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Removal efficiency of cadmium(II) from electroplating wastewater by chemically modified cottonseed cake carbon

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ABSTRACT

The present research aims to reduce the toxicity of cadmium(II) ions to environment and health, the sulfuric acid-treated cottonseed cake (SCSC) used as an adsorbent to remove cadmium(II) ions from aqueous solution and electroplating wastewater. Batch experimental results showed that the optimum equilibrium time and pH were found to be 3 h and 4.0–8.0. The Freundlich and Langmuir models were applied to investigate the equilibrium isotherms and the equilibrium data fitted well with the Langmuir model and the maximum adsorption capacity of SCSC was found to be 156.76 mg g^{-1}. Thermodynamic parameters such as $\Delta G°$, $\Delta H°$, and $\Delta S°$ have also been calculated and found that the adsorption process was spontaneous, feasible, and exothermic in nature. Kinetic data were studies using pseudo-first-order, pseudo-second-order and intraparticle diffusion models and results showed that the adsorption data has the most conformity with pseudo-second-order model followed by film diffusion process. A single-stage batch adsorber was designed for different SCSC dose using the Langmuir equation. The adsorbent efficiency was tested to remove cadmium(II)ions from industrial electroplating wastewater. The regeneration studies are also showed to evaluate the reusability of the adsorbent.

Keywords: Cadmium(II); Isotherm; Cottonseed cake; Adsorption

1. Introduction

Water is one of the most vital natural resources for all life on earth. It is the dispersion medium for all biochemical reactions of the living process and takes part in many of these reactions. Water pollution with heavy metals is one of the most important environmental problems these days. Only <3% of the water resources of the Earth are freshwaters, and only one-hundredths of a percent of these are adapted to human utilization. The valuable resources of rapid and incompetent growth of population, careless management, and excessive consumption in agricultural and industrial activities are facing a serious crisis. Groundwater is at risk of exposure to heavy metals from varies sources, including agricultural runoffs as well as urban and industrial wastewaters [1,2]. Heavy metals are natural components of the Earth's crust, and their concentrations in an aquatic environment have increased due to mining and industrial activities and geochemical processes. They are toxic or poisonous if avail as more than the recommended enough amounts in water bodies. Cadmium is one of the heavy metals and used extensively in various industries such as in batteries, electroplating, pigments, metal coating, and plastics [3].

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The presence of cadmium(II) ions in effluents generates a huge problem for the living organisms and the environment because of their high toxicity and non-biodegradability. According to World Health Organization, the permissible limit of cadmium(II) in drinking water is 0.005 mg L^{-1} [4]. The presence of excess cadmium in drinking water cause liver, kidneys, lungs damage, and anemia [5]. The harmful effects of cadmium include a number of acute and chronic disorders, such as "itai-itai" disease, renal damage, hypertension, emphysema, and testicular atrophy [6]. Therefore, the eradication of cadmium(II) from aqueous solutions is essential for environmental pollution cleaning. There are various technologies for removing heavy metal ions from aqueous solutions, including chemical precipitation, ion exchange, sorption, electrodeposition, and membrane processing [7]. Among these methods, sorption by activated carbon is the most significant method because of its easy operation and high efficiency and has been widely applied in wastewater treatment.

The crystalline structures provide huge porosity and tunable surfaces that make them a promising target in the widespread fields of biomedical, sensing, molecular separation, gas adsorption, chemical catalysis, and pharmacology [8,9]. In order to decrease the experimental cost, several research workers have been attempted to identify different low-cost adsorbents from natural materials and agricultural wastes such as Olive stone [10], Hazelnut husk [11], Groundnut husk [12], Brewery spent barley husk [13], Cherry kernel [14], Saffron leaves [15], *Albizialebbeck* pods [16], Sunflower waste [17], *Sorghumx drummondii* (Sudangrass) [18], *Barbula lambarenensis* biomass [19], *Leucaena leucocephala* biomass [20], *Bauhinia purpurea* Leaves [21], *Albizia lebbeck* and *Melia azedarach* seed shells [22], for the removal of toxic heavy metals from industrial wastewater.

The present study explores the ability of activated carbon prepared from cottonseed cake (SCSC) using sulfuric acid as an activating agent for the removal of cadmium(II) from an aqueous solution and industrial electroplating wastewater. Batch experiments were carried out by varying several key physicochemical parameters such as contact time, solution pH, and adsorbent dose at room temperature. The Freundlich and Langmuir isotherm models were used to calculate the adsorption capacity of SCSC for the removal of cadmium(II) ions at different temperatures. The kinetic data were applied using pseudo-first and second-order and intraparticle model. A single-stage batch adsorber was designed for different adsorbent doses using the Langmuir equation. The adsorbent efficiency was tested to remove cadmium(II) ions from industrial electroplating wastewater in connection with the reuse and selectivity of the adsorbents.

2. Materials and methods

2.1. Reagents and analysis

All chemicals were of analytical reagent grade or highest purity available from Merck Company in India. The concentration of cadmium(II) solutions before and after the equilibrium were determined by Elico-168 atomic adsorption spectrometer (India). The pH of the solution was measured by digital pH meter with combined glass electrode (Systronics-335, Chennai). The Fourier transform infrared (FTIR) spectra were performed using a model Shimadzu 8400S (Japan) Spectrometer with KBr as background. The morphologies of the samples were characterized by Scanning electron microscopy (SEM, model JEOL 6360, Japan). Energy-dispersive X-ray spectroscopy (EDX) was noted to obtain the composition of elements present in the adsorbents.

2.2. Preparation of SCSC

The cottonseed cake was procured from the cottonseed oil factory and washed with distilled water, dried at room temperature. Then, the dried raw material was treated with concentrated sulfuric acid in 1:1 weight ratios and kept in a hot air-oven at 160°C ± 5°C for 24 h. The acid-treated carbon material was washed with distilled water and immersed in 1% sodium bicarbonate for 1 d. After 1 d, the product was washed with an excess of water to remove free acids till the pH become 7.0. Then the washed material was dried and sieved to 20–50 American Society for Testing of Materials mesh size and used for further experiments and named as SCSC.

2.3. Preparation of the cadmium(II) solutions

The stock solution containing 1,000 mg L^{-1} of Cd(II) was prepared by dissolving 2.282 g of cadmium sulfate in 1,000 mL distilled water. The required initial concentration of Cd(II) standards was prepared by appropriate dilution of the above stock Cd(II) solution.

2.4. Batch adsorption studies

Batch studies were conducted in 100 mL of the solution containing 10 mg L^{-1} of cadmium(II) ions under investigation adjusted by varying contact time (0.5–6 h), solution pH (2–10), and carbon dose (50–300 mg) was taken in 300 mL polythene bottles and equilibrated for specific periods of time in a temperature-controlled mechanical shaker. At definite time intervals separation of the adsorbent and solution was carried out by filtration and the residual cadmium(II) concentrations were analyzed using an atomic absorption spectrophotometer. Triplicate runs of each test were conducted and the obtained data have been found to vary to <1% suggesting the accuracy of the results. In order to calculate the cadmium(II) removal (%) efficiency of SCSC was used by the following Eq. (1) [23]:

$$\mathrm{RE} = \frac{C_i - C_t}{C_i} \times 100 \tag{1}$$

where RE is the cadmium removal efficiency (%), C_i and C_t are the initial and equilibrium concentrations of cadmium(II) ions (mg L^{-1}),

2.5. Adsorption isotherms

The adsorption isotherm experiments were carried out in 100 mL of cadmium(II) solution with an initial concentration range of 10–60 mg L^{-1} and at an optimum pH of 5.0 ± 0.3. A known amount of SCSC dose of 150 mg was added to each flack. The mixture was shaken in a temperature-controlled shaker for a period of 24 h at different temperatures 27°C ± 0.5°C, 37°C ± 0.5°C, 47°C ± 0.5°C. After 24 h, the mixture was then filtered and the cadmium(II) concentration was analyzed in the filtrate by atomic absorption spectrometer (AAS). The adsorption capacity efficiency of Cd(II) ions adsorbed per gram of adsorbent (mg g^{-1}) was calculated by:

$$q_e = \frac{C_i - C_t}{M} \times V \tag{2}$$

where q_e is the amount of cadmium(II) adsorbed (mg g^{-1}), V is the volume of the Cd(II) solution (L); M is the mass of the adsorbent used (g), respectively.

2.6. Adsorption kinetics

The kinetic experiments were conducted by shaking 100 mL of cadmium(II) solution with an initial concentration range of 3–10 mg L^{-1} at an optimum pH of 5.0 ± 0.3 and a known amount of SCSC dose of 150 mg was added to each flack and equilibrated in a horizontal mechanical shaker for 1–4 h at room temperature. At the end of the shaking period, the samples were centrifuged and the concentration of metal ions was analyzed by AAS. The amount of metal ion adsorption at time t, q_t (mg g^{-1}), was calculated by the following relationship:

$$q_t = \frac{C_i - C_t}{M} \times V \tag{3}$$

where q_t is the amount of metal ions adsorbed onto the adsorbent at any time t, V is the volume of metal ion solution (L), C_t is the concentration of the metal ion at any time t (mg L^{-1}), M is the mass of the carbon (g), respectively.

3. Results and discussion

3.1. Characterization of the SCSC

The FTIR spectroscopy analysis was employed to determine the active site responsible for the adsorption cadmium(II) ions from aqueous solution based on the changes in vibrational frequencies of the functional groups. The FTIR image of SCSC are shown in Figs. 1a and b. It could be seen from spectra for SCSC that the peak at 3,370–3,470 cm^{-1} corresponds to the OH stretching [24]. The peak at 2,869 cm^{-1} indicated the presence of aliphatic C–H groups in SCSC. The bands appearing at 1,629–1,548 cm^{-1} in SCSC are ascribed to the formation of oxygen functional groups like a highly conjugated C=O stretching in carboxylic acid groups [25]. The peak at 1,369 cm^{-1} in SCSC due to S=O asymmetric stretching of the sulfonic acid group [26]. The presence of hydroxyl, carboxylic, and sulfonic acids groups are confirmed in SCSC by FTIR spectra. These SCSC carbon-containing polar functional groups (–OH, C=O, S=O) could be involved in chemical bonding and may be responsible for the adsorption of metals [27]. Further, according to Pearson's theory, hard acid prefer to interact with hard bases and soft acids with soft bases. Cd is a soft Lewis acid, bind with the functional groups containing "S," which are soft Lewis bases. Hence S=O functional groups, which are present on the adsorbent, show very high coordination with the Cd^{2+} ions [27].

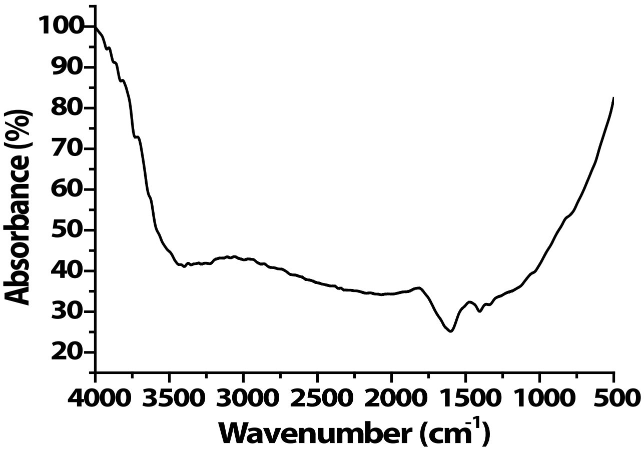

Fig. 1. FT-IR image of SCSC.

The SEM and EDX were used to analysis the surface morphology and elemental analysis of SCSC. The SEM and EDX image for the adsorption of cadmium(II) ions are shown in Figs. 2a–d. The SEM image shows that the surface of the adsorbent appears to be irregular and porous. On the basis of this fact, it can be concluded that the adsorbent has an adequate morphology for Cd(II) ion adsorption. The EDX pattern is used to confirm the adsorption of cadmium(II) ions.

3.2. Effect of contact time

Contact time is an important factor for economical adsorption. To establish an appropriate contact time between the pre-treated adsorbent and metal ion solution, percentage removal of metal ions was measured as a function of time. The effect of contact time on adsorption behavior of 100 ml of a solution containing 10 mg L^{-1} of cadmium(II) ions was studied in different time intervals ranging from 0.5 to 6 h, carbon dose of 100 mg and at pH of 5.0 ± 0.3 are shown in Fig. 3.

The experimental data showed that a rapid increase in the initial cadmium(II) adsorption up to 1 h. After that, the adsorption rate became slower, and finally, no further significant adsorption was noted beyond 3 h. This could be attributed to a larger number of vacant binding sites available for adsorption during the initial stage, which carried out via physical adsorption or ion exchange on the surface of the adsorbent. After prolonging the contact time, the occupation of the remaining vacant sites was difficult as a result of the repulsive forces between Cd^{2+} ions in the solid and liquid phase. Based on these results, a contact time of 3 h for SCSC was assumed to be suitable for all further subsequent studies.

3.3. Effect of pH

The pH is a dynamic and very important environmental factor controlling heavy metals site dissociation, speciation, adsorption, accessibility, and solution chemistry.

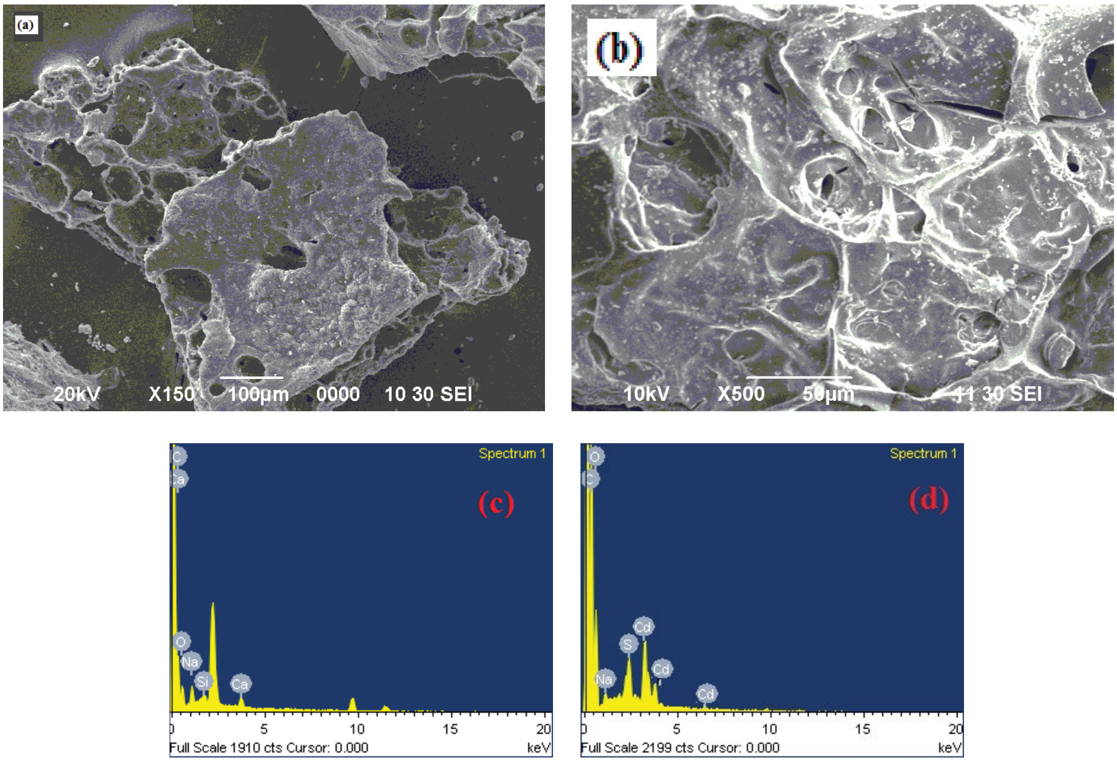

Fig. 2. (a–d) SEM and EDAX image for before and after the adsorption of Cd(II) ions.

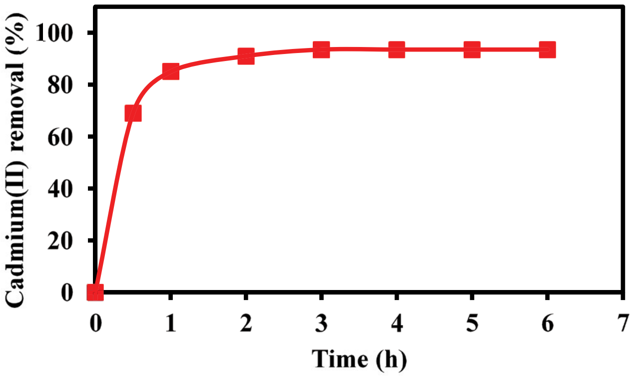

Fig. 3. Uptake of cadmium(II) ions by SCSC as a function of time.

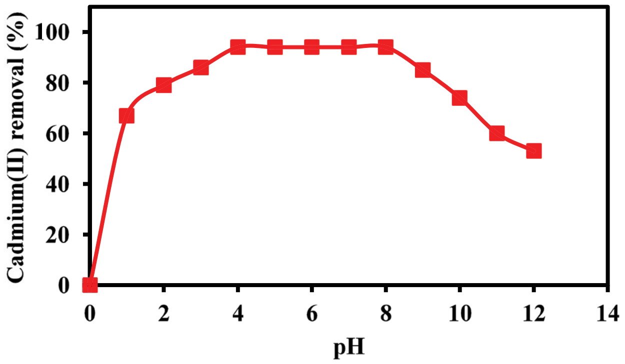

Fig. 4. Uptake of cadmium(II) ions by SCSC as a function of aqueous phase pH.

To investigate the effect of pH on cadmium(II) adsorption rate was studied about 100 ml of a solution containing the concentration of 10 mg L^{-1}, over a pH range of 2.0–10.0, carbon dose of 100 mg, and at a contact time of 3 h are exposed in Fig. 4.

Fig. 4 clearly indicates that the uptake of Cd^{2+} was found to increase with an increase in pH and attained maximum removal of 94% ± 0.3% for SCSC over a pH range of 4.0–8.0. This is due to the fact that at below pH 4, the main species such as H$^+$ ions accumulate at low adsorption levels, thereby creating a positive charge cationic metal surface. As pH increases, the concentration of H$^+$ ions decreased, hence they do not complete with metal ions on the adsorption sites, the more adsorption surface with a negative charge will easily attract the positively charged metal ions. At higher pH, metal hydroxide starts precipitating from the solution, making actual adsorption studies impossible. Therefore, further experiments were carried out at an optimum pH value of 5.0.

3.4. Effect of carbon dose

From an economic point of view, it is essential to study the influence of adsorbent dose to determine the minimum weight of adsorbent required for the effective removal of metal ions. The effect of carbon dose was studied for the adsorption of 100 ml of a solution containing the concentration of 10 mg L^{-1} of cadmium(II) ions, SCSC dose range from 50 to 300 mg at an optimum pH and contact time of 3 h are shown in Fig. 5.

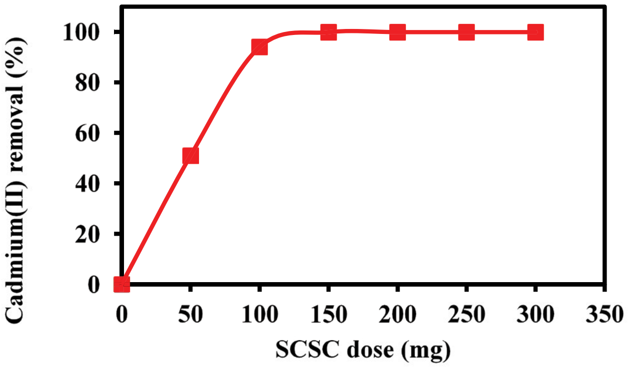

Fig. 5. Uptake of cadmium(II) ions as a function of the amount of SCSC.

The results are shown in Fig. 4 which indicates that adsorption, increased with increasing carbon dose up to a certain value and then became almost constant. It was observed that a minimum SCSC dose of 150 mg is required for the maximum removal of 99.9% ± 0.1% cadmium(II) ions. This may be due to the fact that higher the dosage of adsorbent greater the availability of surface area and the functional groups for metal ions. These chemical groups play an important role in the formation of Van der Waals bonding as the functional groups play the main role in binding metals to the adsorbent during the adsorption process. This provides more possibilities for adsorption to occur since there was less competition between metals for the binding sites.

3.5. Adsorption isotherms

The purpose of the adsorption isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface. The simplest adsorption isotherms are based on the assumption that every adsorption sites are equivalent and that the ability of a particle to bind there is independent of whether or not adjacent sites are occupied. In the present study, two most commonly used adsorption models such as Freundlich and Langmuir isotherms were applied to evaluate adsorbate adsorbent interactions at different temperatures (27°C–47°C). The isotherm parameters such as correlation coefficients (R^2), root mean squared error (RMSE), and the sum of squares error (SSE) values were calculated using MATLAB R2010b from the plot of q_e vs. C_e by non-linear regression analysis.

3.5.1. Freundlich isotherm

The Freundlich adsorption isotherm is an empirical relation between the concentrations of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact. This model allows for several kinds of sorption sites on the solid and represents properly the sorption data at low and intermediate concentrations on heterogeneous surfaces. The following Eq. (4) is used to define the Freundlich isotherm [28]:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{4}$$

where q_e is the amount of the metal adsorbed per unit weight of the adsorbent (mg g^{-1}), C_e is the equilibrium concentration of metal in solution (mg L^{-1}), K_F [(mg g^{-1}; L mg^{-1})$^{1/n}$], and n (g L^{-1}) are the Freundlich constants, which are related to the adsorption capacity and intensity, respectively. The value of n indicates that the favourability of adsorption. The values of $n > 1$ represent the favorable nature of adsorption.

3.5.2. Langmuir isotherm

The Langmuir isotherm, the monolayer model, was developed to represent chemisorptions. The theoretical Langmuir adsorption isotherm [29] is based on the three assumptions namely: adsorption cannot proceed beyond monolayer coverage, all surface sites are equivalent and can accommodate at most one adsorbed atom and the ability of a molecule to adsorb at a given site is independent of the occupation of the neighboring sites. At equilibrium, there is no net charge of surface coverage. The non-linear equation of Langmuir isotherm model is represented by the Eq. (5) as follows [30,31]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{5}$$

where q_m (mg g^{-1}) and K_L (L mg^{-1}) are the Langmuir constants, representing the maximum monolayer adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption, respectively.

The essential characteristics of the Langmuir isotherm can be described by a separation factor, which is called the equilibrium constant, "R_L", defined as [32]:

$$q_e = \frac{1}{1 + K_L C_i} \tag{6}$$

where C_i is the initial concentration of metal in solution (mg L^{-1}), and K_L is the Langmuir constant. The value of R_L indicates the type of isotherm. The values of R_L ranging between 0 and 1 confirm the feasibility of sorption onto biosorbents.

The non-linearized Freundlich and Langmuir adsorption isotherms for the removal of cadmium(II) ions onto SCSC at different temperatures are exposed in Fig. 6. The isotherm constants, correlation coefficients (R^2), RMSE, and the SSE values were calculated using MATLAB R2010b from the plot of q_e vs. C_e by non-linear regression analysis (Fig. 6) and are presented in Table 1.

Among the two isotherms, the R^2 values closer to 1 and less RMSE, SSE value suggests that the Langmuir isotherm model exhibited a better fit for the adsorption of cadmium(II), ions by SCSC at different temperatures (27°C–47°C). The conformity of the adsorption data to the Langmuir isotherm could be interpreted as an indication of a homogeneity adsorption process, leading to monolayer binding. The maximum adsorption capacity (q_m) of cadmium(II) ions onto SCSC was estimated at 156.76 mg g^{-1} at 27°C. The maximum monolayer adsorption capacity (q_m) decreased with an increase in temperature indicating an exothermic process. In addition, the R_L value for the Langmuir isotherm model is in between 0 and 1 at different temperatures, representing a favorable adsorption process.

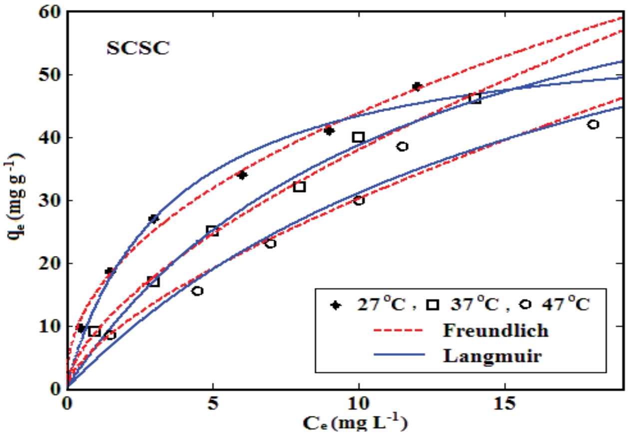

Fig. 6. Freundlich and Langmuir non-linear isotherm of Cd(II) removal onto SCSC.

Table 1
Estimated non-linear isotherm parameters and thermodynamic constants for the removal of Cd(II) ions at different temperature

Isotherm model	Parameters	SCSC		
		27°C	37°C	47°C
Freundlich	K_F	15.13	8.909	6.572
	n (g L^{-1})	2.165	1.589	1.511
	SSE	22.97	11.92	41.14
	RMSE	2.396	2.726	3.221
	R^2	0.978	0.980	0.939
Langmuir	q_m (mg g^{-1})	156.76	135.75	120.50
	K_L (L mg^{-1})	0.287	0.085	0.056
	SSE	6.797	5.816	7.867
	RMSE	1.304	1.212	1.505
	R^2	0.997	0.993	0.990
Thermodynamic constants	$\Delta G°$ (kJ mol^{-1})	–9.494	–6.303	–5.080
	$\Delta H°$ (kJ mol^{-1})	–77.112		
	$\Delta S°$ (kJ mol^{-1}K^{-1})	–0.226		

The comparison of maximum monolayer adsorption capacity of cadmium(II) onto various adsorbents are presented in Table 3. These results indicate that SCSC is a better adsorbent for the removal of cadmium(II) compared to other sorbents. Therefore, it could be concluded that the SCSC has good potential for the removal of cadmium(II) from aqueous solutions.

3.6. Thermodynamics studies

The various thermodynamic parameters, such as the standard Gibbs free energy ($\Delta G°$), the standard enthalpy ($\Delta H°$), and the standard entropy ($\Delta S°$) for the adsorption of cadmium(II) onto SCSC, were estimated using the following Eq. (7):

$$\Delta G° = -RT \ln K \tag{7}$$

Table 2
Comparative evaluation of various low-cost adsorbents for cadmium(II) removal

Adsorbents	Monolayer adsorption capacity, q_m (mg g^{-1})	References
Olive stone	7.80	[10]
Olive fruit stone	24.83	[19]
Silk cotton hull	100.00	[33]
Hazelnut husk	61.35	[11]
Hazelnut husk	20.90	[34]
Groundnut husk	29.78	[12]
Brewery spent barley husk	6.64	[13]
Cherry kernel	198.7	[14]
Red mud	12.05	[35]
Saffron leaves	68.75	[15]
Bamboo powder	8.57	[36]
Albizialebbeck pods	21.22	[16]
Sunflower head carbon	4.30	[17]
Sunflower stem carbon	4.40	[17]
SCSC	156.76	Present study

where K (L g^{-1}) is an equilibrium constant observed by multiplying the Langmuir constant q_m and K_L [37], R is the universal gas constant (8.134 kJ mol^{-1} K) and T is the absolute temperature (Kelvin). The enthalpy ($\Delta H°$) and entropy ($\Delta S°$) parameters were estimated from the following Eqs. (8) and (9):

$$\Delta G° = \Delta H° - T\Delta S° \tag{8}$$

$$\ln K_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{9}$$

The reciprocal of temperature (1/T) was plotted against ln$K$, and a straight line was obtained to calculate the values of $\Delta H°$ and $\Delta S°$ from the slope and the intercept. The results from Table 1 show that the value of $\Delta G°$ is negative at different temperature implies that the process was spontaneous and feasible. The negative $\Delta H°$ value indicates the exothermic nature of adsorption and the negative $\Delta S°$ value can be used to describe the randomness at the SCSC solution interface during the adsorption of cadmium(II) ions.

3.7. Single-stage batch adsorber

Adsorption isotherms can be used to predict the design of single-stage batch adsorptions systems and it is already been described by Mckay et al. [38]. The design purpose is to reduce the metal ion solution of volume V (L), from an initial metal ion concentration of C_0 to C_e (mg L^{-1}) in the adsorption process. The amount of adsorbent used is M (g) and the solute loading on the adsorbent changes from q_0 = 0 to q_e (mg g^{-1}). At time t = 0, q_0 = 0 and as time proceeds the mass balance equated the metal ion adsorbed from the liquid to that picked up by the solid.

The mass balance equation for the sorption system can be written as:

$$V\left(C_0 - C_e\right) = M\left(q_e - q_0\right) = Mq_e \tag{10}$$

Since the equilibrium studies confirmed that the equilibrium data for cadmium(II) ions onto SCSC followed a Langmuir isotherm equation and it can be applied in Eq. (10) and rearranged as:

$$\frac{M}{V} - \frac{C_0 - C_e}{q_e} - \frac{C_0 - C_e}{\dfrac{q_m K_L C_e}{1 + K_L C_e}} \tag{11}$$

Fig. 7 shows that the plot between the calculated amounts of SCSC required to remove cadmium(II) solution of initial concentration 50 mg L^{-1} for 75%, 80%, 85%, 90%, and 95% cadmium(II) removal at different solution volume (1–10 L) for a single-stage batch adsorption system, for which the design procedure is outlined.

3.8. Kinetic studies

Kinetic models are helpful for understanding the mechanism as well as the reaction rate of the sorbate-sorbent, the operating conditions and observed their favorability for practical remediation of metals from natural water. A number of kinetic models are available to understand the behavior of the adsorbent and also to examine the controlling mechanism. In the present study, the adsorption equilibrium data were analyzed using four different kinetic models such as, pseudo-first-order, pseudo-second-order, and intra-particle diffusion models are applied at different metal ion concentrations.

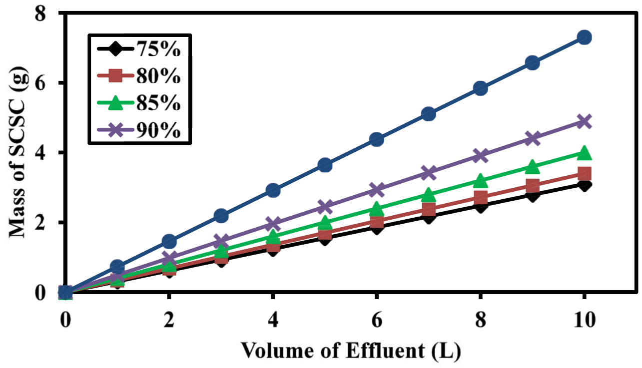

Fig. 7. Volume of Cd(II) solution treated against SCSC dose for different percentage of Cd(II) removal.

3.8.1. Pseudo-first-order equation

Lagergren [39] pseudo-first-order model assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites, that is, rate of change of solute uptake with time is directly proportional to the difference in the saturation concentration and the amount of solid uptake with time. The linearized–integral form of the pseudo-first-order model is expressed as follows:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \tag{12}$$

where k_1 is pseudo-first-order rate constant (min^{-1}), q_e is the adsorption amount at equilibrium (mg g^{-1}), q_t is the adsorption amount at time t (min). The constants such as k_1 and q_e at different metal ion concentrations were determined experimentally by plotting of $\log(q_e–q_t)$ vs. t and are listed in Table 3 and are shown in Fig. 8a.

3.8.2. Pseudo-second-order kinetics

The pseudo-second-order kinetic model proposed by Ho and McKay [40] was based on the assumption that the adsorption follows second-order chemisorptions. The pseudo-second-order kinetic rate expression can be written as follows:

$$\frac{t}{q_t} - \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{13}$$

The plot of t/q_t vs. t produces a straight line (Fig. 8b). The values of the adsorption parameters, q_e and k_2 were

Table 3
Pseudo-first-order and pseudo-second-order kinetic model for the adsorption of Cd(II)

Kinetic model	Parameters	Concentration of Cd(II) solution (mg L^{-1})			
		10	7	5	3
Pseudo-first-order	k_1 (min^{-1})	0.009	0.010	0.011	0.012
	$q_{e(\text{exp})}$ (mg g^{-1})	9.90	6.95	4.97	2.98
	$q_{e(\text{theo})}$ (mg g^{-1})	3.72	3.04	2.04	1.91
	P (%)	62.42	56.26	58.95	35.91
	R^2	0.966	0.983	0.961	0.975
Pseudo-second-order	k_2 (g mg^{-1} min^{-1})	0.006	0.008	0.014	0.015
	$q_{e(\text{theo})}$ (mg g^{-1})	10.00	7.09	4.98	3.05
	P (%)	1.01	2.01	0.20	2.35
	R^2	0.998	0.998	0.999	0.999

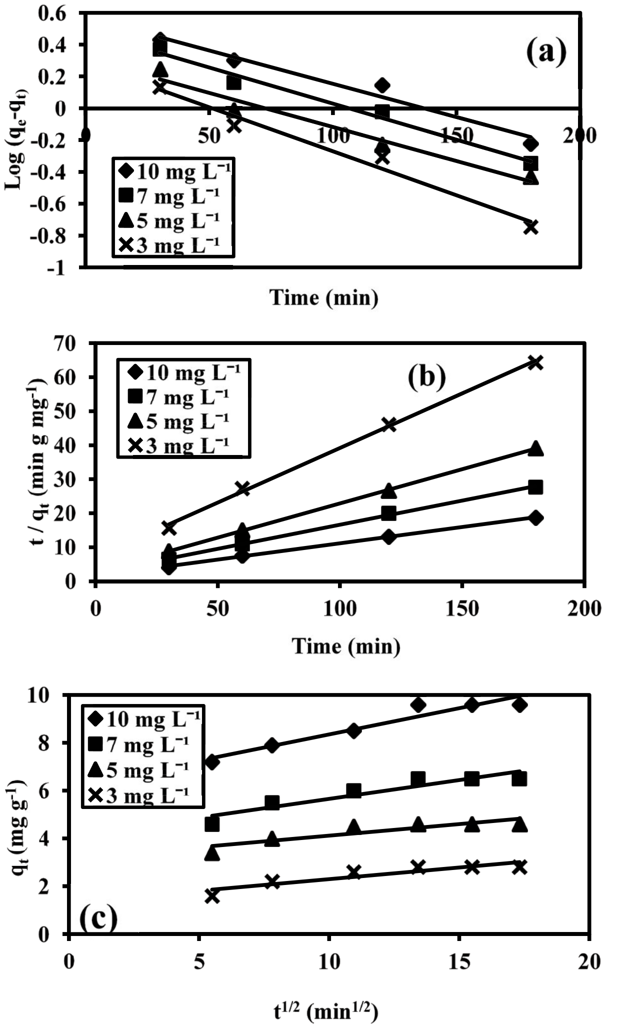

Fig. 8. (a) Pseudo-first-order, (b) pseudo-second-order, and (c) intraparticle diffusion model for the adsorption of Cd(II) ions onto SCSC.

determined from the slope ($1/q$) and intercept ($1/k_2q_e^2$) of the plot, respectively (Table 3). The percentage relative deviation (P %) is used to find out quantitatively the applicability of kinetic models in fitting to data and was calculated by the following Eq. (14):

$$P(\%) = \frac{100}{N\sum\left[\frac{q_{e(\text{exp})} - q_{e(\text{Cal})}}{q_{e(\text{exp})}}\right]} \tag{14}$$

where $q_{e(\text{cal})}$ and $q_{e(\text{exp})}$ are calculated and experimental value of metal ion adsorbed on the adsorbents and are given in Table 3. N is the number of measurements made. Ayranci and Duman [41] reported that the lower value (<5) of percentage deviation (P %) is exhibited a better fit.

The kinetic parameters and correlation coefficients are listed in Table 3. From Table 3, the correlation coefficients (R^2) for pseudo-second-order equation are much closer to unity and percent relative deviation (P %) is also found to be <5%, confirming the applicability of pseudo-second-order. In addition, there is a little difference between the calculated and experimental q_e value, reinforcing the applicability of the pseudo-second-order model for the adsorption of cadmium(II) ions onto SCSC. This suggests that the rate-limiting step of this sorption system may be controlled by chemical sorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate.

3.8.3. Weber–Morris intraparticle diffusion model

For a solid–liquid adsorption process, to analyze the rate-controlling steps such as mass transport and chemical reaction processes is very beneficial for elaborating the adsorption mechanism. The adsorption reaction is usually divided into the following steps [42]:

- Metal ion from the bulk liquid to the liquid film or boundary layer surrounding the adsorbent.
- Transport of solute ions from the boundary film to the external surface of the biosorbent (film diffusion).
- Transfer of ions from the surface to the intra-particular active sites (particle diffusion).
- Adsorption of ions by the active sites of adsorbent.

Weber and Morris [43] model is a widely used intraparticle diffusion model to predict the rate-controlling step and to elucidate the diffusion mechanism, the model is expressed as:

$$q_t = K_d t^{1/2} + I \tag{15}$$

where q_t is the amount of sorbate on the surface of the sorbent at time t (mg g^{-1}), K_d (mg g^{-1} min$^{1/2}$) is the intra-particle diffusion rate constant and I (mg g^{-1}) is a constant that gives an idea about the thickness of the boundary layer. According to this model, the plot of q_t vs. ($t^{1/2}$) is linear and passes through the origin, and then intraparticle diffusion is the sole rate-limiting step.

Fig. 8c shows a plot of the Weber and Morris intraparticle diffusion model for the sorption of cadmium(II) onto SCSC. The deviation in the plots from the origin for all concentrations indicated that pore diffusion was not the only rate-controlling factor, but some other processes like film diffusion were also involved in the sorption process.

3.9. Removal of cadmium(II) from electroplating industry wastewater and desorption studies

The activated carbon is an effective adsorbent only when it removes the maximum possible impurities from industrial wastewater. In order to ascertain the performance of SCSC with respect to wastewater, experiments were conducted for the removal of cadmium(II) ions from electroplating industry wastewater. The electroplating wastewater was collected from the local electroplating industry near Dindugal district, Tamilnadu, India. The physical and chemical characteristics of electroplating wastewater are given in Table 4. In order to find out the optimum carbon dose experiments were carried

Table 4
Physical and chemical characteristics of the examined real sample

Parameter	Concentration of Cadmium-plating industry wastewater
pH	2.00
Total solid (mg L^{-1})	2,500.00
Turbidity (NTU)	17.00
Conductivity (mS cm^{-1})	9.85
Chloride (mg L^{-1})	650.00
Sulfate (mg L^{-1})	890.00
Cadmium (mg L^{-1})	190.00
COD (mg L^{-1})	98.00
Sodium (mg L^{-1})	110.00
Calcium (mg L^{-1})	75.00
Magnesium (mg L^{-1})	128.00

out 1 L wastewater containing the batch reactor having the concentration of 190 mg L^{-1} cadmium(II) ions, adjusted under the optimum pH and equilibrating for 4 h. From Fig. 9a, it has been observed that 99% ± 0.5% removal of cadmium(II) ions could be achieved with an optimum SCSC dose of 1.5 g L^{-1}.

Adsorbent regeneration is an important operating parameter to establish the feasibility and the operating costs of water treatment processes using activated carbons. The performance and efficiency of desorbing agents depend on the carbon type, the concentration of sorbed pollutant, and the operating conditions of the desorption process. The batch desorption experiments were carried out 1 L wastewater containing with the concentration of 190 mg L^{-1} of cadmium(II) ions and added an SCSC dose of 1.5 g, adjusted at optimum pH and agitated for 4 h. After the shaking period, the samples were filtered, and the concentration of metal ions was determined in the filtrate by atomic adsorption spectrophotometer methods.

In the adsorption process, to keep the processing cost down and to open the possibility of recovering the metals extracted from the liquid phase, it is desirable to regenerate the adsorbent material. In this study, 0.5 N HCl was used as a regenerating agent (or eluent). The regenerated carbon was reused for up to five adsorption–desorption cycles and the results are illustrated in Fig. 9b. A slight increase in the sorption of cadmium(II) could be observed after each and every cycle with SCSC, improving the recovery of cadmium(II), ions. This increase in the sorption (99%–99.9%) may occur because additional surface active sites present on the sorbent surface open after repeated regeneration cycles. The reusability results suggested that five adsorption–desorption cycles (Fig. 9b), the SCSC has the greater potential to be used repeatedly for the removal cadmium(II) ions without much significant loss in total adsorption capacity.

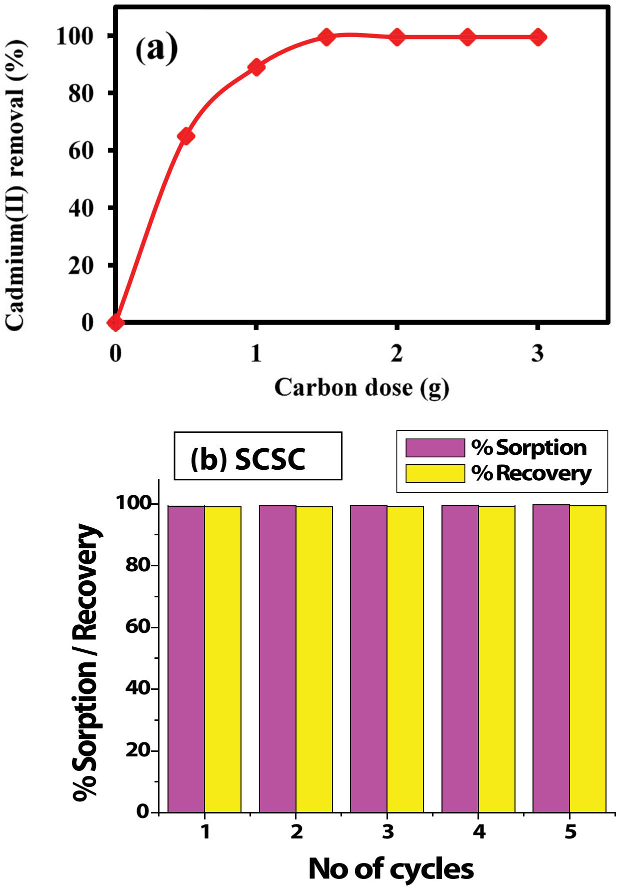

Fig. 9. (a) Effect of SCSC dose for the removal of cadmium(II) ions from electroplating Wastewater and (b) regeneration and recycling of cadmium(II) ions by batch process for SCSC.

4. Conclusion

The present study explores the ability of activated carbon prepared from agricultural by-product like cottonseed cake (SCSC) using sulfuric acid is an activating agent for the removal of cadmium(II) ions from aqueous solution. The optimum contact time and pH were found to be 3 h and 4.0–8.0. The optimum SCSC dose of 150 is required for the maximum removal of 99.9% ± 0.1% cadmium(II) ions. Equilibrium data agreed well with Langmuir isotherm and the adsorption capacity (q_m) of SCSC is 156.76, mg g^{-1}. Thermodynamic studies showed that the adsorption process is spontaneous and exothermic in nature. A single-stage batch adsorber was designed using the Langmuir isotherm equation at room temperature. The adsorption is followed by pseudo-second-order kinetics, which represents the chemisorption with the film diffusion process being a crucial rate-controlling step. The efficiency of the adsorbent was tested for the removal of cadmium(II) ions by electro-plating wastewater. Regeneration studies reported that SCSC might be successfully utilized for more than five cycles for the adsorption of cadmium(II) ions. The above results showed that SCSC is an effective, economical, and environmentally friendly adsorption for the removal of toxic cadmium(II) ions from aqueous solution and electroplating industrial wastewater.

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