



Research Article

Volume 23 Issue 2 - November 2019
DOI: 10.19080/ARTOAJ.2019.23.556230

Agri Res & Tech: Open Access J

Copyright © All rights are reserved by A Ranga Rao

Simultaneous Biosorption of Chromium (III) and Chromium (VI): Application of Multiple Response Optimizations



John Babu D¹, Sumalatha B², Venkata Narayana A¹, Venkateswarulu T.C¹, King Pulipati³ and Ranga Rao A^{1*}

¹Department of Biotechnology, Vignan's Foundation for Science Technology and Research, Andhra Pradesh, India.

²Department of Chemical Engineering, Vignan's Foundation for Science Technology and Research, Andhra Pradesh, India.

³Department of Chemical Engineering, Andhra University College of Engineering, Visakhapatnam, Andhra Pradesh, India.

Submission: October 16, 2019; **Published:** November 06, 2019

***Corresponding author:** A Ranga Rao, Department of Biotechnology, Vignan's Foundation for Science Technology and Research, Andhra Pradesh, India.

Abstract

This work aims, optimization of simultaneous biosorption of Cr(III) and Cr(VI) onto *Gelidilla acerosa*, a marine macro algae using multiple response optimization combined with central composite design of experiments. The three important physicochemical parameters of biosorption such as initial pH, initial concentration of metal solution and biosorbent dosage were optimized. The most favorable condition for simultaneous removal of Cr(III) and Cr(VI) were: pH 2.8, initial concentration 20 mg l⁻¹ and biosorbent dosage 0.05g with maximum overall desirability of 1.0. Surface morphological features of biosorbent were studied using FTIR. The nature of biosorption was analyzed by fitting the equilibrium data to various adsorption isotherms and found that both Langmuir and Freundlich model were best fitted with R²: 0.99 for both chromium ions. The maximum biosorption capacities predicted from Langmuir model were 285.71 mg g⁻¹ for Cr(III) and 270.27 mg g⁻¹ for Cr(VI). The pseudo-second order kinetic model was found to be proper approach to demonstrate biosorption kinetics indicating chemisorption with film diffusion as the rate controlling mechanism. The results demonstrated that multiple response optimization combined with central composite design using desirability function was best approach for optimization of simultaneous biosorption of Cr(III) and Cr(VI) from aqueous medium.

Keywords: Biosorption; Chromium; Central composite design; Multiple response optimizations

Introduction

Water contamination with hazardous heavy metals is one of the most important issues due to its lethal effects to human beings and aquatic ecosystem. The key root of this heavy metal contamination is intensified industrial expansion as every industrial run-off carries toxic heavy metals at different concentrations. Chromium (Cr) is the one of the most profuse metals in the earth's crust and has gained ample attention due its potential toxic nature to human health and environment [1,2]. Though chromium exists in different oxidation states ranging from 0 to +6, hexavalent (Cr(VI)) and trivalent(Cr(III)) oxidation states have significant importance as these two states are most stable in the natural environment [3]. At lower concentrations, Cr(III) is an essential element in the body metabolism as it plays a significant role in the insulin regulation. Little dose of Cr (III) is used in supplements to treat diabetes which is

known to enhances the action of insulin [4,5]. Prolonged exposure to higher concentrations of Cr(III) becomes toxic and leads to skin allergic reactions. Moreover, the microorganisms of aquatic environment may oxidize Cr(III) into Cr(VI) which further enhances the toxicity. Contrary to Cr(III), Cr (VI) ions have high solubility and mobility in water, has no biological activity and penetrates into the human body 10,000 times quicker than Cr (III). Moreover Cr (VI) is mutagenic, carcinogenic and teratogenic to humans, animals and alters plant morphology [6-8].

Chromium is widely used in various industrial and household applications. Across the globe 80% of chromium is used in metallurgical applications [1]. In view of hazards nature of chromium ions to human health and economic importance of recovering chromium from industrial wastewater, several treatment process-

es such as precipitation by alkaline treatment, electrochemical precipitation, ion exchange and adsorption onto nanofibers and activated carbon have been used to remove chromium from contaminated wastewater. However, all these treatment methods are either inefficient or expensive. In addition, these techniques may also generate toxic secondary sludge which needs further expensive sludge disposal strategy [9-11]. On the other hand, adsorption was emerged as a promising technology to treat large quantities of dilute effluents due to its viability, simplicity, inexpensive and eco-friendly nature [12,13]. Biosorption is adsorption of pollutants using naturally available biomasses such as agro waste, algae, microbial consortium and digested sludge. In recent decades biosorption emerged as an effective technique for removal of pollutants from dilute effluents [14,15]. Algae as a renewable, naturally abundantly available biomass, it is well reported by researchers as biosorbent for wastewater treatment. Some marine and freshwater algae (biosorption of Au, Ag, and Co) showed higher biosorption potential than synthetic adsorbents like activated carbon, nanofibers and ion-exchange membranes [16]. It was also reported that in case of highly toxic metals the uptake capacities of brown algae are higher than other algae (green and red algae) [17]. Hence marine brown algae *Gelidilla acerosa*(*G.acerosa*) was selected as biosorbent for this study.

In statistical optimization using response surface methodology (RSM), experimental matrix is generated from design of experiments (DOE), experimental results are fitted to various mathematical models and statistical analysis tools are used to verify the fitness of model and interactions among various variables and responses. Optimization of single response is comparatively simple and requires a smaller number of experiments [18]. However, in many times, more than one response must be optimized simultaneously. In multiple responses optimization, RSM is merged with Derringer's desirability function. The desirability function transforms multiple responses into a single response case (desirability value), which can be optimized using univariate techniques [19].

Biosorption optimization

Table 1: Levels of process variables used in CCD for biosorption of chromium species onto *G.acerosa*.

Factors	Range and levels		
	-1	0	1
X ₁ : pH range	1	3	5
X ₂ : Initial concentration (mg l ⁻¹)	20	60	100
X ₃ : <i>G.acerosa</i> dosage (g)	0.01	0.03	0.05

RSM is a multi-variable optimization tool used to find the optimal response of a process which is a function of several independent variables through fitting the experimental results to polynomial equations. The three major steps of RSM include design of experimental matrix, development of mathematical model and optimization of response of interest [20,21]. In this study, pH (X₁), initial chromium concentration (X₂) and dosage of biosorbent (X₃) are independent variables and uptakes of Cr(III) Y₁ and Cr(VI)

Thus, this work aims to simultaneous biosorption of Cr(III) and Cr(VI) using *Gelidilla acerosa* (*G.acerosa*) as biosorbent. Independent process variables (pH, initial concentrations of chromium species and biosorbent dosage) were optimized by Central Composite Design (CCD) and multiple response optimizations. Biosorption kinetics and isotherms were also studied.

Materials and Methods

Chemicals and biosorbent

Stock solutions of Cr(III) and Cr(VI) (1000ppm) were prepared by dissolving 11.690 & 3.373 g of Cr₂(SO₄)₃.12H₂O & K₂CrO₄ in 1000ml of Double distilled water. Working samples of both chromium solutions were prepared from stock solutions by making accurate dilutions for each batch experiment. Brown marine macro algae (*G.acerosa*) was collected from Gulf of manar, Tamil Nadu, India. Collected algal plants were washed several times with normal and distilled water. Sundried algae were grounded and sieved using standard mesh. Raw biomass without any further treatment was used as biosorbent.

Experiments

The biosorption experiments were conducted by taking 100ml of working samples of different concentrations (20 to 100ppm) in an Erlenmeyer flask, pH (1 to 5) was adjusted with 0.1 normal HCl and NaOH and then pre-determined quantity of alga biomass (0.01 to 0.05g) was added. Solutions were shaken in orbital shaker at 120rpm speed. After filtration, the filtrate was analyzed for remaining chromium using Atomic absorption spectroscopy. The chromium uptake was calculated as follows:

$$q_e = \frac{V(C_o - C_t)}{1000m} \text{ ----- (1)}$$

where C_o and C_t (mg l⁻¹) are the initial and equilibrium chromium concentrations, q_e is chromium uptake (mg g⁻¹), V is working sample volume (ml) and m is weight of biosorbent (g). Triplicate experiments were performed, and average values were reported.

Y₂ are response variables. Experiments were designed using face centered central composite design (FCCCD) of RSM. The ranges and levels (-1, 0, +1) of independent variables are presented in Table 1. The regression equation relating the independent variables and the response of interest i.e., chromium uptake is presented in the form of following equation (2).

$$Y = \beta_0 + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^n \beta_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \beta_{ij} X_i X_j \text{ ----- (2)}$$

Where Y is response of system, β_0 is constant, β_1 is linear constant, β_2 is quadratic constant and is independent variable. MINIT-AB16 was used for experiments design, response fitness analysis and simultaneous response optimization. In multiple responses optimization, the responses were converted into equivalent desirability value (di) which varies from 0 (lowest) to 1 (highest desirability). In this study, maximum metal uptake is the desirability. The individual desirability function ($d_i(Y_i)$) is shown below

$$d_i(Y_i) = \begin{cases} 0 & \text{if } Y_i(X) < Y_{\min,i} \\ \left(\frac{Y_i(X) - Y_{\min,i}}{Y_{\max,i} - Y_{\min,i}}\right)^s & \text{if } Y_{\min,i} \leq Y_i(X) \leq Y_{\max,i} \\ 1 & \text{if } Y_i(X) > Y_{\max,i} \end{cases} \quad (3)$$

where $Y_{\min,i}$ and $Y_{\max,i}$ are minimum and maximum acceptable value of Y_i , respectively. The exponent s is scale of desirability. The desirability function is linear, when s=1. The individual desirability functions are then combined as the geometric mean for calculating overall desirability function (D):

$$D = d_1^{w_1}(Y_1) \times d_2^{w_2}(Y_2) \times \dots \times d_m^{w_m}(Y_m) \quad (4)$$

where $d_i(Y_i)$ and w_i are the desirability of response and weight of various responses, respectively (Liu and Tang 2010). In present study, Cr(III) and Cr(VI) biosorption efficiencies had equal weight ($w_1 = w_2 = 1/2$).

Kinetics of biosorption

Kinetic modeling of biosorption is very much essential to scale-up the process for industrial-scale operations. Moreover, kinetics of a reaction describes nature of the process, reaction pathways and exact interface resistance for mass transfer. Hence, fresh experiments were conducted for kinetics analysis by taking 100ml solutions (20 mg l⁻¹) chromium species with biosorbent dosage of 0.01g at corresponding optimum pH and the data was fitted to pseudo-first-order, pseudo-second order, and intra-particle diffusion models.

$$\log(q_e - q_t) = \log q_e - k_1 (t / 2.303) \quad (5)$$

Results and Discussion

Central Composite Design (CCD)

Table 2: CCD and response of biosorption efficiency of chromium ions in coded and real values.

Exp.No.	X ₁	X ₂	X ₃	pH	C _i (mg/l)	m (g)	% biosorption of Cr(VI)	% biosorption of Cr(III)
1	-1	-1	-1	1	20	0.01	46.35	57.45
2	1	-1	-1	5	20	0.01	30.39	41.93
3	-1	1	-1	1	100	0.01	36.75	47.75
4	1	1	-1	5	100	0.01	20.63	31.54
5	-1	-1	1	1	20	0.05	51.43	62.44
6	1	-1	1	5	20	0.05	35.46	46.74
7	-1	1	1	1	100	0.05	41.72	52.2
8	1	1	1	5	100	0.05	25.94	36.8
9	-1	0	0	1	60	0.03	42.18	53.02
10	1	0	0	5	60	0.03	27.56	38.56

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{t}{q_e}\right) \quad (6)$$

$$q_t = k_{id} t^{1/2} + C \quad (7)$$

Where k_1 and k_2 are the first and second order rate constants, q_e (mg g⁻¹) and (mg g⁻¹) are chromium uptake at equilibrium and time t(min) respectively, k_{id} is diffusion constant, C is the constant related to

film thickness.

Biosorption isotherms

Experimental equilibrium data was generated by conducting a set of experiments at room temperature, optimum pH and biosorbent dosage with variable initial metal ions concentrations and fitted to the Langmuir, Freundlich and Temkin isotherms and details of each isotherm are given below:

$$q_{eq} = \frac{Q_{\max} b C_{eq}}{1 + b C_{eq}} \quad (8)$$

$$q_{eq} = K_f C_{eq}^n \quad (9)$$

$$q_{eq} = \frac{RT}{b} \ln A_T + \frac{RT}{b} \ln C_{eq} \quad (10)$$

Where, C_{eq} is the concentration of chromium in residual solution (mg l⁻¹), q_{eq} is the equilibrium chromium concentration on *G. acerosa* (mg g⁻¹), q_{\max} is the maximum chromium uptake (mg g⁻¹) and b is Langmuir constant (l/mg), K_f is Freundlich constant, n is adsorption intensity (heterogeneity of site energies), A_T is the Temkin constant (l mg⁻¹), b (J mol⁻¹) is heat of sorption, R is universal gas constant (8.314 J mol⁻¹ K⁻¹) and T is temperature (K).

11	0	-1	0	3	20	0.03	81.81	93.2
12	0	1	0	3	100	0.03	72.39	83.38
13	0	0	-1	3	60	0.01	74.25	85.18
14	0	0	1	3	60	0.05	76.81	87.81
15	0	0	0	3	60	0.03	76.85	87.17
16	0	0	0	3	60	0.03	76.62	87.62
17	0	0	0	3	60	0.03	77.27	88.04
18	0	0	0	3	60	0.03	75.95	86.93
19	0	0	0	3	60	0.03	76.24	87.15
20	0	0	0	3	60	0.03	76.54	87.18

Effects of the three individual variables pH, initial chromium ions concentration and biosorbent dosage on biosorption efficiency (%) were examined using CCD. Complete design matrix generated using FCCCD in terms of coded, actual values of variables and responses reported from experiments were shown in Table 2. It shows that, biosorption of Cr (III) varied from 31.54% to 93.20% and 20.63% to 81.81% for Cr (VI). Significances of model and process variables were determined by ANOVA and found that all individual variables had significant effect, whereas quadratic and interaction terms had no effect on biosorption. Low value of lack of fit and high values of R^2 and R^2_{adj} demonstrates the consistency of models. The regression models equations were:

$$Y_1 = 12.70 + 57.781 X_1 - 0.2271 X_2 + 166.7 X_3 - 10.2780 X_1 * X_1$$

$$+ 0.000868 X_2 * X_2 - 1017 X_3 * X_3 - 0.00061 X_1 * X_2 + 1.97 X_1 * X_3 - 0.014 X_2 * X_3 \text{ ----- (11)}$$

$$Y_2 = 1.23 + 57.657 X_1 - 0.2074 X_2 + 173.0 X_3 - 10.269 X_1 * X_1 + 0.000722 X_2 * X_2 - 1039 X_3 * X_3 + 0.00005 X_1 * X_2 + 1.03 X_1 * X_3 + 0.020 X_2 * X_3 \text{ ----- (12)}$$

where Y_1 and Y_2 are biosorption efficiencies of Cr(III) and Cr(VI) respectively. X_1 , X_2 and X_3 are pH, initial concentration of chromium (mg l^{-1}) and biosorbent dosage (g) respectively. The optimum conditions for the maximum efficiency were pH: 3; biosorbent dosage: 0.03g; initial concentration: 20mg l^{-1} for both Cr(III) and Cr(VI), can result in maximum biosorption efficiency 93.20% (185.12 mg g^{-1}) and 81.81% (163.63mg g^{-1}) for Cr(III) and Cr(VI), respectively.

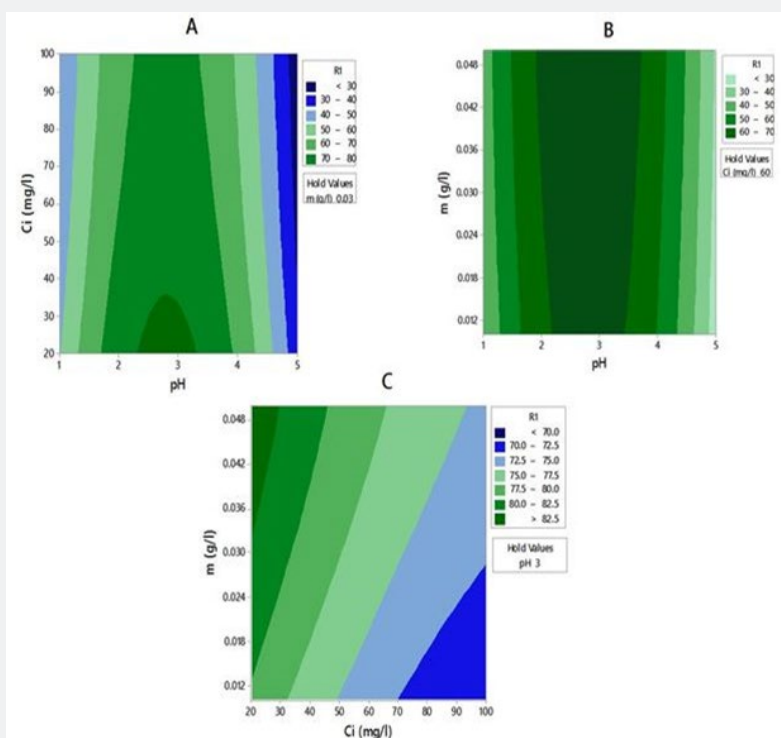


Figure 1: Contour plot of effect of (A) pH/Initial concentration, (B) pH/Biosorbent dosage, (C) Initial concentration/Biosorbent dosage on biosorption efficiency of Cr(III).

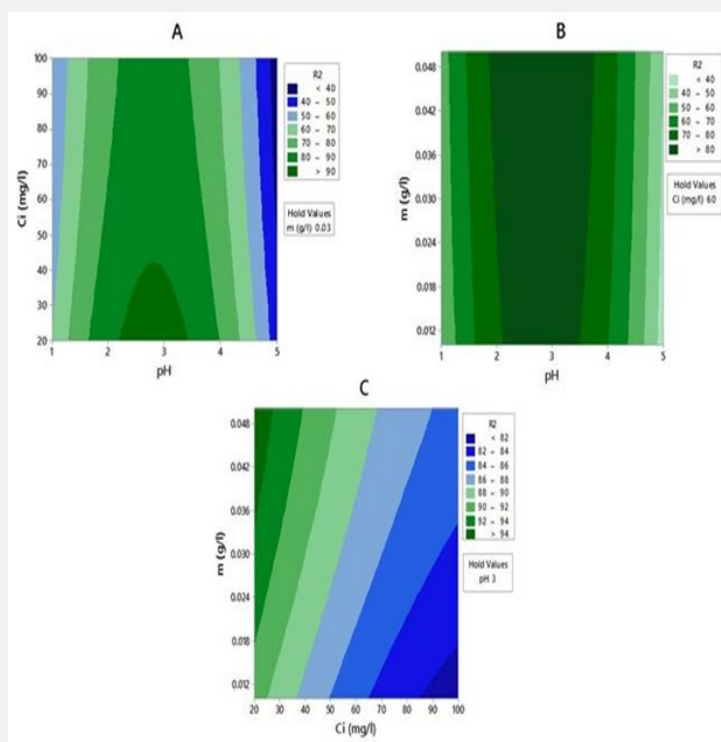


Figure 2: Contour plot of effect of (A) pH/Initial concentration, (B) pH/Biosorbent dosage, (C) Initial concentration/Biosorbent dosage on biosorption efficiency of Cr(VI).

Effects of process variables on biosorption efficiency

Figures 1 & 2 A & B show the influence of initial pH of chromium solution on biosorption efficiency at constant chromium concentration and biosorbent dosage. The biosorption efficiencies of Cr(III) and Cr(VI) were increased with pH(1-3) and reached maximum at pH 3. At lower pH, in the acidic medium the biomass surface will be protonated; hence the positive surface of biomass effectively holds the chromium ions. Moreover, at lower pH large number of H⁺ ions present in the solution will be neutralized by the OH⁻ ions present on the surface of biomass which promotes the migration of negatively charged chromium ions towards binding sites on biomass surface. Hence these two factors promote maximum biosorption at lower pHs [22]. With increase in pH(3-5), the surface of biosorbent becomes negatively charged which hinders biosorption through electro static repulsion, as a result biosorption efficiency decreases [23]. Effect of concentrations of chromium species on biosorption efficiency were shown in Figures 1 & 2 A & C. Biosorption efficiency was gradually decreased with the increase of concentration. At lower concentrations because of presence of good number of binding sites and less number of chromium ions biosorption efficiency is high, whereas at higher concentrations due to lack of sufficient binding sites and repulsion between biosorbed molecules and bulk phase the biosorption efficiency decreases [24]. Effects of *G.acerosa* dosage on chromium removal efficiency were presented in Figures 1 & 2 B & C. It was noticed that with increase of biosorbent, biosorption

efficiency was increased. With the increase of biosorbent dosage number of available metal binding sites and therefore metal removal efficiency increases [25].

Simultaneous responses optimization

Optimization of single response using statistical optimization techniques is simple and well reported in literature, but in effluent treatment optimization of multiple responses is much needed. As shown in Table 2, maximum biosorption efficiency of Cr(III) and Cr(VI) was not under similar conditions. Therefore, multiple response optimization with desirability function was used to predict the common optimum point for simultaneous biosorption of Cr(III) and Cr(VI). The desirability values for maximum biosorption of Cr(III), Cr(VI) and overall desirability value for simultaneous maximum biosorption were calculated. Optimization of simultaneous biosorption of chromium ions with desirability function was depicted in Figure 3. As shown in the figure individual and overall desirability values of 1.0 indicate that optimization of individual responses and simultaneous biosorption of Cr(III) and Cr(VI) are effective. Hence, pH 2.8, initial chromium species concentrations 20 mg l⁻¹ and *G.acerosa* dosage 0.05g were chosen as optimum conditions for simultaneous biosorption. At this optimum process conditions, maximal predicted responses for simultaneous biosorption were Y₁ =95.73% and Y₂ =84.51%. The validity of optimization process was examined by conducting a set fresh experiments (triplicate) at the above predicted values and reported 92.25% and 82.47% of Cr(III) and Cr(VI) removal respectively.

The experimental results are very closer to the predicted values. Hence, the predicted values of independent variables at maximum chromium removal were considered as optimum process conditions for biosorption of chromium onto *G.acerosa*.

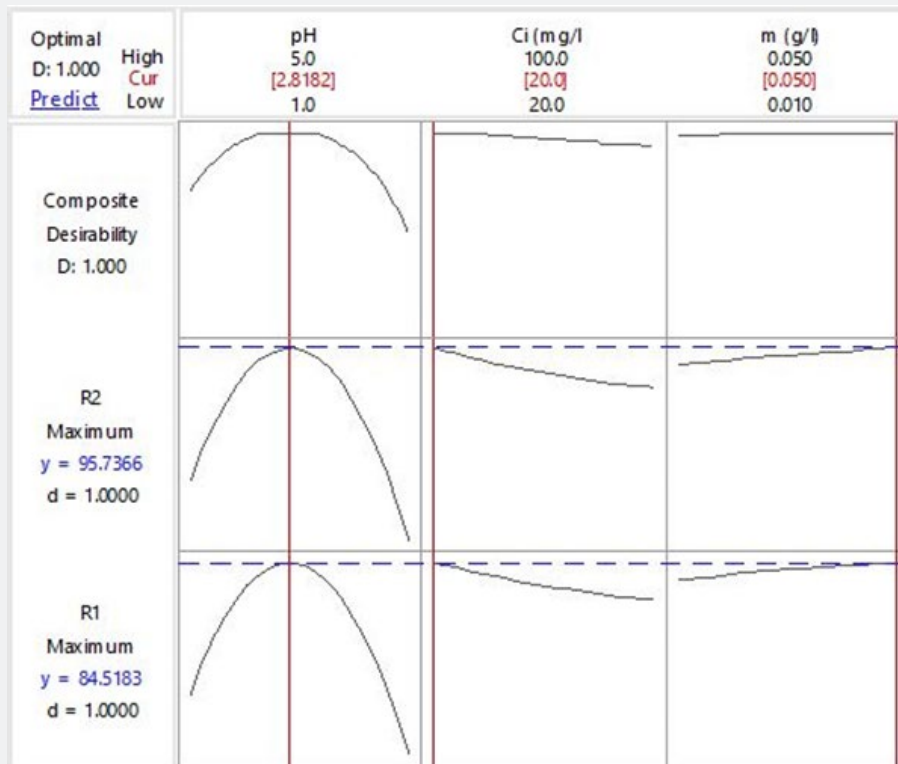


Figure 3: Profiles for predicted values and desirability function for biosorption efficiency of Cr(III) and Cr(VI).

Kinetic study

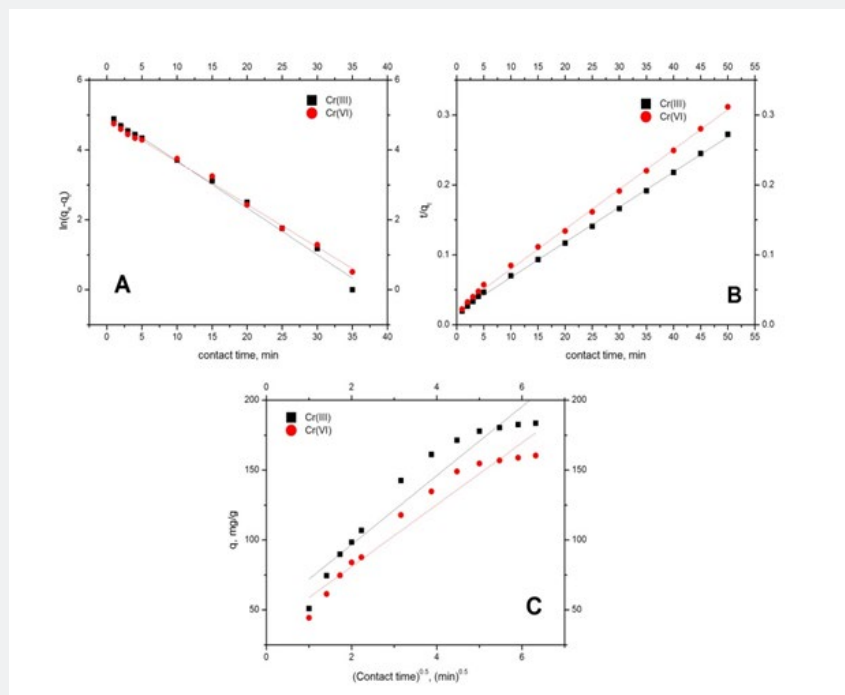


Figure 4: Biosorption kinetic models (a) pseudo-first order, (b) Pseudo-second order, (c) Intra- particle diffusion.

Kinetic modeling is fundamental in order to determine the affinity or capacity of the sorbent which in turn governs the residence time in the design of biosorption process. The fitness of kinetic data to pseudo first, second order rate equations and intra particle model was described in Figure 4 and corresponding rate constants, predicted chromium uptakes and R² values were reported in Table 3. Though the values of first order model are in the range of 0.99 to 0.98 but the predicted metal uptakes are far away from the experimental values. Hence, pseudo first order rate equation is not appropriate for determining kinetics. Whereas for

pseudo second order, high correlation coefficients and very close predicted and experimental chromium uptake values shows the significance of the model for representing kinetics of biosorption of chromium. Therefore biosorption of chromium ions onto *G.acerosa* follows pseudo second order model. The intra-pore diffusion of chromium ions was investigated by fitting the kinetic data to intra particle diffusion model Figure 5(a) shows that the kinetic data is not well correlated to the intra particle diffusion model and also plots are not passing through origin, indicating the biosorption of chromium is controlled by film diffusion.

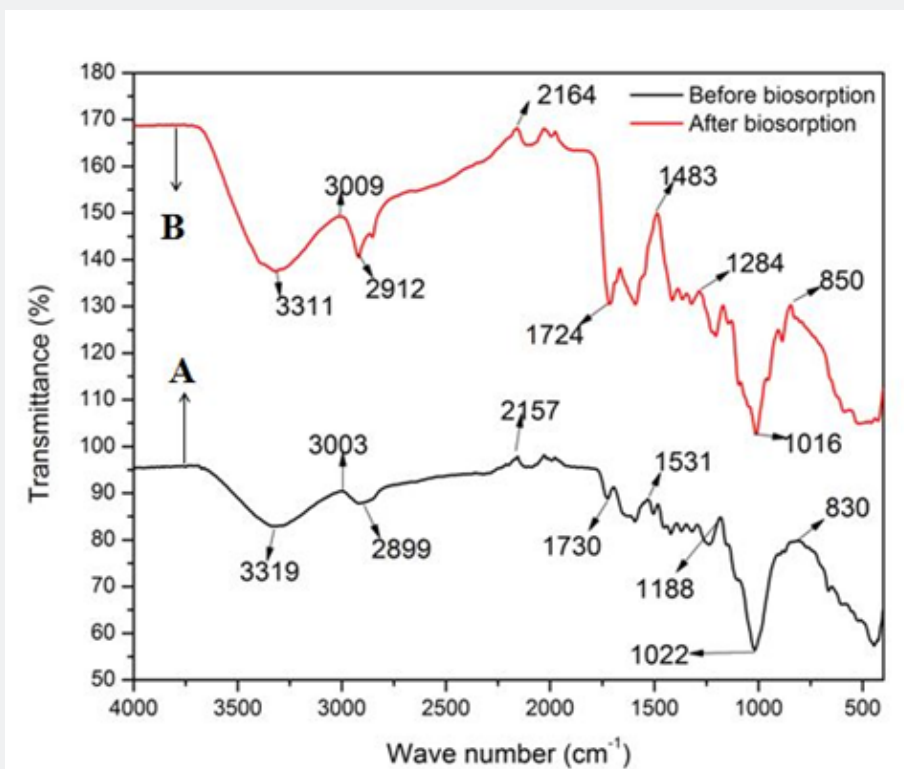


Figure 5: FTIR spectrograph of *G. acerosa* (a) before biosorption (b) after biosorption of chromium.

Table 3: Kinetic and isotherm models for biosorption of Cr(III) and Cr(VI).

Model	Parameter	Cr (III)	Cr (VI)
Kinetics			
Pseudo-first order	q _e	152.17	132.55
	K ₁	0.134	0.122
	R ₂	0.992	0.996
Pseudo-second order	q _e	185.18	161.29
	K ₂	0.0011	0.0014
	R ₂	0.999	0.998
Intra particle	K _{id}	24.65	22.11
	C	47.5	36.85
	R ₂	0.925	0.944
Isotherms			

Langmuir	Q _{max}	285.71	270.27
	b	0.388	0.185
	R ₂	0.996	0.992
Freundlich	n	6.41	4.716
	K _f	171.22	119.58
	R ₂	0.997	0.998
Tempkin	B	65.16	53.93
	A _T	68.03	7.17
	R ₂	0.997	0.987

Biosorption isotherms

Langmuir, Freundlich and Temkin isotherms were fitted to experimental equilibrium data to illustrate the biosorption nature of chromium onto *G.acerosa*. The plots pertain to Langmuir and

Freundlich and Temkin models were shown in Figure 6 and the equilibrium constants, regression coefficients and were shown in Table 3. The Freundlich model was better approximation to describe the biosorption isotherms than the other models.

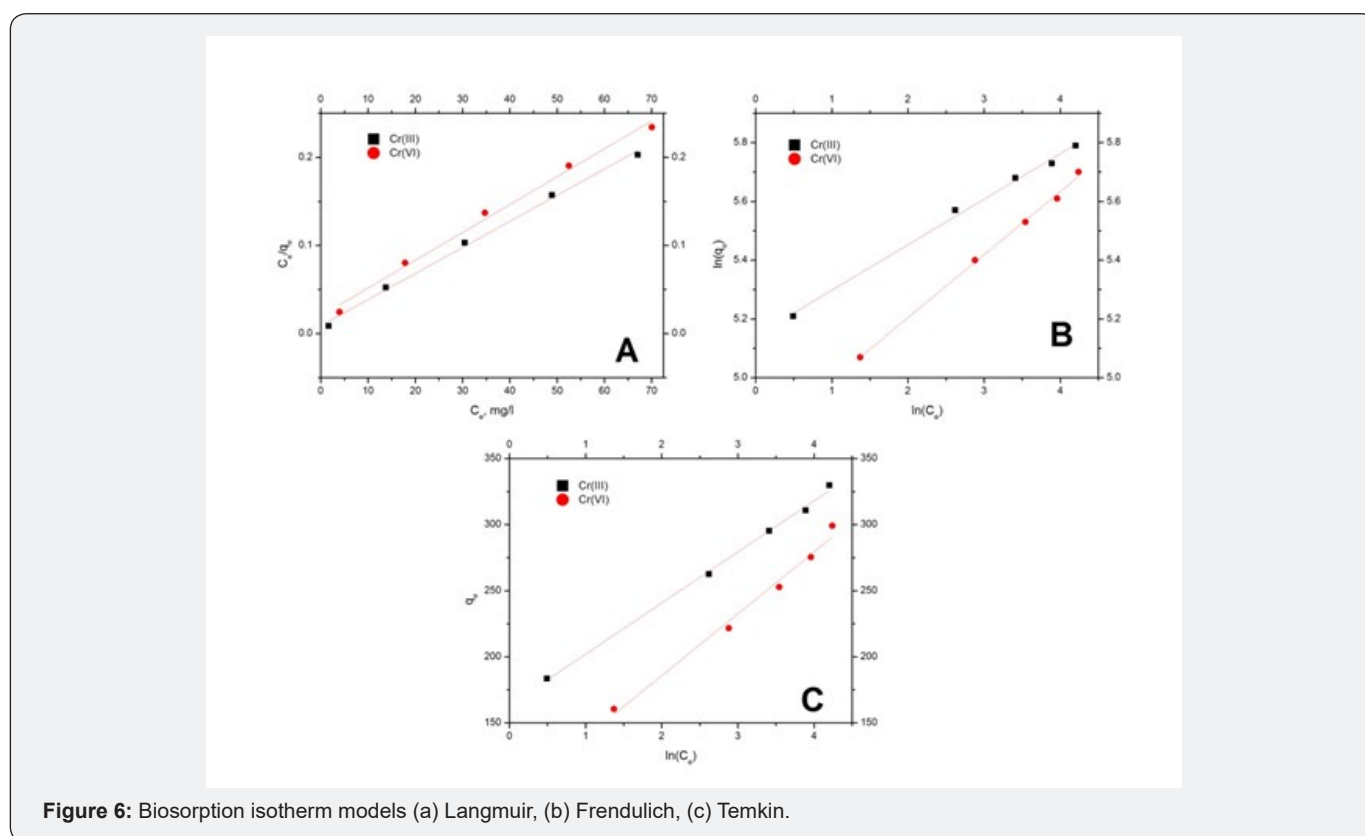


Figure 6: Biosorption isotherm models (a) Langmuir, (b) Freundlich, (c) Temkin.

Characterization of *G.acerosa* using FT-IR

FT-IR spectra of *G.acerosa* before and after biosorption of chromium were recorded at frequencies from 4000 to 400 cm^{-1} and presented in Figure 5. The spectra disclosed presence of various functional groups like carboxyl, hydroxyl, amino and carbonyl on the biosorbent surface. Algal cell wall is composed of many functional groups like hydroxyl, carboxyl, amine, sulphate and phosphate that play major role in metal binding [26]. Several peaks observed in Figure 5(a) indicating the prevalence of vari-

ous functional groups which are responsible for binding of chromium. The medium peak at 3319 cm^{-1} represents N-H stretching vibration that showed the presence of amine group on the surface of biosorbent. The peaks at 3003 and 2899 cm^{-1} represent C-H bonds that indicate the presence of carboxylic groups [26,27]. 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 [28]. The peaks at wave numbers of 1730, 1531 cm^{-1} are indicative of the presence of S, C=O and NO_2 groups [29]. Strong

stretching vibrations in the range of 1250-970 cm^{-1} are indication of the presence of alcohols and phenols. The peak at 830 cm^{-1} is associated with absorbance of O-H group indicating the presence of carboxylic groups. Therefore it is inferred that the surface of *G.acerosa* comprises of functional groups like carboxylic acids, amino, alkenes and alkyl groups. Comparison of FTIR spectra of *G.acerosa* loaded with chromium (Figure 5(b)) with that of unloaded revealed significant changes. Formation of new peaks at 1438 and 1248 cm^{-1} and disappearance of peak at 1724 cm^{-1} are the clear indications of possible chemical reaction between chromium ions and surface functional groups. Further shifting of peaks in the range of 3500 to 2800 cm^{-1} pertaining to carboxylate group reveals that involvement of C-H group in adsorption of chromium ions onto the biosorbent. Moreover, shifting of peak from 830 cm^{-1} to 850 cm^{-1} also discloses the binding of chromium ions to amine group present on the surface of spent *G.acerosa* [31].

Conclusion

This work demonstrated the simultaneous optimization of biosorption efficiency of Cr(III) and Cr(VI) using *G.acerosa* by applying CCD and multiple response optimizations. The optimum process conditions for simultaneous biosorption of Cr(III) and Cr(VI) were pH 2.81, initial chromium ions concentration 20 mg l^{-1} and *G.acerosa* dosage 0.05g. The maximum biosorption efficiencies of Cr(III) and Cr(VI) reported under this optimum process conditions were 95.73% (183.83 mg g^{-1}) and 84.51% (160.47 mg g^{-1}) respectively. Kinetic study showed that pseudo second order model provided better fit and fitness to the intra particle diffusion model revealed that film diffusion is the biosorption rate controlling step. Isotherm study showed that Freundlich isotherm model better explains biosorption equilibrium. The combination of RSM and multiple response optimization in present work led to finding optimized conditions for the simultaneous biosorption of Cr(III) and Cr(VI). These results indicate that marine algae *G.acerosa* without any pretreatment is a favorable sorbent material for biosorption of Cr(III) and Cr(VI).

References

- Miretzky P, Cirelli AF (2010) Cr (VI) and Cr (III) removal from aqueous solution by raw and modified lignocellulosic materials: a review. *J Hazard Mater* 180(1-3): 1-19.
- Avudainayagam S, Megharaj M, Owens G, Kookana RS, Chittleborough D, et al. (2003) Chemistry of chromium in soils with emphasis on tannery waste sites. *Rev Environ Contam. Toxicol* 178: 53-91.
- Chen S, Yue Q, Gao B, Li Q, Xu X, et al. (2012) Adsorption of hexavalent chromium from aqueous solution by modified corn stalk: a fixed-bed column study. *Bioresour Technol* 113: 114-120.
- Cohen MD, Kargacin B, Klein CB, Costa M (1993) Mechanisms of chromium carcinogenicity and toxicity. *Crit Rev Toxicol* 23(3): 255-281.
- Losi ME, Amrhein C, Frankenberger WT (1994) Environmental biochemistry of chromium. *Rev Environ Cont Toxicol* 136: 91-121.
- Bennett RM, Cordero PRF, Bautista GS, Dedeles GR (2013) Reduction of hexavalent chromium using fungi and bacteria isolated from contaminated soil and water samples. *Chem Ecol* 29: 320-328.
- Thatoi H, Das S, Mishra J, Rath BP, Das N (2014) Bacterial chromate reductase, a potential enzyme for bioremediation of hexavalent chromium: a review. *J Environ Manag* 146: 383-399.
- Abyaneh AS, Fazaelpoor MH (2016) Evaluation of rhamnolipid (RL) as a biosurfactant for the removal of chromium from aqueous solutions by precipitate flotation. *J Environ Manag* 165: 184-187.
- Cardoso VDA, De Souza AG, Sartoratto PP, Nunes LM (2004) The ionic exchange process of cobalt, nickel and copper (II) in alkaline and acid-layered titanates. *Colloids. Surf A Physicochem Eng Asp* 248(1-3): 145-149.
- Kandah MI (2004) Zinc and cadmium adsorption on low-grade phosphate. *Sep Purif Technol* 35(1): 61-70.
- Gupta VK, Ali I (2008) Removal of endosulfan and methoxychlor from water on carbon slurry. *Environ Sci Technol* 42(3): 766-770.
- Ferraz AI, Amorim C, Tavares T, Teixeira JA (2015) Chromium (III) biosorption onto spent grains residual from brewing industry: equilibrium, kinetics and column studies. *Int J Environ Sci Technol* 12: 1591-1602.
- Gupta VK, Pathania D, Agarwal S, Sharma S (2013) Removal of Cr (VI) onto *Ficus carica* biosorbent from water. *Environ Sci Pollut Res* 20(4): 2632-2644.
- Kuppusamy S, Thavamani P, Megharaj M, Venkateswarlu K, Lee YB, et al. (2016) Potential of *Melaleuca diosmifolia* leaf as a lowcost adsorbent for hexavalent chromium removal from contaminated water bodies. *Process Saf Environ Prot* 100: 173-182.
- Spasojevic PM, Panic VV, Jovic MD, Markovic J, Van Roost C, et al. (2016) Biomimic hybrid polymer networks based on casein and poly (methacrylic acid). Case study: Ni²⁺ removal. *J Mater Chem A* 4: 1680-1693.
- Kumar KS, Dahms HU, Won EJ, Lee JS, Shin KH (2015) Microalgae-A promising tool for heavy metal remediation. *Ecotoxicol Environ Saf* 113: 329-352.
- Mata YN, Blazquez ML, Ballester A, Gonzalez F, Munoz JA (2008) Characterization of the biosorption of cadmium, lead and copper with the brown alga *Fucus vesiculosus*. *J Hazard Mater* 158(2-3): 316-323.
- Witek-Krowiak A, Chojnacka K, Podstawczyk D, Dawiec A, Pokomeda K (2014) Application of response surface methodology and artificial neural network methods in modelling and optimization of biosorption process. *Bioresour Technol* 160: 150-160.
- Grosso C, Ferreres F, Gil-Izquierdo A, Valentão P, Sampaio M, et al. (2014) Box-Behnken factorial design to obtain a phenolic-rich extract from the aerial parts of *Chelidonium majus* L. *Talanta* 130: 128-136.
- Chatterjee S, Kumar A, Basu S, Dutta S (2012) Application of Response Surface Methodology for Methylene Blue dye removal from aqueous solution using low cost adsorbent. *Chem Eng J* 181-182: 289-299.
- Sadhu K, Mukherjee A, Shukla SK, Adhikari K, Dutta S (2014) Adsorptive removal of phenol from coke-oven wastewater using Gondwana shale, India: experiment, modeling and optimization. *Desalin Water Treat* 52(34-36): 6492-6504.
- Gorzin F, Bahri RAMM (2018) Adsorption of Cr (VI) from aqueous solution by adsorbent prepared from paper mill sludge: Kinetics and thermodynamics studies. *Adsorpt Sci Technol* 36(1-2): 149-169.
- Hiremath PG, Theodore T (2016) Zirconium-Doped Fungal Sorbents: Preparation, Characterization, Adsorption Isotherm, and Kinetic and Mathematical Modelling Study for Removal of Fluoride. *Advances in Chemistry*.
- Fathi MR, Asfaram A, Farhangi A (2015) Removal of Direct Red 23 from aqueous solution using corn stalks: isotherms, kinetics and thermodynamic studies. *Spectrochim Acta Part A* 135: 364-372.

25. Chowdhury MRI, Mulligan CN (2011) Biosorption of arsenic from contaminated water by anaerobic biomass. *J Hazard Mater* 190(1-3): 486-492.
26. Jerold M, Sivasubramanian V (2016) Biosorption of malachite green from aqueous solution using brown marine macro algae *Sargassum swartzii*, *Desal. Water Treat* 57: 25288-25300.
27. Dulla JB, Sumalatha B, King P, Yekula PK (2018) Investigation on biosorption of Cd (II) onto *Gelidiella acerosa* (brown algae): Optimization (using RSM & ANN) and mechanistic studies. *Desalin Water Treat* 107: 195-206.
28. Meseguer VF, Ortuño JF, Aguilar MI, Pinzón-Bedoya ML, Lloréns M, Sáez J, et al. (2016) Biosorption of cadmium (II) from aqueous solutions by natural and modified non-living leaves of *Posidonia oceanica*. *Environ Sci Pollut Res* 23(23): 24032-24046.
29. Khan TA, Mukhlif AA, Khan AA, Sharma DK (2006) Isotherm and kinetics modeling of Pb (II) and Cd (II) adsorptive uptake from aqueous solution by chemically modified green algal biomass. *Model Earth Syst Environ* 2: 1-13.
30. Liu RS, Tang YJ (2010) Tuber *melanosporum* fermentation medium optimization by Plackett-Burman design coupled with Draper-Lin small composite design and desirability function. *Bioresour Technol* 101(9): 3139-3146.
31. Sari A, Mendil D, Tuzen M, Soylak M (2008) Biosorption of Cd (II) and Cr (III) from aqueous solution by moss (*Hylocomium splendens*) biomass: equilibrium, kinetic and thermodynamic studies. *Chem Eng J* 144(1): 1-9.



This work is licensed under Creative Commons Attribution 4.0 License
DOI: [10.19080/ARTOAJ.2019.23.556230](https://doi.org/10.19080/ARTOAJ.2019.23.556230)

Your next submission with Juniper Publishers will reach you the below assets

- Quality Editorial service
- Swift Peer Review
- Reprints availability
- E-prints Service
- Manuscript Podcast for convenient understanding
- Global attainment for your research
- Manuscript accessibility in different formats
(Pdf, E-pub, Full Text, Audio)
- Unceasing customer service

Track the below URL for one-step submission
<https://juniperpublishers.com/online-submission.php>