

Kinetics, mechanism, isotherm and thermodynamic analysis of adsorption of cadmium ions by surface-modified *Strychnos potatorum* seeds

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(Received 11 April 2012 • accepted 24 May 2012)

Abstract—The surface-modified *Strychnos potatorum* seeds (SMSP) were used as an effective low-cost adsorbent for the removal of cadmium ions from aqueous solution. SMSP was characterized by Fourier transform infrared spectroscopy and scanning electron microscopic analyses. The effect of operating variables such as solution pH, adsorbent dose, contact time, initial cadmium ions concentration and temperature on the removal of cadmium ions were studied in a batch mode adsorption operation. The optimum conditions for the adsorption of cadmium ions onto the SMSP were found to be: pH of 5.0, SMSP dose of 2 g/L, contact time of 30 min, temperature of 30 °C for an initial cadmium ions concentration of 100 mg/L. Kinetic data were analyzed using the pseudo-first order and pseudo-second order kinetic equations, intraparticle diffusion model, Boyd kinetic model and shrinking core model. The characteristic parameters for each model have been estimated. Adsorption of cadmium ions onto the SMSP follows the pseudo-second order kinetic model. The rate-limiting steps in the adsorption process were found to be external and internal diffusion. Equilibrium data were well described by the Langmuir isotherm model than the Freundlich isotherm model, which yields a maximum monolayer adsorption capacity of 200 mg/g. Thermodynamic parameters such as standard free energy change, enthalpy change and entropy change were also estimated. The results show that the removal of cadmium ions by the SMSP was found to be spontaneous and exothermic.

Key words: Adsorption, Cadmium Ions, Isotherms, Kinetics, Mechanism, Thermodynamics

INTRODUCTION

The wastewater from the metal plating, battery, metallurgical alloying, mining, ceramics, pigment and chemical industries mainly consists of heavy metals such as cadmium ions, and this wastewater has permanent toxic effects on all living organisms, as well as constituting a threat to the environment even at a low concentrations. Therefore, the elimination of cadmium ions from the water and wastewater is highly important to protect the public health and other living organisms. According to the Bureau of Indian Standards (BIS), the permissible limit of cadmium in drinking water is 0.003 mg/L (BIS 1992). Many conventional technologies such as precipitation, coagulation, reverse osmosis, ultrafiltration, electrodialysis, and solvent extraction can be used to remove the heavy metal ions from the water and wastewater. But these conventional technologies are relatively expensive, inefficient and generate secondary pollutants. Adsorption was found to be an important and effective technology for the control of pollution due to the heavy metal ions. Generally, the activated carbons are used as an effective adsorbent for the large number of heavy metal ions because of their higher adsorption capacities. However, the cost of the activated carbon is relatively high, which limits its applications [2]. This gives an idea for the search for new low-cost adsorbents which replace the existing commercial materi-

als. Some of the low cost adsorbents available for the removal of cadmium ions and also other metal ions from the aqueous solution are almond shell [2], hazelnut shell [2], coconut copra meal [3], corn-cob [4], grape stalk waste [5], juniper fiber (untreated) [6], juniper fiber (treated) [6], mungbean husk [7], olive cake [8], papaya wood [9], peanut hulls [10], petiolar-felth sheath of palm [11], pinus sylvestris [12], rice husk (raw) [13], rice husk (modified) [13], rice polish [14], spent grain [15], tobacco dust [16], wheat bran [17], cashew nut shell [18], sulphuric acid treated cashew nut shell [19], rice husk [20], bael tree leaf powder [21], aluminium pillared clay [22], montmorillonitic clay [23,24], calcareous clay [23,24], natural clay [25], and acid-activated clay [26].

The main objective of the present study is to evaluate the adsorption behavior of cadmium ions onto the SMSP. The influence of operating variables such as solution pH, adsorbent dose, contact time, initial cadmium ion concentration and temperature on the cadmium ions adsorption has been investigated. The adsorption kinetic data were applied to the pseudo-first order and pseudo-second order kinetic equations, intraparticle diffusion model, Boyd kinetic model and shrinking core model, to evaluate the adsorption kinetic mechanism that controls the adsorption process. The Langmuir and Freundlich adsorption isotherm models were used for fitting the adsorption isotherm or equilibrium data, to calculate the adsorption capacity of the adsorbent and also to know the type of adsorption process. Thermodynamic studies were also performed to evaluate the thermodynamic parameters and also to know the type of adsorption

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process (either exothermic or endothermic).

EXPERIMENTAL

1. Preparation of Surface Modified *Strychnos potatorum* Seeds

Strychnos potatorum (Nirmali) tree is grown in southern and central part of India, Sri Lanka, and Burma. It is known as Nirmali tree or Clearing nut tree. *Strychnos potatorum* seeds were collected from Pudukkottai District, Tamilnadu, India and were used as a raw material for the preparation of surface modified adsorbent. The seeds of *Strychnos potatorum* were thoroughly washed with double distilled water to remove the impurities and were then allowed to dry at sun light. This material is called as raw *Strychnos potatorum* seeds (RSP). The surface modified *Strychnos potatorum* seeds were prepared by treating one part of *Strychnos potatorum* seeds and two parts by weight of concentrated sulfuric acid for about 24 h. To remove the excess sulfuric acid, the dehydrated *Strychnos potatorum* seeds were rinsed with double distilled water until the pH of the supernatants remained constant at the pH of 7.0. This material was dried at 80 °C for 3 h, ground and then sieved to obtain the size of 42 mesh fractions. The surface modified *Strychnos potatorum* seeds were abbreviated as SMSP and used as an adsorbent for the removal of cadmium ions from the aqueous solution.

2. Preparation of Cadmium Ion Solution

Cadmium ions solution used in this batch adsorption study was obtained by the dilution of cadmium ions stock solution (500 mg/L) prepared by dissolving the 1.1405 g of $3\text{Cd}(\text{SO}_4)\cdot 8\text{H}_2\text{O}$ salt (Merck Chemicals, India) in 1 liter of double distilled water.

3. Analytical Procedure

The concentration of cadmium ions in the supernatant was determined by AA6300 Atomic absorption spectrometer, AAS (Shimadzu, Japan). The solution pH was measured with a Hanna pH meter using a combined glass electrode (HI 98107, Hanna Equipments Private Limited, Mumbai, India). FTIR analysis was used to identify the different chemical functional groups available in the solid adsorbent (PE IR SPECTRUM ASCII PEDS 1.60 spectrometer). The surface morphology of the adsorbent was analyzed using a Quanta 200 FEG scanning electron microscope at an accelerating voltage of 20 kV, and with the working distance of 20 μm for the adsorbent.

4. Batch Adsorption Studies

The adsorption of cadmium ions onto the SMSP was investigated in a batch adsorption mode of studies. The effect of operating variables such as solution pH, adsorbent dose, contact time, initial cadmium ions concentration and temperature on the cadmium ions removal was studied. The effect of pH on the cadmium ions removal was investigated in the pH range of 2.0-7.0 for the operating conditions: initial cadmium ion concentration=100 mg/L, adsorbent dose=0.2 g, contact time=30 min, volume=100 mL and temperature=30 °C. The initial solution pH was brought to the desired pH value for the cadmium ions by adding 0.1 M HCl or 0.1 M NaOH. The mixture (adsorbent+adsorbate) was taken in a series of 250 mL Erlenmeyer flasks and it was shaken in a rotary shaker at 80 rpm for about 30 min. Then the mixture was centrifuged and the concentration of cadmium ions in the supernatant was analyzed by using AAS. Each determination was repeated thrice, and the result obtained is the average of the values. Batch adsorption studies were carried out with

SMSP in different adsorbent doses, from 0.05 to 0.4 g in a 100 mL solution containing 100 mg/L of cadmium ions at pH 5.0, for a contact time of 30 min at 30 °C. The mixtures were then shaken, centrifuged, and the supernatants were analyzed as mentioned above. Batch adsorption studies were carried out with SMSP by varying the contact time from 5 to 60 min at 30 °C, while keeping the other parameters such as pH, SMSP dose and initial cadmium ion concentration constant at 5.0, 0.2 g and 100-500 mg/L, respectively. The mixtures were then shaken and withdrawn at different contact time intervals and centrifuged. The supernatants were analyzed as mentioned above. Batch adsorption studies were carried out by contacting 0.2 g of the SMSP with 100 mL of cadmium ion solution of different initial cadmium ion concentrations (100-500 mg/L) at pH 5.0 and at a temperature of 30 °C. The mixtures were shaken for 30 min at a speed of 80 rpm and then centrifuged. The supernatants were analyzed as mentioned above. Batch adsorption studies were performed with the SMSP at different temperatures of 30, 40, 50 and 60 °C for a fixed initial cadmium ion concentration (100-500 mg/L) with a SMSP dose of 0.2 g and pH 5.0. The contents were shaken for 30 min at a speed of 80 rpm and centrifuged. The supernatants were analyzed as mentioned above. The percentage removal of cadmium ions was calculated by using the following relationship:

$$\% \text{ Removal} = \frac{C_o - C_f}{C_o} \times 100 \quad (1)$$

Where C_o and C_f are the initial and final cadmium ions concentration in the solution (mg/L), respectively. The amount of cadmium ions adsorbed onto the SMSP at time t , q_t , was calculated by the following relationship:

$$q_t = \frac{(C_o - C_t)V}{m} \quad (2)$$

Where C_t is the concentration of cadmium ions in the solution at time t (mg/g), V is the volume of the solution (liter) and m is the mass of the SMSP (g). The amount of cadmium ions adsorbed onto the SMSP at equilibrium, q_e , was calculated by the following relationship:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (3)$$

Where C_e is the equilibrium concentration of cadmium ions in the solution (mg/L).

RESULTS AND DISCUSSION

1. Characterization of the RSP and SMSP

The adsorption capacity of the adsorbent mainly depends upon the porosity and also the chemical reactivity of the functional groups present on its surface. The different chemical functional groups present in the adsorbent were observed by FTIR analysis. The FT-IR spectra of the RSP and SMSP are shown in the Fig. 1(a) and 1(b). The FTIR spectra of the RSP are shown in Fig. 1(a). The intense peak at $3,399 \text{ cm}^{-1}$ was due to OH stretching vibration of water and stretching vibration of amine. Presence of NH_2 was confirmed by N-H bending vibration at $1,524 \text{ cm}^{-1}$ and C-N stretching vibration at $1,249 \text{ cm}^{-1}$. Presence of H_2O was also confirmed by its bending vibration at $1,633 \text{ cm}^{-1}$. The peaks at $2,924$ and $2,854 \text{ cm}^{-1}$ were

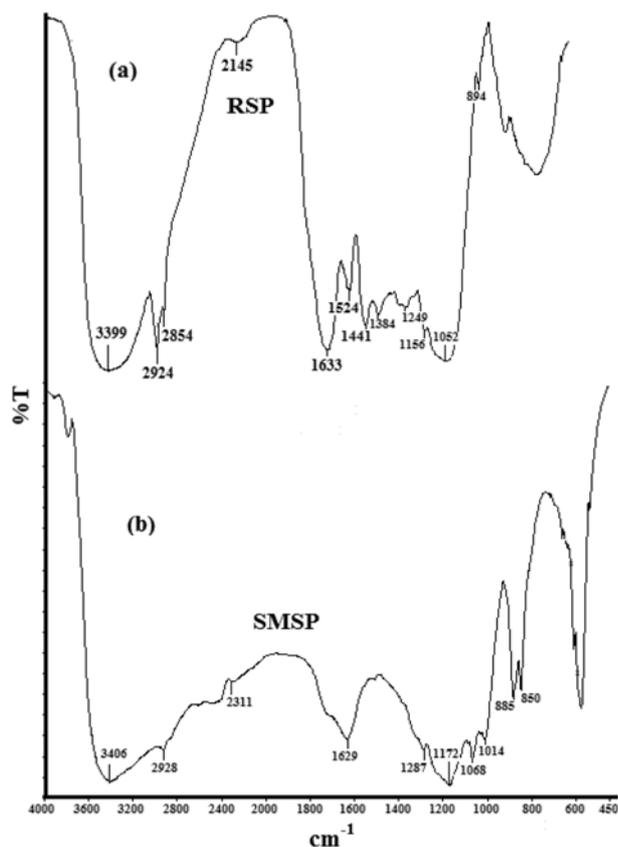
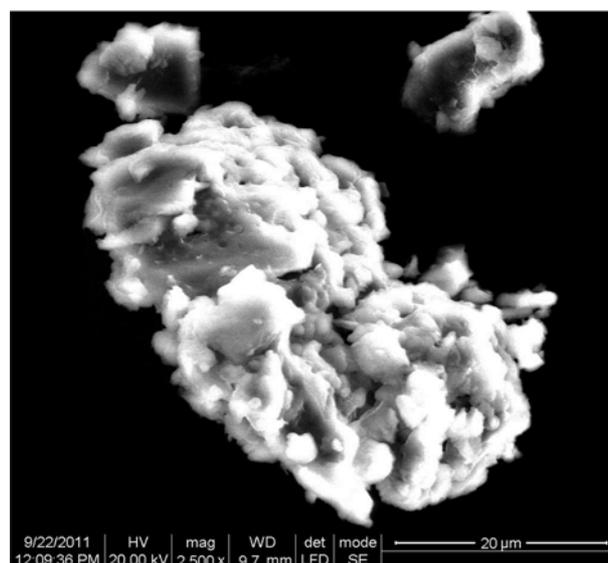
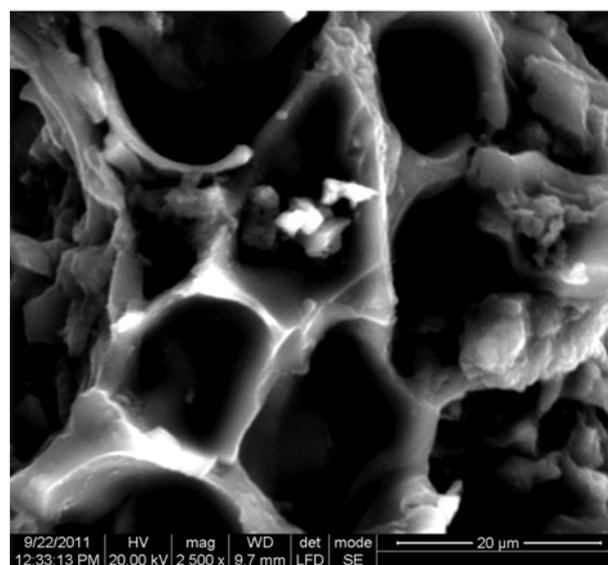


Fig. 1. FT-IR spectrum of (a) RSP and (b) SMSP.

due to -CH_2 vibration of alkyl group. The CH_2 bending vibration occurred at $1,441\text{ cm}^{-1}$ and $1,384\text{ cm}^{-1}$. The intense peak at $1,052\text{ cm}^{-1}$ was due to -CO stretching vibration of ether groups. So, the IR Spectra reveal that the seed mainly carries aliphatic grouping with ether linkages and amine groups. The FTIR spectra of the acid treated sample are shown in Fig. 1(b). It shows -OH stretching vibration of H_2O at $3,046\text{ cm}^{-1}$ and its bending vibration at $1,629\text{ cm}^{-1}$. Presence of amino group was evident by its C-N stretching vibration close to $1,300\text{ cm}^{-1}$. Alkyl group -CH_2 stretching vibration occurred just below $3,000\text{ cm}^{-1}$, but the intensity was slightly less than the seed powder. Presence of Carbonyl group C=O is evident by the peak close to $1,700\text{ cm}^{-1}$. The C-O stretching vibration of ethers yields a peak at $1,172\text{ cm}^{-1}$ and $1,068\text{ cm}^{-1}$. The peaks at 885 and 850 cm^{-1} were assigned to cyclic ethers, since the alkyl groupings were nearly absent as their bending vibration was completely absent; thus carbonization is established. The results observed from the FTIR studies indicate that SMSP has a variety of functional groups, such as hydroxyl, carbonyl and amine groups, which may be involved in the adsorption of cadmium ions onto the SMSP. The FTIR spectrum of SMSP was different as compared with RSP spectrum because there is a change in the FTIR spectrum of SMSP observed, which confirms the modification due to the effect of sulfuric acid with the RSP. This surface modification was further confirmed by the scanning electron microscopic analysis of the adsorbent. Fig. 2(a) and 2(b) show the SEM images of RSP and SMSP, respectively. From Fig. 2, it is clear that the SMSP has a considerable number of porous sites on its surface than the RSP, which indicates that the SMSP has a more adequate morphology for the cadmium ions ad-



(a)



(b)

Fig. 2. (a) SEM Image of RSP, (b) SEM Image of SMSP.

sorption.

2. Effect of Operating Variables on the Cadmium Ions Adsorption

The adsorption of cadmium ions as a function of solution pH is given in Fig. 3(a). It was suggested that the cadmium ions removal and equilibrium adsorption capacity (q_e) was increased with the increase in solution pH and then it was decreased when the solution pH was beyond 5.0. At lower pH values, the SMSP surface became more positively charged, thus reducing the attraction of cadmium ions by the SMSP. At higher pH values, the SMSP surface is more negatively charged, which attracts a greater number of cadmium ions [5,7]. However, a further increase in the solution pH causes the formation of metal hydroxide complexes [5,7], which decreases the concentration of the free cadmium ions, thereby decreasing the equilibrium adsorption capacity. The maximum adsorption of cadmium ions was observed at the solution pH of 5.0. Based on the

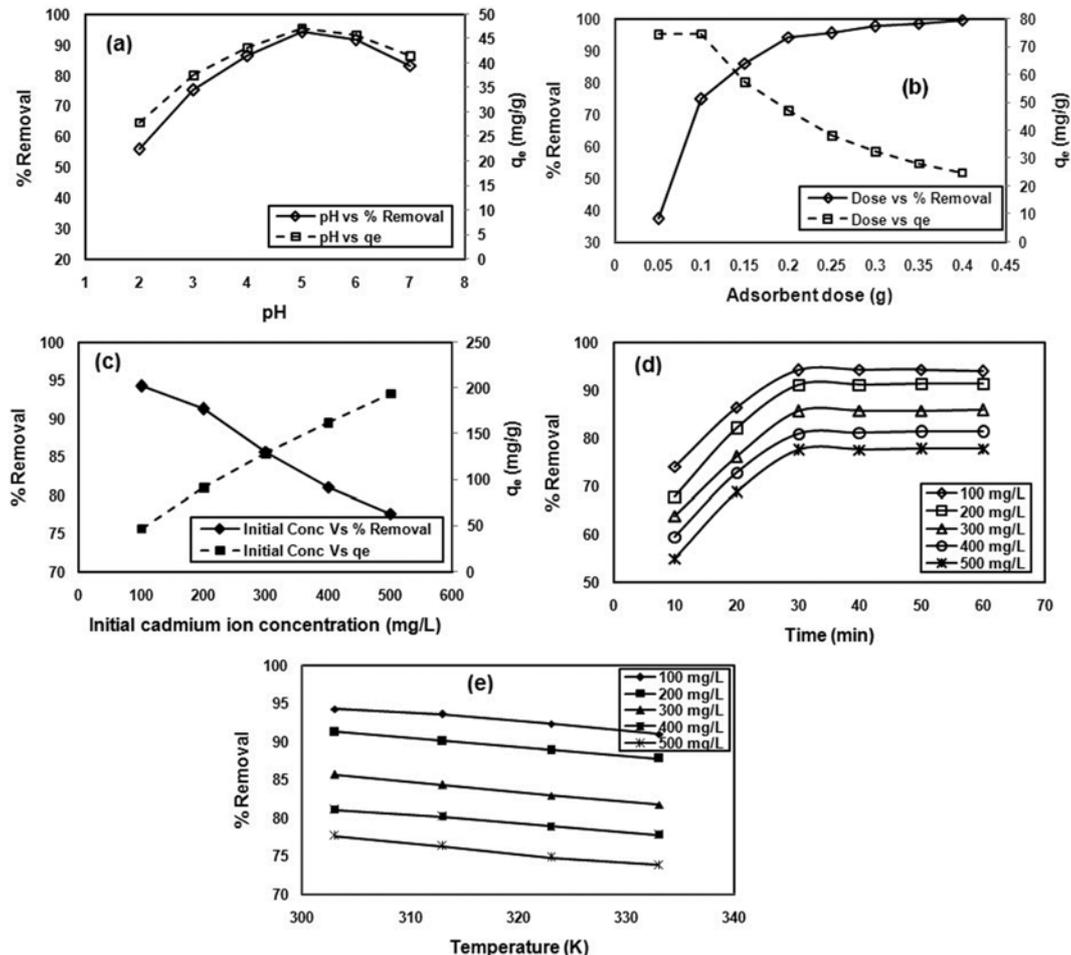


Fig. 3. Effect of operating variables on the cadmium ions adsorption.

removal of cadmium ions and uptake capacity of SMSP for cadmium ions in aqueous solution, an optimum pH of 5.0 was selected for the further experimental studies.

The effect of adsorbent dose on the adsorption of cadmium ions onto the SMSP is shown in Fig. 3(b). The removal of cadmium ions was increased from 37.23 to 99.77% with the increase in adsorbent dose from 0.05 to 0.4 g; however, the uptake capacity of SMSP decreased from 744.68 to 249.41 mg/g. It suggested that the removal of cadmium ions increases with an increase in adsorbent dosage, but the adsorption density decreases [7]. The decrease in adsorption density may be attributed to some of the active sites that remain unsaturated during the adsorption of cadmium ions onto the SMSP. The number of available active sites increases with the increase in adsorbent dosage, which results in an increase in the removal of cadmium ions. Based on the results observed, it was found that 0.2 g was selected as an optimum adsorbent dosage for the further experimental studies.

The effect of initial cadmium ions concentration on the adsorption of cadmium ions onto the SMSP is shown in Fig. 3(c). From Fig. 3(c), it is observed that the removal of cadmium ions decreases from 94.23 to 77.56% with the increase in initial cadmium ion concentration from 100 to 500 mg/L; however, the uptake capacity increases from 47.12 to 193.91 mg/g. The increase in the uptake capacity with an increase in initial cadmium ions concentration is a result

of the increase in driving force due to the concentration gradient developed between the bulk cadmium ions solution and the surface of the SMSP. At higher cadmium ion concentration, the available active sites on the SMSP are surrounded by the more cadmium ions, which leads to an increase in the uptake of cadmium ions onto the SMSP. Therefore, the value of the uptake capacity increases with the increase in initial cadmium ion concentration [7]. The removal of cadmium ions decreases with the increase in initial cadmium ions concentration, and this may be due to the fixed quantity of adsorbent dosage used in this study.

The effect of contact time on the adsorption of cadmium ions onto the SMSP is shown in Fig. 3(d). From Fig. 3(d), it is observed that the removal of cadmium ions is rapid for the first 10 min because at the beginning of the adsorption process the active sites on the SMSP surface are more available; thus cadmium ions could interact easily with the available active sites. After that the adsorption process continued at a slower rate and finally it attained equilibrium by means of the saturation of the available active sites on the SMSP surface [2]. Equilibrium was attained within 30 min of contact time; thus, further adsorption studies were conducted for a contact time of 30 min.

The effect of temperature on the adsorption of cadmium ions onto the SMSP is shown in Fig. 3(e). From Fig. 3(e), it is observed that the removal of cadmium ions decreases with the increase in tem-

perature from 30 to 60 °C, which indicates that the adsorption of cadmium ions onto the SMSP is exothermic in nature [8]. The maximum removal of cadmium ions is observed at 30 °C.

3. Adsorption Kinetics and Mechanism

The batch adsorption kinetics of cadmium ions onto the SMSP have been studied in terms of pseudo-first order [27] and pseudo-second order [28] kinetic models. The pseudo-first order Eq. (4) and the pseudo-second order Eq. (5) kinetic equations are given by the following relationship:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{5}$$

Where q_e is the equilibrium adsorption capacity (mg/g), q_t is the adsorption capacity at time t (mg/g), k_1 is the pseudo-first order reaction rate constant (min^{-1}), t is the time (min), k_2 is the pseudo-second order reaction rate constant ($\text{g/mg}\cdot\text{min}$) and $h=k_2\cdot q_e^2$, is the initial

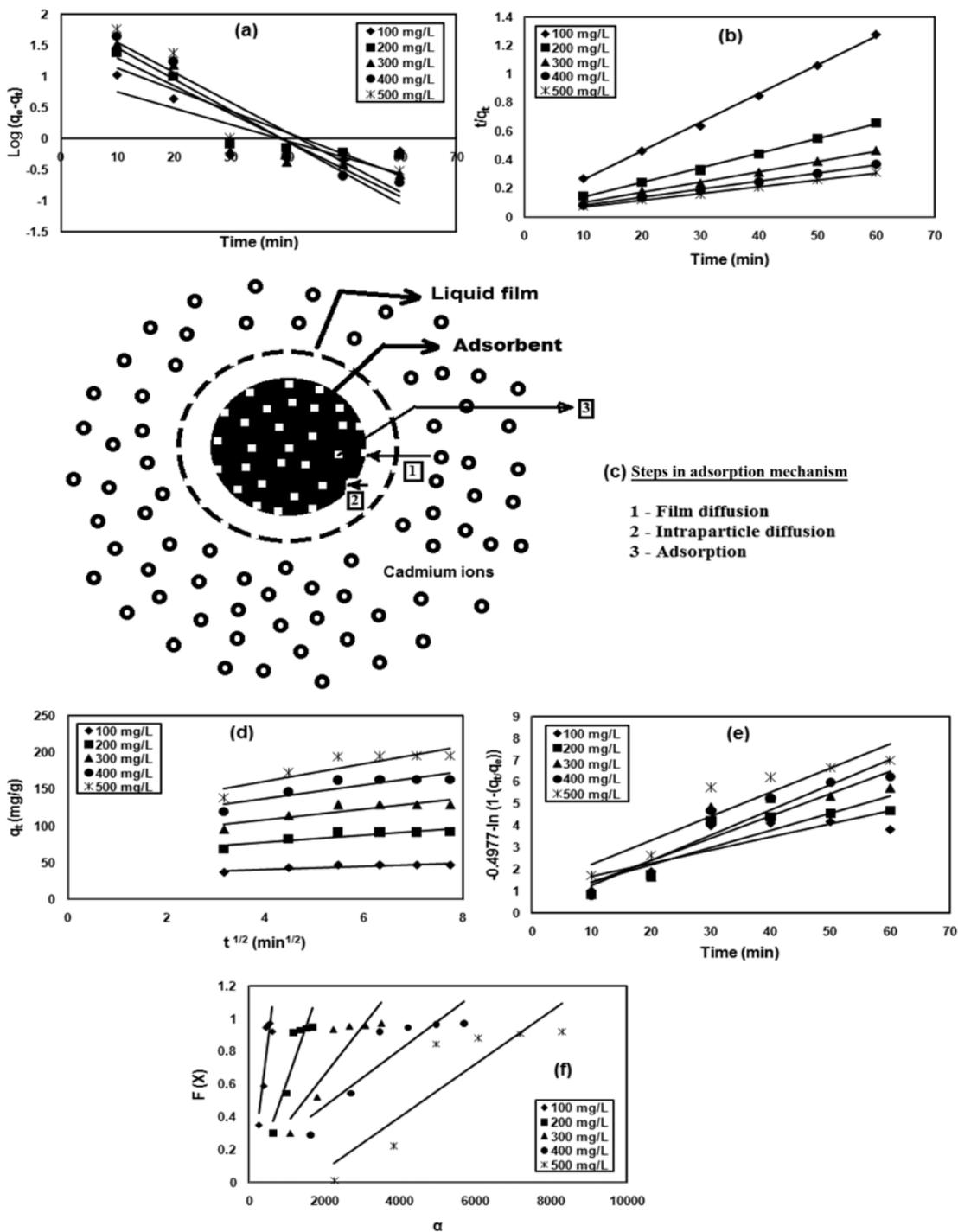


Fig. 4. Adsorption kinetics and mechanism (cadmium ions concentration=100-500 mg/L, pH=5.0, SMSP dose=0.2 g, volume of sample= 100 mL, equilibrium time=30 min and temperature 30 °C).

Table 1. Adsorption kinetics and mechanism for the adsorption of cadmium ions onto the SMSP

Kinetic model	Parameters	Concentration of cadmium ions solution (mg/L)				
		100	200	300	400	500
Pseudo-first order kinetic equation	k_1 (min^{-1})	0.0599	0.0783	0.1011	0.1082	0.1152
	q_e , cal (mg/g)	10.046	29.854	54.201	90.365	105.439
	R^2	0.667	0.789	0.816	0.890	0.858
Pseudo-second order kinetic equation	k_2 (g/mg·min)	0.00735	0.00279	0.00208	0.00166	0.00128
	q_e , cal (mg/g)	49.751	98.345	133.333	169.492	208.333
	h (mg/g·min)	18.182	27.027	37.037	47.619	55.555
	q_e , exp (mg/g)	47.653	92.043	129.112	162.998	194.935
	R^2	0.998	0.998	0.997	0.997	0.997
Adsorption mechanism						
Intraparticle diffusion model	k_p (mg/g·min ^{1/2})	2.108	4.953	7.080	9.147	12.031
	C	32.750	57.640	80.350	100.2	112.3
	R^2	0.758	0.774	0.786	0.772	0.775
Boyd kinetic model	B	0.060	0.079	0.102	0.110	0.115
	D_i ($\times 10^{-12}$ m ² /s)	3.174	4.179	5.396	6.084	5.819
	R^2	0.677	0.789	0.816	0.890	0.858
Shrinking core model	D ($\times 10^{-10}$ m ² /s)	14.357	13.874	11.149	9.3558	7.564
	R^2	0.778	0.822	0.796	0.801	0.793

adsorption rate (mg/g·min). The values of k_1 , k_2 , h , q_e , R^2 were calculated from the linear plots of $\log(q_e - q_t)$ vs t (Fig. 4(a)) and t/q_t vs t (Fig. 4(b)), and these values are listed in Table 1. The coefficient of determination (R^2) values obtained for the pseudo-first order kinetic model were found to be lower than that of pseudo-second order kinetic model, and the obtained experimental q_e values for the pseudo-first order kinetic model did not agree with the calculated q_e values. This indicates that the adsorption of cadmium ions onto the SMSP does not follow the pseudo-first order kinetic model. The R^2 values obtained for the pseudo-second order kinetic model were found to be higher than that of the pseudo-first order kinetic model. It also shows good agreement between the experimental and calculated q_e values. The small deviation of the experimental and calculated q_e values may be due to the uncertainty inherent in obtaining the experimental q_e values. The result shows that the adsorption of cadmium ions onto the SMSP follows well the pseudo-second order kinetic model.

Generally, the adsorption kinetic models are used to explain whether the system (cadmium ions - SMSP) is following either pseudo-first order or pseudo-second order kinetics. But these models are not able to explain the adsorption mechanism and also the rate controlling steps in the removal of cadmium ions by the SMSP. This adsorption mechanism can be explained with the intraparticle diffusion model [29], Boyd kinetic plot [30] and shrinking core model [31-33]. In the solid-liquid adsorption process, the adsorbate transfer is generally characterized by either film or intraparticle diffusion or both. The adsorption mechanism on the removal of cadmium ions from aqueous solution using the SMSP particles is discussed with the three consecutive steps and is given in Fig. 3(c). The adsorption kinetic data were applied with the intraparticle diffusion model to examine the adsorption mechanism and the plots (q_t vs $t^{1/2}$) are shown in Fig. 3(d). Weber and Morris intraparticle diffusion model is written as follows:

$$q_t = k_p t^{1/2} + C \quad (6)$$

Where q_t is the adsorption capacity at time t (mg/g), k_p is the intraparticle diffusion rate constant (mg/g min^{0.5}), t is the time (min) and C is the film thickness. The values of k_p , C and R^2 were calculated from the linear plot of q_t versus $t^{1/2}$ (Fig. 3(d)) and are listed in Table 1. The higher the value of C and the higher is the effect of boundary layer on the adsorption process. If the rate controlling step in the adsorption of cadmium ions onto the SMSP is the intraparticle diffusion, then the plot of q_t versus $t^{1/2}$ should be a straight line and it should pass through the origin. The deviation of this plot from the linearity indicates that the rate controlling step should be film diffusion controlled. It was observed from the Fig. 3(d), that the plots possess multi-linear portions (i.e., two steps were involved in the adsorption of cadmium ions onto the SMSP process). The first linear portion is due to the film diffusion and the second linear portion is due to the intraparticle diffusion. The deviation of the linear plot (q_t versus $t^{1/2}$) from the origin indicates that the intraparticle diffusion was not only the rate controlling step or all other steps may be involved simultaneously.

The adsorption kinetic data were analyzed with the Boyd kinetic model to determine the actual slowest step (i.e., rate controlling step) in the adsorption of cadmium ions onto the SMSP process, and the results are shown in Fig. 4(e). The Boyd kinetic model is written as follows:

$$\frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \exp(-Bt) \quad (7)$$

Eq. (7) can be rearranged into the following modified form:

$$Bt = 0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right) \quad (8)$$

Where q_e is the adsorption capacity at equilibrium (mg/g), q_t is the

adsorption capacity at time t , and Bt is a mathematical function of q_t/q_e . If the plots of $-0.4977 - \ln(1 - (q_t/q_e))$ versus t are linear and pass through the origin, the actual slowest step in the adsorption process is the intraparticle diffusion. It can be seen from the Fig. 4(e) that the plots are linear, but it did not pass through the origin. This indicates that the adsorption process is controlled by film diffusion. The value of effective diffusion coefficient, D_i (m^2/s) was estimated by using the following equation (Table 1):

$$B = \frac{\pi^2 D_i}{r^2} \tag{9}$$

Where r is the radius of the SMSP particles.

The adsorption kinetic data were further analyzed with the shrinking core model and the results are shown in Fig. 4(f). The adsorption kinetic models have been developed to estimate the mass transfer characteristic parameters in the adsorption process. This kinetic model was applied to the fluid-particle chemical reactions by Levenspiel [31]. If the adsorption process is controlled by the diffusion of cadmium ions through the liquid film (film diffusion control), then the extent of the adsorption of the cadmium ions onto the SMSP process as a function of time will be given by the following equation:

$$X = \frac{3D}{\delta RC} \alpha \tag{10}$$

If the film diffusion is the rate controlling step in the adsorption process, a plot of X versus α gives a straight-line relationship. If the process is controlled by diffusion through the reacted shell (particle diffusion control), then the model is given by the following expression:

$$F(X) = 1 - 3(1 - X)^{2/3} + 2(1 - X) = \frac{6D}{R^2 C_o} \alpha \tag{11}$$

In case of the particle diffusion control, a plot of $F(X)$ versus α gave a straight-line relationship (Fig. 4(f)) and the diffusivity of the cadmium ions in the SMSP could be determined from the slope of the plots of the Fig. 4(f) and it is given as follows:

$$D = (\text{Slope}) \frac{C_o R^2}{6} \tag{12}$$

Where

$$X \text{ is the extent of reaction} = \frac{(C_o - C)}{(C_o - C_{eq})} \tag{13}$$

$$\alpha = \int_0^t C \, dt \tag{14}$$

Where C_o is the initial cadmium ions concentration (mg/L), C_o° is the average cadmium ions binding site density of the SMSP (mg/L), C is the final cadmium ions concentration (mg/L), C_{eq} is the cadmium ions concentration at equilibrium (mg/L), D is the diffusion coefficient (m^2/s) and R is the radius of SMSP (m). From the Fig. 4(f), it was observed that the slope of the straight-line portion decreases with the increase in the initial cadmium ions concentration (Table 1). It can be seen from the Fig. 4(f), a best fit was observed in the case of intraparticle diffusion (i.e., rate controlling step) for the adsorption of cadmium ions onto the SMSP. The diffusivity of cadmium ions onto the SMSP was estimated (Table 1).

4. Adsorption Isotherms

The adsorption isotherm gives the relationship between the distribution of the adsorbate molecules in the liquid phase (C_e) and the solid phase (q_e) at equilibrium condition. The analysis of the adsorption equilibrium or isotherm data by fitting them to the various adsorption isotherm models is an important step in choosing the perfect model that can be applied for the design purpose. In this study, adsorption equilibrium data were applied to the two well known adsorption isotherm models, Langmuir [34] and Freundlich [35] adsorption isotherm models, to check the types of the adsorption process. The linear form of Langmuir adsorption isotherm model is obtained under the ideal assumption of a totally homogeneous adsorption surface and it is given as follows:

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \frac{1}{C_e} + \frac{1}{q_m} \tag{15}$$

Where q_m is the maximum monolayer adsorption capacity (mg/g), K_L is the Langmuir constant related to the affinity of the cadmium ions to the SMSP (L/mg) and C_e is the concentration of cadmium ions in the solution at equilibrium (mg/L). Fig. 5(a) shows the Langmuir plots and the parameter values are tabulated in Table 2. Higher coefficient of determination values (R^2) indicates that the adsorption of cadmium ions onto the SMSP follows the Langmuir adsorption isotherm model. The important characteristics of the Langmuir adsorption isotherm model can be expressed in terms of a dimensionless constant, separation factor (R_L), given as follows:

$$R_L = \frac{1}{1 + K_L C_o} \tag{16}$$

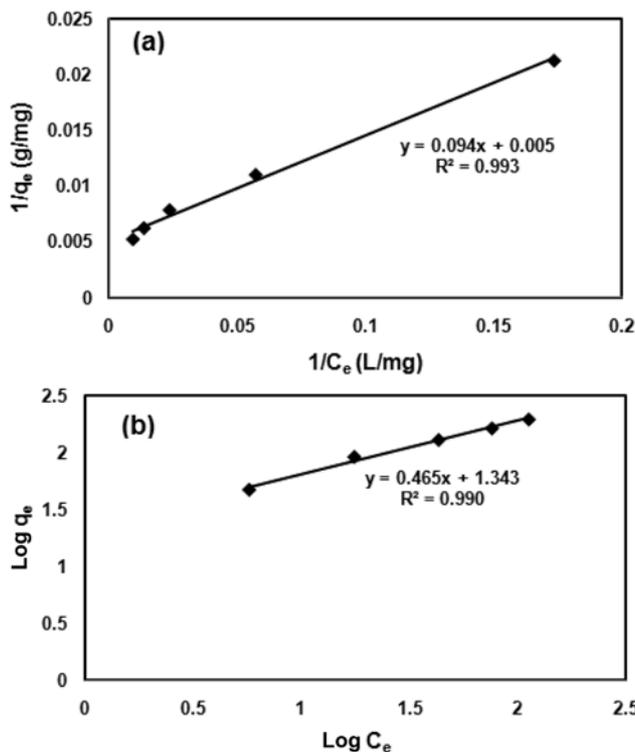


Fig. 5. Adsorption isotherms (Cadmium ions concentration=100-500 mg/L, pH=5.0, SMSP dose=0.2 g, volume of sample=100 mL, equilibrium time=30 min and temperature 30 °C).

Table 2. Adsorption isotherm models for the adsorption of cadmium ions onto the SMSP

Adsorption isotherm model	Parameters	Values	R ²
Langmuir	q _m (mg/g)	200	0.993
	K _L (L/mg)	0.053	
Freundlich	K _F ((mg/g)(L/mg) ^(1/n))	22.029	0.990
	n (g/L)	2.150	

The value of the separation factor (R_L) indicates the type of adsorption isotherm to be unfavorable (R_L>1), linear (R_L=1), favorable (0<R_L<1) or irreversible (R_L=0). The separation factor (R_L) was found to be 0.1587 to 0.036 for the initial cadmium ion concentration of 100-500 mg/L. It was observed that the obtained R_L values are in the range of 0-1, which indicates favorable adsorption. The linear form of Freundlich adsorption isotherm model is suitable for a highly heterogeneous adsorption surface and it is given as follows:

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \quad (17)$$

Where K_F is the Freundlich constant ((mg/g)(L/mg)^(1/n)) related to

Table 3. Comparison of maximum monolayer adsorption of cadmium ions onto various adsorbents

Adsorbents	q _m (mg/g)	Reference
Sulphuric acid treated cashew nut shell	436.7	[19]
SMSP	200	Present study
Olive cake	65.4	[8]
Mungbean husk	35.41	[7]
Tobacco dust	29.6	[16]
Juniper fiber (treated)	29.54	[6]
Grape stalk waste	27.87	[5]
Cashew nut shell	22.11	[18]
Rice husk (modified)	20.24	[13]
Papaya wood	17.35	[9]
Spent grain	17.3	[15]
Pinus sylvestris	9.26	[12]
Juniper fiber (untreated)	9.18	[6]
Rice husk (raw)	8.58	[13]
Peanut hulls	5.96	[10]
Hazelnut shell	5.42	[2]
Corn cob	5.09	[4]
Almond shell	3.18	[2]

Table 4. Thermodynamic parameters of cadmium ions adsorption by the SMSP

Initial conc. of cadmium ions solution (mg/L)	ΔH° (kJ/mol)	ΔS° (J/mol/K)	ΔG° (kJ/mol)			
			30 °C	40 °C	50 °C	60 °C
100	-13.849	-22.249	-7.042	-6.978	-6.678	-6.391
200	-10.431	-14.992	-5.897	-5.724	-5.571	-5.449
300	-8.210	-12.235	-4.502	-4.381	-4.237	-4.144
400	-5.867	-9.056	-3.661	-3.627	-3.533	-3.468
500	-5.702	-6.682	-3.125	-3.036	-2.919	-2.863

the bonding energy and n is a measure of the deviation from linearity of adsorption (g/L). Fig. 5(b) shows the Freundlich plots and the parameter values are tabulated in Table 2. A value of n greater than one represents a favorable adsorption process. The obtained R² value for the Freundlich adsorption isotherm model was found to be low when compared with the Langmuir adsorption isotherm model. This indicates that the Langmuir adsorption isotherm model is the best suitable model for the adsorption of cadmium ions onto the SMSP process. A comparison of the maximum monolayer adsorption capacity of SMSP with the other low-cost adsorbent materials reported in literature is presented in Table 3, which clearly shows that the SMSP was identified as better sorbent as compared with other adsorbents. Nevertheless, since SMSP is an agricultural waste of no commercial value, it should have a greater potential in water and wastewater treatment applications, as compared with other low-cost adsorbents.

5. Adsorption Thermodynamics

Adsorption thermodynamic parameters such as free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated (Fig. 6) to evaluate the thermodynamic feasibility and also the spontaneous nature of the adsorption process (Table 4):

$$\Delta G^\circ = -RT \ln K_c \quad (18)$$

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (19)$$

Where R is the gas constant (8.314 J/mol/K), T is the temperature (K), K_c is the equilibrium constant (=C_{Ac}/C_e), C_{Ac} is the amount of cadmium ions adsorbed onto the SMSP per liter of solution at equilibrium (mg/L), and C_e is the cadmium ion concentration in the solution at equilibrium (mg/L). From Table 4, it was observed that

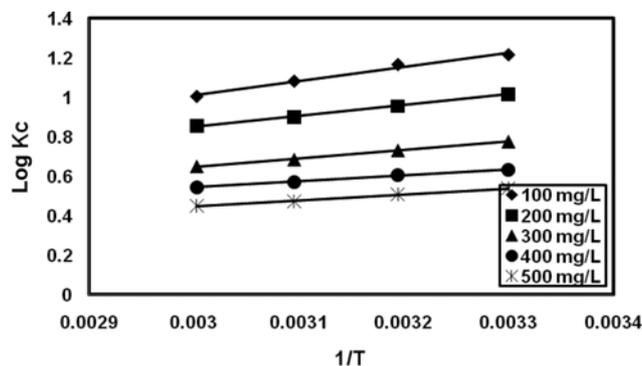


Fig. 6. Thermodynamic study (Cadmium ions concentration=100-500 mg/L, pH=5.0, SMSP dose=0.2 g, volume of sample=100 mL, and equilibrium time=30 min).

the negative value of ΔH° indicates that the adsorption process is exothermic in nature [8]. The negative value of ΔG° indicates the feasibility of the adsorption process and also indicates the spontaneous nature of the adsorption [8]. As seen from the Table 3, the ΔG° values decreased with the increase in temperature from 30 to 60 °C. This indicates that the lower temperature (30 °C) favors the adsorption easier. The negative value of ΔS° indicates that the adsorption process is enthalpy driven [8].

CONCLUSION

The surface of the *Strychnos potatorum* seeds was successfully modified using concentrated sulfuric acid, and the surface modification process was confirmed by the FTIR and SEM analyses of the before and after modification. The surface-modified *Strychnos potatorum* seeds (SMSP) show the higher adsorption capacity towards the removal of cadmium ions. The adsorption equilibrium data of the cadmium ions removal using the SMSP was well described by the Langmuir adsorption isotherm model. The adsorption kinetic data was found to follow the pseudo-second order kinetic model with the high coefficient of determination values (R^2) and also the similar values of theoretically calculated equilibrium adsorption capacity and the experimental equilibrium adsorption capacity. The adsorption process was found to be controlled by the both film and the intraparticle diffusions, and this was observed from the results of the intraparticle, Boyd kinetic and shrinking core models. In addition, the adsorption of cadmium ions onto the SMSP was found to be spontaneous and exothermic in nature. Finally, it was concluded that the SMSP can be utilized as an effective low-cost adsorbent for the removal of cadmium ions from the aqueous solution.

ACKNOWLEDGEMENTS

The authors are grateful for the financial support from the SSN Trust, Chennai.

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