ($\Delta G°$ -4.846 $kJmol^{-1}$, $\Delta H°$ 10.60 $kJmol^{-1}$ and $\Delta S°$ 0.052 $kJK^{-1}mol^{-1}$) showed that the biosorption of Cd (II) is feasible, spontaneous, endothermic and highly disordered in nature under the experimental conditions. These findings indicate that the leaf of *Calotropis procera* could be employed in the removal of Cd (II) from industrial effluents. @JASEM

Key words: *Calotropis procera*, Cadmium, Adsorption isotherm.

Industrialization, a welcome sign of civilization has brought serious environmental problems all over the world. Heavy metals form a major constituent of most industrial effluents which is posing a great threat to public health. Cadmium pollution originates from metal plating, metallurgical alloying, mining, and other industrial operations, its toxicity may be observed in a variety of syndromes and effects such as renal dysfunction, hypertension, hepatic injury, lung damage and tetratogenic effects. (Vieira et al., 2007). Conventional methods which have been used for the removal of toxic metals such as cadmium from aqueous environment include ion exchange, reverse osmosis, evaporation, membrane filtration processes, chemical precipitation, adsorption and so on. However, these methods are expensive and more often, lead to secondary pollution problem. They also become inefficient when the concentration of the heavy metals in the effluent is low. Biosorption has been employed as an alternative method for removal of toxic metal ions from dilute aqueous solutions and industrial effluents (Sari et al., 2008; Sethunathan et al., 2005;Vieira et al., 2007;Anyurt et al., 2009 & Atolaiye et al., 2009). The biosorption process is technically feasible, eco-friendly and economical, due to the availability of biomaterials and their reusability (Romera et al., 2007). Improved selectivity for specific metals of interest, removal of heavy metals from effluent irrespective of its toxicity, short operation time and no production of secondary pollutants are the advantages of this biological method of heavy metal recovery (Sari et al., 2008; Mungasavalli et al.,2007). Various biomaterials such as algae, bacteria, mosses, plant materials and agricultural wastes have been found useful for removal of Cd(II) from aqueous solutions (Munagapati et al., 2010; Anayurt et al., 2009; Sari & Tuzen, 2008; Laurent et al., 2010). *Calotropis procera* is a species of flowering plant in the dogbane family, Apocynaceae, that is native to North Africa, Tropical Africa, Western Asia, South Asia, and Indochina. It is commonly known as Apple of Sodom. To the best of our knowledge, there has been no report on the use of the leaf of *Calotropis procera* for sorptive removal of cadmium (II) from solution. Literature has revealed that all parts of this plant are useful for diverse purposes such as in medicine, fuel, food processing, spear poisons and a lot more. However, the leaf is not too useful as it is known to be poisonous as fodder. Therefore, harvesting plant for use in medicine and other applications leaves the leaf as litter which constitutes environmental nuisance. Therefore this work was aimed at investigating the biosorption potential of C*alotropis procera* leaf in the removal of Cd (II) from dilute aqueous solutions.

MATERIALS AND METHODS

All chemicals used in this work were of analytical reagent grade and were used without further purification. Jenway 3510 model pH meter was used to measure pH values in the aqueous phase and a Buck scientific Flame Atomic Absorption spectrometer (FAAS) model 2004 was used for residual metal ion analysis. Spectroscopy grade standards were used to calibrate the instrument which was periodically checked for instrument response. All measurements were done in air/acetylene flame. The batch experiments were carried out in triplicates and the mean calculated for each set of values. For functional group analysis, Fourier-Transform Infra-Red (FT-IR) spectra of unloaded and metal-loaded biomass were recorded at 4000 - 400 cm^{-1} wave

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number range using a Nicolet Avater 3300 Thermo Electron Corporation IR spectrometer.

Leaves of *Calotropis procera* were plucked from Moniya in Ibadan, Nigeria. They were rinsed thoroughly with tap water to remove sand and other particulate matter and then rinsed twice with deionized water. They were thereafter sun-dried for six days. The dried leaves were pulverized and sieved through a 150 µm size mesh screen and stored in air-tight polythene bags till time of usage.

8mM stock solutions of $Cd(NO)_3.4H_2O$ was prepared by dissolving a calculated mass of the salt in deionized water using a standard volumetric flask. Serial dilutions of 0.1 mM, 0.3 mM, 0.5 mM, 0.7 mM, 1.0 mM, 2.0 mM, 3.0 mM were prepared from the stock solution. All aqueous solutions were prepared with deionized water.

FT-IR analysis of unloaded and cadmium-loaded *Calotropis procera* at the optimum pH was carried out to ascertain the functional groups on the walls of the biosorbent which are responsible for the biosorption process. This was done by mixing approximately 1 mg dried sample of unloaded and cadmium-loaded *Calotropis procera* with 5 mg KBr (1:5), ground to fine powder and pressed under vacuum to a pellet. The pellet was then analyzed in the range 4000-400 cm^{-1}.

In order to explore the effects of pH, contact time, biosorbent dose, initial metal ion concentration and temperature, a series of batch studies were conducted. Batch biosorption experiments on the effect of pH were conducted by agitating 0.05 g of the biosorbent for each batch equilibrium experiment in 20 ml metal solution of desired concentration at varying pH (pH 2- 8). Subsequently, the other experiments were carried out in similar manner by varying a parameter and keeping others constant. Each experiment was carried out in triplicate, and the optimum value for each study was used for the successive ones. The amount of Cd (II) adsorbed by biomass was calculated using a mass balance equation expressed in equation (1).

$$q_e = \left(\frac{C_e - C_o}{m} \right) v \qquad (1)$$

where q_e = metal ion uptake at equilibrium (mg/g), C_e is the metal ion concentration remaining in solution at equilibrium, C_o is the initial metal ion concentration in solution (mg/L), v is the volume of metal solution used (L) and m is the mass of biomass used. The biosorption efficiency was calculated with equation (2).

$$E = 100 \left(\frac{C_o - C_e}{C_o} \right) \qquad (2)$$

RESULTS AND DISCUSSION

FT-IR Analysis of unloaded and cadmium-loaded *Calotropis procera:* In order to ascertain the functional groups that are responsible for the biosorption of the metal ions in this study and possibly to explain the mechanism of the biosorption, FT-IR study was carried out on both the unloaded and the metal loaded biomass at the optimum pH. The *FT-IR* spectrum (Fig. 1) of unloaded biomass shows a number of distinct absorption bands indicating the complex nature of the biomass. Several distinct and sharp absorptions around 3448 cm^{-1} are indicative of $-OH$ and $-NH_2$ groups. Weak bands around 2910 cm^{-1} in both indicate presence of C-H stretch of alkane. The absorption bands around 1637 cm^{-1} in both spectra depict mainly C=O stretch bands while the bands around 1560 cm^{-1} suggest –NH, -CN and -NO stretch. Pandey et al., 2007, have reported similar bands in leached and unleached root biomass of *Calotropis procera*. Bands around 1100 cm^{-1} in unloaded biomass could be attributed to –C-O-H stretch of sugar.

Using Cd (II) as a case study, comparing the spectra of Cd (II)-loaded biomass with that of the unloaded, it is observed that the band at 3448 cm^{-1} broadens and its intensity is reduced and the band shifts to a lower wave number after Cd(II) biosorption. Also the band at 2910 cm^{-1} becomes more intense. These results indicate that the free carboxyl groups changed into carboxylate, which occurred during the reaction of the metal ions and carboxyl groups of the biosorbent. An ion-exchange process occurred when the metal ions in the solution was transferred from solution to biosorbent leading to the formation of chemical bond.

Effect of pH: The pH of the solution has been identified as one of the most important parameters that affect biosorption of metal ions by biomass. This is due to the fact that it regulates the availability of the functional groups at the active sites on the biosorbent. At highly acidic pH there is high level of protonation of the functional groups on the cell walls which makes the functional groups unavailable for binding metal ions. In addition, it causes competition between the protons and the metal ions in solution thereby reducing the level of the metal ions uptake at the active sites in the biosorbent.

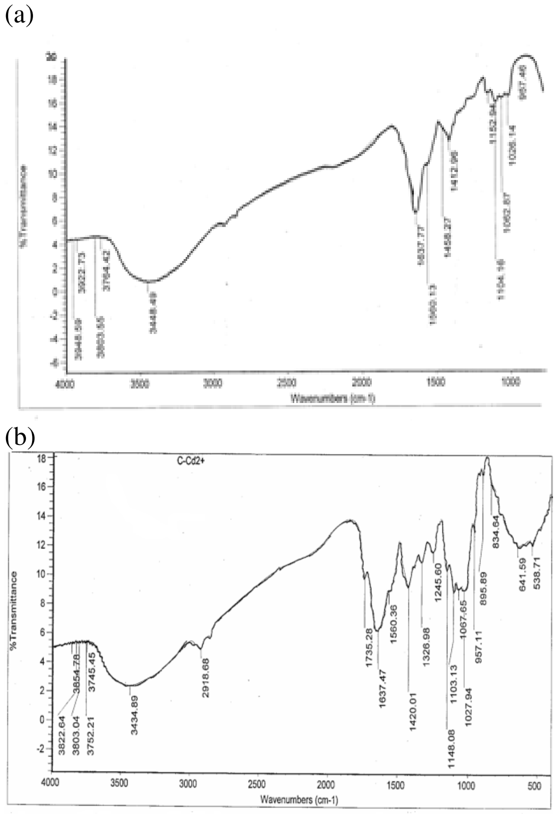

Fig. 1. FT-IR spectra of unloaded (a) and Cd (II)-loaded (b) leaf of *Calotropis procera* at pH 5.

As shown in Fig. 2, the percentage of Cd(II) ion biosorbed increased as pH increased from pH 2 with the maximum biosorption occurring at pH 5.. Further increase in the pH beyond pH 5 led to a decline in the amount of metal ion biosorbed. Similar trends have been reported for the pH dependence on biosorption of Cd(II) by cells of *Spirulina platensis* immobilized in alginate and silica gel (Rangsayatorn et al., 2002). Also, the pH dependence of Cd(II) biosorption by macroalgae and by red algae (Sari & Tuzen, 2008) showed similar results. In these cases pH 5 was reported as optimum pH for Cd (II) biosorption. This result therefore shows that weak acidic pH favours Cd(II) biosorption on *Calotropis procera*. At low pH value there are many H^+ ions in the solution competing with the Cd (II) ions and are more favourably bound to the negatively charged active sites on the adsorbent making these sites less available for the Cd (II) cations. On the other hand, at high pH, metal hydroxides are formed and both species are adsorbed at the surface of adsorbent either by ion exchange mechanism or by hydrogen bonding. This therefore causes a competition at the active sites (Sari & Tuzen, 2008). Hence, the decrease in metal uptake is observed at high pH values similar to what has been reported in literature (Razmouski & Sciban, 2008; Dang et al., 2009; Babarinde et al., 2008).

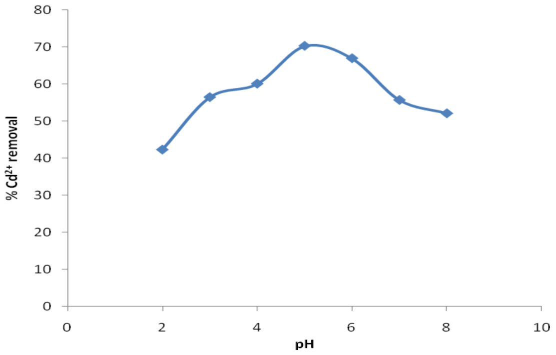

Fig. 2. Effect of initial solution pH on biosorption of Cd(II) onto the leaf of *Calotropis procera*. (temp. 27°C, initial metal ion concentration 0.3 mM, contact time 120 min).

Effect of contact time: The rate of biosorption is important for designing batch biosorption studies. Consequently, the effect of contact time on the biosorption of Cd(II) was investigated in this study.

The result of this effect is presented in Fig. 3 which shows that the optimum time for Cd(II) ions biosorption is 60 minutes. It is observed that further increase in time did not cause any enhancement in the biosorption of the cadmium ions because at such optimum time, there is saturation of the active sites on the biomass.

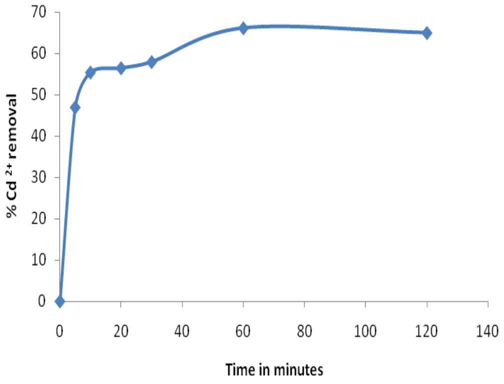

Fig. 3. Effect of contact time on the biosorption of Cd(II) by *Calotropis procera.* (adsorbent concentration 50 mg/L, initial metal ion conc. 0.3 mM, temperature 27 °C and optimum pH).

Biosorption kinetics: The biosorption of cadmium (II) from its aqueous solution increased rapidly with increase in time within the first 20 minutes after which the optimum time was reached. The rapidity in the biosorption of the ions from solution at the initial state reflects the availability of abundant active binding sites on the cell wall of the biomass. The rate of biosorption does not increase after the optimum time due to the fact that the available binding sites on the biomass were used up therefore, further increase in contact time did not cause any enhancement in the biosorption of the metal ions. The results of this kinetic study were tested with three kinetic models. The pseudo-first-order, pseudo-second-order and the intraparticle diffusion equations were applied to the kinetic study as shown in Eqs. (3), (4) and (5), respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (4)$$

$$R = K_s t^b \qquad (5)$$

where k_1 is the Lagergren rate constant of the biosorption (min^{-1}); k_2 is the pseudo-second-order rate constant ($\mathrm{g\ mg}^{-1}\ \mathrm{min}^{-1}$); q_e and q_t are the amounts of metal ions sorbed ($\mathrm{mg\ g}^{-1}$) at equilibrium and at time t, respectively. R is the percent metal biosorbed, K_s is the intraparticle diffusion constant, t is the contact time, while b is the gradient of the linear plot as shown in eqn. (6). In the linear form, Eq. (4) turns to Eq. (6).

$$\log R = b \log t + \log K_s \qquad (6)$$

A plot of $log(q_e - q_t)$ against t, for pseudo first order kinetics clearly indicates (not shown) that the pseudo-first-order equation did not provide a good description of the sorption process**.**

However, a plot of t/q_t against t, for pseudo-second-order model adequately provided a good fit as shown in Fig. 4. The pseudo-second-order model suggests that the biosorption process follows a pseudo-second-order mechanism. Therefore, the rate of occupation of biosorption sites is proportional to the square of the number of unoccupied sites (Zafar et al., 2006; Overah, 2011). The value of q_e and k_2 were determined from the slope and intercept of the plot of t/q_t against t. These values as well as the correlation co-efficient values (R^2) are presented in Table 1**.** The linearity of the plot as indicated by $R^2 \approx 1$ shows the applicability of the model for this biosorption process.

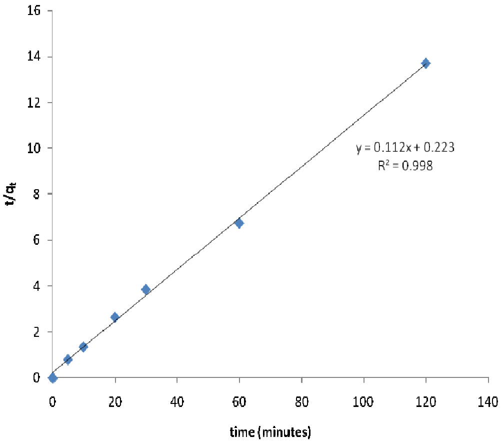

Fig. 4. The pseudo-second-order plot for the biosorption of Cd (II) by *Calotropis procera* leaf. (Conditions: optimum pH; optimum biomass dose, 110 mg ; adsorbate conc 0.3mM; time, 120 mins; temperature, 27°C.)

Table 1. The kinetic parameters from the pseudo-second-order model for the biosoprtion of Cd (II) by *Calotropis procera* leaf.

Metal ion	q_e(mg g^{-1}) (calc)	q_e(mg g^{-1}) (expt)	k_2 (g mg^{-1} min^{-1})	R^2	SD
Cd(II)	8.929	8.912	0.0562	0.998	0.1753

For the intraparticle diffusion model, the plot of log t against $log\ R$ gives linear relationship as shown in Fig. 5. The values of the rate constant and correlation coefficient are presented in Table 2

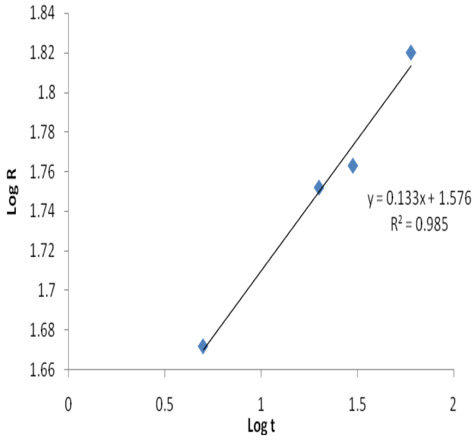

Fig. 5. Plot of the Intraparticle diffusion model for the biosorption of Cd (II) by *Calotropis procera* leaf.

Table 2. The kinetic parameters from the intraparticle diffusion model for the biosoprtion of Cd(II) by *Calotropis procera* leaf.

Metal ion	B	K_s	R^2	SD
Cd (II)	0.133	4.8355	0.985	0.0090

Effect of Biosorbent Dose: The effect of biomass dosage on Cd (II) biosorption was investigated in the range of 10 mg – 150 mg as presented in Fig. 6. The results show that biosorption efficiency is highly dependent on the dose of biomass. The Percentage Cd (II) biosorbed increased with increase in biosorbent dose up to 110 mg above which the efficiency of biosorption reduced. Therefore the biosorbent dose of 110 mg was used as optimum dose the biosorption of the cadmium ions on *Calotropis procera*. An increase in biomass concentration generally increases the amount of biosorbed metal ion because of increase in surface area of the biosorbent, which consequently increases the number of available binding sites (Esposito et al., 2001; Razmouski & Sciban, 2008). The decrease in biosorption efficiency with further increase in biomass dose above 110 mg could be explained as a consequence of a partial aggregation of biomass, which results in a decrease in effective surface area for the biosorption process (Karthikeyan et al., 2007). However, biosorption capacity or uptake (q_e) decreased as the biosorbent dose increased from 10-150 mg as presented in fig 6. This may be due to the fact that some adsorption sites may remain unsaturated during the adsorption process where as the number of sites available for sorption increases by increasing the sorbent dose. This can be attributed to an insufficiency of metal ions in solution with respect to available binding sites (Fourest & Roux, 1992).

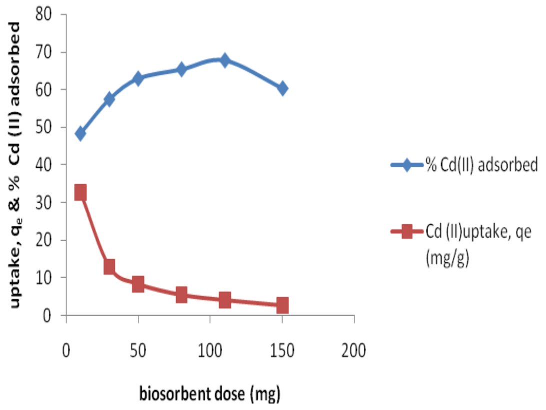

Fig. 6. Effect of biosorbent dose on uptake,q_e and biosorption efficiency for the biosorption of Cd(II) on *Calotropis procera* (Conditions: Temperature, 27°C; initial metal ion concentration, 0.3 mM; agitation time, 120 mins; optimum pH).

Effect of metal ion concentration: The effect of initial metal ion concentration on the uptake of Cd(II) onto the leaf of *Calotropis procera* at various initial metal ion concentrations was studied in the concentration range of 0.1 to 3.0 mM. The results are shown in Fig. 7. The Cd (II) sorption capacity or uptake q_e increases from 1.71 mg/g to 45.76 mg/g with increase in initial metal ion concentration. This increase can be attributed to competition for the available binding sites, that is, most binding sites are unoccupied. High initial concentration provides an important driving force to overcome mass transfer resistance of metal ion between the aqueous and solid phases (Onyancha et al., 2008; Ilhan, 2004).

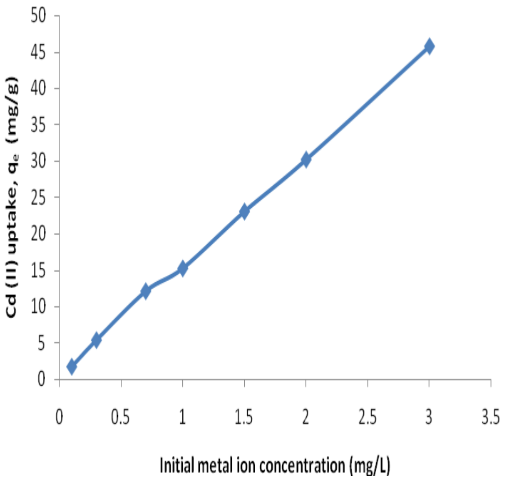

Fig. 7. Effect of initial metal ion concentration on biosorption of Cd(II) on *Calotropis procera* (Conditions: Temperature, 27°C, optimum biosorbent dose, time and pH).

Biosorption isotherms: The biosorption isotherms for the uptake of Cd(II) has been studied using initial concentration between 0.1 and 3.0 mM. The biosorption equilibrium data have been conveniently represented by biosorption isotherms, which correspond to the relationship between the biosorbate concentration for the solutiuon at equilibrium (C_e) and the mass of the biosorbate biosorbed per unit mass of the biosorbent (q_e). Basically, the Freundlich and the Langmuir theoretical models were succesfully applied to this study.The Freundlich model gives an emperical relationship for the sorption of sorbate to heterogenous sorbent surface with the assumption that different sites with several energies are involved. On the other hand, the Langmuir model describes the biosorption as a monolayer sorption onto surfaces having finite number of identical sorption sites. These two isotherms are mathematical represented by equations (7) and (8), respectively.

$$\log \Gamma = \frac{1}{n} \log C_e + \log K_f \qquad (7)$$

where K_f is a constant related to the biosorption capacity (mg g^{-1}) and 1/n is an empirical parameter related to the biosorption intensity.

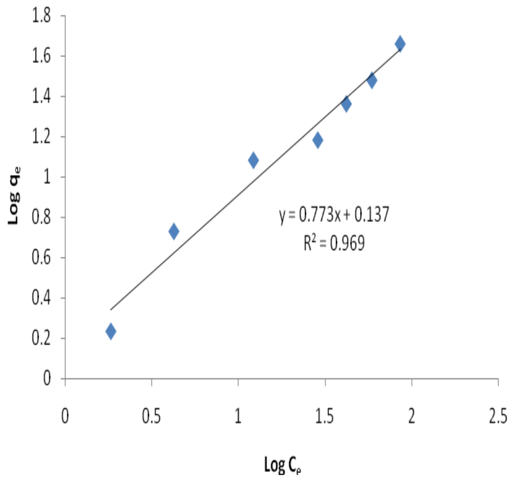

Fig. 8. Freundlich isotherm for the biosorption of Cd(II) on *Calotropis procera* (Conditions: Temperature, 27°C, optimum biosorbent dose, time and pH).

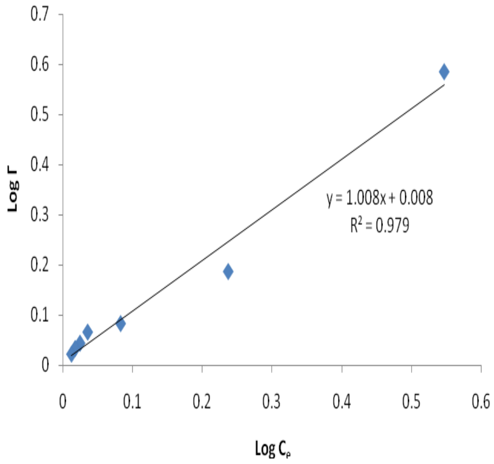

Fig. 9. Langmuir isotherm for the biosorption of Cd(II) on *Calotropis procera* (Conditions: Temperature, 27°C, optimum biosorbent dose, time and pH).

Table 3. Freundlich and Langmuir isothermal biosorption parameters for the biosorption of Cd(II) by *Calotropis procera* (Conditions: Temperature, 27°C, optimum biosorbent dose, time and pH).

Freundlich isotherm model				Langmuir isotherm model			
n	K_f	R^2	S.D.	b_m	Γ_m	R^2	S.D.
1.293	1.372	0.9696	0.0148	0.0080	123.46	0.9793	0.0013

The Freundlich isotherm for the biosorption of Cd(II) is shown in Fig. 8

$$\frac{1}{\Gamma} = \frac{1}{b_m}\frac{1}{C_e} + \frac{1}{\Gamma_m} \qquad (8)$$

where b_m is a coefficient related to the affinity between the sorbent and sorbate, Γ_m is the maximum sorbate uptake under the given condition. The Langmuir isotherm for the biosorption of Cd(II) is shown in Fig. 9. The Freundlich and Langmuir isothermal biosorption parameters for the biosorption of Cd(II) by *Calotropis procera* are presented in Table 3. The biosorption parameters compare well with the results reported for the biosorption of Cd(II) and Pb(II) with *Acacia leucoephala* (Munagapati et al., 2010)

Biosorption Thermodynamics: The Fig. 10 shows the dependence of the biosorption of Cd (II) by *Calotropis procera* on temperature. The plot indicates that increase in temperature caused increase in the biosorption until a peak was reached after which increase in temperature led to decrease in the percentage of Cd (II) ions biosorbed. The temperature, 27°C at which maximum biosorption was obtained is considered the optimum temperature. The biosorption of Cd(II) by *Calotropis procera* can be represented as the reaction involving the biosorption of metal ion (represented as M^{2+} for a divalent metal ion) from the liquid phase to the solid phase, biosorbent, with lone pair of electron (represented as Ä). It is considered as reversible reaction with an equilibrium being made between the two phases as schematically shown below:

$$\ddot{A} + M^{2+} \rightleftharpoons A\text{-}M \qquad (9)$$

For such equilibrium reactions, the distribution constant, K_c, is used to evaluate the thermodynamic parameters since it depends on temperature. It is calculated using equation (10).

$$K_c = \frac{C_{ad}}{C_e} \qquad (10)$$

K_c is related to change in free energy by equation (11) while the latter is related to other thermodynamic parameters by equation (12).

$$\Delta G^o = -RT \ln K_c \qquad (11)$$

$$\Delta G^o = \Delta H^\circ - T\Delta S^\circ \qquad (12)$$

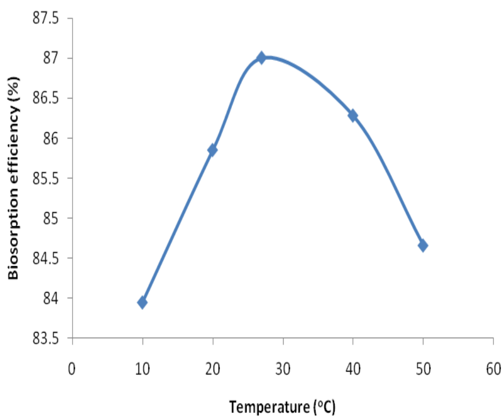

Fig. 10. Effect of temperature on the biosorption of Cd(II) on *Calotropis procera* (Conditions: intial metal ion concentration, 0.3 mM; optimum pH, agitation time and biosorbent dose).

In order to describe the thermodynamic behaviour of the biosorption of Cd (II) on the biomass, thermodynamic parameters including the enthalpy and entropy were calculated from the slope and intercept of ln K versus 1/T as shown in fig. 11. The thermodynamic parameters for the biosorption of cadmium (II) ions on *Calotropis procera leaf* is shown in table 4. The positive value of enthalpy change (ΔH^o) indicates that the biosorption process is endothermic and the positive value of change in entropy (ΔS^o) implies an increase in the randomness at the solid/solution interface during the biosorption process.

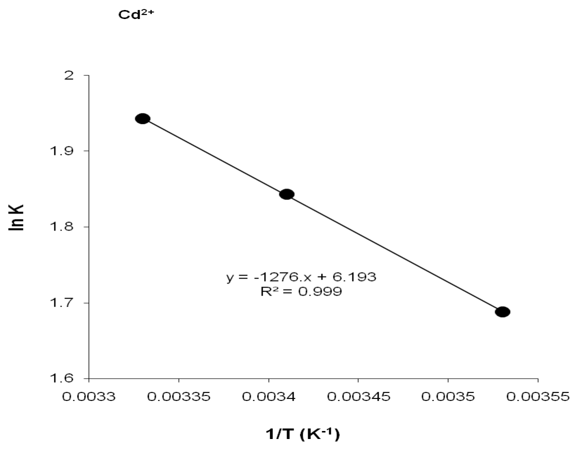

Fig. 11. *Arrhenius plot of the biosorption of* Cd^{2+} *by Calotropis procera leaf*

The Gibbs free energy change, ΔG^0, is an indication of spontaneity of a chemical reaction and therefore is an important criterion for feasibility. The negative values of the Gibbs free energy change as shown in table 4 confirm the feasibility and spontaneous nature of the biosorption process.

TABLE 4: thermodynamic parameters for the biosorption of Cd (II) on *Calotropis procera leaf*

R^2	ΔH^0 ($kJmol^{-1}$)	ΔS^0($kJK^{-1}mo^{-1}$)	ΔG^0 at T=283K	ΔG^0 at T=293K	ΔG^0 at T=300K	ΔG^0 at T=313K	ΔG^0 at T=323K
0.9999	10.60	0.052	-4.210	-4.597	-4.846	-4.686	-4.350

Conclusions: Biosorption of Cd (II) by *Calotropis procera* leaf biomass is found to be influenced by the solution pH, biosorbent dose, contact time, temperature and initial metal ion concentration. The kinetic studies indicate that the biosorption process follows pseudo-second-order and intraparticle diffusion models but the pseudo-second-order kinetics was better. Equilibrium studies show that the biosorption of Cd (II) ions is well represented by both Freundlich and Langmuir isotherms but the Langmuir model gave a better fit. The values of the thermodynamic parameters show the spontaneous, endothernic and highly disordered nature of the biosorption of Cd (II) from aqueous solution.

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