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ORIGINAL ARTICLE

Isotherm and kinetic modeling of sorption of Cadmium onto a novel red algal sorbent, *Hypnea musciformis*

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Abstract

In this work, sorption of cadmium from aqueous solution using a novel sorbent, *Hypnea musciformis*, was carried out. In order to optimize the operating variables namely, pH (3–6), sorbent dosage (0.5–2.5 g/L) and agitation speed (60–100 rpm), Box–Behnken Design was employed. The optimum conditions for the maximum cadmium percentage removal was 4.6, 1.67 g/L and 81 rpm for pH, sorbent dosage and agitation speed, respectively. At the optimal operating conditions, studies were carried out for effects with respect to various concentrations of cadmium and temperature for isotherm, kinetics and thermodynamic studies. The data obtained have been analysed by isotherm models such as Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherms. The most fitted equation for describing the isotherm profile was the Langmuir model ($R^2 = 0.9990$) with the maximum sorption capacity of 105.49 mg/g. The kinetics studies exposed that the process of sorption of cadmium onto red algae has been satisfactorily described for pseudo-second order. The calculated thermodynamic parameters such as ΔG°, ΔH° and ΔS° showed that the sorption of cadmium onto red algae was feasible, spontaneous and endothermic.

Keywords Adsorption · Metal · Cadmium · Algae · Isotherm · Kinetics

Introduction

Cadmium, one of the high priority toxic heavy metal responsible for polluting the ecosystems with the maximum potential threat to humans and the environment. Cadmium has been incorporated in the red list of priority pollutants by Department of Environment, UK (UK Red List Substances 1991) and in List I (the ''black list'') of Directive 76/464/EEC Council directive 1976). USEPA has also classified cadmium as group B1 carcinogen (USEPA 1999). The industries dealing with electroplating, smelting, paint pigments, batteries, fertilizers, alloy and mining industries (Iqbal and Edyvean 2005) are the major sources of cadmium into the environment through wastewater streams. Cadmium is non-biodegradable (Wu et al. 2012), toxic even at low concentration and enters the food chain (Da Silva et al. 2003) and causes serious human diseases and disorders. The cadmium exposure leads to adverse health effects to human viz. renal dysfunction, liver damage, bone degradation, hypertension and can disrupt protein metabolism (Bernard 2008; Nordberg et al. 1993; Vimala and Das 2011).

Sorption of heavy metals from aqueous solutions has been assured as a very sanguine process in the removal of heavy metal contaminants. Also it proved to be an efficient, competitive, clean and inexpensive technology for the treatment of low-concentration effluents (Volesky et al. 1999; Pagnanelli et al. 2002). The sorption process gives rise to certain potential advantages over conventional treatment methods include : low operating cost, minimization of chemical or biological sludge, highly effective efficiency of heavy metal removal from diluted solutions, regeneration of sorbents, possibility of metal recovery and being eco-friendly (Ahluwalia and Goyal 2007). Lot of research has been undertaken for developing and employing cost effective sorbents for the treatment of wastewaters carrying heavy metal cadmium (Aksu 2001). In this study, a novel sorbent is employed for the removal of Cadmium from aqueous solution. The process variables were optimized using RSM and

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at the optimized conditions equilibrium, kinetic and thermodynamic studies were carried for the sorption process.

Materials and methods

Preparation of sorbent

The fresh red algal, *Hypnea musciformis*, was collected from the coats of Mandapam, Ramanathapuram district, Tamilnadu, India. It was washed thoroughly with distilled water to remove sand, salts and other impurities adhered. Then the sorbent was sun dried and further dried in oven at 50 °C for 48 h to remove the moisture. The dried sorbent was then ground using domestic mixer. The particle size of the ground sorbent was determined using Zetasizer (6.12), Nano series, Malvern instruments Ltd, UK. The mean particle diameter of the ground sorbent was found to be 1503 nm.

Preparation of metal ion solution

The stock solution of cadmium (II) of 1000 ppm concentration was prepared by dissolving 2.1 g of analytical grade cadmium nitrate in 1 L of distilled water.

Characterization of sorbent

Scanning electron microscopy (SEM)

The surface morphology of red alage was assessed by scanning electron microscope (JSM-5610 LV, JEOL, USA), with voltage of 10 KV and at high vacuum mode.

Fourier transform infrared (FTIR) spectroscopy

FTIR was used to determine the presence of functional groups on the sorbent surface for both raw and cadmium loaded sorbent. FTIR analyses were conducted by KBr pellets method using FTIR spectrophotometer (Thermo scientific- Nicolet iS5 FTIR, USA) in the wave number region of 4000–400/cm^{-1} .

BET

The surface area, average pore diameter and pore volume were determined by Brunauer Emmett and Teller method using Micrometrics ASAP 2020 and the observed values are 0.8576 m^2/g, 269.24 Å and 0.0057 cm^3/g respectively. Nitrogen was used as adsorptive agent for the algal sample of 0.625 g.

Experimental design

Box- behnken design (BBD) was followed for optimizing the sorption of cadmium by red algae *Hypnea musciformis*. Batch experiments were conducted base on BBD, to study the effects of three variables including pH, sorbent dosage (g/L) and agitation speed (rpm) on percentage removal of cadmium. The range of independent variables along with the experimental design were given in Table 1. A statistical program package (design expert 7.1.5) was used for regression analysis of the data obtained and to estimate the coefficient of the regression equation. The equation was validated by ANOVA. At the optimal operating conditions, experiments were performed at various concentrations of cadmium and temperature for isotherm, kinetics and thermodynamic studies.

Sorption studies procedure

Based on Box Behnken design (BBD), experiments were conducted in 250 ml Erlenmeyer flasks containing 100 ml of 100 ppm Cadmium solution. The solution was agitated in incubated orbital shaker (Labline instruments, India) for a period of 60 min and 30 °C in order to study the effects of pH, sorbent dosage and agitation speed. After 1 h of agitation, the algae was separated from the aqueous experimental sample solution using whatman filter paper (No. 41). The presence of cadmium concentration in the aqueous solution was analyzed by using ICP-AES (Perkin Elmer, Germany). The percentage of cadmium removal was calculated as

Table 1 BBD based experimental design and its response for Cadmium removal

Run order	A	B (g/L)	C (rpm)	Cadmium removal (%)	
				Experimental	Predicted
1	4.5	1.5	80	84.5	84.43
2	3	2.5	80	57.9	55.15
3	4.5	1.5	80	84.3	84.4
4	6	0.5	80	47.1	49.85
5	6	2.5	80	54.9	55.87
6	3	1.5	100	59.2	62.31
7	3	0.5	80	40.3	39.33
8	4.5	0.5	100	74.3	72.16
9	4.5	2.5	100	83.5	83.14
10	6	1.5	100	59.4	58.79
11	3	1.5	60	52.8	53.41
12	4.5	2.5	60	81.2	83.34
13	6	1.5	60	71.3	68.19
14	4.5	1.5	80	84.5	84.4
15	4.5	0.5	60	72.1	72.46

$$\text{Cd removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100, \quad (1)$$

where C_o (mg/L) is the initial concentration of cadmium and C_e (mg/L) is the final or equilibrium concentration of cadmium. The amount of adsorbed cadmium per unit mass of adsorbent (qe, mg/ g) was determined according to equation:

$$q_e \text{ (mg/g)} = \frac{(C_0 - C_e)V}{m}, \quad (2)$$

Where v is the volume of solution in liter and m is the amount of sorbent in gram.

Sorption and desorption procedure

For desorption studies, 10 mL of 0.1–0.5 M HCl concentration was utilized for the sorption and desorption experiments for ten cycles. One cycle consists of sorption followed by desorption. For the subsequent use of sorbent, they were washed with excess of HCl solution and distilled water, sequentially.

Results and discussion

Box–Behnken design was carried out for studying the effects of 3 independent variables and the results obtained from the BBD experiments, along with the theoretically predicted responses were shown in Table 1. The quadratic regression model was used to explain the mathematical relationship between the independent variables and the dependent responses for cadmium removal in terms of coded factor. It is:

$$Y = 84.43 + 2.81\,A + 5.46\,B - 0.13\,C - 2.45\,AB - 4.58AC + 0.025\,BC - 25.74A^2 - 8.64B^2 + 1.98C^2,$$

where, Y is the percentage removal of cadmium and A, B and C are coded values of pH, sorbent dosage(g/L) and agitation speed (rpm), respectively.

The ANOVA results for cadmium removal were shown in Table 2. The values of “probability > F” less than 0.05 indicate that the model terms are significant. In this study A, B, AC, A^2 and B^2 were significant model terms. This implies that the linear and square effects of pH and sorbent dosage were more significant factors. The interactive effect of pH and agitation speed was also significant. The goodness of fit of the model was checked by coefficient of determination (R^2). For a good statistical model R^2 value should be closed to 1. In our model, R^2 was found to be 0.9852, which implies that more than 98% of experimental value was compatible with the predicted value. Adeq precision greater than 4 indicating an adequate signal. The “predicted R^2 “of 0.763 was found to be in reasonable agreement with “adjusted R^2” of 0.9585.

Table 2 ANOVA for cadmium removal using red algal biomass *Hypnea musciformis*

Source	Sum of squares	df	Mean square	F-value	P value
Model	3094.90	9	343.88	36.91	0.0005
A	63.28	1	63.28	6.79	0.0479
B	238.71	1	238.71	25.62	0.0039
C	0.13	1	0.13	0.013	0.9123
AB	24.01	1	24.01	2.58	0.1693
AC	83.72	1	83.72	8.99	0.0302
BC	0.0025	1	2.5E-3	2.684E-4	0.9876
A^2	2446.65	1	2446.65	262.63	<0.0001
B^2	275.74	1	275.74	29.60	0.0028
C^2	14.52	1	14.52	1.56	0.2671
Residual	46.58	5	9.32		
Lack of fit	46.55	3	15.52	1163.81	0.0009
Pure error	0.028	2	0.013		0.0005
Cor total	3141.48	14			

SD – 3.05, R^2 – 0.9852; Mean – 52.90; adj R^2 – 0.9585; CV% – 4.55, pred R^2 – 0.763; PRESS – 744.90; adeq Precision – 18.101

The interactive effects of operating variables on cadmium removal efficiency are illustrated in three dimensional response surface plots (Fig. 1a, b). The interactive effect of pH and sorbent dosage on the cadmium removal efficiency was studied in the pH range of 3–6 and the results are shown in the Fig. 1a. From the plot, it was observed that the sorption efficiency increases with the increase in pH from 3 to 4.6. This is due to the fact that, as the number of negatively charged sites increased due to deprotonation of the hydrogen ions from the functional group present on the sorbent. At pH 4.6, a maximum cadmium removal efficiency of 84.5% was achieved. However at solution pH less than 3 (highly acidic), the removal efficiency of cadmium was found to be less than 45%. This is because of the competition between hydronium ions (H_3O^+) and cadmium ions to the few negatively charged sites of the sorbent. Further increase in pH beyond 4.6, the sorption efficiency of cadmium decreases due to the precipitation of cadmium as hydroxide or in the form of Cd $(OH)_2$. Therefore, the pH is pegged at 4.6 for further experimental studies. It can be inferred from the results that the solution pH was one of the most important factor which influences metal sorption and also the surface properties of the sorbent. Similar observations were reported for red sorbent (Wael and Ibrahim 2011).

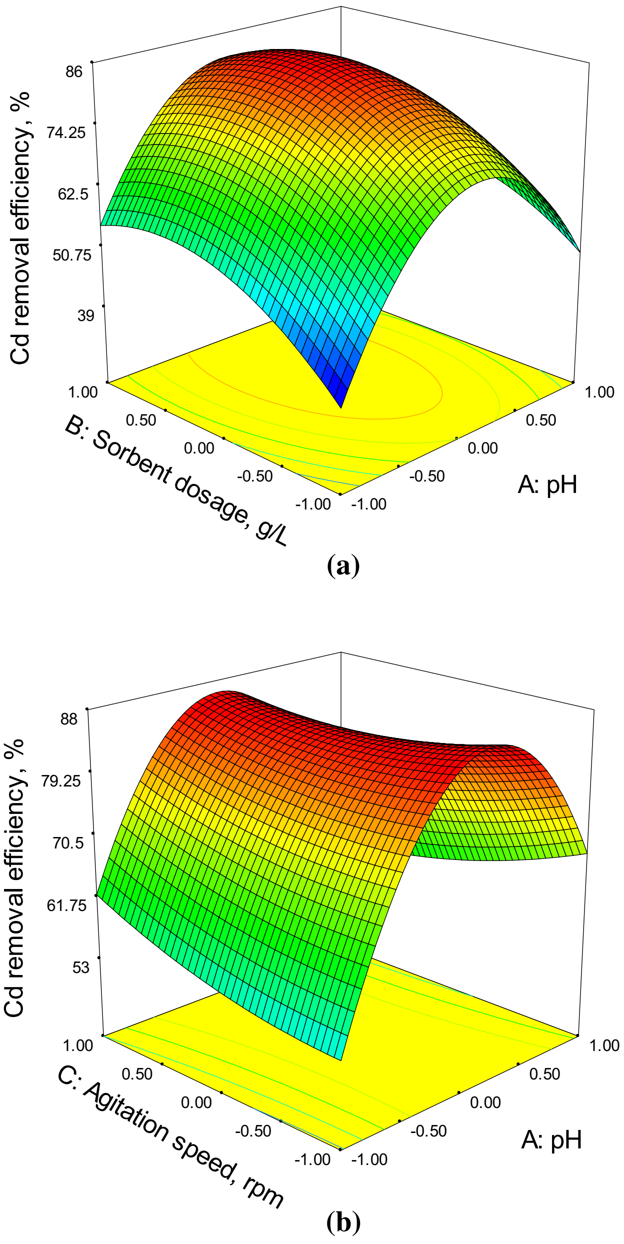


Fig. 1 Response surface plot of Cd(II) sorption onto red biomass *Hypnea musciiformis* ; **a** interactive effects of pH and sorbent dosage ; **b** interactive effects of pH and agitation speed

The effect of sorbent dosage on the cadmium removal efficiency was studied in the range of 0.5–2.5 g/L. The results are shown in Fig. 1a. From the plot, the maximum removal efficiency was observed at 1.67 g/L. The sorption of metal efficiency increases with increase in sorbent from 0.5 to 1.67 g/L and decreases with further increase in sorbent dosage. Partial aggregation of the sorbent which minimizes the effective surface area could be the reason for the decrease in cadmium removal efficiency at higher sorbent dosage (Karthikeyan et al. 2007). Therefore, the optimum dosage of sorbent is 1.67 g/L for further experimental studies.

The effect of agitation speed was studied by changing the agitation speed in the range of 60 to 100 rpm. The results obtained are shown in Fig. 1b. From the plot, it was inferred that maximum sorption of cadmium occurred at 81 rpm. The sorbent accumulates at the bottom of the flask instead of spreading in the sample solution, at low agitation speed. As a result, the lower layer wraps up the active sites of the sorbent within that and hence they are not exposed to the phenomenon of cadmium ion removal while the upper layer active sites of sorbent adsorb the cadmium ion. At higher agitation speed, cadmium removal efficiency decreases, may be due to the desorption tendency of sorbent (Saha and Datta 2009).

Sorption isotherm study

The sorption capacity of a sorbent can be described by equilibrium sorption isotherm, which is characterized by definite constants whose values express the surface properties and affinity of the sorbent. In this study, four sorption isotherm models namely Langmuir, Freundlich, Dubinin-Radushkevich and Temkin were selected to evaluate the batch experimental data.

Langmuir isotherm

The Langmuir isotherm assumes that sorption occurs at specific homogenous sites on the sorbent and is used successfully in many monolayer sorption process. The linear form of Langmuir isotherm (Liu and Liu 2008) is expressed by

$$\frac{1}{q_e} = \frac{1}{q_m k_L C_e} + \frac{1}{q_m}, \tag{3}$$

where q_e is the equilibrium concentration of the metal on the sorbent (mg/g), q_{max} is the monolayer sorption capacity (mg/g), C_e is the equilibrium concentration of the metal in the solution (mg/ L) and k_L is the Langmuir sorption constant (L/mg) related to the free energy of sorption. The plots of $\frac{1}{qe}$ versus $\frac{1}{Ce}$ were drawn as shown in Fig. 2a for six different initial metal concentration at constant temperature. In general, good sorbents have high q_{max} and a high correlation co-efficient (R^2). The values of q_{max}, R^2,and b are tabulated in Table 3. The high correlation co-efficient ($R^2 = 0.994$) indicates that the sorption of the cadmium metal on to the red algae *Hypnea musciformis*, best suits the Langmuir model. Table 4 presents the comparison of sorption capacity (q_{max}, mg/g) of various red algae for cadmium.

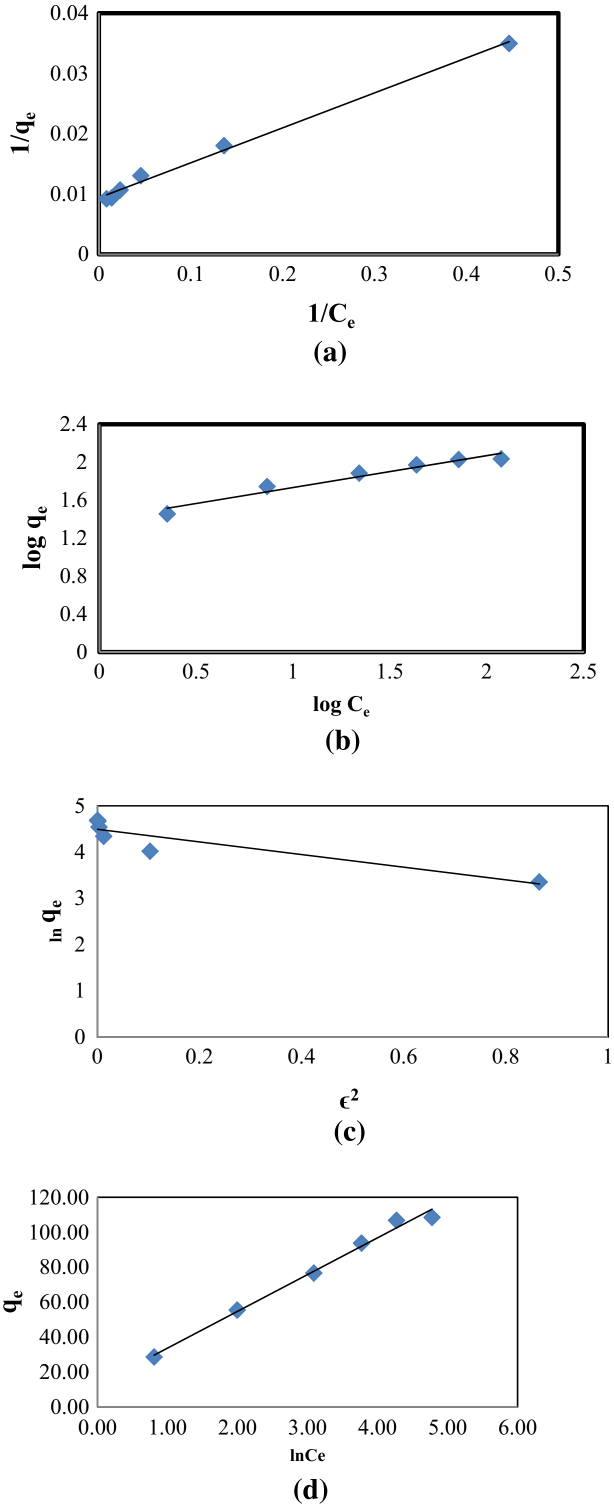


Fig. 2 **a** Langmuir **b** Freundlich **c** Dubinin- Radushkevich and (d) Temkin isotherms for cadmium sorption onto red biomass *Hypnea musciformis*: pH 4.6; biomass dosage: 1.67 g/L ; temperature: 30°C ; agitation speed 81 rpm

Table 3 Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm constants for Cadmium sorption onto red biomass *Hypnea musciformis*

Isotherm model	Parameters	Values
Langmuir	$q_{m\ (mg/g)}$	105.49
	$K_{L\ (L/mg)}$	0.163
	R^2	0.994
Freundlich	$K_{f\ (L/mg)}$	25
	1/n	0.336
	R^2	0.951
Dubinin- Redushkevich	$q_{m\ (mg/g)}$	89.3
	β (mol^2/ kJ$^{2)}$	1.364
	E (kJ/mol)	0.61
	R^2	0.843
Temkin	B	21.03
	$K_{T\ (L/mg)}$	1.832
	R^2	0.99

Table 4 Comparison of adsorption capacities of various red algae for the removal of Cadmium

Biosorbent	q_{max} (mg/g)	References
Gracilariafisheri	70.81	Chaisuksant (2003)
Gracilaria sp	33.72	Ping Xin Sheng et al. (2004)
Gracilariachangii	25.85	Hashim and Chu (2004)
Gracilariaedulis	26.98	
Gracilariasalicornia	17.98	
Asparagpsisarmata	32.3	Romera et al. (2007)
Chondruscrispus	75.2	
Ceramiumvirgatum	39.7	Sari and Tuzen (2008)
Mastocarpusstellatus	66.32	Herrero et al. (2008)
Hypneavalentiae	17.4	Aravindh et al. (2010)
J. rubens	30.5	Wael and Ibrahim (2011)
P. capillacea	33.5	
C. mediterranea	64.1	
G. oblongata	85.5	
Chondracanthuschamissoi	85.42	Yipmantin et al. (2011)
Hypneamusciformis	105.49	This study

Freundlich isotherm

The Freundlich isotherm is an empirical equation used to describe the adsorption on heterogenous surfaces (Freundlich 1906) and its linear form is represented by:

$$\log q_e = \log K_f + \log C_e, \tag{4}$$

where K_f is the Freundlich isotherm indicating adsorption capacity and $\frac{1}{n}$ is the sorption intensity. The values of K_f and $\frac{1}{n}$ were calculated from the intercept and slope of the plot between log q_e versus log C_e (Fig. 2(b)). The values of K_f ,$\frac{1}{n}$ and the correlation coefficient (R^2) are given in Table 3. Generally, $\frac{1}{n}$ values between 0 and 1 indicate good sorption (Vasudevan et al. 2009). In this study, $\frac{1}{n}$= 0.336 indicates that the sorption of cadmium onto the red algae was favorable. However, compared to the R^2 values, the Langmuir isotherm equation fits the experimental values better than the Freundlich isotherm equation.

Dubinin-Radushkevich (D-R) isotherm

D-R isotherm was applied to determine the nature of sorption processes as physical or chemical using the experimental data and it's linear form (Dubnin 1960) is :

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \tag{5}$$

where, q_e is the amount of metal ions adsorbed on per unit weight of algae (mg/g), q_m is the maximum sorption capacity (mg/g), β is the activity co- efficient related to mean sorption energy (mol^2/ kJ^2) and ε is the Polanyi potential described as

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right), \tag{6}$$

where, R is the universal gas constant 8.314×10^{-3} in kJ/mol K, T is the temperature in Kelvin and C_e is the equilibrium concentration of the cadmium in solution (mg/L).

The mean free energy of sorption per molecule of sorbate required to transfer one mole of ion from the infinity in the solution to the surface of sorbent and can be determined by the equation:

$$E = \frac{1}{\sqrt{-2\beta}}. \tag{7}$$

Dubinin- Radushkevich (D-R) isotherm constant β, and q_m were evaluated from the slope and intercept of plot $\ln q_e$ versus ε^2 (Fig. 2c) and the results are presented in Table 3. The energy value, E = 0.61 kJ/mol, obtained is less than 8 kJ/mol indicates that the adsorption is a physical process. Also the sorption capacity was lower than the Langmuir model.

Temkin isotherm

The Temkin isotherm equation assumes that the heat of absorption of all the molecules in layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy (Temkin and Pyzhev 1940). The Temkin isotherm is represented by the following equation:

$$q_{e=} \frac{RT}{b} \ln \left(K_T C_e\right) \tag{8}$$

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \tag{9}$$

Equation (9) can be arranged linearly as

$$q_e = B \ln K_T + B \ln C_e, \tag{10}$$

where, T is the temperature in Kelvin, R is the Universal gas constant in kJ/mol K, K_T is the equilibrium binding constant in L/mg, b is the variation of sorption energy in J/mol. $B = \frac{RT}{b}$, is the Temkin constant related to the heat of sorption.

Figure 2(d) shows the plot of q_e versus ln C_e. The isotherm constants were found and given in Table 3. The correlation factors show that the Langmuir model approximation to the experimental values was better than the Temkin model. Consequently, among the four isotherm modes used, the Langmuir model offers the best correlation factor.

Effect of temperature and thermodynamic study

The effect of temperature on the sorption of cadmium ions was studied in the temperature range of 298.15–313.15 K. An increase in temperature from 298.15 to 313.15 K increases the uptake capacity from 51.69 to 57.62 mg/g of cadmium by red algae. This effect is due to the rate of sorbate diffusion across the external boundary layer and in the internal pores of the sorbent particles because, liquid viscosity decreases as the temperature increases. Thermodynamic behavior of the sorption of cadmium onto red algae were calculated from following equation:

$$\Delta G^{\circ} = -RT \ln k \tag{11}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - \Delta S^{\circ}, \tag{12}$$

Where, R is the universal gas constant (8.314×10^{-3} kJ/mol K), T is the temperature in Kelvin and k is the equilibrium constant, calculated as the surface and solution metal distribution ratio ($k = q_e/C_e$) (Aravindhan et al. 2007), ΔG° is the Gibbs free energy (kJ/mol), ΔH° is the enthalpy change (kJ/mol) and ΔS° is the entropy change (kJ/mol K).

The thermodynamic feasibility and the nature of the sorption process can be described from the Eq. (15). The intercept and slope of the plot ΔG° versus T, gives the values of ΔH° and ΔS° respectively, for the adsorption process of cadmium using red algae *Hypnea musciformis*. The calculated thermodynamic parameters are presented in Table 5. The positive values of ΔH° suggest the endothermic nature of the sorption and the positive values of ΔS° show the increasing randomness at the solid-solution interface during the sorption process (Li et al. 2009). The negative values of ΔG° indicate the spontaneous nature of the sorption process and the higher negative value reflects a more energetically favorable adsorption (Chegrouche et al. 2009).

Table 5 Thermodynamic parameters for the sorption of Cadmium onto *Hypnea musciformis*

Metal ion	Temp (K)	ΔG^o (kJ/mol)	ΔS (kJ/mol k)	ΔH (kJ/mol)
Cd(II)	298.15	– 20.418		
	303.15	– 22.505	0.301	69.23
	308.15	– 23.601		
	313.15	– 25.077		

Sorption kinetics

The sorption kinetics behavior of cadmium ions onto red algae was analyzed to examine the mechanism of the sorption process and to test the experimental data, by adopting three kinetic models: pseudo first order, pseudo second order and intra-particle diffusion. Kinetic data are often used for the scale-up of sorption system.

Pseudo first order model

The linear form of pseudo first order model (Ho 1999) as described by Lagergren is expressed as

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t, \tag{13}$$

Where K_1 is the rate constant of the first order equation (/min),q_t and $q_e$are the amount of the cadmium ions sorbed at given time and equilibrium (mg/g) respectively and t is the time in minutes. The values of K_1 and q_e were calculated from the slope and intercept, respectively of the plot log (q_e– q_t) versus t, as shown in Fig. 3a. The values of q_e, K_1, and the correlation coefficient (R^2) are given in Table 6.

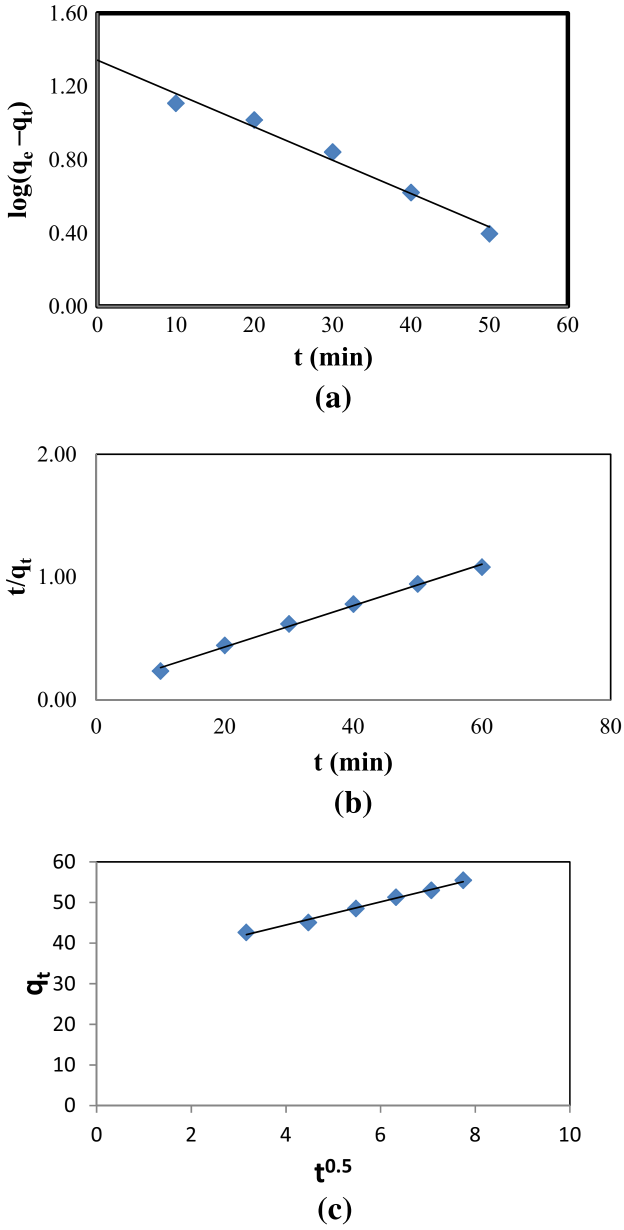


Fig. 3 **a** Pseudo first order **b** pseudo second order and **c** intra particle diffusion kinetic plots for cadmium sorption onto red biomass *Hypnea musciformis*: pH 4.6; biomass dosage: 1.67 g/L; temperature: 30 ºC; agitation speed: 81 rpm; initial concentration: 100 mg/l

Pseudo second order model

Linear form of pseudo second order can be expressed as (Ho and McKay 1999) ;

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t, \tag{14}$$

where $K_2$is the rate constant of second order equation (g/mg min), q_t and q_e are the amount of the cadmium ions sorbed at given time and equilibrium (mg/g) respectively and t is the time in min. The values of K_2 and q_e were calculated from the slope and intercept, respectively of the plot $\frac{t}{q_t}$ versus t, as shown in Fig. 3 b. The values of q_e, K_2, and the correlation coefficient (R^2) are given in Table 6. When compared with the correlation coefficients, R^2 from the Table 6, it is observed that pseudo second order model fits with the experimental data better than the pseudo first order.

Intra particle diffusion model

Intra particle diffusion model, described by Weber and Morris (1963), is tested for the diffusion mechanism and it is given by:

$$q_t = K_{id}t^{0.5} + C, \tag{15}$$

Table 6 Kinetic parameters of Cadmium sorption onto red biomass *Hypnea musciformis*

Kinetic model	Parameters	Cd(II) sorption
Pseudo first order	K_1 (/min)	0.042
	R^2	0.977
Pseudo second order	K_2 ((g/mg)min)	0.003
	R^2	0.995
	qe,cal (mg/g)	62.50
Intra particle diffusion	K_{id} ((mg/g)min$^{-0.5}$)	2.851
	R^2	0.990

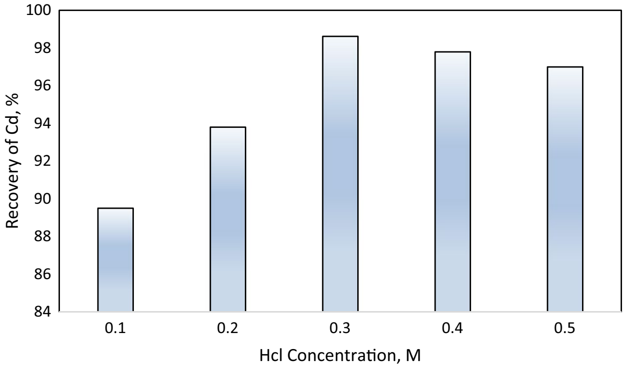


Fig. 4 Effect of Hcl concentration on desorption of Cd

where K_{id} is the intra particle diffusion rate constant in mg/g/min and C is the intercept which gives intra particle accumulation in the boundary layer.

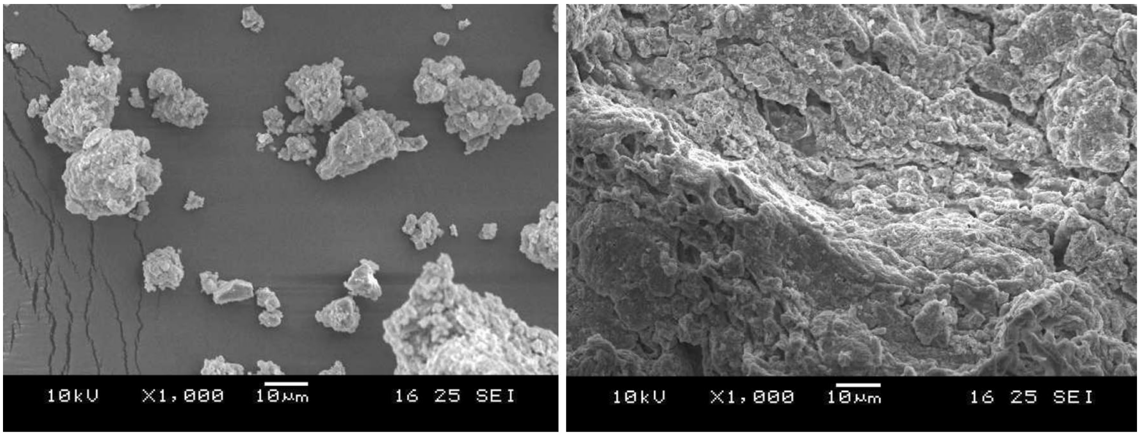
The values of K_{id} and $t^{0.5}$ can be calculated from the plot q_t versus $t^{0.5}$ as shown in Fig. 3 c and reported in Table 6. Results clearly suggest that intra particle diffusion was not only the sole rate controlling factor. However, based on the results from the table pseudo second order model has higher correlation coefficient value indicating that the sorption of cadmium on the red algae follows pseudo second order kinetic model, suggesting chemisorption mechanism. Higher values of R^2 show a better fitness of the sorption data (Deng et al. 2007).

Desorption Studies

Desorption of cadmium ion from the Cd loaded red algae was studied using HCl and the results were sown in Fig. 4. From the results, it was inferred that increase in hydrochloric acid concentration upto 0.3 M increases the desorption rate and then became stable. A maximum percentage recovery of 98.62% Cd was achieved with 0.3M HCL solution. The Cd ions adsorbed onto the sorbents were eluted with 0.3M HCL for the resuse of red algae. From the results it was observed that, in the first cycle, a maximum of 98.62% of the adsorbed Cd ions was desorbed from the sorbents. As the number of cycle increases the Cd sorption decreased to 81.55% at the end of tenth cycle. This loss may be because of the amount of sorbent lost during the sorption–desorption process. The results are in well agreement with the literatures (Jayakumar et al. 2015a, b). The results indicate that the red algae can be utilized repeatedly for sorption process with little loss in their initial adsorption capacities.

Scanning electron microscope analysis

The morphological changes of sorbent surface before and after cadmium loading was analyzed by the electron microscopic images. Red algae surface cells before cadmium loading were rough and rigid as shown in Fig. 5 a. After cadmium loading the surface becomes smooth and swollen,

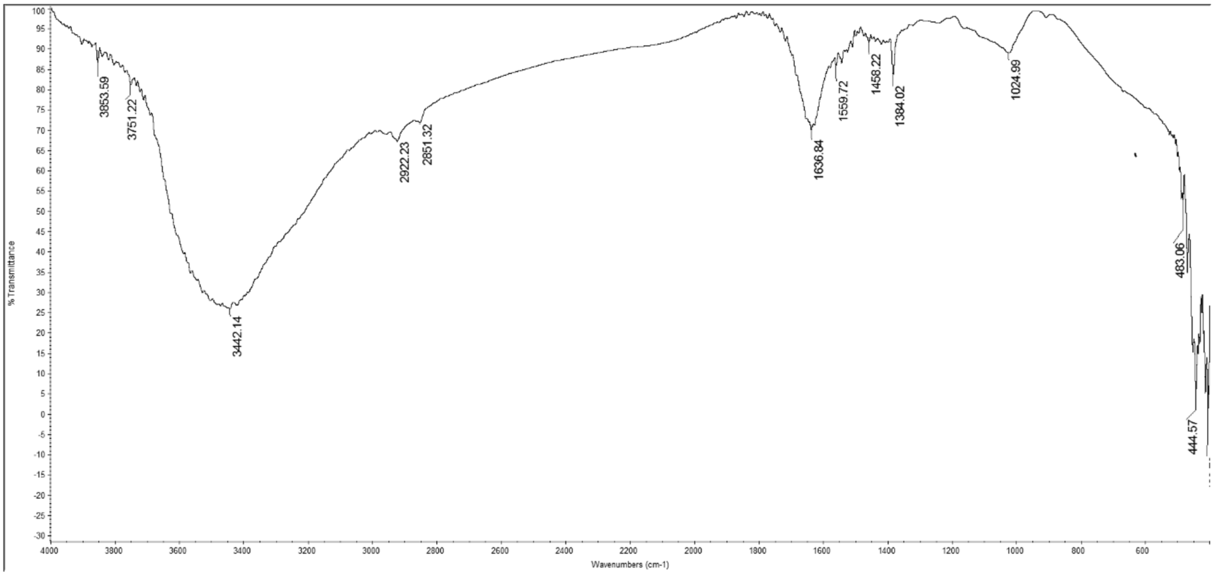


(a) **(b)**

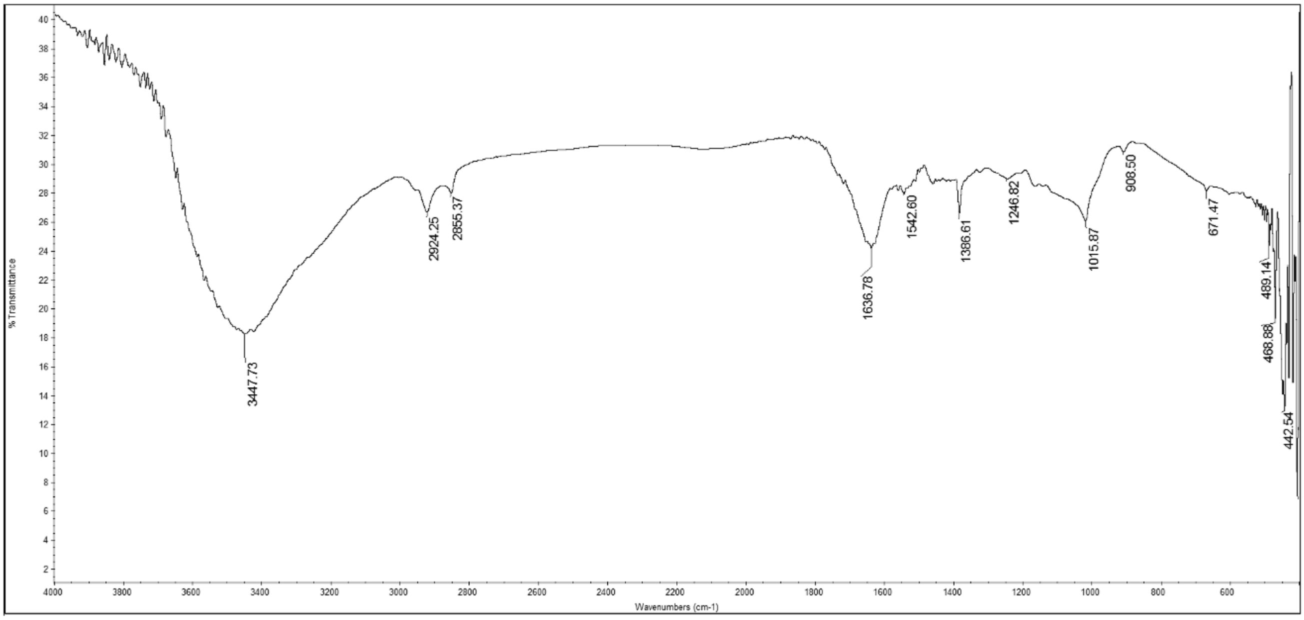
Fig. 5 SEM images for Cd(II) on *Hypnea musciformis*: **a** before sorption and **b** after sorption which can be observed from the Fig. 5b. This confirms the sorption of cadmium onto the surface of the sorbent.

Fourier transform infrared spectrometer (FTIR)

FT-IR spectrum identifies the functional group present in the uptake of cadmium onto red sorbent. Figure 6a, b shows the FTIR spectra of fresh and cadmium loaded red algae in the range of 4000−400/cm. The strong band shift from 3424.05 to 3432.75 cm^{-1} corresponds to bonded hydroxyl (0-H) group (Su et al. 2008). The peak shift from 2920.20 to 2926.28/cm can be assigned to C-H stretching of aliphatic group (Vaghetti et al. 2009). Band shift from 1647.33 to 1635.79/cm can be ascribed to C=O stretching of carboxyl group (Sawant et al. 2011). A slight change in the wave number from 1384.17 to 1384.58/cm can be attributed to O–H bending of the phenolic & carboxylic group (Centeno and Shamir 2008). Peak change from 1073.22 to 1032.08 can be assigned to C–O stretching of carboxylic group (Martin et al. 2005). The infrared spectral wavelengths of each sorption peak and the corresponding



(a) Before sorption



(b) After sorption

Fig. 6 FTIR images for Cd(II) on *Hypnea musciformis* **a** before sorption and **b** after sorption

Table 7 FTIR spectral characteristic of red biomass *Hypnea musiformis*

Wavelength range (cm^{-1})	Values		Assignment
	Before sorption	After sorption	
3500–3200	3424.05	3432.75	Bonded –OH group
2900–2800	2920.2	2926.28	C–H stretching
1680–1630	1647.33	1635.79	C=O stretching
1400−1300	1384.17	1384.58	Bending –OH group
1200–800	1073.22	1032.08	C–O stretching

functional groups were shown in Table 7. Therefore, observations from the FTIR analysis clearly shown that the important functional groups such as hydroxyl, carboxylic, C=O and C–O groups were responsible for the binding of cadmium heavy metal on to the red algae.

Conclusions

In an attempt to explain the effect of main operating parameters such as pH, adsorbent dose and agitation speed and their interactions on the phenomenon of removal of cadmium, the present study of RSM, based on the three-factor-three-level BBD was put into use as a tool for the experimental design. The outcome of RSM indicated that the cadmium removal efficiency was significantly affected by all the variables. The chosen red algae is found to be highly potential and most suitable for an efficient removal of cadmium from solution. According to the ANOVA results, the model presents a high R^2 value (0.97) for cadmium removal efficiency. At optimum initial cadmium concentration (100 mg /L), pH (4.6), agitation speed (81 rpm), and sorbent dosage (1.67 g /L), a maximum removal efficiency of 92.65% was achieved. Sorption of Cd was analyzed using Langmuir, Freundlich, Dubinin-Radushkevich,Temkin, isotherm models and found that the Langmuir model presented a better fit. SEM confirmed the presence of Cd ions on the sorbent surface. Temperature affects the sorption process and the thermodynamic parameters show the spontaneous character of the sorption reaction. From the kinetics study, it was found that the sorption follows pseudo second order and intra particle diffusion models. The reusability of the sorbent was good after ten consecutive adsorption–desorption cycles without any considerable loss in sorption capacity.

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