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Cadmium removal from aqueous solutions using biosorbent *Syzygium cumini* leaf powder: Kinetic and equilibrium studies

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Abstract−*Syzygium cumini* L. leaf powder and Cd(II) loaded samples were characterized using FTIR and SEM techniques. The biosorption of cadmium ions from aqueous solution was studied in a batch adsorption system as a function of pH, contact time, adsorbate, adsorbent, anion and cation concentrations. The biosorption capacities and rates of transfer of cadmium ions onto *S. cumini* L. were evaluated. The kinetics could be best described by both linear and nonlinear pseudo-second order models. The isothermic data fitted to various models in the order Freundlich>Redlich-Peterson>Langmuir>Temkin. The maximum adsorption capacity of *S. cumini* L. leaves at room temperature was estimated to be 34.54 mg g^{-1}. The negative values of ΔG^0 indicated the feasibility of the adsorption process. The endothermic nature was confirmed by the positive value of the enthalpy change (ΔH^0=3.7 kJ mol^{-1}). The positive value of entropy change (ΔS^0=16.87 J mol^{-1} K^{-1}) depicted internal structural changes during the adsorption process.

Key words: *Syzygium cumini* L., Adsorption, Equilibrium Isotherm Models, Langmuir, Temkin, Kinetic Models

INTRODUCTION

Toxic heavy metal ions are introduced into the aquatic streams by a variety of industrial activities. Hence removal and recovery of such ions from mine wastewaters, soils and waters has been important from the economic point of view and also for finding solutions to solve environmental problems [1,2]. Heavy metals and other metal ions exist as contaminants in aqueous waste streams of many industries. Mining and metallurgy of cadmium, cadmium electroplating, battery and accumulator manufacturing, pigments and ceramic industries waste waters contain high concentrations of Cd^{2+} ions [3]. Main techniques utilized for treatment of Cd^{2+} bearing waste streams include precipitation, adsorption, ion exchange, membrane separation, solvent extraction, etc.

Heavy metals such as cadmium, mercury, arsenic, copper, zinc, and cadmium are highly toxic when adsorbed into the body [4], causing acute poisoning, cancer, brain damage, etc. 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 [5,6]. The "*Itai-Itai*" disaster occurred due to cadmium contamination in the Jintsu river of Japan [7]. 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 [8]. 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. Even though various regulatory bodies set limits for heavy metal discharge into aquatic streams, metal ions are being added to water stream at a much higher concentration than the prescribed limit, thus causing health hazards. Among the various water-treatment techniques described, adsorption is generally preferred due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness [9].

The search for low-cost adsorbents that have metal binding capacities has intensified and materials locally available in large quantities such as natural materials, agricultural waste or industrial by products can be utilized as low-cost adsorbents. Kuyucak [10] indicated that the cost of biomass production played an important role in determining the overall cost of a biosorption process. Therefore, low cost biomass becomes a crucial factor when considering practical application of biosorption.

The present work is an attempt in that direction to find an alternate, cheap, green adsorbent. With that objective in mind, we conducted experiments to investigate the potential use of untreated *Syzygium cumini* L. for removal of cadmium from aqueous solution. Though *S. cumini* L. has been used for lead adsorption [11], there is no information about its adsorption potential towards cadmium.

MATERIALS AND METHODS

1. Preparation of Biosorbent

The green *Syzygium cumini* L. (SCL) 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 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 by using a domestic mixer-grinder. The dried leaves of 75-212 μm particle size were used as biosorbent for cadmium adsorption without any pretreatment.

2. Chemicals

Stock solution of cadmium concentration 1,000 mg L^{-1} was prepared by dissolving 4.5637 g of $3CdSO_4 \cdot 8H_2O$ (Loba-chemie Indoaus-

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tranal Co.) in 2,000 mL of distilled water. The pH of solutions for adsorption experiments was adjusted with 0.1 N HCl or NaOH.

3. Biosorption Experiments

Biosorption experiments were performed at room temperature (30±1 °C) in a water bath shaker (maker Remi) at constant speed (260 rpm) using 100 mL Borosil conical flasks containing 50 mL solution of different cadmium concentrations. After 30 min of contact time (according to the preliminary sorption dynamics tests with 0.25 g *S. cumini* L. leaves biomass), equilibrium was reached and the reaction mixture was separated. The metal content in the solution was determined by using an atomic absorption spectrometer (Perkin Elmer AAnalyst 200, USA) at a wavelength of 228.80 nm. The amount of metal adsorbed by *SC*L leaves was calculated from the differences between metal quantity added to the biomass and metal content left in solution using the following equation:

$$q_t=(C_0-C_f)V/m \tag{1}$$

Where q_t is the metal uptake at any time 't' (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.

4. Instrumental Analysis

The adsorbent *Syzygium cumini* L. (SCL) 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 4,000 cm^{-1} with a resolution of 1 cm^{-1} using four scans with background subtraction. For SEM 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). It was then 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 SCL obtained was 53.3 m^2 g^{-1}.

RESULTS AND DISCUSSION

1. Characterization of Adsorbent *Syzygium cumini* L. (SCL)

The FTIR spectra of SCL before and after cadmium adsorption are shown in Fig. 1. The following identification is related to the SCL: broad and intense peak at 3,467 cm^{-1} assigned to the stretching of O-H group due to inter-and intra hydrogen bonding of polymeric compounds (macromolecular association), such as alcohols, phenols and carboxylic acids, as in pectin, cellulose and lignin. The O-H stretching vibrations occur within a broad range of frequencies indicating the presence of "free" hydroxyl groups and bonded O-H bands of carboxylic acids [12]. The band at 2,935 cm^{-1} indicates symmetric or asymmetric C-H stretching vibration of aliphatic acids [13]. The band at 2,860 cm^{-1} is the symmetric stretching vibration of CH_2 due to C-H bonds of aliphatic acids [14]. The band observed at 1,736 cm^{-1} is for the stretching vibration of C=O bond due to non-ionic carboxyl groups (-COOH, $-COOCH_3$), and may be assigned to carboxylic acids or their esters [13]. Bands appearing at 1,635 cm^{-1}, 1,456 cm^{-1}, 1,381 cm^{-1} correspond to ionic carboxylic groups (-COO-), and aliphatic acid group, vibration at 1,248 cm^{-1} to deformation vibration of C=O and stretching formation of -OH of carboxylic acids and phenols [14]. The 1,115 cm^{-1} band may be due to the presence of >C=S group. It is well indicated from FTIR spectrum of SCL that carboxyl and hydroxyl groups are present. These groups in biopolymers may function as proton donors; hence deprotonated hydroxyl and carboxyl groups may be involved in coordination with metal ions [15]. On comparing the IR spectra of SCL before and after adsorption, it is seen (Table 1) that after adsorption the bands had shifted to lower values. These shifts may be attributed to the changes in counter ions associated with carboxylate and hydroxyiate anions. This indicates that the main contributors in Cd(II) uptake may be acidic, carboxyl and hydroxyl groups [15].

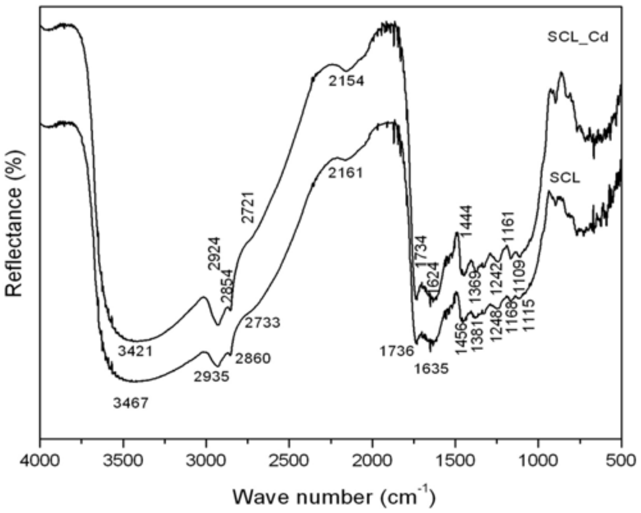

Fig. 1. FTIR spectra of *Syzygium cumini* L. leaf powder loaded with and without Cd(II).

Microstructures of the leaf accomplished with compositional map for Cd are illustrated in Fig. 2(a), 2(b) and 2(c). When the texture is compared with the unloaded leaves, it is observed that the particles have agglomerated and formed distinct grains after cadmium adsorption. The cadmium distribution on the porous grains (Fig. 2(c)) shows

Table 1. Shift of FTIR peaks after cadmium adsorption

Wave numbers cm^{-1}		
Original sorbent	Cadmium loaded sorbent	Shift
3467	3421	46
2935	2924	11
2860	2854	6
2733	2721	12
2161	2154	7
1736	1734	2
1635	1624	11
1456	1444	12
1381	1369	12
1248	1242	6
1168	1162	6
1115	1109	6

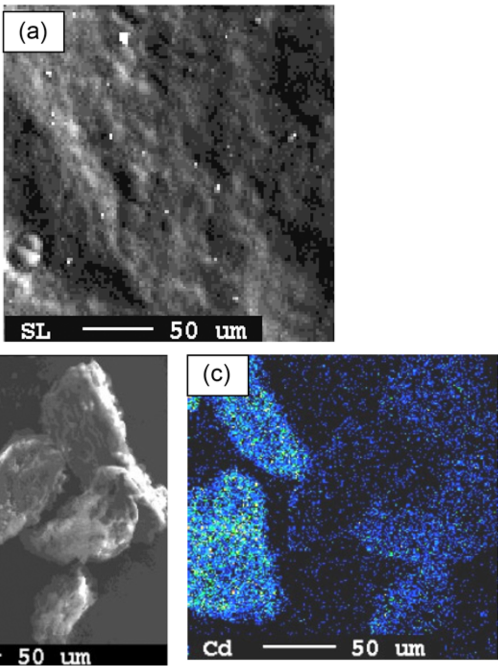

Fig. 2. Scanning Electron Micrographs of *Syzygium cumini* L. leaf (a) and leaf powder loaded with Cd (b), (c).

higher level when compared to the less porous particles.

2. Adsorption Studies

2-1. Effect of Contact Time

To find the mechanism of adsorption and potential rate controlling step, kinetic models have been used to test experimental data. When batch stirred tank reactors (BSTR) are used to generate the data, all the material surface binding sites are made readily available for metal uptake so the effect of external film diffusion on biosorption rate can be assumed not significant and ignored in any engineering analysis [16]. From the contact time results, it was found that the amount of metal adsorbed, q_t (mg g^{-1}) increased with increased contact time. The adsorption rate within the first 15 min was observed to be very high and thereafter the reaction proceeded at a slower rate and finally reached a plateau value. The data obtained from the adsorption of cadmium ions on *S. cumini* L. powder showed that a contact time of 30 min was sufficient to achieve equilibrium and the adsorption did not change significantly with further increase in contact time. Therefore, the uptake and unadsorbed cadmium concentrations at the end of 30 min are given as the equilibrium values (q_e=12.45 mg g^{-1}; C_e=37.74 mg L^{-1}), respectively.

2-1-1. Kinetic Models

The kinetics data was analyzed by 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. Linearized pseudo-first-order [17] and pseudo-second-order [18] kinetics equations are given in Eqs. (2) and (3), respectively.

$$\ln(q_e-q_t)=\ln q_e-k_1 t \tag{2}$$

$$t/q_t=1/k_2 q_e^2+t/q_e \tag{3}$$

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

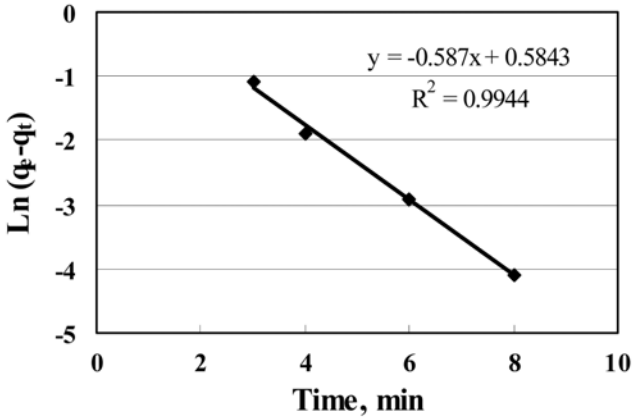

Fig. 3. Pseudo-first-order kinetics for the adsorption of cadmium by *S. cumini* L. leaf powder. Conditions: Cd 100 mgL^{-1}, pH 5.5, temp. 30±1 °C, solution 50 mL and SCL 0.25 g of −75 μm.

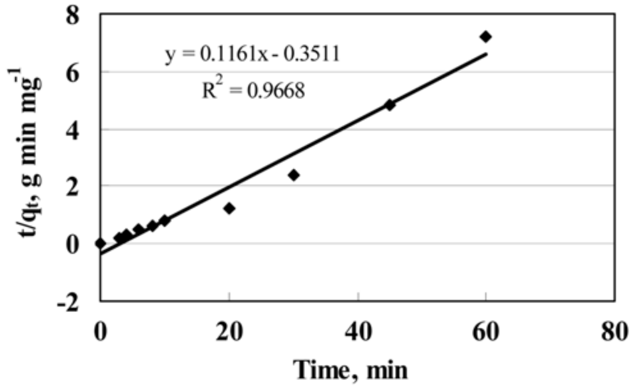

Fig. 4. Pseudo-second-order kinetics for the adsorption of cadmium by *S. cumini* L. leaf powder. Conditions: Cd 100 mgL^{-1}, pH 5.5, temp. 30±1 °C, solution 50 mL and SCL 0.25 g of −75 μm.

Fig. 3 shows the Lagergren pseudo-first-order kinetic plot for the adsorption of cadmium onto *S. cumini* L. The pseudo-first-order rate constant k_1 value was calculated from the slope of Fig. 3. The calculated k_1 value and the corresponding linear regression correlation coefficient values are shown in Table 2. Although the linear regression correlation coefficient R^2 was 0.994, the equilibrium uptake q_e was 1.79 mg g^{-1} only, which is less than the experimental value (12.45 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. 4). The pseudo-second-order rate constant k_2, the calculated q_e value and the corresponding linear regression coefficient value R^2 are given in Table 2. This model fits the data well q_e (12.45 mg g^{-1}) and regression coefficient R^2=1. Further, the data were fitted by using the non-linear regression method proposed by Ho [19]. It too fitted the experimental data very well.

2-2. Effect of pH

Namasivayam and Ranganathan [20] have reported that precipi-

Table 2. Kinetic parameters for cadmium onto *Syzygium cumini* L.

Pseudo-first order -	
Rate constant, k_1 (min^{-1})	0.587
Amount of cadmium adsorbed on adsorbent, q_e (mg g^{-1})	1.79
Regression coefficient, R^2	0.994
Pseudo-second-order	
Rate constant, k_2 (g $mg^{-1}min^{-1}$)	2.93
Amount of cadmium adsorbed on adsorbent, q_e (mg g^{-1})	12.45
Regression coefficient, R^2	1.0
Non-linear	
Rate constant, k_2 (g $mg^{-1}min^{-1}$)	1.067
Amount of cadmium adsorbed on adsorbent, q_e (mg g^{-1})	12.50
Regression coefficient, R^2	0.999

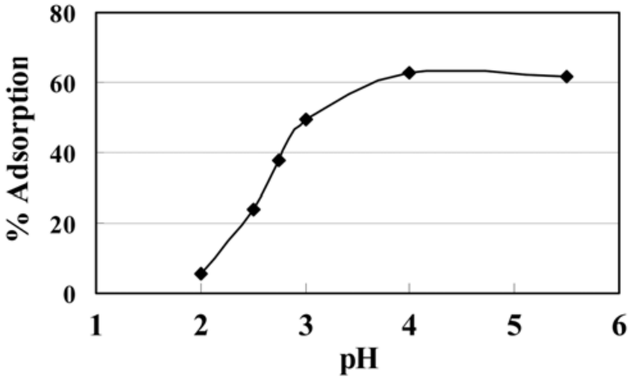

Fig. 5. Effect of pH on cadmium adsorption by *S. cumini* L. leaf powder. Conditions: Cd 100 mgL^{-1}, Solution 50 mL, temp. 30±1 °C and SCL 0.25 g of −75 μm, time 30 min.

tation of cadmium starts at pH 8.2. Hence, the pH effect was studied in the range of 2-5.5 and the results are reported in Fig. 5. Cadmium adsorption increased with the increase of initial pH of the solution. Uptake of cadmium by SCL was only 5.61% at pH 2.0 but increased to 62.27% at pH 5.5. At lower pH value, there is always competition between hydrogen and cadmium ions for the adsorption sites and the strong hydrogen ions restrict the approach of metal cations as a consequence of the repulsive force [21,22]. It was reported that at low pH, most of the carboxylic groups are not dissociated and cannot bind the metal ions in solution [22]. As the pH increased, the ligands such as carboxylate groups in SCL 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 biosorption onto the cell surface. The pH_{PZC} measurements were made with and without cadmium adsorption. Results indicated that after cadmium loading the pH_{PZC} value decreased by 0.69 units, i.e., from 7.53 to 6.94. The shift in the pH may indicate that the sorption of Cd(II) is taking place by chemisorption [23].

2-3. Effect of Initial Cadmium Concentration

Fig. 6 shows the effect of metal ion concentration on the adsorption of cadmium by *S. cumini* L. The data show that the metal uptake increased and the percentage cadmium adsorption decreased with the increase in metal ion concentration. This increase (7.68-29.52 mg g^{-1}) is a result of increase in the driving force, i.e., concentration gradient to overcome all mass transfer resistances of the metal between the aqueous and solid phases. Hence, a higher initial cadmium concentration will enhance the sorption process until saturation uptake occurs. However, the percentage adsorption of cadmium ions on *S. cumini* L. decreased from 76.77 to 29.52, which is expected and is attributed to lack of sufficient surface area to accommodate much more metal available in the solution.

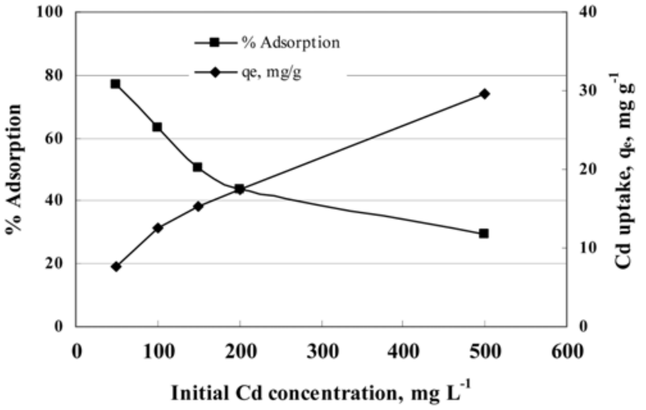

Fig. 6. Effect of metal ion concentration on the adsorption of cadmium by *S. cumini* L. leaf powder. Conditions: Solution 50 mL, pH 5.5, temp. 30±1 °C and SCL 0.25 g of −75 μm, time 30 min.

2-3-1. Equilibrium Isotherms

The equilibrium adsorption of cadmium on the *S. cumini* L. as a function of the initial concentration of cadmium was studied. There was a gradual increase of adsorption for cadmium ions until equilibrium was attained. The data were fitted to four types of equilibrium models namely Langmuir, Freundlich, Redlich-Peterson and Temkin. The Langmuir [24] adsorption isotherm is based on the assumption that maximum adsorption is achieved on the basis of saturation of monolayer of solute on the adsorbent surface. It also assumes that all adsorption sites are identical, each site retains one molecule of the given compound and all sites are energetically and sterically independent of the adsorbed quantity. The Langmuir isotherm can be expressed as

$$q_e=q_m bC_e/(1+bC_e) \tag{4}$$

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. For fitting the experimental data, the Langmuir model was rearranged as

$$1/q_e=1/q_m+C_e/bq_m \tag{5}$$

The Freundlich [25] model is fairly satisfactory empirical isotherm and can be used for non-ideal adsorption that involves heterogeneous surface energy systems. This model is represented by the equation:

$$q_e=K_f C_e^{1/n} \tag{6}$$

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). For fitting the experimental data, the Freundlich model was linearized as follows:

$$\ln q_e = \ln K_f + 1/n \ln C_e \tag{7}$$

The magnitude of the exponent ‘n’ gives an indication on the favorability of adsorption. It is generally stated that values of ‘n’ in the range of 2-10 represent good, 1-2 moderately difficult and less than 1 poor sorption characteristics [26].

The Redlich-Peterson [27] model is represented by the equation:

$$q_e = AC_e/(1+BC_e^g) \tag{8}$$

where A (L g^{-1}) and B (L mg^{-1}) are the Redlich-Peterson isotherm constants and g is the Redlich Peterson isotherm exponent, which lies between 0 and 1. The linearized form of equation is given by:

$$\ln (AC_e/q_e - 1) = g \ln(C_e) + \ln(B) \tag{9}$$

The Redlich-Peterson isotherm equation contains three unknown parameters A, B, and g. Therefore a minimization procedure is adopted to maximize the coefficient of determination, between the theoretical data for q_e predicted from the linearized form of Redlich-Peterson isotherm equation and the experimental data.

The Temkin isotherm [28] is based on the assumption that the heat of sorption would decrease linearly with the increase of the coverage of adsorbent. It has generally been applied in the following linear form:

$$q_e = RT/b_T \ln (A_T C_e) \tag{10}$$

where A_T is the Temkin isotherm constant (L mg^{-1}) and b_T is the Temkin constant related to the heat of adsorption (J mol^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}) and T absolute temperature (K).

Table 3. Langmuir, Freundlich, Redlich-Peterson and Temkin isotherm constants and correlation coefficients

Langmuir	
q_m (mg g^{-1})	34.54
b (L mg^{-1})	0.014
R^2	0.959
Freundlich	
K_f ($mg^{1-1/n}L^{-1}g^{-1}$)	3.01
n	2.61
R^2	0.99
Redlich-Peterson	
A (L mg^{-1})	1.0
B (L mg^{-1})	0.067
g	0.905
R^2	0.977
Temkin	
A_T (L mg^{-1})	0.222
b_T ($Jmol^{-1}$)	410.02
R^2	0.922

The results of Langmuir, Freundlich, Redlich-Peterson and Temkin isotherm constants are given in Table 3. It is found that the adsorption of cadmium on the *S. cumini* L. was correlated well with all four isotherms in the order Freundlich>Redlich-Peterson>Langmuir >Temkin based on the correlation coefficients. The Langmuir monolayer capacity was estimated to be 34.54 mg g^{-1}. The equilibrium curves for Cd(II) adsorption for different isotherm models are compared with the experimental results in Fig. 7.

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L [29], defined as $1/(1+bC_0)$, where b is Langmuir constant and C_0 is 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 values obtained (Table 4) indicate favorable isotherm shape ($0<R_L<1$) for adsorption of Cd(II) on SCL in the concentration range studied.

2-4. Thermodynamic Parameters

The effect of temperature on Cd(II) adsorption by SCL revealed the adsorption to be endothermic as the adsorption capacity increased with increase in temperature. Thermodynamic parameters such as the change in enthalpy, ΔH^0, change in entropy ΔS^0, and change in free energy, ΔG^0, were determined by the following relations:

$$K_c = C_{Ae}/C_e \tag{11}$$

$$\Delta G^0 = -RT \ln Kc \tag{12}$$

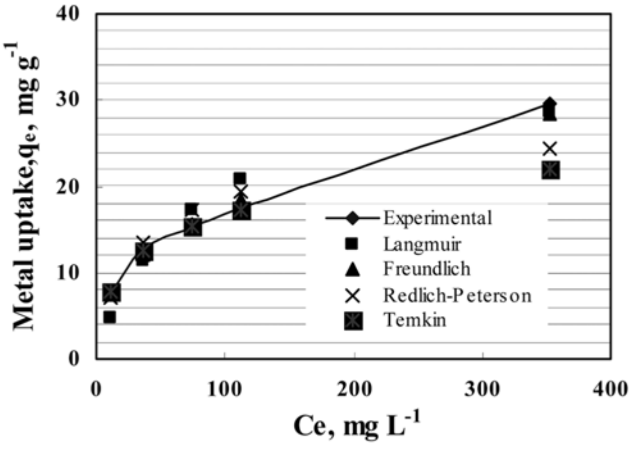

Fig. 7. Equilibrium isotherms for cadmium adsorption onto *S. cumini* L. leaf powder.

Table 4. Separation factor values for cadmium adsorption by *S. cumini* L.

Temp. °C	b×10^{-3} (L mg^{-1})	*R_L				
		50 mgL^{-1}	100 mgL^{-1}	150 mgL^{-1}	200 mgL^{-1}	500 mgL^{-1}
30	13.546	0.596	0.425	0.330	0.270	0.129
40	16.226	0.552	0.381	0.291	0.236	0.110
50	16.109	0.554	0.383	0.293	0.237	0.110

*Separation factor=R_L=1/(1+bCo)

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0 \qquad (13)$$

Where Kc is the equilibrium constant, C_{Ae} is the solid phase concentration at equilibrium (mg L^{-1}), T is the temperature in Kelvin, and R is the gas constant. ΔG^0 values were calculated by using Eq. (12) from the equilibrium constant (Kc) obtained for each temperature for an initial cadmium concentration of 100 mg L^{-1} and were estimated to be −1.40, −1.58 and −1.74 kJ mol^{-1} at 30, 40 and 50 °C, respectively. The values of ΔG^0 decreased with increase in temperature, indicating that adsorption of cadmium by *S. cumini* L. is spontaneous and the spontaneity increased with the increase in temperature.

A plot of ΔG^0 vs. temperatures was found to be linear as shown in Fig. 8. The values of ΔH^0 and ΔS^0 were determined from the intercept and slope of the plot respectively. The value of the enthalpy change (ΔH^0=3.7 kJ mol^{-1}) indicates the adsorption to be endothermic. The increase in adsorption of Cd(II) with temperature might have been due to changes in pore size and enhanced rate of intraparticle diffusion [30]. The entropy change (ΔS^0=16.87 J mol^{-1} K^{-1}) corresponds to increase in the degree of freedom of adsorbed species. Positive values of ΔS^0 have also been reported in the literature for the adsorption of spent grain [31], natural and oxidized corn cob [32] and rice husk [33].

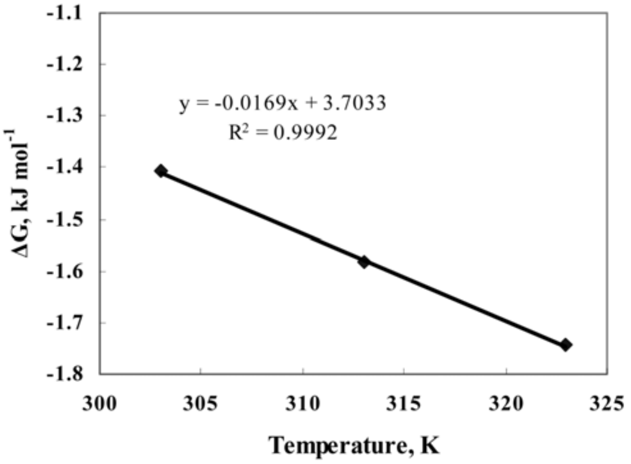

Fig. 8. Plot of Gibbs free energy change: ΔG^0 vs. temperature.

2-5. Effect of Adsorbent Dosage

Fig. 9 depicts 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 amount of cadmium adsorbed increased from 62.49 to 90.71% with an increase in adsorbent dosage from 0.25 to 4 g per 50 mL of adsorbate. The increase in the amount of solute adsorbed was obvious due to increasing biomass surface area. A similar trend was also observed for cadmium removal using *eucalyptus bark* as adsorbent [34].

2-6. Effect of Presence of Anions and Lead on Adsorption of Cadmium

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. The effect of chloride, sulfate and lead ions on adsorption of cadmium was studied by addition of desired amounts of sodium chloride, sodium sulfate or lead. The results are shown in Figs. 10. Generally the presence of chloride or sulfate ions inhibits cadmium uptake. A similar trend was also reported in the literature [34-37]. As the concentration of lead increased from 20 mg L^{-1} to 100 mg L^{-1} lead uptake decreased from 91.59 to 82.05%. The reason may be the availability of fewer adsorption sites. Since lead is extracted in preference to cadmium, partly the active sites are preferentially occupied by lead ions, thereby decreasing the cadmium adsorption. Such observations have been made for teak leaves by Rao et al. [38], for sugar beet pulp by Pehlivan et al. [37] and for ferrihydrite by Mohapatra et al. [36].

Loading capacities of some adsorbents for Cd(II) uptake are compared in Table 5. Except for first three adsorbents, the loading capacity obtained in the present work is greater. The two adsorbents, namely rice husk and wheat bran, which show higher cadmium uptake need pretreatment and kraft lignin is to be extracted. In the present work the leaves have been used without any modification.

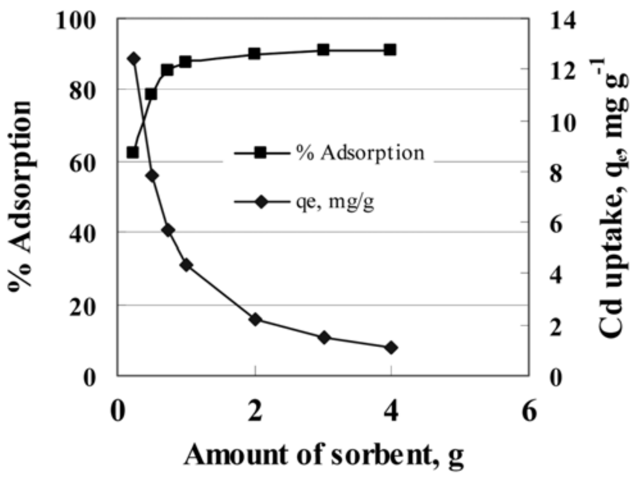

Fig. 9. Effect of adsorbent dosage on adsorption of cadmium. Conditions: Cd 100 mgL^{-1}, pH 5.5, temp. 30±1 °C, solution 50 mL, SCL size −75 μm, time 30 min.

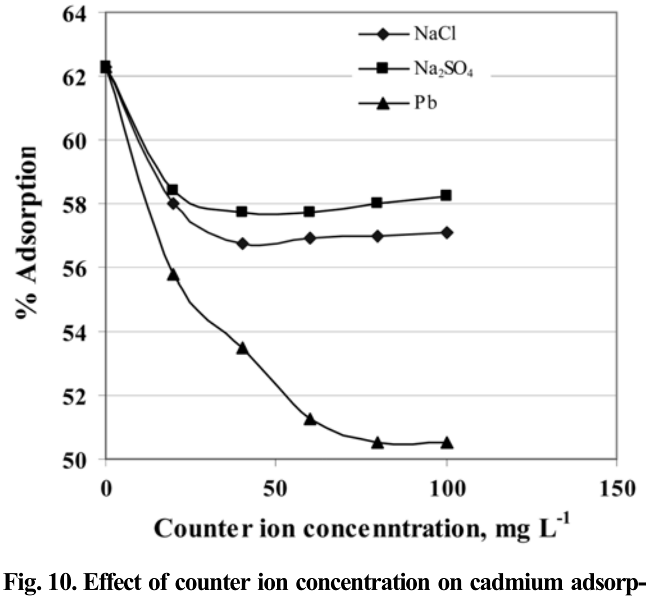

Fig. 10. Effect of counter ion concentration on cadmium adsorption on SCL. Conditions: Solution 50 mL, Cd 100 mgL^{-1}, pH 5.5, SCL 0.25 g of −75 μm, time 30 min.

Table 5. Maximum adsorption capacities of various adsorbents for cadmium adsorption

Biosorbent	q_m (mg g^{-1})	Reference
Kraft lignin	137.14	[39]
Rice husk	103.09	[33]
Sulfuric acid-treated wheat bran	101	[40]
Syzygium cumini L.	34.54	Present work
Grape stalk waste	27.88	[41]
Techtona grandis l.f	23.20	[38]
NaOH-treated spent grain	17.3	[31]
Tree fern	16.3	[42]
Wheat bran	15.71	[43]
Tea-industry waste	11.29	[44]
Petiolar felt-sheath of palm	10.8	[45]

CONCLUSIONS

The effects of process parameters such as time, pH, metal ion, adsorbent and anion/cation concentrations on process equilibrium were studied. The effect of contact time revealed that equilibrium is achieved within 30 minutes. The biosorption process could be best described by both linear and nonlinear pseudo-second-order models. The Cd(II) uptake increased by increasing pH from 2.0 to 5.5. The uptake of cadmium ions by *S. cumini* L. increased by increasing the metal ion concentration or adsorbent concentrations. Maximum loading of SCL (34.54 mg g^{-1}) is more than many adsorbents reported. The isothermic data was fitted to various models. The order of fitting these isotherms was found to be Freundlich> Redlich-Peterson>Langmuir>Temkin. adsorption models. The value of the enthalpy change (ΔH^0=3.7 kJ mol^{-1}) indicated that the process is endothermic. The negative values of ΔG^0 indicated the spontaneous nature of adsorption, and the positive values of ΔS^0 suggested an increase in the degree of freedom of adsorbed species. Presence of chloride or sulfate showed marginal adverse effect on cadmium uptake. Cadmium adsorption was inhibited in the presence of lead ion. Lead was adsorbed in preference to cadmium. The SCL was characterized by FTIR and SEM both with and without cadmium loading. These studies further supported the presence of cadmium in the loaded samples. The present study shows that the *S. cumini* L. is an effective biosorbent for adsorption of cadmium ions from aqueous solutions.

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NOMENCLATURE

A : Redlich-Peterson constant [Lg^{-1}]
A_T : Temkin adsorption intensity [L mg^{-1}]
B : Redlich-Peterson constant [L mg^{-1}]
b : Langmuir constant related to the free energy of adsorption [L mg^{-1}]
b_M : Langmuir constant related to the free energy of adsorption [L mol^{-1}]
b_T : Temkin constant related to the heat of adsorption [J mol^{-1}]
C_{Ae} : solid phase concentration at equilibrium [mg L^{-1}]
C_e : equilibrium concentration of the adsorbate in solution [mg L^{-1}]
C_f : final concentration of the adsorbate in solution [mg L^{-1}]
C_0 : initial concentration of the adsorbate in solution [mg L^{-1}]
g : redlich-peterson isotherm exponent
k_1 : Lagergren pseudo-first-order rate constant [min^{-1}]
k_2 : pseudo-second-order rate constant [g $mg^{-1}min^{-1}$]
Kc : equilibrium constant
K_f : Freundlich constant indicative of the relative adsorption capacity of adsorbent [$mg^{1-1/n}$ $L^{1/n}$ g^{-1}]
m : mass of adsorbent [g]
n : Freundlich constant indicative of the intensity of the adsorption
q_e : amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium [mg g^{-1}]
q_m : maximum adsorption capacity of the adsorbent [mg g^{-1}]
q_t : amount of adsorbate adsorbed per unit mass of adsorbent at any time t [mg g^{-1}]
R^2 : Regression coefficient
R : universal gas constant [J mol^{-1} K^{-1}]
R_L : dimensionless separation factor of Hall
T : temperature [K]
t : time [min]
V : solution volume [L]
ΔG^0 : Gibb's free energy change [kJ mol^{-1}]
ΔH^0 : enthalpy change [kJ mol^{-1}]
ΔS^0 : entropy change [J mol^{-1} K^{-1}]

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