



Biosorption of hexavalent chromium by free and immobilized dead *Sargassum sp*: a study on isotherms and kinetics

Sheryll Judith Dsilva^{a,†}, Ashish A. Prabhu^{b,†}, B.C. Suhas^a, B.E. Rangaswamy^a, Venkata Dasu Veeranki^{b,*}

^aDepartment of Biotechnology, Bapuji Institute of Engineering Technology Davangere, Karnataka, India,

emails: sheryll.biotec@gmail.com (S.J. Dsilva), suhasbc.Biet@gmail.com (B.C. Suhas), swamyber@hotmail.com (B.E. Rangaswamy)

^bBiochemical Engineering Laboratory, Department of Biosciences and Bioengineering, Indian Institute of Technology Guwahati, Assam, India, email: ashishbiotec@gmail.com, Tel. +91-361-258 2212; Fax: +91-361-258 4212; email: veeranki@iitg.ernet.in

Received 24 January 2016; Accepted 12 July 2016

ABSTRACT

In the present investigation, batch studies were carried out to remove hexavalent chromium (Cr(VI)) from the aqueous solution using *Sargassum sp* biomass in free and immobilized form. The effect of various operating parameters such as pH, biomass dosage, temperature and initial Cr(VI) concentration was studied. Two and three parameter isotherm models were used to fit the equilibrium data and regeneration studies were carried out for reusability of *Sargassum sp* biomass. Three parameter models showed better fit for immobilized *Sargassum sp* biomass ($R^2 > 0.995$). Among two parameter models, Langmuir model was found to be the best fit for the experimental equilibrium biosorption data with the predicted maximum total Cr(VI) biosorption capacity of 41.67 and 71.42 mg/g for free and immobilized *Sargassum sp* biomass, respectively. The pseudo second order model was better described ($R^2 > 0.9$) the Cr(VI) biosorption kinetic data for both free and immobilized biomass. The Fourier transform infrared spectroscopy suggested that amido-, hydroxyl-, C=O and C–O groups were involved in the biosorption of Cr(VI). This study showed that *Sargassum sp* biomass was an attractive and efficient biosorbent that could have been used as an alternative to treatment.

Keywords: *Sargassum sp*; Hexavalent chromium; Immobilization; Isotherm; Kinetics

1. Introduction

With the rapid development of industrialization and urbanization worldwide, drastic elevation in toxic heavy metals is being witnessed. This heavy metal deposition in the nature leads to bioaccumulation phenomenon [1,2]. Heavy metals such as cadmium, copper, chromium, lead, mercury and nickel are toxic to the environment even at their low concentration. Chromium is one of such toxic heavy metals, which is extensively used in industries like leather tanning, electroplating, wood preservation, metal finishing and chromate

preparation [3]. In aquatic environment, chromium exists in two oxidation states Cr(III) and Cr(VI) [1]. Release of Cr(VI) in the water bodies can cause malicious effects on human health with manifestations such as hemorrhage, severe diarrhea, vomiting, nausea, ulcers, lung carcinoma, tissue necrosis and finally leads to death [3–6]. According to the World Health Organization (WHO) drinking water guidelines, the maximum allowable limit for total chromium in inland surface waters is 0.1 mg/L and for potable water is 0.05 mg/L [7].

In order to reduce the hazardous effect of Cr(VI), considerable research has been carried out over the last few decades [8]. Traditionally, the removal of Cr(VI) from wastewaters carried out in two step method. The first step is the chemical reduction of Cr(VI) to Cr(III), followed by the precipitation of

* Corresponding author.

[†]Authors with equal contributions.

Cr(III) as Cr(OH)₃ [9]. Other conventional technologies such as chemical precipitation, ion exchange, chemical oxidation/reduction, reverse osmosis, electro dialysis, ultra filtration, etc are used to remove the Cr(VI) from aqueous solution, but it is seen that in some of these processes Cr(III) gets re-oxidized to form Cr(VI) again, and most of these methods are laborious and costly [8–10].

Metal removal through adsorption has gained much attention, due to its advantages such as efficient treatment of waste water through cost effective adsorbent, flexibility in designing and operation [11,12]. Biological sources are considered as an important biosorbent for the removal of heavy metal, due to its availability, renewable nature and cost effectiveness [13–15]. Biosorbents, such as Seaweeds [16–19], agriculture by-products and wastes [20–22] have been used extensively for the removal of Cr(VI) from aqueous solution. One of the most commonly used biosorbents is brown algae, as its cell wall consists of alginate or salts of alginate with other functional groups such as amine, carboxylic, sulphonic acid and hydroxyl groups in the polysaccharides, which are responsible for higher metal sorption capacity. The highly porous and rigid structure allows the transport of small ionic species and also facilitates rapid metal ion mass transfer and effective metal binding [21,22].

In standard metal sorption process, it is very difficult to use microbial biomass of any kind in direct form due to its small particle size, low strength and density which makes its separation tedious [24]. Immobilization of microbes is reported to be a more effective method for removal of heavy metals from solutions as it possess advantages such as efficient regeneration of biomass, easy separation of biomass, effluent and high biomass loading [23–28]. For immobilization, several natural and synthetic matrices have been studied. Sodium alginate is one of the most widely preferred matrices which is used for entrapment of biomass [24,25,27].

While using the dead biomass of algae, which are biologically inactive and the metal uptake process is completely dependent on passive adsorption, and can be correlated through various mathematical isotherms [29]. In the present study, attempts were made to explore the feasibility of using calcium alginate entrapped *Sargassum sp* for removing chromium ions from solutions, and to understand various factors effecting the absorption capacity of both immobilized and free algal biomass. The mechanism of biosorption of Cr(VI) on immobilized and free algal biomass was investigated by the study of kinetic constants and equilibrium isotherm models.

2. Materials and methods

2.1. Chemical reagents

Potassium dichromate (K₂Cr₂O₇), Calcium Chloride (CaCl₂), sodium alginate and 1,5 Diphenylcarbazide and phosphoric acid were procured from himedia, India and were of analytical grade.

2.2. Preparation of stock solution

A Stock solution of Cr(VI) of 1,000 ppm was prepared by dissolving potassium dichromate in distilled water. Cr(VI) solutions of different concentrations were obtained by diluting the stock solution.

2.3. Pretreatment of biomass

The seaweed (*Sargassum sp.*) biomass was collected from the west coastal region, Udupi, Karnataka, India. The biomass was washed thoroughly with distilled water to remove impurities and cations such as Ca²⁺ and Na⁺, the seaweeds were subjected to air drying for 2 d followed by oven drying (at 60°C ± 2°C) for 5 h and stored in desiccators. Dried biomass was chopped and grounded in a pestle and mortar. The powdered biomass was sieved to obtain the fractions of 0.3–0.7 mm, subsequently protonation of the biomass was carried out by soaking the above treated biomass with 0.1 M HCl at a 1:50 (w/v) ratio. The biomass was then washed with distilled water and dried at 50°C overnight. The prepared biomass was stored in an air-tight plastic container before it is used in biosorption experiments.

2.4. Immobilization of biomass

The biomass was washed thoroughly with distilled water and centrifuged at 10,000 RPM for 10 min. Immobilization of biomass was done by preparing 4 g of alginate (sodium salt) dissolved in 100 ml of distilled water with constant stirring to avoid formation of lumps. Equal amounts of pre treated algal biomass (4 g) were mixed with sodium alginate solution while stirring to ensure a uniform mixture. The immobilized beads of size 3 mm were prepared by dropping a mixture of sodium alginate and algal biomass suspension into a 0.3 M calcium chloride solution by a syringe. The beads thus formed were left to harden for 1 h and were maintained in the same salt solution. The beads were washed with distilled water and stored at 4°C for further use.

2.5. Batch biosorption studies

The removal of Cr(VI) from aqueous solution using the seaweed (*Sargassum sp.*) biomass was examined in a batch mode operation. The effect of various parameters of Cr(VI) biosorption on the seaweed (*Sargassum sp.*) biomass were observed by varying the solution of pH (2, 4, 6, 8), initial concentration of chromium (VI) ions (25, 50, 75, 100, 125, 150, 175, 200 ppm), biomass dosage (0.1, 0.2, 0.3, 0.4, 0.5 g (dry cell weight)) and temperature (25°C, 30°C, 40°C, 45°C, 50°C, 60°C). The batch sorption studies was carried out in a 250 ml conical flask containing 50 mL Cr(VI) solution of various concentration. The suspension was maintained under agitation on a reciprocal shaker at 150 RPM for 24 h. Later the chromium solution was subjected to filtration using cellulose filter membrane (0.45 µm). The concentrations of the Cr(VI) ions in the filtrate were analyzed using standard colorimetric method after complexation with 1,5-diphenylcarbazide in an acidic medium, using a UV-visible spectrophotometer at 540 nm (Cary 50 Bio UV-visible, Varian, Palo Alto, CA, USA) [6,13].

The amount of Cr(VI) adsorbed, q_e (mg/g), was calculated by use of the mass balance equation:

$$q = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

The percentage removal of Cr(VI) was calculated by use of the equation:

$$\text{Removal (\%)} = \left(\frac{C_i - C_e}{C_i} \right) \times 100 \quad (2)$$

where q is the biosorption capacity (mg/g), C_0 and C_e are the initial and equilibrium concentrations of Cr(VI) in mg/L, V is the volume of Cr(VI) solution (L) and m is the weight of the *Sargassum sp* (dry cell weight) in g.

2.6. Adsorption isotherm models

Adsorption equilibrium is a fundamental property of any adsorption studies. Sorption isotherms represent the distribution of the solute at equilibrium between the solid phase (the sorbent) and the liquid phase (the solution). All these isotherms can be explained in various mathematical forms, some of which are simply based on the concept of physical adsorption and desorption, while some others are empirically based and intend to correlate with the experimental data. In the present study we have tried to fit various adsorption isotherm models in order to verify which of the models fit the data with more accuracy [30,31].

2.6.1. Two-variable isotherms

2.6.1.1. Langmuir isotherm The Langmuir isotherm is applicable for monolayer adsorption onto a surface which contains finite number of identical sites. Furthermore this model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate on the plane of the surface [32]. Based upon these assumptions, Langmuir isotherm is given by:

$$q = \frac{q_{\max} b C_e}{1 + b C_e} \quad (3)$$

where C_{eq} is the equilibrium concentration of adsorbate (mg/L), q is the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g), q_{\max} is the maximum monolayer coverage capacity (mg/g), b is the Langmuir isotherm constant (L/mg).

The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L , which is a dimensionless constant referred to as separation factor or equilibrium parameter [33].

$$R_L = \frac{1}{1 + (b \times C_0)} \quad (4)$$

where C_0 is the initial concentration, R_L is the constant related to the energy of adsorption (Langmuir Constant). R_L value indicates the adsorption nature to be either unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0 < R_L < 1$ and irreversible if $R_L = 0$.

2.6.1.2. Freundlich isotherm The Freundlich isotherm model is used for heterogeneous surface energy systems and

for the description of multilayer adsorption with interactions between adsorbed molecules and it expresses surface heterogeneity, exponential distribution of active sites and energy of adsorption [34]. The Freundlich isotherm can be described by:

$$q = k_f C_e^{(1/n)} \quad (5)$$

where k_f is the Freundlich isotherm constant (mg/g), n is the adsorption intensity; C_e is the equilibrium concentration of adsorbate (mg/L) q is the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).

2.6.1.3. The Temkin isotherm Temkin Isotherm contains a factor that explicitly takes an account of adsorbent – adsorbate interactions by ignoring the extremely low and large values of concentrations. This model assumes that the adsorption heat of all molecules decreases linearly with the increase in coverage of the adsorbent surface and that adsorption is characterized by a uniform distribution of binding energies, up to a maximum binding energy [35]. Temkin Isotherm can be given as:

$$q_e = \frac{RT}{b} \ln(A_T C_e) \quad (6)$$

A_T is the Temkin isotherm equilibrium binding constant (L/g), b is the Temkin isotherm constant, R is the universal gas constant (8.314 J/mol/K), T is the Temperature at 303 K.

2.6.1.4. Dubinin–Radushkevich isotherm model Dubinin–Radushkevich (D-R) isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [36]. The model has often been successfully fit with high solute activities and the data with intermediate range of concentrations. The D-R isotherm model considers that adsorbent size is comparable to the micropore size and the adsorption equilibrium relation for a given adsorbate-adsorbent combination can be expressed by using the adsorption potential (ϵ),

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$$

where R , T and C_e represent the gas constant (8.314 J/mol K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L), respectively.

The D-R isotherm assumes a Gaussian-type distribution for the characteristic curve and the model can be described by:

$$q_e = q_s \exp(-B \epsilon^2) \quad (8)$$

where q_e is the amount of adsorbate in the adsorbent at equilibrium (mg/g); q_s is the theoretical isotherm saturation capacity (mg/g); B is the Dubinin–Radushkevich isotherm constant (mol²/kJ²) and ϵ is the Dubinin–Radushkevich isotherm constant [36–38]. E (kJ/mol) per molecule of sorbate at the

moment of its transfer to the solid surface from the bulk solution and can be computed using the following equation:

$$E = \frac{1}{\sqrt{2B}} \quad (9)$$

2.6.1.5. Elovich isotherm model Elovich model is based on the principle that the adsorption sites increase exponentially with adsorption, which implies a multilayer adsorption [39]. It is expressed by the relation:

$$\frac{q_e}{q_m} = K_E C_e \exp\left(-\frac{q_e}{q_m}\right) \quad (10)$$

where K_E denotes the Elovich equilibrium constant (L/mg) and q_m represent the Elovich maximum adsorption capacity (mg/g).

2.6.1.6. Jovanovic isotherm model The Jovanovic isotherm is similar to that of the Langmuir model, except that the allowance is made in the former for surface binding vibrations of adsorbed species [40]. This model is represented by the nonlinear relationship:

$$q_e = q_{mj} (1 - e^{-(K_j C_e)}) \quad (11)$$

where K_j denotes the Jovanovic isotherm constant (L/g) and q_{mj} is the maximum adsorption capacity (mg/g).

2.6.2. Three-variable isotherms

2.6.2.1. The Redlich–Peterson isotherm model The Redlich–Peterson isotherm is a three parameter model which includes the features of both Langmuir and Freundlich isotherms. This isotherm can be used to represent the biosorption equilibrium over a wide range of adsorbate concentrations [41]. This isotherm is expressed as follows:

$$q_e = \frac{K_{RP} C_e}{1 + \alpha_{RP} C_e^g} \quad (12)$$

where K_{RP} represents the Redlich–Peterson model isotherm constant (L/g), α_{RP} is the Redlich–Peterson model constant (L/mg), and the exponent g lies between 0 and 1. When $g = 1$, the Redlich–Peterson equation becomes the Langmuir equation and when $g = 0$, it becomes Henry's law.

2.6.2.2. Sips model The sips isotherm at low adsorbate concentrations reduces to Freundlich isotherm, while at higher adsorbate concentrations it shows characteristic of the Langmuir isotherm [42]. The isotherm is represented by the equation:

$$q_e = \left(\frac{q_{ms} K_s C_e^{ms}}{1 + K_s C_e^{ms}} \right) \quad (13)$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e the equilibrium concentration of the adsorbate (mg/L),

q_{ms} the Sips maximum biosorption capacity (mg/g), K_s the Sips equilibrium constant (L/mg), and ms the Sips model exponent.

2.6.2.3. The Koble–Corrigan isotherm model Koble–Corrigan isotherm is a three parameter model, which is a combination of the Langmuir and Freundlich isotherm models and is mostly applied to heterogeneous biosorption [43]. The model is given by the equation

$$q_e = \frac{a C_e^n}{1 + b C_e^n} \quad (14)$$

where a , b and n are the Koble–Corrigan variables.

2.6.2.4. Regression analysis The two parameter isotherm constants were determined by linear regression analysis, while the three parameter model constants were estimated using iterative method by Levenberg–Marquardt algorithm in MATLAB (2010a) curve fitting tool box [44]. The equations were solved to find the values of kinetic parameters that minimize the objective function. The sum of the squares of differences (SSD) between experimental and theoretical data for specific growth rates, is given by the Eq. (16):

$$SSD = \sum_{i=1}^N (Y_a - Y_p)^2 \quad (15)$$

where, Y_a is the actual output, Y_p is the predicted output and N is the number of data points

2.7. Kinetic studies of Cr(VI) biosorption by free and immobilized *Sargassum sp* biomass

Kinetic models help in the better understanding of metal biosorption mechanism by the aid of which, we can accurately evaluate the performance of biosorbents for metal removal. In our study the kinetics has been modeled with two conventional models: (a) the pseudo-first order rate equation (the so-called Lagergren equation) [45], (b) the pseudo-second order rate equation [46]. Lagergren model considers that the rate of occupation of adsorption sites is proportional to the number of unoccupied sites, Eq. (14):

$$\frac{dq}{dt} = k_{1,ads} (q_e - q) \quad (16)$$

where q_e and q are the amounts of adsorbed metal ions on the biosorbent at equilibrium and at any time t , respectively (mg/g), and $k_{1,ads}$ is the Lagergren rate constant of the first-order biosorption. Integrating Eq. (16) between the limits, $t = 0$ to $t = t$ and $q = 0$ to $q = q_t$, the Eq. (17) is obtained:

$$\log(q_e - q) = \log q_e - \frac{k_{1,ads}}{2.303} t \quad (17)$$

Linear plots of $\log(q_e - q)$ vs. t indicate the applicability of this kinetic model. However, to adjust the Eq. (16) to the experimental data, the value of q_e (equilibrium sorption capacity) must be pre-estimated by extrapolating the experimental data $t = \infty$.

The pseudo-second-order kinetic model assumes that the rate of occupation of the adsorption sites are proportional to the square of the number of unoccupied sites [13], Eq. (18):

$$\frac{d}{dt} = k_{2,ads}(q_e - q)^2 \quad (18)$$

where $k_{2,ads}$ is the rate constant of second-order bio-sorption (g/mg.min). Integrating Eq. (18) for the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q_e$ to Eq. (19), which corresponds to the integrated rate law for a second-order reaction:

$$\frac{t}{q} = \frac{1}{k_{2,ads} \times q_e^2} + \frac{1}{q_e} t \quad (19)$$

The plot t/q vs. t should give a straight line if the second-order kinetics are applicable and q_e and $k_{2,ads}$ can be determined from the slope and intercept of the plot, respectively. It is important to notice that for the application of this model the experimental estimation of q_e is not necessary.

2.8. Desorption and regeneration of biosorbent

The desorption experiments were performed according to Rangabhashiyam and Selvaraju, [13]. The reusability of free and immobilized *Sargassum sp* biomass was evaluated by subjecting the biomass to successive biosorption-desorption process, which was repeated for four cycles. 0.1 M HCl solution was used as desorption agent. 0.3 g of immobilized beads (wet weight) and free biomass was placed into a 50 mL conical flask of 100 mg/L of Cr(VI) solution for a period of 24 h. The beads loaded with Cr(VI) were constantly stirred on a thermostat shaking incubator at 120 rpm for 3 h at 30°C with 50 mL of HCl solution. The residual metal concentration of the solution was then determined. The beads after desorption were repeatedly washed with deionized water for reuse.

2.9. Characterization of *Sargassum sp* biomass

Fourier transform infrared spectroscopy (FT-IR) spectra of *Sargassum sp* biomass (Free and immobilized) before and after Cr(VI) biosorption were collected in 400–4,500/cm using FT-IR spectrophotometer (PerkinElmer Spectrum Version 10.4.3).

3. Results and discussions

3.1. Effect of initial Cr(VI) concentration

The effect of initial Cr(VI) concentration on free and immobilized *Sargassum sp* dead biomass was studied. The results revealed that the biosorption capacity of both free and immobilized *Sargassum sp* increased with increasing initial Cr(VI) concentration (Fig. 1). But immobilized algal beads showed a higher biosorption capacity of Cr(VI) of 68.33 mg/g compared to the free biomass (43.33 mg/g) and further increase in metal concentration resulted in reduced uptake by the biomass in both free and immobilized forms. This increase in adsorptivity of Cr(VI) is associated with higher probability of collision between Cr(VI) ions and algal biomass, which provides an important driving force to overcome the mass transfer

resistance of metal ions between the aqueous and solid phases [11,46]. Whereas the percentage removal of Cr(VI) decreased up to 43.10% in free biomass and 53.6% in immobilized biomass (Data not shown). During the initial stage of biosorption, a large number of binding sites on the cell wall were available which could rapidly bind to the metal ions. In the later phase, as the metal binding sites get saturated, the adsorption rate becomes less effective [28]. Thus the present observations agree with the previous studies [28,47].

3.2. Effect of biomass dose on Cr(VI) sorption

The biosorption of Cr(VI) by free and immobilized *sargassum sp*, was studied by varying the biomass dosage in 50 ml of 100 mg/L Cr(VI) solution. The biomass dosage was varied from 0.1 to 0.5 g, while maintaining other parameters such as contact time, pH, agitation rate and temperature at 24 h, pH = 2, 150 RPM and 30°C, respectively. The percentage removal of Cr(VI) as a function of adsorbent dosage for both free and immobilized biomass was shown in Fig. 2. The results depicted that with the increase in biomass concentration of

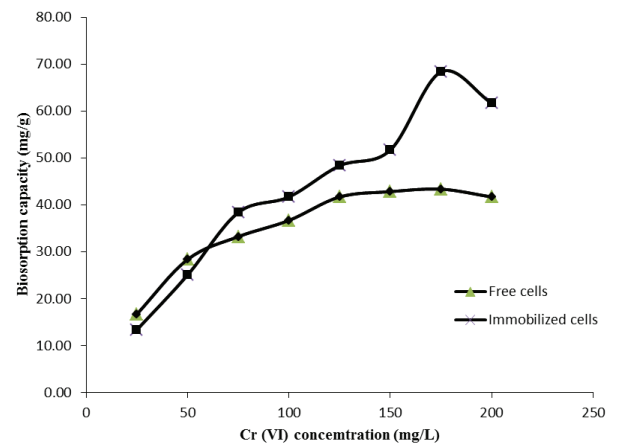


Fig. 1. Effect of initial Cr(VI) concentration on free and immobilized *Sargassum sp*.

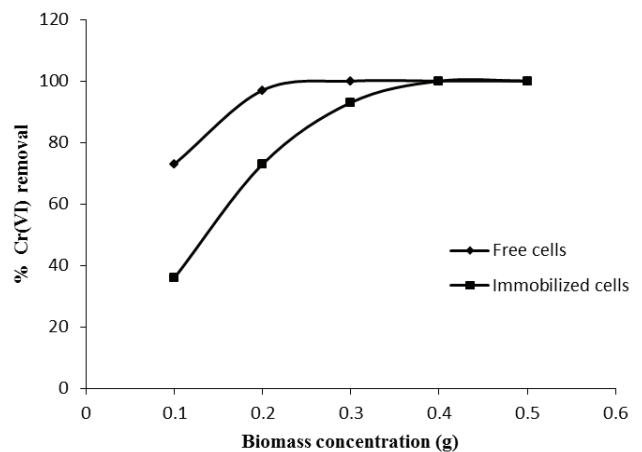


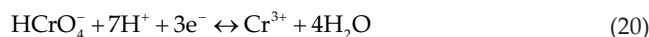
Fig. 2. Effect of biomass dose of free and immobilized *Sargassum sp* on Cr(VI) removal.

free and immobilized biomass, the percentage removal of Cr(VI) also increased, this may be due to the greater availability of binding sites for Cr(VI) [8]. It was observed that the free biomass showed a higher metal removal capacity at biomass concentration of 0.3 g, whereas the immobilized biomass attained similar metal removal capacity with biomass concentration of 0.4 g, this may be due to the external mass transfer imposed by alginate layer. Also, the ions compete for the availability of sites which causes a decrease in the specific removal capacity with the increase in adsorbent dosage. Similar observation was made by Marta et al. [9].

3.3. Effect of pH on Cr(VI) sorption

pH of aqueous solution is considered as an important environmental factor which not only helps in site dissociation, but also affects the solution chemistry of heavy metals such as complexation by organic and/or inorganic ligands, hydrolysis, precipitation, redox reactions. Apart from this, the pH strongly influences speciation and biosorption availability of heavy metals [49]. In the present study, the effect of pH on Cr(VI) removal was studied. The pH was varied from (2 to 8) by maintaining parameters such as Biomass concentration, contact time, pH, agitation rate and temperature at 0.1 g (dry cell weight), 24 h, pH = 2, 150 RPM and 30°C, respectively. Fig. 3 depicts the removal of chromium from free and immobilized *Sargassum sp* biomass. In both free and immobilized biomass, the Cr(VI) removal was increased by lowering the pH of the solution, nevertheless as the pH increased, the reduction in adsorption capacity of biomass was evident. The maximum Cr(VI) removal was observed at pH 2 for both free biomass (55%) and immobilized biomass (74%). The uptake of Cr(VI) by the biomass follows three steps: In the first step, the sorption of HCrO_4^- anions onto the biomass takes place, followed by reduction of Cr(VI) to Cr(III) and in the final step, the adsorption of Cr(III) onto biomass takes place. According to this mechanism, a lower pH favours Cr(VI) in two different ways: at lower pH the protonation of the components of the cell wall takes place, which induces positive charge on the surface and favors the adsorption of HCrO_4^- . On the other hand, the presence of

a larger number of protons in the solution favours the reduction reaction, as per the Eq. (20):



According to the equation above, maintaining an acidic condition in the solution, increases the reduction potential of $\text{HCrO}_4^-/\text{Cr}^{3+}$, thereby strengthening the oxidizing character of HCrO_4^- ions with respect to the biomass. When the pH of the solution increases, the reduction potential decreases, so Cr(VI) stays in its hexavalent form [9]. The results are appropriate according to Marta et al. [9] and Yeslić et al. [2]. These results suggest that the pH affects the solubility of metals and the ionization state of functional groups like carboxylate, phosphate and amino groups of the cell walls.

3.4. Effect of temperature on Cr(VI) sorption

Temperature is one of the important factors affecting the biosorption efficiency, as many of the mechanisms related to metal sorption are temperature dependent. With the view of finding the optimum temperature for maximum biosorption of Cr(VI), studies were carried out by varying the temperature from 25°C to 60°C, while maintaining other parameters such as Biomass concentration, contact time, pH and agitation rate at 0.1 g (dry cell weight), 24 h, 2 and 150 RPM, respectively. Dependence of Cr(VI) sorption on temperature was shown in Fig. 4. It was evident that in free biomass, maximum Cr(VI) removal capacity was observed at 40°C and in immobilized biomass, it was observed at 45°C. Furthermore as the temperature was increased, reduction in Cr(VI) removal occurred. This increase in sorption capacity indicates the endothermic nature of the process which is due to the enhanced magnitude of the reverse step in the mechanism as the temperature increases. With the increment in the temperature, the available active sites in the biosorbent increases. On the other hand, as the thickness of the algal cell wall decreases, the effect of resistance to the transference decreases which in turn leads to the enhancement in the sorption capacity [2].

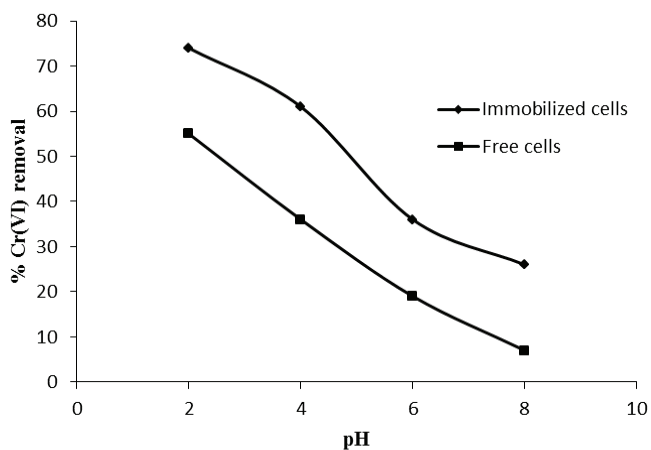


Fig. 3. Effect of pH of free and immobilized *Sargassum sp* on Cr(VI) removal.

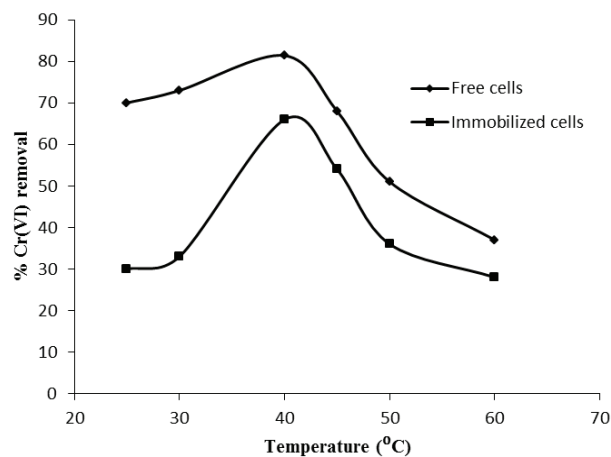


Fig. 4. Effect of temperature of free and immobilized *Sargassum sp* on Cr(VI) removal.

3.5. Adsorption isotherms

Various two parameter and three parameters models were used to obtain the equilibrium data for free and immobilized biomass. The experiments were performed by varying the concentration of Cr(VI) and with the fixed concentration of cell (0.1 g (dry cell weight)). The two parameter model was determined by linear regression, while the three parameter model was determined by non linear curve fitting analysis using Levenberg–Marquardt (LM) method, which is an approximation to Newton's method. The isotherm constants of different models and corresponding correlation coefficient values are shown in Table 1. It was observed that among the two parameter isotherms, Langmuir isotherm fits better with q_{\max} and b values of 41.67, 71.42 and 0.24, 0.02 for free and immobilized biomass respectively, with correlation coefficient of 0.97 and 0.99 for free and immobilized biomass respectively, indicating a better fit of the mono-layer Langmuir model for the biosorption of Cr(VI). The R_L values 0.04 and 0.25, which are less than unity, indicate that the sorption of Cr(VI) is favorable in both free and immobilized biomass. It was evident that the maximum sorption capacity of immobilized biomass was more as compared to the free biomass indicating that the entrapment of biomass in calcium

alginate increased the Cr(VI) sorption capacity of biomass. The Freundlich isotherm constants K_f and n are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity. The adsorption capacity K_f for Cr(VI) was higher for immobilized biomass as compared to the free biomass (Table 1), the coefficient n , indicates the affinity of the sorbent for the metal. In our study, the n value of free and immobilized biomass were 4.6 and 2.74, respectively which indicated cooperative adsorption. If n lies between one and ten, it indicates a favorable sorption process [39,48,49]. The Temkin isotherm constants were related to the heat of biosorption (kJ/mol), b_T , the equilibrium binding constant, A_T (L/mg) for free and immobilized biomass were calculated and shown in Table 1. The Free sorption energy (E) of the D-R isotherm model for free and immobilized biomass was found to be almost similar with the values of 0.3 and 0.13 KJ/mol, which indicated that physisorption had played a significant role in the adsorption process [51]. The maximum biosorption capacity q_m from the Elovich isotherm model for free and immobilized *Sargassum sp* was 7.19 and 22.72 (mg/g), respectively, while for Jovanovic model the equilibrium biosorption capacity for free and immobilized *Sargassum sp* was found to be 21.69 and 17.77 (mg/g).

Table 1
Isotherm constants for the adsorption of Cr(VI) by Free and immobilized *Sargassum sp*

Model	Parameters	Free cells	R^2	Immobilized cells	R^2
Langmuir	q_{\max} (mg/g)	41.67	0.96	71.42	0.99
	b (L/mg)	0.24		0.02	
	R_L	0.04		0.25	
Freundlich	n	4.63	0.87	2.74	0.94
	k_f	15.34		8.04	
Temkin	b (J/mol)	463.58	0.89	87.19	0.975
	A_T (L/g)	15.86		0.23	
Dubinin–Radushkevich	q_s (mg/g)	78.72	0.78	79.75	0.965
	K_{ad} (mol ² /KJ ²)	1.00 E–07		1.00 E–07	
	E (KJ/mol)	0.3		0.13	
Elovich	K_E (L/mg)	17.37	0.703	0.15	0.795
	q_m (mg/g)	7.19		22.72	
Javanovic	q_{mj} (mg/g)	21.69	0.538	17.77	0.837
	K_j (L/g)	–0.0,002		–0.0,005	
Redlich–Peterson	K_{RP} (L/g)	39.86	0.69	1.38	0.99
	a_{RP} (L/mg)	1.55		0.02	
	g	0.9		0.99	
Sips	q_{ms} (mg/g)	53.69	0.68	70.52	0.99
	k_s (L/mg)	0.52		0.02	
	m_s	0.36		0.99	
Koble–corrigan	a	27.83	0.68	1.42	0.99
	b	0.51		0.03	
	n	0.35		0.99	

Table 2
Kinetic model fitting for Cr(VI) by free and immobilized *Sargassum sp*

	$q_{e,exp}$ (mg/g)	$k_{1,ads}$ (g/mg.h)	Pseudo first order model		Pseudo second order model		
			$q_{e,cal}$ (mg/g)	R^2	$k_{2,ads}$ (g/mg.h)	$q_{e,cal}$ (mg/g)	R^2
Free cells	40.69	0.031	48.4	0.967	0.002	55.5	0.996
Immobilized cells	35	0.027	54.9	0.942	0.001	62.5	0.982

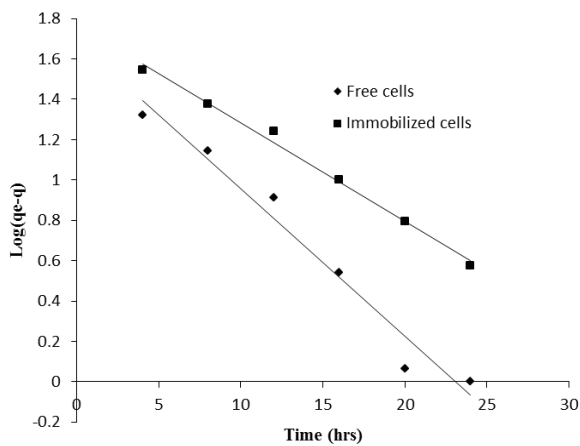


Fig. 5. Linearized plot of Pseudo first order kinetics for uptake of Cr(VI) by free and immobilized *Sargassum sp*.

The correlation coefficient of Jovanovic and Elovich isotherm model for both free and immobilized *Sargassum sp* was very low compared to other two parameter models.

The three parameter model showed better correlation coefficient compared to the two parameter model ($R^2 > 0.99$) for immobilized biomass. Whereas free biomass showed poor correlation coefficient with all the three parameter models. Redlich–Peterson showed that the best fit to the experimental data for immobilized biomass, in both free and immobilized *Sargassum sp* that the Redlich–Peterson variable g is nearly equal unity. So, the Redlich–Peterson isotherm behaves similar to the Langmuir isotherm, which implies that in both free and immobilized *Sargassum sp* the surface was homogenous for Cr(VI) biosorption. In sips isotherm model, the maximum biosorption capacity was found to be 53.69 and 70.52 mg/g (Table 2) for free and immobilized *Sargassum sp*, respectively. The Koble–corrigan model showed high correlation coefficient ($R^2 > 0.99$) for immobilized cell. The value of n was 0.35 and 0.99 for free and immobilized *Sargassum sp* suggesting that the biosorption of free and immobilized *Sargassum sp* was heterogeneous.

3.6. Kinetic studies

The linear plots of first order and second order kinetics for free and immobilized biomass of *Sargassum sp* is shown in Figs. 5 and 6, respectively. The rate constants for free and immobilized biomass along with the correlation coefficients are mentioned in Table 2. The Lagergren first-order kinetics failed to estimate q_e in both free as well as immobilized

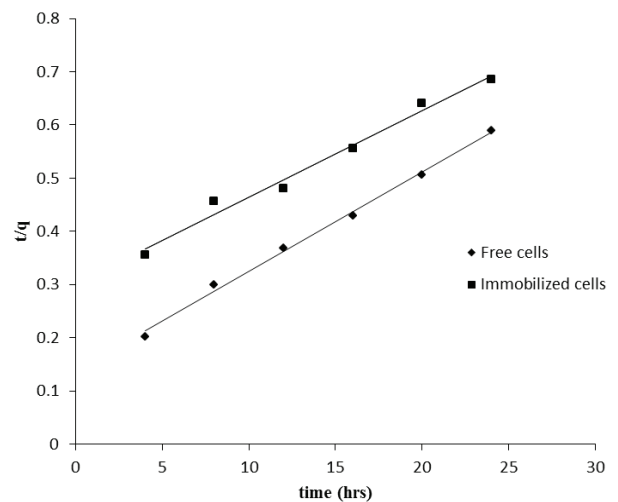


Fig. 6. Linearized plot of Pseudo second order kinetics for uptake of Cr(VI) by free and immobilized *Sargassum sp*.

biomass, from the Table 2. In pseudo-second-order kinetics model, the q_e values for both free and immobilized biomass agreed very well with the experimental ones and the correlation coefficient for free and immobilized *Sargassum sp* are 0.952 and 0.915, respectively. The studies suggest that the sorption of Cr(VI) ions follows the Pseudo second-order kinetics model, which relies on the assumption that biosorption may be the rate-limiting step. This study agrees with other studies which shows that Pseudo second-order kinetics model is more efficient for modeling kinetic profiles than the Pseudo first order kinetics model [52].

3.7. Regeneration studies

Most of the biosorption studies were focused on the biosorbent materials which were reusable and had low cost. Hence, an effective desorption technique must be considered in order to avoid secondary pollution, which recovered targeted metals and recycled biosorbent [52,53]. In present study, the reusability of free and immobilized *Sargassum sp* was carried out by performing biosorption–desorption cycles of Cr(VI) had repeated up to four times using the same preparations. The biosorption capacity of free *Sargassum sp* toward Cr(VI) removal was decreased in the order of 33, 30.23, 25.33 and 20.45 mg/g, while the biosorption capacity of immobilized *Sargassum sp* was decreased from 28.2, 24.69, 21.66 and 20.33 mg/g, respectively from 1 to 4 consecutive biosorption–desorption cycles. The decrease in the adsorption is due to

changes on the cell wall structure which occurred during repetition of the cycles and some of Cr(VI) ions are being held in the intrapores [12].

3.8. FTIR spectrum of *Sargassum* sp

The absorbance spectrum of Cr(VI) untreated and treated free and immobilized biomass are showed in Figs. 7(a)–(d), respectively. The broader band at a range of (3,334–3,434 cm^{-1}) was assigned to the stretching of hydrogen-bonded O–H, N–H of secondary amides and NH_3^+ . The band gave peak at the range of 1,740, 1,582 and 1,425 cm^{-1} were attributed to asymmetric and symmetric stretching vibration of C = O groups. Whereas, the band at 1,027.58 cm^{-1} was assigned to the stretching of C–O groups on the biomass surface. The Cr(VI) was treated with free and immobilized

biomass, whichn showed that shift in the band from 3,434.23 to 3,368.02 cm^{-1} in free biomass and 3,344.74 to 3,375.23 cm^{-1} in immobilized biomass, and the bands observed at 1,740.4, 1,582.3 cm^{-1} to 1,604.35, 1,211.53 cm^{-1} in free biomass, while in immobilized biomass the shift was observed from 1,698.19, 1,425.06 cm^{-1} to 1,590.57, 1,420.33 cm^{-1} , respectively. Also the peak at 1,027.58, 1,025.03 cm^{-1} in free and immobilized biomass was shifted to 1,025.03 and 1,020.69 cm^{-1} respectively. These results suggested that the amido-, hydroxyl-, C=O and C–O groups could have reacted with Cr(VI) intensively [55].

4. Conclusion

Biosorption through various biological materials such as bacteria, algae, yeast and fungi has been used due to their low cost, high adsorption capacity and availability in large

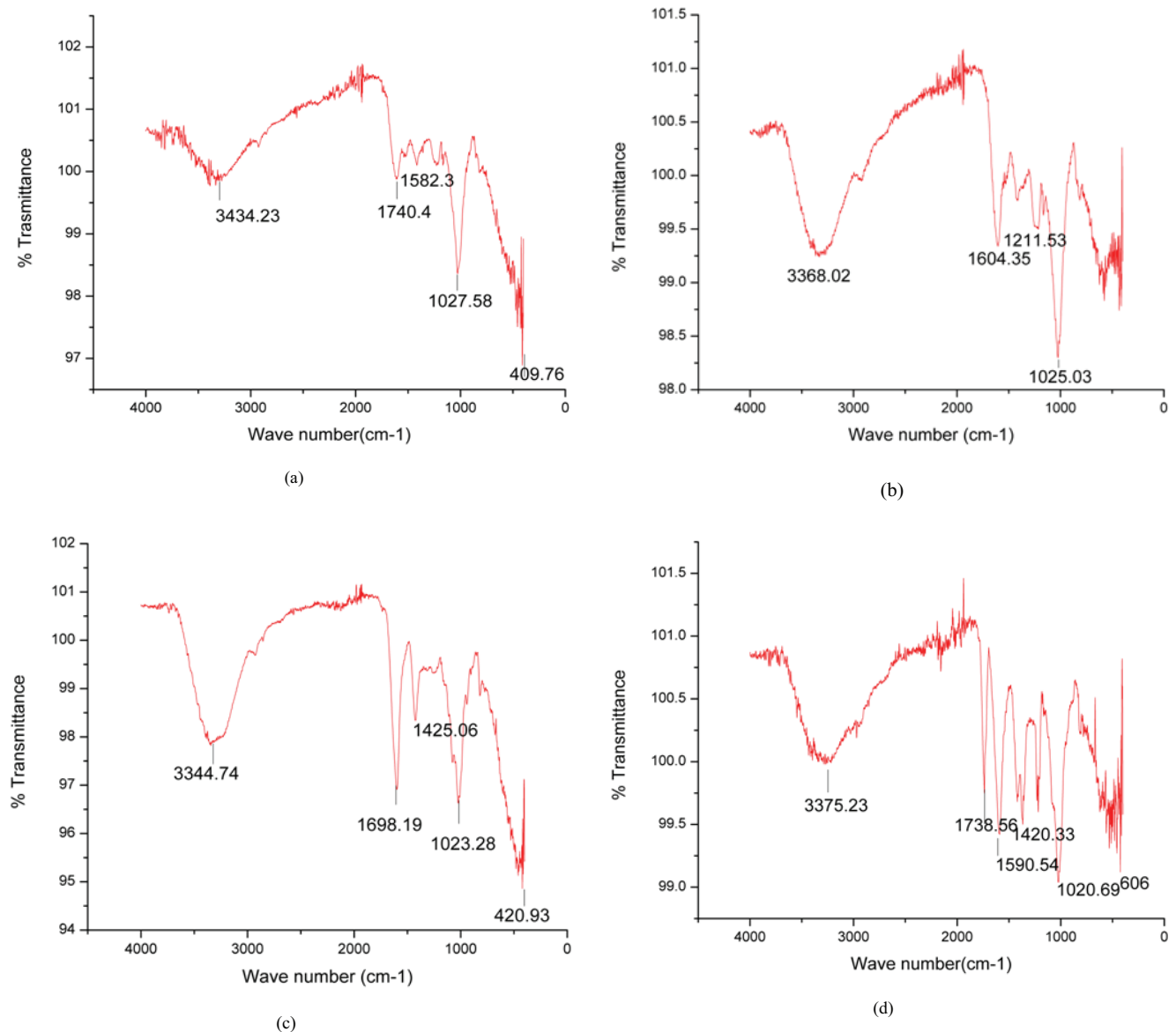


Fig. 7. FTIR spectrum: (a) unloaded Cr(VI) free biomass (b) loaded Cr(VI) free biomass, (c) unloaded Cr(VI) immobilized biomass, (d) loaded Cr(VI) immobilized biomass.

quantity. The present study is focused on the biosorption of Cr(VI) from algal biomass obtained from *Sargassum sp* in free and immobilized form. The process parameters are pH of the solution, biomass dosage and temperature affected biosorption capacity of both free and immobilized form of biomass. Various two and three parameter isotherm models were used to fit the equilibrium data. All three parameter models had showed better fit ($R^2 = 0.995$) for immobilized biomass compared to two parameter models. In two parameter models, Langmuir isotherm model had showed better fit with the correlation coefficient of 0.96 and 0.99 and with maximum adsorption capacity of 41.67 and 71.42 mg/g for free and immobilized biomass, respectively. Kinetics best fit with the pseudo second order model for both free and immobilized *Sargassum sp* biomass, respectively with the maximum adsorption capacity of 55.5 and 62.5 mg/g, respectively.

References

- A.M.F. Orozco, E.M. Contreras, N.E. Zaritzky, Modelling Cr(VI) removal by a combined carbon-activated sludge system, *J. Hazard. Mater.*, 150 (2008) 46–52.
- Y. González Bermúdez, I.L. Rodríguez Rico, E. Guibal, M. Calero de Hoces, M.Á. Martín-Lara, Biosorption of hexavalent chromium from aqueous solution by *Sargassum muticum* brown alga. Application of statistical design for process optimization, *Chem. Eng. J.*, 183 (2012) 68–76.
- L. Yang, J.P. Chen, Biosorption of hexavalent chromium onto raw and chemically modified *Sargassum sp.*, *Bioresour. Technol.*, 99 (2008) 297–307.
- B. Dhal, H.N. Thatoi, N.N. Das, B.D. Pandey, Chemical and microbial remediation of hexavalent chromium from contaminated soil and mining/metallurgical solid waste: a review, *J. Hazard. Mater.*, 250–251 (2013) 272–291.
- L. Khezami, R. Capart, Removal of chromium(VI) from aqueous solution by activated carbons: kinetic and equilibrium studies, *J. Hazard. Mater.*, 123 (2005) 223–231.
- K. Mohanty, M. Jha, B.C. Meikap, M.N. Biswas, Removal of chromium (VI) from dilute aqueous solutions by activated carbon developed from *Terminalia arjuna* nuts activated with zinc chloride, *Chem. Eng. Sci.*, 60 (2005) 3049–3059.
- “WHO, Guidelines for Drinking-Water Quality, 2nd edition,” WHO. Available online at: http://www.who.int/water_sanitation_health/dwq/gdwq2v1/en/. 2016
- A. Prabhu, Evaluation of process parameters for biosorption of chromium (VI) using full factorial design and response surface methodology, *Environ. Sci.*, 9 (2014) 263–273.
- M. López-García, P. Lodeiro, R. Herrero, M.E. Sastre de Vicente, Cr(VI) removal from synthetic and real wastewaters: The use of the invasive biomass *Sargassum muticum* in batch and column experiments, *J. Ind. Eng. Chem.*, 18 (2012) 1370–1376.
- M.G.A. Vieira, R.M. Oisiovi, M.L. Gimenes, M.G.C. Silva, Biosorption of chromium(VI) using a *Sargassum sp.* packed-bed column, *Bioresour. Technol.*, 99 (2008) 3094–3099.
- D.G.S.S. Ahluwalia, Removal of heavy metals by waste tea leaves from aqueous solution, *Eng. Life Sci.*, 5 (2005) 158–162.
- S. Rangabhashiyam, E. Suganya, N. Selvaraju, Packed bed column investigation on hexavalent chromium adsorption using activated carbon prepared from *Svietenia Mahogani* fruit shells, *Desal. Wat. Treat.*, 57 (2016) 13048–13055.
- S. Rangabhashiyam, N. Selvaraju, Evaluation of the biosorption potential of a novel *Caryota urens* inflorescence waste biomass for the removal of hexavalent chromium from aqueous solutions, *J. Taiwan Inst. Chem. Eng.*, 47 (2015) 59–70.
- S. Rangabhashiyam, N. Selvaraju, Adsorptive remediation of hexavalent chromium from synthetic wastewater by a natural and ZnCl₂ activated *Sterculia guttata* shell, *J. Mol. Liq.*, 207 (2015) 39–49.
- S. Rangabhashiyam, E. Suganya, N. Selvaraju, L.A. Varghese, Significance of exploiting non-living biomaterials for the biosorption of wastewater pollutants, *World J. Microbiol. Biotechnol.*, 30 (2014) 1669–1689.
- D. Kratochvil, P. Pimentel, B. Volesky, Removal of trivalent and hexavalent chromium by seaweed biosorbent, *Environ. Sci. Technol.*, 32 (1998) 2693–2698.
- R. Elangovan, L. Philip, K. Chandraraj, Biosorption of chromium species by aquatic weeds: kinetics and mechanism studies, *J. Hazard. Mater.*, 152 (2008) 100–112.
- D.C. Lee, C.J. Park, J.E. Yang, Y.H. Jeong, H.I. Rhee, Screening of hexavalent chromium biosorbent from marine algae, *Appl. Microbiol. Biotechnol.*, 54 (2000) 597–600.
- J.P. Chen, L. Yang, Chemical modification of *Sargassum sp.* for prevention of organic leaching and enhancement of uptake during metal biosorption, *Ind. Eng. Chem. Res.*, 44 (2005) 9931–9942.
- J.L. Gardea-Torresdey, K.J. Tiemann, V. Armendariz, L. Bess-Oberto, R.R. Chianelli, J. Rios, J.G. Parsons, G. Gamez, Characterization of Cr(VI) binding and reduction to Cr(III) by the agricultural byproducts of *Avena monida* (Oat) biomass, *J. Hazard. Mater.*, 80 (2000) 175–188.
- S.K. Prabhakaran, K. Vijayaraghavan, R. Balasubramanian, Removal of Cr(VI) ions by spent tea and coffee dusts: reduction to Cr(III) and biosorption, *Ind. Eng. Chem. Res.*, 48 (2009) 2113–2117.
- S.P. Dubey, K. Gopal, Adsorption of chromium(VI) on low cost adsorbents derived from agricultural waste material: a comparative study, *J. Hazard. Mater.*, 145 (2007) 465–470.
- T.A. Davis, B. Volesky, R.H.S.F. Vieira, *Sargassum* seaweed as biosorbent for heavy metals, *Water Res.*, 34 (2000) 4270–4278.
- M. Tsezos, Adsorption by microbial biomass as a process for removal of ions from process or waste solutions, *Res. Gate*, 18 (1986) 201–218.
- S.C. Wilkinson, K.H. Goulding, P.K. Robinson, Mercury removal by immobilized algae in batch culture systems, *J. Appl. Phycol.*, 2 (1990) 223–230.
- A.C.A. da Costa, S.G.F. Leite, Metals biosorption by sodium alginate immobilized *Chlorella* homosphaera cells, *Biotechnol. Lett.*, 13 (1991) 559–562.
- M.Z.-C. Hu, M. Reeves, Biosorption of uranium by *Pseudomonas aeruginosa* strain CSU immobilized in a novel matrix, *Biotechnol. Prog.*, 13 (1997) 60–70.
- S.K. Mehta, J.P. Gaur, Removal of Ni and Cu from single and binary metal solutions by free and immobilized *Chlorella vulgaris*, *Eur. J. Protistol.*, 37 (2001) 261–271.
- E. Valdman, S.G.F. Leite, Biosorption of Cd, Zn and Cu by *Sargassum sp.* waste biomass, *Bioprocess Eng.*, 22 (2000) 171–173.
- M.C. Ncibi, Applicability of some statistical tools to predict optimum adsorption isotherm after linear and non-linear regression analysis, *J. Hazard. Mater.*, 153 (2008) 207–212.
- S. Rangabhashiyam, N. Anu, N. Giri, N. Selvaraju, Relevance of isotherm models in biosorption of pollutants by agricultural byproducts, *J. Environ. Chem. Eng.*, 2 (2014) 398–414.
- M. Prasad, H. Xu, S. Saxena, Multi-component sorption of Pb(II), Cu(II) and Zn(II) onto low-cost mineral adsorbent, *J. Hazard. Mater.*, 154 (2008) 221–229.
- F. Renault, N. Morin-Crini, F. Gimbert, P.-M. Badot, G. Crini, Cationized starch-based material as a new ion-exchanger adsorbent for the removal of C.I. Acid Blue 25 from aqueous solutions, *Bioresour. Technol.*, 99 (2008) 7573–7586.
- I.D. Mall, V.C. Srivastava, G.V.A. Kumar, I.M. Mishra, Characterization and utilization of mesoporous fertilizer plant waste carbon for adsorptive removal of dyes from aqueous solution, *Colloids Surf. Physicochem. Eng. Asp.*, 278 (2006) 175–187.
- A.A. Nunes, A.S. Franca, L.S. Oliveira, Activated carbons from waste biomass: an alternative use for biodiesel production solid residues, *Bioresour. Technol.*, 100 (2009) 1786–1792.
- M.E. Argun, S. Dursun, C. Ozdemir, M. Karatas, Heavy metal adsorption by modified oak sawdust: thermodynamics and kinetics, *J. Hazard. Mater.*, 141 (2007) 77–85.

- [37] M.M. Dubinin, Modern state of the theory of volume filling of micropore adsorbents during adsorption of gases and steams on carbon adsorbents, *Zh Fiz Khim*, 39 (1965) 1305–1317.
- [38] J.P. Hobson, Physical adsorption isotherms extending from ultrahigh vacuum to vapor pressure, *J. Phys. Chem.*, 73 (1969) 2720–2727.
- [39] S.Y. Elovich, O.G. Larinov, Theory of adsorption from solutions of non electrolytes on solid (I) equation adsorption from solutions and the analysis of its simplest form, (II) verification of the equation of adsorption isotherm from solutions, *Res. Gate*, 2 (1962) 209–216.
- [40] S. Rangabhashiyam, E. Nakkeeran, N. Anu, N. Selvaraju, Biosorption potential of a novel powder, prepared from *Ficus auriculata* leaves, for sequestration of hexavalent chromium from aqueous solutions, *Res. Chem. Intermed.*, 41 (2014) 8405–8424.
- [41] O. Redlich, D.L. Peterson, A useful adsorption isotherm, *J. Phys. Chem.*, 63 (1959) 1024.
- [42] R. Sips, On the structure of a catalyst surface, *J. Chem. Phys.*, 16 (1948) 490–495.
- [43] R.A. Koble, T.E. Corrigan, Adsorption isotherms for pure hydrocarbons, *Ind. Eng. Chem.*, 44 (1952) 383–387.
- [44] Y. Yasin, F.B.H. Ahmad, M. Ghaffari-Moghaddam, M. Khajeh, Application of a hybrid artificial neural network–genetic algorithm approach to optimize the lead ions removal from aqueous solutions using intercalated tartrate-Mg–Al layered double hydroxides, *Environ. Nanotechnol. Monit. Manage.*, 1–2 (2014) 2–7.
- [45] F. Zan, S. Huo, B. Xi, X. Zhao, Biosorption of Cd^{2+} and Cu^{2+} on immobilized *Saccharomyces cerevisiae*, *Front. Environ. Sci. Eng.*, 6 (2011) 51–58.
- [46] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process Biochem.*, 34 (1999) 451–465.
- [47] G. Dönmez, Z. Aksu, Removal of chromium(VI) from saline wastewaters by *Dunaliella* species, *Process Biochem.*, 38 (2002) 751–762.
- [48] K.F. Tan, K.H. Chu, B.S. Gupta, M.A. Hashim, Studies on fixed-bed biosorption and elution of copper using polyvinyl alcohol-immobilized seaweed biomass, *J. Environ. Sci. Health Part A*, 37 (2002) 1621–1632.
- [49] A. Esposito, F. Pagnanelli, F. Vegliò, pH-related equilibria models for biosorption in single metal systems, *Chem. Eng. Sci.*, 57 (2002) 307–313.
- [50] N. Tamilselvan, K. Saurav, K. Kannabiran, Biosorption of Cr(VI), Cr(III), Pb (II) and Cd (II) from aqueous solutions by *Sargassum wightii* and *Caulerpa racemosa* algal biomass, *J. Ocean Univ. China*, 11 (2011) 52–58.
- [51] R. Han, P. Han, Z. Cai, Z. Zhao, M. Tang, Kinetics and isotherms of Neutral Red adsorption on peanut husk, *J. Environ. Sci. China*, 20 (2008) 1035–1041.
- [52] E. Valdman, L. Erijman, F.L.P. Pessoa, S.G.F. Leite, Continuous biosorption of Cu and Zn by immobilized waste biomass *Sargassum* sp., *Process Biochem.*, 36 (2001) 869–873.
- [53] K.H. Chu, M.A. Hashim, S.M. Phang, V.B. Samuel, Biosorption of cadmium by algal biomass: adsorption and desorption characteristics, *Water Sci. Technol.*, 35 (1997) 115–122.
- [54] S. Pradhan, L.C. Rai, Copper removal by immobilized *Microcystis aeruginosa* in continuous flow columns at different bed heights: study of the adsorption/desorption cycle, *World J. Microbiol. Biotechnol.*, 17 (2001) 829–832.
- [55] Y. Wang, Y. Li, F.J. Zhao, Biosorption of chromium(VI) from aqueous solutions by *Sargassum thunbergii* Kuntze, *Biotechnol. Biotechnol. Equip.*, 28 (2014) 259–265.