Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2018.22145

107 (2018) 195–206
March

Investigation on biosorption of Cd (II) onto Gelidiella acerosa (brown algae): Optimization (using RSM & ANN) and mechanistic studies

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Received 17 October 2017; Accepted 28 February 2018

ABSTRACT

Cadmium biosorption capacity of the biosorbent prepared from *Gelidiella acerosa* (brown algae) from synthetic cadmium solutions at optimum process conditions was investigated. The surface functional groups of the biosorbent responsible for biosorption were identified using FTIR analysis and the surface texture and porosity of the biosorbent was analyzed by SEM analysis. Response surface methodology (RSM) and artificial neural network (ANN) combined with central composite design (CCD) were used for modeling and optimization of biosorption and to study interaction effects of the three effective process variables such as solution pH, initial cadmium ion concentration and biosorbent dosage. Prediction capacities of RSM and ANN were compared and found that RSM showed better prediction performance than ANN. Kinetic data were well fitted to second order rate equation showing maximum biosorption capacity of 21.73 mg/g for 100 mg/l metal solution concentration. It was further confirmed by fitting the data to Elovich model. Biosorption mechanism was investigated using Intra-particle diffusion and Boyd models. The optimum cadmium removal efficiency of the biosorbent was found as 90.25%.

Keywords: ANN; Biosorption; Cadmium; Gelidiella acerosa; Kinetics; RSM

1. Introduction

Due to rapid industrialization, all kinds of pollution including toxic metal pollution have been increasing from the past few decades and causing destabilization of ecosystem. Cadmium is known as the most toxic metal found in industrial wastewater [1]. It enters into the aquatic systems through various industrial effluents like metal coating, battery manufacturing, fertilizer etc. It enters the food chain through the crops cultivated in cadmium contaminated water and soil [2–4]. Excessive concentration of cadmium in drinking water causes a number of health issues, mainly cancer, malfunction of kidneys, damage of bones and many other diseases [5]. Formation of stones in the kidneys through disorder in calcium metabolism is also caused due to the excessive intake of cadmium [6].

Different approaches and several strategies have been followed to develop the best choice of mitigating the heavy metal contamination in wastewater. Many of the techniques that are physical, chemical and biological have been practicing for longer periods of time in order to treat heavy metal contaminated water. Several methods which were used for the treatment of wastewater include precipitation, ion exchange, coagulation, reverse osmosis etc. [7–10] were found to have economical constraints and technical limitations which include costly chemicals, filter membranes, inefficient for dilute solutions, secondary sludge treatment, etc. [11–14].

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Biosorption is a passive non-metabolic mediated process of metal ions binding by various biological materials in aqueous solutions. Different kinds of biological materials belong to various sources such as agricultural waste products [15,16], dead microorganisms [17,18] and digested sludge [19,20] were investigated by many researchers.

Utilization of algal biomass has been increasing because of its huge applications in various fields like biodiesel production, food products, bio-fertilizers, synthesis of useful proteins etc. Biosorbents prepared from various sources like plant waste material, microorganism and algae were used to eliminate heavy metals from the environment. Among these, biosorbents prepared from algal biomass were reported as most promising source with high metal removal capacity [21,22]. The cell wall of algal biomass consists of proteins, lipids and amino acids which are formed by various functional groups such as carboxyl, hydroxyl etc. These functional groups at favorable pH and other parameters bind to heavy metals by ion exchange and forms metal complexes in solution [23]. Though good quantum of literature is available on biosorption of heavy metals using algal biomass, another effort was made to estimate the metal removal potential of *Gelidiella acerosa (G. acerosa).*

Due to the involvement of various biological components in metal removal, biosorption mechanism becomes more complex and non-linear. Optimization of process parameters is essential to maximize the biosorption efficiency and to make the process as economically viable. The classical method of optimization is having many disadvantages like ignoring interaction effect, require more experimental runs, etc. Therefore optimization of non-linear processes using classical "one factor at a time" method is not advisable. To overcome this problem multivariate optimization tools have been used to find out optimum combination of parameters and interaction among parameters. Factorial design and response surface methodology (RSM) are the most popular designs used for optimization of multi variable processes [24]. Recently artificial neural networks (ANN) was particularly used for optimization of non-linear processes in all fields of science and technology [25]. Some interesting features of ANN like analogous data analysis, comprehensive approximation ability, training from past data, no need of empirical relation and more precise prediction made it as powerful optimization technique [26]. ANN requires experimental data to train the network and to validate predicted output. Hence combination of RSM and ANN i.e., using the experimental data of RSM for training and validation of ANN could give more accurate results.

In the present study, dead *G. acerosa* (brown algae) which is raw material for agar industries was used as biosorbent for efficient removal of cadmium from an aqueous solution. The objectives of the present investigation are optimization of process variables for optimum cadmium removal and estimation of biosorption kinetics of cadmium with possible mechanism.

2. Materials and methods

2.1. Preparation of biosorbent

Caramel green *G. acerosa* was collected from beach area of Visakhapatnam, India. These plants were washed first with tap water to remove the dirt and then with distilled water. Later these plants were dried in daylight for about 10 d. Dried plant material was then crushed and pulverized in domestic grinder. This granulated biomass of *G. acerosa* was sieved and graded into the required particle sizes range and straightly employed as biosorbent in the present study.

2.2. Preparation of metal solution

The standard solution of Cd (II) of concentration 1000 ppm was prepared by dissolving 2.31 g of 99% 3 $CdSO_4 \cdot 8H_2O$ in 1000 ml of distilled water. From this standard solution, working solutions (100, 80, 60, 40, 20 mg/l) of lower concentrations were prepared by appropriate dilution. The initial pH of the metal solution was calibrated by adding HNO_3 (0.1 N) and NaOH (0.1 N). The chemicals used for this experimental work were procured from Merck India Ltd., India. Each experiment was conducted three times and the mean values were reported. Blank tests were also carried out to ensure the experimental results.

2.3. Biosorption experiments (Batch mode)

Batch biosorption experiments were conducted by varying pH, initial Cd (II) ion concentration and biomass dosage while keeping the volume of reaction mixture as 30 ml. Mixing was carried out in orbital shaker at 120 rpm. All the experiments were conducted for an equilibrium contact time of 30 min at room temperature. Samples were collected and filtered using What man filter paper (No. 1). Residual Cd (II) in solution was measured using atomic absorption spectroscopy.

2.4. Metal uptake

The amount of metal deposited on biosorbent surface was determined by measuring the solution concentration difference. The metal solution concentration (C_i (mg/L)) before and after biosorption (C_f (mg/L)) was measured and the metal uptake q_e (mg metal adsorbed/g adsorbent) was calculated from the following equation:

$$q_e = \frac{V\left(C_i - C_f\right)}{1000W} \tag{1}$$

where V is the volume of metal solution taken (ml) and w is the amount of biosorbent (g) added to solution.

2.5. Central composite design (CCD)

CCD a standard experimental design of RSM was used to develop the empirical relation between process variables and response. Experimental design matrix designed by CCD for three variables and each with three levels (–1, 0, +1) was used to find out the optimum values of pH, metal ion concentration and biomass dosage. The ranges and levels of independent process parameters are given in Table.1. The mathematical equation relating three independent process variables and the response function i.e., percentage removal of metal ions has been expressed by the following quadratic model,

Table 1
Levels of different process variables used in CCD for biosorption of cadmium onto *G. acerosa*

Factor	Symbol	Levels		
		–1	0	1
pH	A	2	4.5	7
Initial concentration, mg/l	B	20	60	100
Biosorbent dosage, g	C	0.1	0.3	0.5

$$Y = \beta_0 + \beta_1 a + \beta_2 b + \beta_3 c + \beta_{11} a^2 + \beta_{22} b^2 + \beta_{33} c^2 + \beta_{12} ab + \beta_{13} ac + \beta_{23} bc \quad (2)$$

where Y is the output of the process, β_n is the coefficient associated with factor n, and the letters a, b, c are the process variables in the model.

2.6. Artificial neural network

ANN is a computer model developed with the inspiration of network and functioning of human neurological system. It became a fascinating tool for modeling and simulation of complex non-linear processes [27]. Its basic topology includes an input layer, hidden layers and an output layer. Each of these layers is inter-connected by a number of neurons, which will transfer the information between layers in the form of their weights [28]. In this study, the selected input variables are initial pH of solution, initial concentration of metal ion and biosorbent dosage, the % removal of Cd (II) as output (target) for ANN modeling. Training, testing and validation of network were conducted based on the same CCD data used for RSM. The Levenberg–Marquardt back-propagation algorithm was applied for network training. A tansigmoid transfer function (tansig) at hidden layer and a linear transfer function (purelin) at output layer were selected [29]. All ANN calculations were carried out using NN tool of MATLAB.

2.7. Kinetic models

Equilibrium and kinetic studies were carried out to predict biosorption mechanism and to determine various important parameters like initial adsorption rate, order of metal uptake kinetics, rate constant, rate controlling mechanism, diffusion coefficient, etc. An empirical relation for first order kinetics is represented by:

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

Pseudo second order equation is given by:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^{\,2}}\right) + \left(\frac{t}{q_e}\right) \quad (4)$$

where k_1 and k_2 are the first and second order rate constants, q_e and q_t are metal uptake at equilibrium and time t respectively for both models.

2.8. Intra-particle diffusion model

It was used to investigate the effect of diffusion of metal ions in to the pores of adsorbent on rate of biosorption. This model is represented by the following equation [30].

$$q_t = k_{id} t^{\frac{1}{2}} + C \quad (5)$$

where q_t is metal uptake at time t (min), k_{id} is rate constant and C is the value of intercept which measures the boundary layer thickness. Suitability of this model is checked by linearity test of the plot between q_t and $t^{0.5}$.

2.9. Boyd model

In order to find out the actual slow step in the biosorption process, the kinetic data were further analyzed using Boyd model [31] given by:

$$F = \left(1 - \frac{6}{\pi^2}\right)\exp\left(-\beta_t\right) \quad (6)$$

where F is the metal uptake relative to equilibrium uptake and β_t is a mathematical function measured from Eq. (7):

$$\beta_t = -0.4977 - \left(1 - F\right) \quad (7)$$

β_t value was calculated from the data and plotted against time, then the rate controlling step was determined from the linearity of the plot.

2.10. Elovich model

Elovich equation was also widely used by many researchers to demonstrate second order reaction kinetics of heterogeneous reactions. This was first applied to describe the kinetics of chemisorption mechanism of gas molecules onto a solid surface [32]. In recent years it had been successfully applied by the investigators to describe the chemisorption behavior of biosorption. The Elovich equation can be written in the linear form as:

$$q_t = \left(\frac{1}{b}\right)\ln\left(ab\right) + \frac{1}{b}\ln t \quad (8)$$

where '*a*' is the initial sorption rate and '*b*' is the constant related to the extent of surface coverage and activation energy for chemisorption.

3. Results and discussion

3.1. Characterization of G. acerosa algae

Algal cell wall is composed of many functional groups like hydroxyl, carboxyl, amine, sulphate and phosphate that play major role in metal binding [33]. FTIR spectra of *G. acerosa* algae before and after cadmium biosorption were recorded at frequencies from 4000 to 400 cm^{-1} and shown in Fig. 1. Several peaks (Fig. 1a) were observed indicating the presence of various functional groups which are responsible for binding of cadmium. The broad peak at 3421.66 cm^{-1} represents O-H stretching vibration that showed the presence

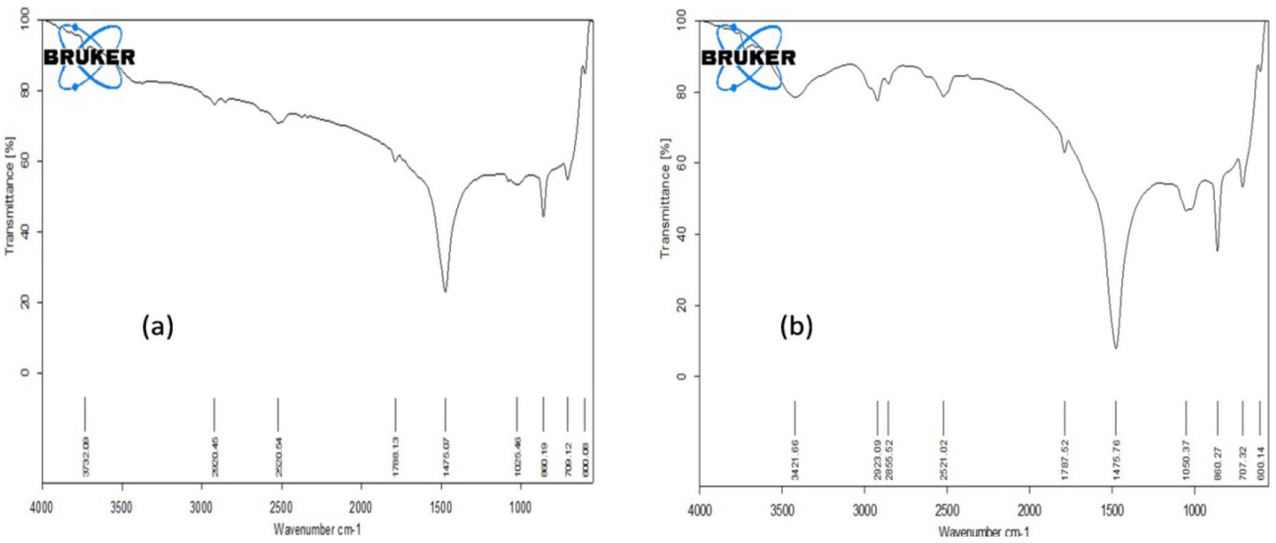

Fig. 1. FTIR spectra of *G. acerosa* (a) before biosorption and (b) after biosorption of cadmium.

of alcohols and phenols on the surface of biosorbent. The peaks in the range of 2923–2856 cm^{-1} showed the stretching of O-H and N-H bonds indicate the presence of carboxylic and amino groups [33]. In most of the brown algae, 70% of cell wall functional groups are carboxylic and amino groups, these groups play vital role in metal binding [34]. The peaks at wave numbers of 2521.09, 1737.52, 1475.78, 1050.37 cm^{-1} are indicative of the presence of S-H, C-O, C-H, C=C groups [35]. The peaks in the range of 700–900 cm^{-1} are originated from the stretching mode of C=C, C-l bonds. The peak at 600.14 cm^{-1} was associated with absorbance of C-l group indicating the presence of halo compounds. Therefore surface functional groups known as carboxylic acids, amino, alkenes and alkyl groups which are the functional groups of cell wall are responsible for biosorption of cadmium.

Comparison of FTIR spectra of *G.acerosa* loaded with cadmium (Fig. 1b) with that of unloaded reveled significant changes. Formation of new peaks around 3730 cm^{-1} and disappearance of peak at 3421.66 cm^{-1} is the clear indication of possible chemical reaction between metal ions and surface functional groups. The absorption peaks of C-H & O-H stretching vibrations are slightly shifted from 2923.09 to 2920.45 cm^{-1}. The large shift of C-O stretch from 1737.52 to 1788.13 cm^{-1} clearly indicates the strong involvement of carboxylic acids, esters and aldehydes in biosorption process [36]. Major shift of peak from 1050.37 to 1025.48 cm^{-1} indicates the more involvement of more alcoholic groups in biosorption process. The peak changes in the range of 600–800 cm^{-1} are the evidences of involvement of halo compounds and alkene groups in the metal removal.

The SEM analysis of *G. acerosa* was carried out to study the surface texture and porosity of biosorbent. The result obtained is shown in Fig. 2a. It clearly illustrates that the surface area of *G. acerosa* is highly heterogeneous and uneven with porous structure. It is apparent from the figure that *G. acerosa* has very rough surface with good number of pores where there is good possibility for biosorption of metals. SEM micro graphs of *G. acerosa* biosorbent after biosorption of cadmium is shown in Fig. 2b. The micro graph clearly shows the presence of shiny particles over the surface loaded with cadmium.

3.2. Optimization of process parameters

3.2.1. Response surface methodology (RSM)

Central composite design was used to develop quadratic model by considering pH (A), initial concentration (B) and biosorbent dosage (C) as variables. A total of 20 experiments designed by CCD which includes eight factorial, six axial and six center points were conducted and the obtained results were used for the analysis. Complete design matrix generated using CCD with coded variables, response reported from experiments and predicted response for biosorption of cadmium onto *G. acerosa* is given in Table 2.

3.2.2. Regression analysis

Regression analysis was carried out to find out the fitness of the response function, i.e., percentage biosorption of cadmium. An empirical relationship between the response and input variables in coded terms developed by RSM was given by the following response surface reduced quadratic model equation:

$$\%\ Removal = +74.50 - 13.53 * A - 18.12 * B + 1.52 * C + 0.46 * A * B + 0.08 * A * C - 0.015 * B * C - 21.09 * A^2 - 2.09 * B^2 + 1.15 * C^2 \quad (9)$$

The above equation shows that how the individual variables or double interactions influence the biosorption of cadmium from an aqueous solution. From this equation it could be observed that factors A and C had positive effect means proportional effect, while factor B had negative effect i.e., reverse effect on biosorption of cadmium. Similar results were reported [37] for biosorption of chromium onto chitosan carbonized rice husk.

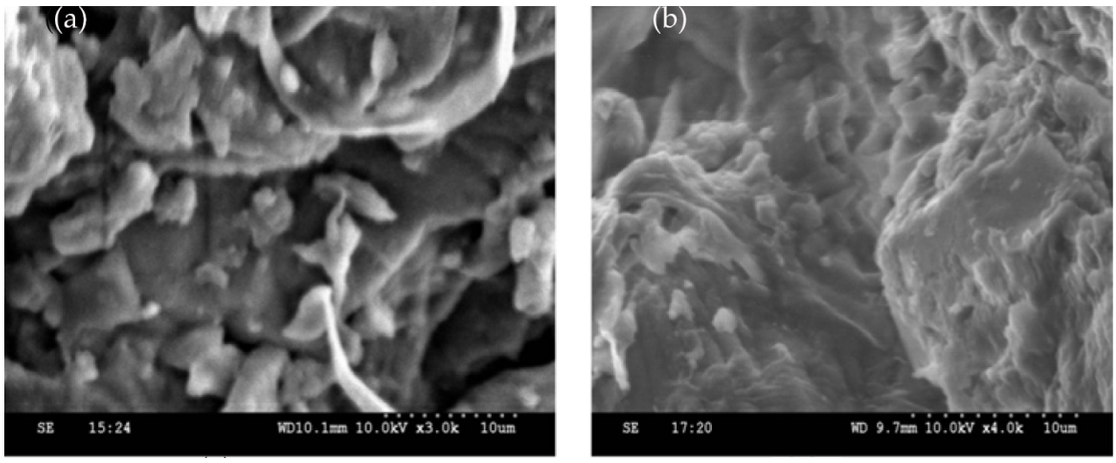

Fig. 2. SEM micro graph of *G. acerosa* (a) before biosorption, (b) after biosorption of cadmum (biosorbent size = 75 µm).

Table 2
Comparison of experimental values of CCD with predicted values of RSM and ANN for biosorption of cadmium onto *G. acerosa*

Standard order	pH	Initial concentration (mg/l)	Biosorbent dosage(g)	% Removal		
				Experimental	RSM predicted	ANN predicted
1	–1	–1	–1	83.13	83.10	83.40
2	1	–1	–1	55.01	54.98	55.01
3	–1	1	–1	46.02	45.99	58.00
4	1	1	–1	19.72	19.69	19.76
5	–1	–1	1	86.04	86.01	86.78
6	1	–1	1	58.24	58.21	58.21
7	–1	1	1	48.87	48.84	48.87
8	1	1	1	22.89	22.86	23.02
9	–1	0	0	66.82	66.93	66.81
10	1	0	0	39.76	39.88	39.86
11	0	–1	0	90.4	90.52	89.01
12	0	1	0	54.17	54.29	54.35
13	0	0	–1	74.01	74.12	73.92
14	0	0	1	77.04	77.16	77.08
15	0	0	0	74.31	74.50	74.73
16	0	0	0	75.09	74.50	74.73
17	0	0	0	73.94	74.50	74.73
18	0	0	0	74.72	74.50	74.73
19	0	0	0	75.24	74.50	74.73
20	0	0	0	74.16	74.50	74.73

3.2.3. ANOVA for response surface quadratic model

Significance of each individual process variables and overall model significance was studied using Analysis of variance (ANOVA) and the results are presented in Table 3. The F-values and lack of fit tests explicit the significance of model and insignificance of lack of fit which further confirms the fitness of the model. Moreover very small "model P-value" (< 0.0001), large "lack of fit P-value" (0.989) and high determination coefficient (0.999) are also the evidences of significance of models. Later significance of each individual parameter and their interaction was studied using

Table 3
ANOVA for quadratic surface model for biosorption of cadmium onto *G. acerosa*

Source	Sum of squares	df	Mean square	F Value	p-value Prob > F
Model	7493.66	9	832.63	5539.66	< 0.0001
A-pH	1829.53	1	1829.53	12172.24	< 0.0001
B-Initial metal concentration	3281.53	1	3281.53	21832.74	< 0.0001
C-Biosorbent dosage	23.07	1	23.07	153.51	< 0.0001
AB	1.66	1	1.66	11.02	0.0078
AC	0.051	1	0.051	0.34	0.5724
BC	1.800E-003	1	1.800E-003	0.012	0.9150
A2	1223.06	1	1223.06	8137.29	< 0.0001
B2	12.06	1	12.06	80.23	< 0.0001
C2	3.61	1	3.61	24.03	0.0006
Residual	1.50	10	0.15		
Lack of fit	0.13	5	0.026	0.094	0.9894
Pure error	1.37	5	0.27		
Cor total	7495.17	19			

P-values of respective factor. For the present study A, B, C, AB, A^2 are significant model terms [37]. Though the individual parameter effects of pH, initial concentration and biosorbent dosage were significant, combined effect of pH and initial concentration was more significant. Square effect of pH had also shown moderate significance on biosorption. Overall, the ANOVA analysis indicates the suitability of the model for simulation of the biosorption process of cadmium by *G.acerosa* within the limits of the experimental factors.

3.2.4. Optimization of process variables and authentication

After developing mathematical model for the biosorption of cadmium onto *G. acerosa*, optimization was carried out to predict maximum metal uptake by *G. acerosa*. Predicted solution by RSM is shown as contour plot in Fig. 3. The maximum cadmium removal predicted from RSM is 90.51% at optimum process conditions of pH of 5.85, initial concentration of 24.8 mg/l and biosorbent dosage of 0.48 mg/l. To assess the validity of optimization of process using RSM, a new experiment was conducted at above mentioned predicted optimum process conditions. Cadmium removal obtained in this experiment is 90.25%, which is approximately equal to that of the predicted value from RSM. Hence the values of process variables where maximum metal removal was predicted by RSM were considered as optimum process conditions for biosorption of cadmium onto *G. acerosa*.

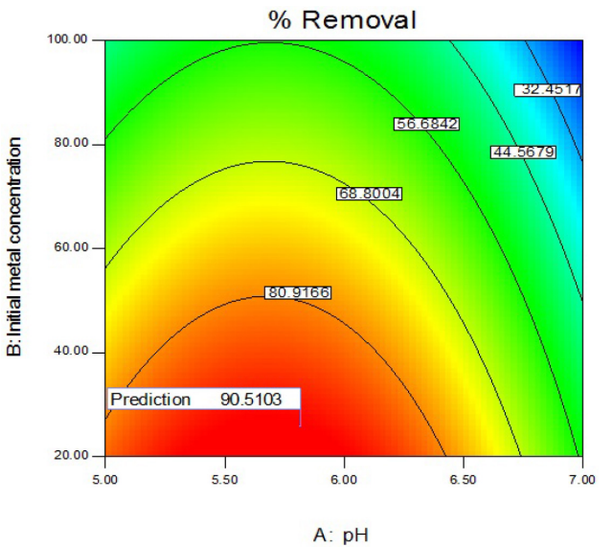

Fig. 3. Contour plot of optimization of biosorption of cadmium onto *G. acerosa*.

3.2.5. Interactive effects of two variables

Three dimensional response surface plots were used to study the interaction effects of process variables on biosorption. Fig. 4a shows the three-dimensional response surface plot of interactive effect of initial metal ion concentration and initial pH of the solution. This plot clearly visualizes the dominance of pH over initial concentration in terms of percentage of metal removal. Instead of decrease in percentage removal a moderate increase was observed with an increase in initial concentration, later decrease in percentage of removal was noticed. In overall the effect of initial metal ion concentration was neutralized by the effect of pH. Three-dimensional surface plot of interactive effect of pH and the biosorbent dosage on cadmium removal is shown in Fig. 4b. It clearly manifests the effect of pH over effect of biosorbent dosage. It could be observed that at higher biosorbent dosage, the percent removal of cadmium was

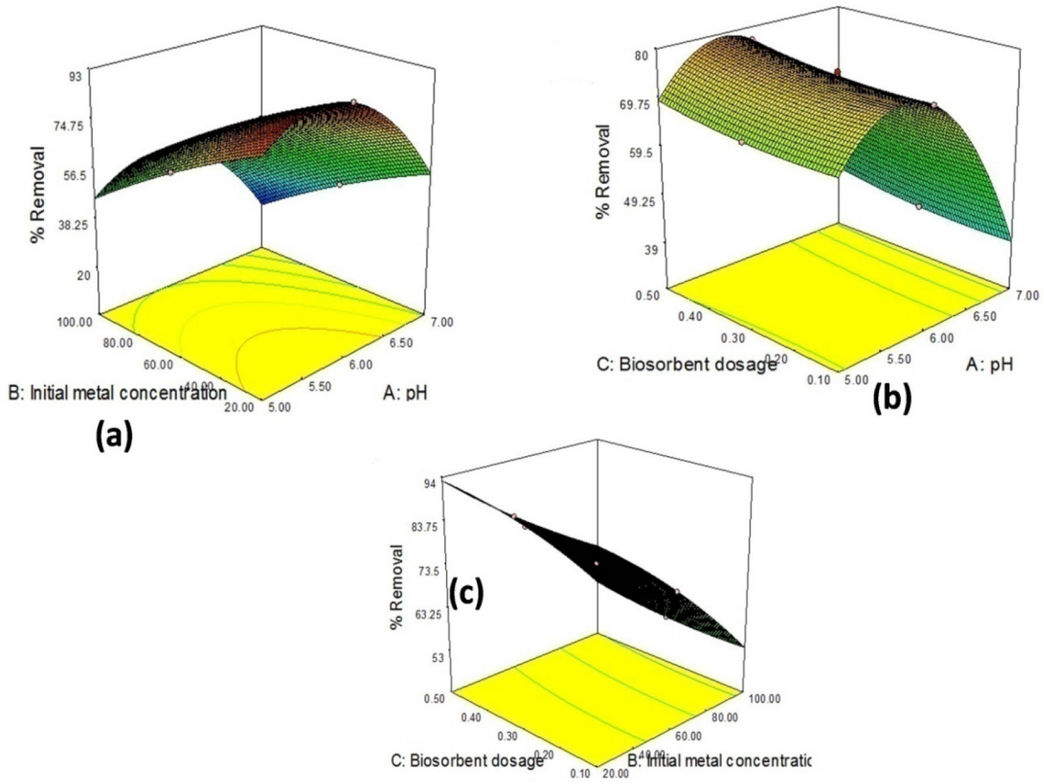

Fig. 4. Surface plot for interactive effects of (a) initial concentration and pH, (b) biosorbent dosage and pH, (c) initial concentration and biosorbent dosage on biosorption of cadmium onto *G. acerosa*.

high, possible reason for this was availability of more binding sites and increase of negative charge on surface of biosorbent with an increase of pH, both together contributed for increase of metal removal. The interactive effects of the biosorbent dosage and initial metal ions concentration can be inferred from the response plot of Fig. 4c holding pH at central values. From the figure it could be observed that both biosorbent dosage and initial concentration as individual parameter had no significant affect on metal removal, so the interaction effect of both variables was also insignificant. From ANOVA also it can be confirmed that the p-value of the factor BC is very high, which shows the insignificant effect of that factor. In overall the interactive effect of biosorbent dosage and initial concentration had almost no significance on cadmium removal.

3.2.6. Optimization of process parameters using Artificial Neural Network (ANN)

The ANN models were developed, trained and validated for optimization of process variables for biosorption of cadmium onto *G. acerosa*. Experimental data generated for RSM using CCD were used as input and target data for network training. To enhance prediction capability of network, experimental data were divided into three sub sets as training (70%), testing (15%) and validation (15%). The network was trained using back-propagation method which is based on Levenberg-Marquardt algorithm. The variation of determination coefficients is presented in Fig. 5, showing values above 0.99 in training, testing, validation, and overall model. The optimum training combination was used to simulate the variables of the experimental sets and the predicted values are presented in Table 2.

The experimental results were compared with predicted values of both the RSM and ANN, and performances of models in terms of R^2 values were evaluated. Both the models showed good efficiency in predicting the percentage of biosorption of cadmium. However the R^2 values of RSM (0.999) were higher than ANN (0.98) (Fig. 6) indicating the higher prediction ability of RSM over ANN. Optimum process conditions for the percentage of biosorption of cadmium were determined using RSM and ANN optimization methods and confirmation experimental runs were also conducted at these optimum levels. The results showed that the values of percentage of biosorption of cadmium determined from RSM are in close agreement with the experimental results than the values of percentage of biosorption determined from ANN method. Hence the optimization values predicted from RSM were considered as optimum process variables for biosorption of cadmium onto *G. acerosa*.

3.3. Kinetic studies

Kinetics of biosorption describing the solute uptake rate, which in turn governs the residence time of the bio-

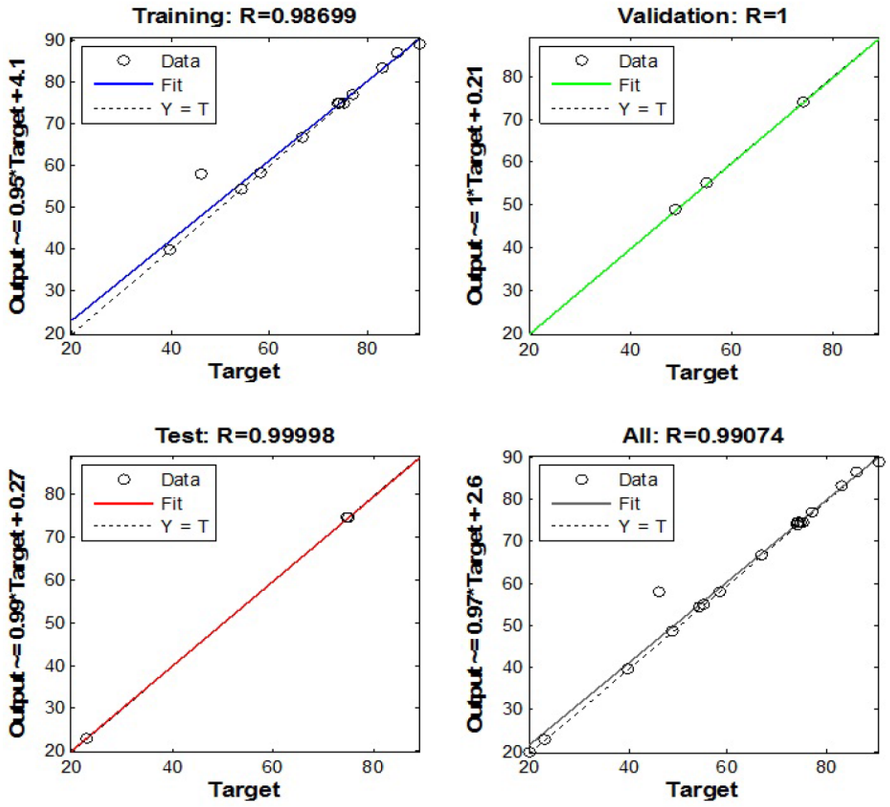

Fig. 5. Values of R^2 for training, validation, testing and model with 10 neurons in hidden layer of ANN for biosorption of cadmium.

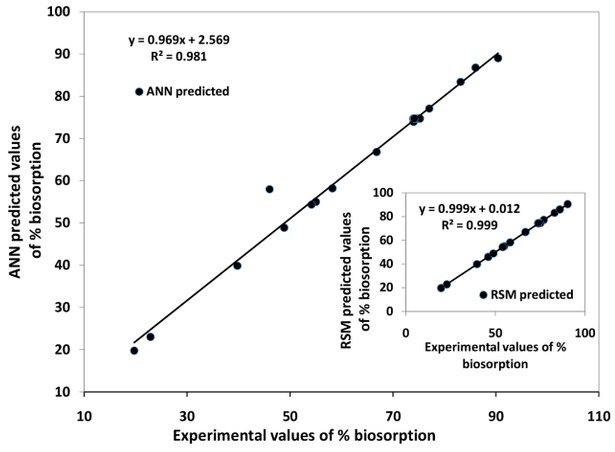

Fig. 6. Comparison of experimental values with predicted values of ANN and RSM for biosorption of cadmium onto *G. acerosa*.

sorption reaction, is one of the important characteristics defining the efficiency of biosorption. Hence in the present study, the kinetic analysis for removal of cadmium by biosorbent was carried out with different initial cadmium concentrations ranging from 20–100 mg/l at an initial pH of 6 and temperature of 303 K.

The fitness of kinetic data to pseudo first and second order rate equations was described in Fig. 7 and corresponding rate constants, predicted cadmium uptake and R^2 values are reported in Table 4. In case of pseudo first order model R_1^2 values were found in the range of 0.99–0.98 which shows the significance of model, but the predicted maximum metal uptake values were significantly differed with the experimental values. According to Sinha et al. [38], if the predicted metal uptake is not equal to the experimental value the kinetic equation is not appropriate, even if the plot has a high regression coefficient. Hence pseudo first order rate equation is not suitable for determining kinetics. In case of pseudo second order, high correlation coefficients and very close predicted and experimental metal uptake values show the significance of the model for representing kinetics of biosorption of cadmium. Therefore biosorption of cadmium onto *G. acerosa* follows pseudo second order model with chemisorption as a rate limiting step [39]. Further kinetic data were fitted to Elovich model to confirm the chemisorption. As shown in Fig. 8 the plots are linear with good correlation coefficient (R^2 in the range of 0.985). So the fitness of data to Elovich model suggest that the biosorption of cadmium follows chemisorption, involving valence forces through sharing or exchange of electrons between biosorbent and biosorbate [40].

As shown in Table 4, the rate constant (k_{II}) values were decreased from 0.052 to 0.006 1/ g min with an increase of initial cadmium ion concentration where as the initial sorption rate increased from 1.186 to 4.201 mg/g min. This can be interpreted as with an increase in initial metal concentration, concentration gradient increases between bulk solu-

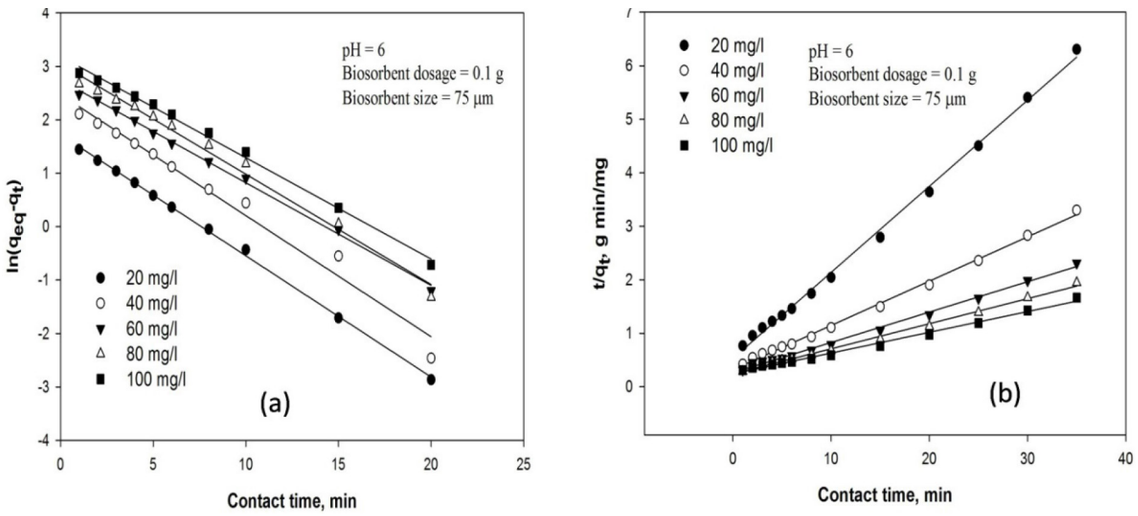

Fig. 7. (a) Pseudo first order (b) pseudo second order kinetics for biosorption of cadmium onto *G. acerosa*.

Table 4
Pseudo first and second order kinetic constants for biosorption of cadmium onto *G. acerosa*

Ci (mg/l)	Experimental	Pseudo-first-order			Pseudo-second-order		
	q_e [mg/g]	q_e [mg/g]	K_1 [1/min]	R^2	q_e [mg/g]	k_{II} [g/mg min]	R^2
20	5.492	3.309	0.227	0.998	6.25	0.0520	0.997
40	10.603	5.555	0.226	0.997	11.363	0.0221	0.997
60	15.133	6.694	0.192	0.997	15.625	0.0128	0.996
80	18.012	8.276	0.206	0.988	18.867	0.0094	0.996
100	21.039	9.107	0.189	0.986	21.739	0.0063	0.995

tion and biosorbent surface, which is the driving force for metal uptake. However at high concentrations, high probability of metal ion collisions makes metal ions diffusion towards the surface ligands or micro pores difficult and hence reduces the overall rate of kinetics.

The intra-pore diffusion of cadmium ion is investigated by fitting the kinetic data to intra particle diffusion model. Fig. 4 shows the fitness of kinetic data to the intra particle diffusion model. If the intra-particle diffusion is the only rate-controlling step then the plot should pass through the origin, else the boundary layer diffusion affects the biosorption to some degree. From Fig. 9a it was clear that the linear curves are not passing through the origin which indicates the existence of external pore diffusion in biosorption. Similar trend was reported by jafari et al. [41] for biosorption of cadmium onto brown seaweed and by Ofomaja [42] for removal of lead using mansonia wood saw dust.

Further investigation was carried out by fitting the kinetic data to Boyd model to find out exact rate limiting step. B_t values were calculated from the data and then plotted against contact time. The rate controlling step of biosorption can be determined from the linearity of the plot. If the plot is linear and passes through the origin, the pore diffusion is the rate controlling step otherwise surface (film) diffusion is the rate controlling step. As shown in Fig. 9b,

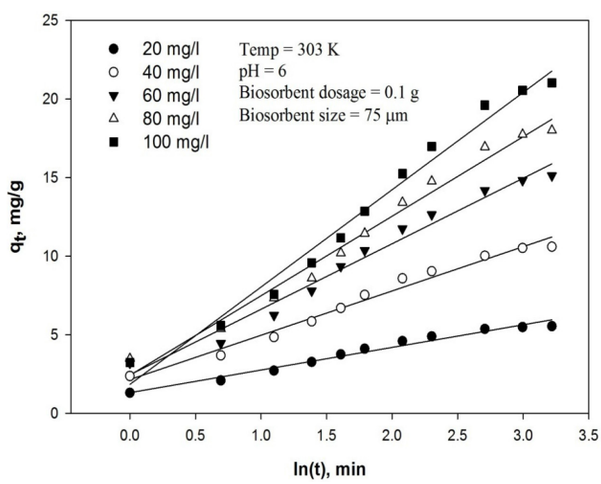

Fig. 8. Elovich model for biosorption of cadmium onto *G. acerosa*.

the plot of B_t vs. contact time was linear with correlation coefficient (R^2 = 0.998), but it was not passed through the origin which indicates that the process is controlled by external mass transport, where particle diffusion is rate controlling step.

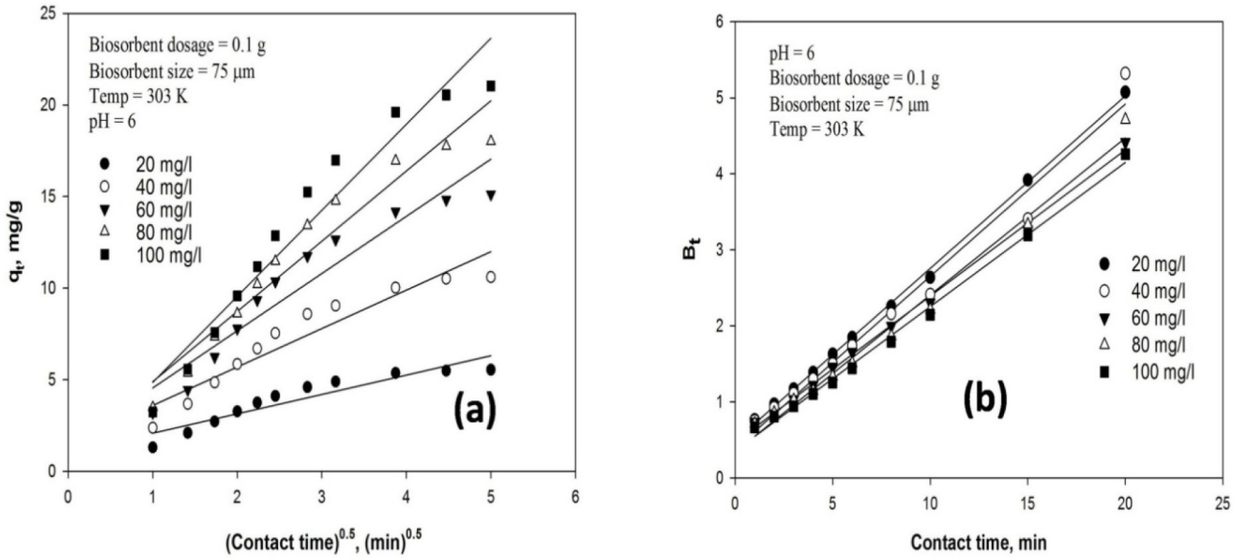

Fig. 9. (a) Intra particle diffusion model, (b) Boyd model for biosorption of cadmium onto *G. acerosa*.

Table 5
Comparison of maximum biosorption capacity of cadmium onto various biosorbents

Biosorbent	q_{max} (mg/g)	Reference
Olive pomace	7	43
Wheat straw	4.25	44
Tree fern	16.3	45
Coconut copra meal	4.99	46
Eucalyptus bark	14.53	47
Almond shell 0	3.18 0	48
Corncob 0	5.09 0	49
Rice husk (raw) 0	8.58	50
Gelidiella acerosa	21.739	Present study

3.4. Comparision of G. acerosa. with other biosorbents

The maximum cadmium biosorption capacity of *G.acerosa* was compared with various biosorbents and summarized in Table 5. The biosorption capacity of *G. acerosa* was found to be comparable and moderately higher than those of many biosorbents.

4. Conclusions

Optimization of biosorption potential of biosorbent prepared from *G. acerosa* for the removal of cadmium from an aqueous metal solution was investigated. The surface functional groups responsible for biosorption of cadmium onto *G. acerosa* were identified using FTIR and found that carboxylic acids, amino, alkenes and alkyl groups are involved in metal binding. The surface texture and porosity of the biosorbent was analyzed by SEM analysis and found that the biosorbent surface is highly heterogeneous and uneven with porous structure. The initial cadmium ion concentration, solution pH and biosorbent dosage were considered as variables for optimization using RSM and ANN. The effect of three individual factors and interaction effect between pH and initial concentration showed significant effect on biosorption. RSM showed better performance in predicting optimum process variables. Kinetic data were well correlated by pseudo second order model indicating chemisorption and search for mechanism demonstrated that particle diffusion as the rate controlling step.

Acknowledgement

We would like to thank entire team of Center of Excellence for Advanced Materials, Manufacturing, Processing and Characterization (CoExAMMPC) of Vignan's Foundation for Science and Technology, Guntur and Advanced Analytical Laboratory of Andhra University, Visakhapatnam for their support in entire instrumental analysis.

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