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Biosorption of hexavalent chromium from aqueous solution using chemically modified *Spirulina platensis* algal biomass: an ecofriendly approach

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ABSTRACT

Biosorption is the process of removing heavy metals and other toxic chemicals from environment using live or dead biomass. In this study, algal biomass of *Spirulina platensis* was chemically modified by acid/ECH treatment that altered the functional groups present on the cell membrane of biomass. By applying Langmuir isotherm model to the biosorption data, it was suggested that the efficiency of biosorption process of metal uptake by acid treatment of *S. platensis* was increased by more than 3-fold and maximum biosorption occurred at pH 3. The order of biosorption of Cr^{6+} was found to be $HCl > HNO_3 > H_2SO_4 >$ raw algal biomass > ECH treated algal biomass by 15 h of contact time with q_{max} of 5 mg g^{-1}. Fourier transform infrared analysis of modified algal biomass shows that lipids, carbohydrates, and proteins present in the membrane were probably involved in the biosorption process and acid-treated modified algal biomass could be used in the bioremediation of industrial effluents.

Keywords: Biosorption; *Spirulina platensis;* Chemical modification; Langmuir; FTIR

1. Introduction

Heavy metals discharged from various industrial processes act as an important route for water pollution, which is a major threat to environment as metal accumulation occurs in food chain. Cr^{6+} is one of the heavy metals responsible for contamination of water bodies [1] and considered as one of the 16 toxic pollutants due to its carcinogenic and teratogenic effect on human health [2]. Although Cr exists in several valence states (−2 to +6), the less toxic Cr^{3+} and more toxic Cr^{6+} are the major pollutants found in the environment.

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According to WHO drinking water guidelines, the allowed limit for Cr^{6+} is 0.05 mg L^{-1} and total chromium (Cr^{3+}, Cr^{6+}, and others) is 2 mg L^{-1} [3]. Therefore, it is essential and necessary to treat the industrial wastes before discharging into environment [4]. Removal of heavy metals by using conventional methods like ion exchange, chemical oxidation, and chemical precipitation are expensive. Further, the methods appear to be cumbersome and cause hazardous effects to the environment. Hence, biosorption acts as an alternative approach for effective removal of heavy metals and could be used in the treatment of industrial wastes. Biosorption occurs in two stages: first, being rapid occurs by the direct interaction between biomass and heavy metal(s), and second, being the transport of heavy metal(s) into cytoplasm of dead biomass. Biosorption has several advantages, but important one being its low cost; high efficient removal of metal ions at low concentration of biosorbent and minimization of chemical/biological sludge. Further, the biosorption process requires no additional nutrients and if required, there is every possibility of metal recovery from biomass [5–7]. In biosorption process, both live and dead cell mass of micro-organisms/fungi and plants are used as adsorbing agents [8,9]. Use of non-viable biomass is preferred as toxic metals in solution may have an effect on the metabolic activity of live cells, and may in turn affect the adsorbent process [10–12]. Many groups reported that live bacteria, such as *Pseudomonas*, *Bacillus, Desulfovibrio, Desulfomicrobium,* and *Pyrobaculum islandicum* etc., could be used as adsorbents for heavy metal removal from aqueous solution [13]. Studies suggested that the use of algal and fungal biomass were preferred in the efficient removal of heavy metals by biosorption [14–16] and among them, particularly seaweeds are found to be highly efficient as they produce exopolysaccharides. Exopolysaccharides act as surface-active agents in heavy metal removal process and the adsorption being non-metabolic, energy independent and the interaction occurs between metal cations and negative charge present on the functional groups of exopolysaccharides.

A recent study from our laboratory and others suggested that live *Spirulina platensis* could be used as a biosorbent in the laboratory-scale treatment of the industrial wastewater for the effective removal of Cr^{6+} [17,18]. Microalgae *S. platensis* could be abundantly produced for several commercial uses and can be considered as a source of adsorbent for heavy metal removal [19,20]. Chemical modification of a bioadsorbent is an ecofriendlier approach, to increase the efficiency of adsorption process by overcoming some of the problems associated with live biomass. Studies from various groups have shown that the pretreated algal biomass enhance and strengthens the biosorption process and its applications [2]. A recent study [21] shows that dry biomass of *S. platensis* rehydrated for 48 h, effectively removes copper by shortening the adsorption time, and increase in its percentage of metal removal. Pretreatment like heat treatment [22] denatures some biomolecules or NaOH treatment [23] increases the negative charge on the cell surface or acid treatment opens up the sites for adsorption or Ca^{2+} treatment [24] increases the ion exchange capacity or ECH treatment [25] cross-links and hardens the cell surface have been successfully used for biosorption processes of many metal ions. However, studies on the use of chemically modified *S. platensis* algal biomass for Cr^{6+} and other heavy metals removal from aqueous solution found to be limited.

Hence, this study was undertaken to enhance Cr^{6+} biosorption capacity of *S. platensis* biomass by various chemical treatment. First algal biomass was pretreated with either ECH to cross-link the groups present on the surface or pretreated with various acids ($HCl/HNO_3/H_2SO_4$) that open up and change the surface characteristics that may influence metal absorption process. Second, the different parameters like optimization of biosorption process, contact time required, and pH on uptake of Cr^{6+} by modified algal biomass were investigated. Finally, the Langmuir isotherm model was applied to fit the biosorption data obtained to measure the efficiency of the adsorption process.

2. Materials and methods

2.1. Chemicals

Sodium bicarbonate, sodium nitrate, sodium chloride, calcium chloride, boric acid, copper sulfate, dipotassium hydrogen phosphate, EDTA, sodium molybdate, zinc sulfate, ferrous sulfate, manganous chloride, potassium chromate, potassium dichromate, 1,5-diphenylcarbazide (DPC), ethyl alcohol, sulfuric acid, hydrochloric acid, nitric acid, magnesium sulfate, dimethyl sulfoxide, and sodium hydroxide were procured from Himedia (Mumbai, India) and Epichlorohydrin was purchased from SRL. Pvt. Ltd (Mumbai, India).

2.2. Zarrouk's medium (Z medium)

Z medium is composed of macronutrients and micronutrients, and prepared as per the protocol described earlier [17]. Working Z medium was prepared by mixing 999 mL of macronutrients and 1 mL of micronutrients under sterile conditions.

2.3. Culture of S. platensis and collection of algal biomass

S. platensis was cultured and maintained in our laboratory using Z medium in several Erlenmeyer flasks provided with light intensity of 2,000 lux at 28°C in growth chambers for 15 d [17]. After sufficient growth of *S. platensis*, the algal biomass was filtered using Whatmann No. 1 filter paper, oven dried at 70°C, and referred as *Spirulina* algal biomass (SAB). The yield of SAB was found to be 2 g L^{-1} of cultures and was further used for chemical treatment.

2.4. Chemical modification of algal biomass

2.4.1. Treatment with acids

SAB (2 g) was mixed with or without 1 M HNO_3 or 1 M H_2SO_4 or 1 M HCl in 250 mL Erlenmeyer flasks and incubated overnight at ambient temperature in a shaker. Acid-treated algal biomass samples were filtered using Whatmann No. 1 filter paper, washed, oven dried at 70°C for 2 h, and later used in biosorption studies. SAB treated with water and processed as above was used as control and referred as raw algal biomass (RAB).

2.4.2. Treatment with epichlorohydrin

RAB of *S. platensis* (2 g) was suspended in 100 mL of dimethylsulfoxide (DMSO) in 250 mL Erlenmeyer flasks and incubated overnight at ambient temperature in a shaker. Epichlorohydrin (50 mL) was added and incubated further at room temperature for 2 h in a shaker. To the ECH-treated mixture, 25 mL of 0.1 N NaOH was added and agitation was continued further for 6 h at ambient temperature. The treated algal biomass was centrifuged at 2,000 rpm for 15 min in REMI-R8C centrifuge at room temperature and pellet was oven dried at 70°C for 2 h and used in biosorption studies.

2.5. Biosorption of Cr^{6+} from aqueous solution using chemically modified-algal biomass

RAB (1 g) or chemically modified-*S. platensis* biomass (1 g) (acid treated or ECH treated) was added to Erlenmeyer flasks containing 100 mL of 50 ppm $K_2Cr_2O_7$ (Cr^{6+}) solution. Flasks were incubated at room temperature with continuous agitation in a shaker for different time intervals (0–72 h). The samples (2 mL) were withdrawn into 15 mL Falcon tubes centrifuged at 5,000 × g for 10 min. Supernatant was used for the estimation of Cr^{6+} by DPC method.

2.6. Biosorption of Cr^{6+} by chemically modified-Spirulina biomass at different pH

For determination of optimum pH required for the maximum biosorption of Cr^{6+}, the different acid-treated *S. platensis* or ECH-treated samples were incubated with aqueous solution of Cr^{6+} (50 ppm) with different pHs (pH 1, 3, and 5) and the flasks were agitated in a shaker at room temperature. At 15 h, the samples (2 mL) from each flask were withdrawn into 15 mL Falcon tubes and the samples were centrifuged at 5,000 × g for 10 min. Amount of Cr^{6+} present in the supernatant was determined using DPC method.

2.7. Estimation of the amount of Cr^{6+} by DPC method

Amount of Cr^{6+} present in the samples were determined by DPC method as described earlier [17]. In brief, supernatant of RAB or modified Cr^{6+}-treated *S. platensis* algal samples (0.5 mL) obtained at different time intervals were taken in 20 mL tubes. To each tube, 2.5 mL of DPC reagent was added and the volume in each tube was made up to 8 mL by adding distilled water. The Cr^{6+} concentrations present in different samples were determined by the absorption of pink-colored complex formed between DPC and Cr^{6+} against standard using spectrophotometer at 540 nm. Efficiency of biosorption of different treated algal biomass was calculated by applying Langmuir adsorption model.

2.8. Fourier transform infrared analysis

Fourier transform infrared (FTIR) analysis was carried out for each of the modified algal sample to analyze the different functional groups modified by ECH/acid treatment. For the analysis, 30 mg of each of the different acid-treated samples or RAB sample was encapsulated in KBr, and the translucent disks were prepared and used. The spectral peaks correspond to probable functional modified groups of the samples were shown in Table 2 [26].

2.9. Biosorption isotherm and the metal uptake using Langmuir adsorption model

The Langmuir adsorption isotherm [27,28] is given by the following equation:

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

where q_{max} (mg g^{-1}) is the maximum adsorption capacity, b (L mg^{-1}) is the Langmuir constant, and q is the adsorption isotherm (amount of Cr^{6+} adsorbed) at equilibrium which also represents the metal uptake calculated from the difference in metal concentration in the aqueous solution before and after sorption using the following equation:

$$q = \frac{V(C_i - C_e)}{W} \quad (2)$$

where V is the volume of aqueous solution (L), C_i and C_e are the initial and equilibrium concentrations of the aqueous solution (mg L^{-1}), respectively, and W is the dry weight of the *S. platensis* algal biomass (g), and q was calculated using the data and as described earlier for other adsorbent system [29]. Normally, the

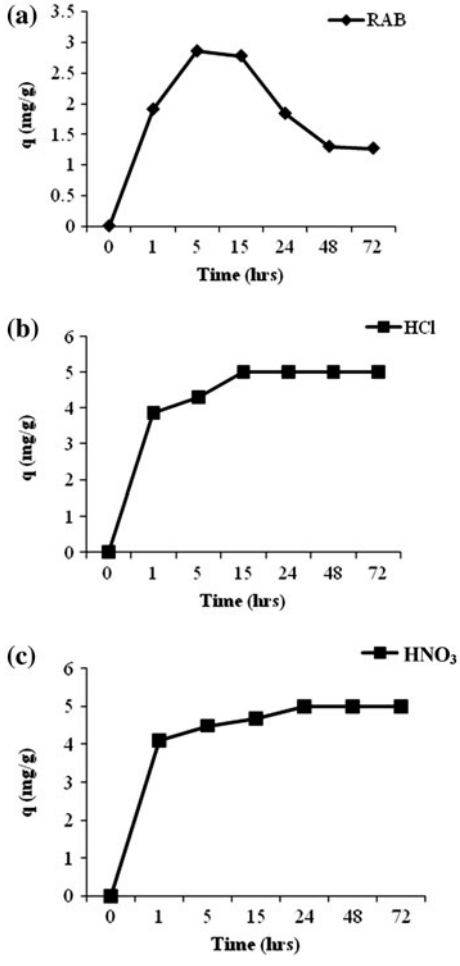

Fig. 1. Biosorption of Cr^{6+} by *S. platensis*. (a) RAB alone, treated with (b) 1 M HCl, (c) 1 M HNO_3, (d) 1 M H_2SO_4, and (e) ECH. Cr^{6+} (50 ppm) was incubated with or without modified *S. platensis* biomass for different time intervals. Cr^{6+} as $K_2Cr_2O_7$ was estimated by DPC method.

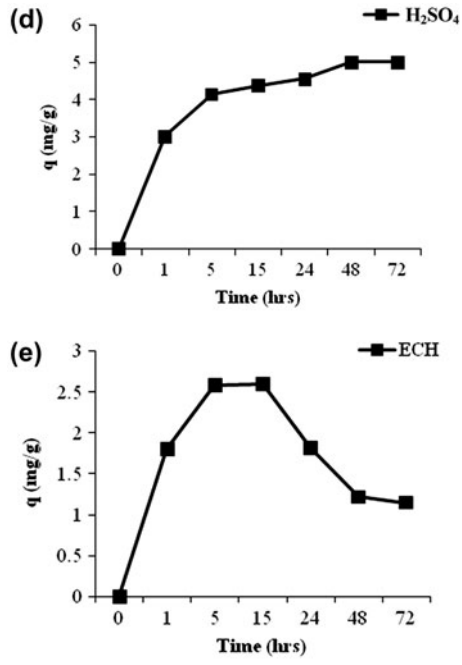

Fig. 1. (*Continued*)

Langmuir model is applied in modified algal systems to study the relationship between the sorbed concentration of Cr^{6+} and concentration of metal present at the equilibrium. The graphs were plotted with q (mg g^{-1}) vs. time (h) and q (mg g^{-1}) vs. pH of different of acid-treated/ECH-treated *S. platensis* samples and the results were interpreted using Table 2 [26].

3. Results

3.1. Biosorption of Cr^{6+} by S. platensis

In our study, the Langmuir model was applied to get the information on the uptake capabilities of modified biosorbent over control and equilibrium attainment during biosorption process [30,31]. It was shown that with RAB (control), initially the uptake of Cr^{6+} was linear, increases with contact time up to 5 h with raising equilibrium, plateaus by 7 h, probably because of the fixed number of adsorption sites with the q_{max} of 3 mg g^{-1} (Fig. 1(a)). However, with the increase in the contact time, the q value was decreased showing desorption and reversible attainment of new low equilibrium constant.

3.2. Chemical treatment of S. platensis algal biomass and its effect on biosorption of Cr^{6+}

Chemical modification of powdered *S. platensis* algal biomass was done using HCl or HNO_3 or H_2SO_4

to check which acid is more efficient in altering the surface chemistry of biomass and increase the efficiency of metal uptake. Results of our study show that the uptake of Cr^{6+} by all the acid-treated (HCl/HNO_3/H_2SO_4) algal biomass show almost the same q at 48 and 72 h, respectively. In HCl-treated algal sample, initially there was a rapid uptake of Cr^{6+} within 1 h, later continued with the sorption process, and reached maximum value by 15 h (Fig. 1(b)). However, in HNO_3- and H_2SO_4-treated samples, q was reached at 36 and 48 h, respectively (Fig. 1(c) and (d)). Maximum of q shown by modified or unmodified algal biomass may be due to saturation of adsorption sites.

Table 1 summarizes the Langmuir constants obtained for control, different acid-treated and ECH-treated algal biomass. Comparing the q values of treated algal biomass, at 15 h, the HCl-treated sample shows the maximum of q, which suggested that HCl-treated sample reached the equilibrium q_{max} of 5 mg g^{-1} biomass (Fig. 2). Our study shows that ECH has little or no effect on the sorption kinetics of Cr^{6+} compared to control. Although biosorption of Cr^{6+} by ECH-treated increases with increase in contact time, reaches equilibrium by 15 h, followed by desorption at 24 and 48 h (Fig. 1(e)). During biosorption, a rapid equilibrium is established between adsorbed and unadsorbed metal ion for algal biomass in solution. At a certain point of contact time, the adsorbed reaction reached equilibrium and the RAB show maximum of absorption efficiency ($q = 3$ mg g^{-1}). However, as the contact time increased, the equilibrium was shifted towards left and true equilibrium was reached by desorption, both in control and in ECH treated *S. platensis* (Fig. 1(a) and (e)).

Table 1
Absorption efficiency capacity obtained by Langmuir isotherm model for different biomasses of *S. platensis*

Sl. No.	Biomass	q_{max} (mg g^{-1})
1	RAB	3.0
2	HCl-treated biomass	5.0
3	HNO_3-treated biomass	5.0
4	H_2SO_4-treated biomass	5.0
5	ECH-treated biomass	3.0

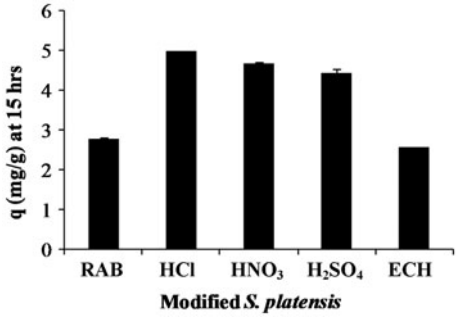

Fig. 2. Biosorption of Cr^{6+} at 15 h by different chemically modified *S. platensis*. Cr^{6+} (50 ppm) was incubated with or without modified *S. platensis* biomass for 15 h. Cr^{6+} as $K_2Cr_2O_7$ was estimated by DPC method.

3.3. Effect of pH on biosorption of Cr^{6+} by modified algal S. platensis biomass

In biosorption process, the pH affects metal ion solubility and also the net charge present on the biosorbent since proton can be added or released [32]. The pH of solution greatly influences the metal uptake or release. In our study, biosorption experiments were carried out at pH 1, 3, and 5 using buffer. The study shows that the absorption efficiency of *S. platensis* algal biomass and pH are interdependent and the efficiency varies significantly with varying pH (Fig. 3). Also, chemical modification of *S. platensis* shows a remarkable difference in the absorption efficiency with respect to varying pHs. At pH 3.0, all the acid-treated algal biomass show max biosorption efficiency for Cr^{6+} and the order of biosorption was found to be H_2SO_4 > HCl > HNO_3-treated algal samples. However, ECH-treated *S. platensis* shows least biosorption at pH 3.0. RAB of *S. platensis* also show maximum absorption efficiency at pH 5 almost equivalent to HCl/H_2SO_4-treated *S. platensis* algal biomass. Biosorption efficiency of RAB for Cr^{6+} was significantly increased (59%) at pH 5.0 compared to RAB used at pH 7

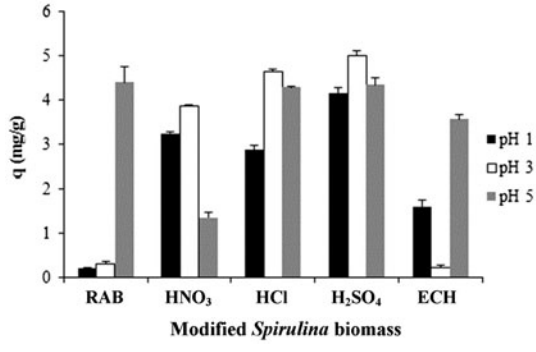

Fig. 3. Biosorption of Cr^{6+} at pH 1, 3, and 5 using chemically modified *S. platensis*. Cr^{6+} solution was incubated with different modified *S. platensis* algal biomass for 15 h at different pH (pH 1, 3, 5) at room temperature. Cr^{6+} as $K_2Cr_2O_7$ was estimated by DPC method.

(Fig. 3). However, there was every possibility of desorption as the biosorption is occurring at narrow range of pH that needs to be investigated. The pH of solution was also found to have no influence on the q value and max of 5.0 mg g^{-1} was achieved at pH 5 by H_2SO_4-treated and other acid-treated samples (Fig. 1), which suggested that there are finite number of binding sites for Cr^{6+}. Similar increased biosorption of Cr^{6+} by untreated yeast biomass at pH 4.2 was observed [33]. Increased biosorption of Pb^{2+} and Zn^{2+} was also observed at pH 4.0 and 8.0, respectively, using *S. platensis* [34].

3.4. FTIR analysis

Analysis of FTIR spectra of control and modified algal biomass samples show that there were strong absorption peaks at 1,070, 1,650, 2,325, 2,932, and 3,350 cm^{-1} (Fig. 4). The probable altered groups in the algal cell mass responsible for the peaks are presented in Table 2 [26].

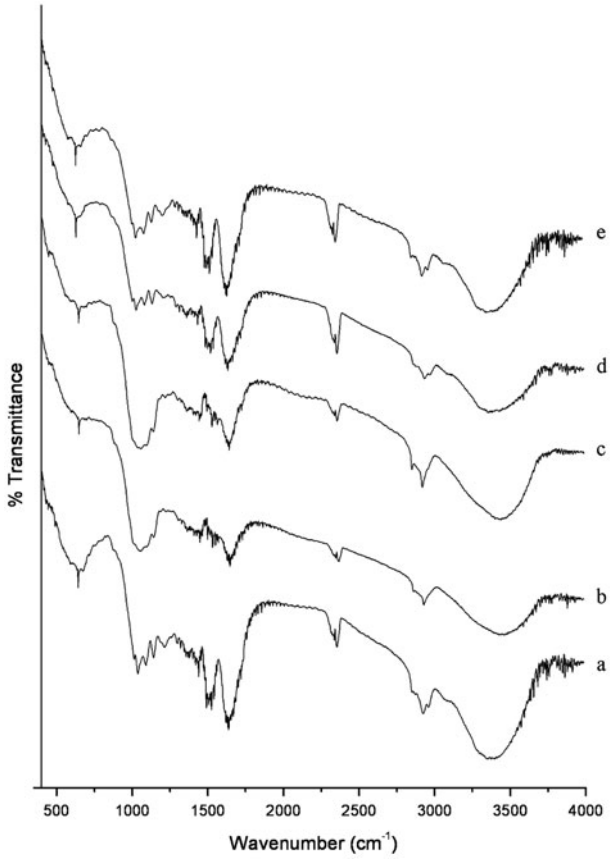

Fig. 4. FTIR analysis (a) raw biomass, (b) HCl, (c) HNO_3, (d) H_2SO_4, and (e) ECH. Different acid/ECH-treated *S. platensis* algal biomass (30 mg) was encapsulated in KBr and translucent disks were used for FTIR analysis.

FTIR analysis shows that there was no difference in the spectra of control and ECH-treated algal samples except for the marginal increase at 1,070 and 1,650 cm^{-1} (Fig. 4(a) and (e)). Our results also show that there was not much of a difference in the biosorption of Cr^{6+}. However, marginal decrease in the biosorption at pH 5 by ECH-treated samples compared to control confirms the modification of algal biomass at 1,070 and 1,850 cm^{-1}. Absorption peak at 2,932 cm^{-1} was observed in all the control and treated algal cell biomass samples that suggested the presence of CH_2 asymmetric stretching and vibrations. A similar peak was observed at 2,929 cm^{-1} for RAB/ECH-treated samples of *Cystoseira indica* [29]. Absorption peak between 3,180 and 3,680 cm^{-1} treated samples were assigned to P–H group [35]. The peaks obtained between 1,400 and 1,750 cm^{-1}(i.e. 1,732 cm^{-1}) attributed by C=O stretching, chelate stretching, and COOH groups. Similar peaks were also observed in control and modified *C. indica* samples [29,36]. However, analysis of FTIR spectra of all the acid-treated algal samples suggested that there was a significant increase in the absorption at 1,070 cm^{-1} (Fig. 4 (b)–(d)). Absorption peaks at 2,325, 2,932, and 3,350 cm^{-1} show varied results. At 2,325 cm^{-1}, HCl and HNO_3 acid-treated algal samples show decreased absorption, while H_2SO_4-treated samples show marginal increase. Acid HCl and H_2SO_4-treated samples show marginal decrease in the absorption peak of 2,932 cm^{-1}, while HNO_3-treated samples show marginal increase. At 3,350 cm^{-1}, there was a significant decrease in the absorption peak by HCl/H_2SO_4-treated algal samples, and HNO_3 acid-treated sample shows no effect.

4. Discussion

Toxic heavy metals like Cr^{6+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, etc. that were discharged as wastes into industrial effluent is a major cause of water pollution [37,38]. Currently, adsorption process using activated charcoal is a recognized method for the efficient removal of heavy metals, while the high cost limit its use. Earlier study from our laboratory shows that live *S. platensis* acts as a biosorbent for the efficient removal of Cr^{6+} and Pb^{2+}. However, almost five days were required for the maximum biosorption of Cr^{6+} from aqueous solution. Further, as we used live *S. platensis*, the biosorption process demands the continuous supply of media and also large surface area for the treatment of industrial wastes. The method was found to be cumbersome, requires more time, and not economical. Table 3 summarizes the q_{max} of different algal samples and raw

Table 2
FTIR spectra obtained for raw and chemically modified *S. platensis*

Sl. No.	Peak range (cm^{-1})	Modified group	Typical band
1	1,000–1,200	Nucleic acids, carbohydrate	P=O stretching, V(C–O–C)
2	1,300–1,500	Protein, lipid	$\sigma_{as}(CH_2)$ and $\sigma_s(CH_3)$ bending, (CH_2) bending of methyl
3	1,500–1,700	Protein amide II, protein amide I	σ(N–H) bending, V(C–N) stretching, V(C=O) stretching
4	2,000–3,000	Lipid–carbohydrate	$Vas(CH_2)$ and $Vs(CH_2)$ stretching
5	3,000–3,600	Water, protein	V(O–H) stretching, V(N–H) stretching

Table 3
Biosorption of Cr^{6+} by different untreated biomasses obtained by different groups

Sl. No.	Biomass	q_{max} (mmol g^{-1})	Reference
1	*Chlorella vulgaris*	0.534–1.575	[43]
2	*Sargassum* sp. (brown algae)	1.3–1.3257	[43]
3	*Scenedesmus obliquus* (green algae)	1.131	[43]
4	RAB *S. platensis*	0.465	[17]

biomass of used *S. platensis* for biosorption Cr^{6+}. The q_{max} value obtained for *S. platensis* suggested that they are less efficient compared to *Sargassum*, brown algal biomass. Hence, we made an attempt to modify the dried *S. platensis* algal biomass by treatment with acid or ECH and used for Cr^{6+} removal. In all the acid-treated algal biomass with the increase in the contact time, the metal ion uptake also increases initially and, but to attainment of equilibrium, biosorption becomes almost stable at the later time points. Treatment of algal biomass with acid protonate the side chains of negatively charged aspartate or glutamate or carboxyl group of C-terminal amino acid residues present in proteins reducing the net negative charges present on the surface. At 1 h of contact time, nitric acid-treated algal biomass show 2-fold increase in biosorption, while HCl show little less but H_2SO_4-treated samples show 1.5-fold increase in biosorption compared to control. At later time points, all the acid-treated *S. platensis* algal samples show slow increase in biosorption and equilibrium was achieved for HNO_3-treated sample by 24 h and almost stabilized q was obtained at later time points of 48 and 72 h for all the acid-treated algal biomass.

The order of biosorption at 15 h time point was found to be $HCl > HNO_3 > H_2SO_4$-treated *S. platensis* (Fig. 2). Results of our study suggest that Cr^{6+} biosorption occur in two stages, an initial rapid uptake due to surface adsorption and subsequent slow uptake due to membrane transport of metal ion into cytoplasm portion of dead cells, and the similar mechanism was also observed in other algal samples [39–41]. At alkaline pH, epichlorohydrin treatment facilitates chemical cross-linking of hydroxyl groups of polysaccharide chains present in the membrane. DMSO treatment exposes the metal binding groups before cross-linking. The results also show that there was 98% less q values in ECH-treated algal biomass compared to acid-treated sample, which suggested that the cross-linked *S. platensis* was not suitable for Cr^{6+} removal. In contrast, epichlorohydrin-treated *C. indica*, biomass show increased biosorption of Cr^{6+} and different adsorption kinetics [29,42]. This difference in the kinetics of biosorption of Cr^{6+} by *C. indica* algal biomass may be due to different membrane compounds with altered surface properties. Different freeze-dried algal biomass were found to absorb cadmium, lead, nickel, and zinc from aqueous solution and varied q_{max} between 0.02 and 0.85 mmol g^{-1} was achieved for Pb^{2+} by *Dunaliella bioculata* and *Scytonema hofmani*, respectively [43]. *C. indica*, a brown seaweed with marine habitat; probably show impressive biosorption capacity, high tolerance for metal ion(s) compared to *S. platensis*, a blue green microalgae with fresh water habitat [29]. Algal or plant biomass mainly composed of exopolysaccharides and proteins with functional carboxyl groups that exhibit acidic properties. Adsorption of metal ion depends on its solubility, the concentration of counter ions, and the degree of ionization of adsorbent as well as adsorbate [33]. Hence, metal sorption by the biomass depends on pKa [44–47], and at pH below 2, high proton concentration minimizes metal sorption, while at and above pH 6, precipitation of metal ions are favored [48]. Water polluted with Cr^{6+} is anionic in nature as it occurs mainly as complex CrO_4^{2-} and $HCrO_4^-$ ions. The acidic pH of buffers used for biosorption reduces the negative charge present on the algal biomass, which acquires positive charge that greatly influences the uptake of Cr^{6+} ions. Therefore, biosorption experiments were carried out at pH 1, 3, and 5 to optimize the conditions required for biosorption. The experiments carried out on the removal of heavy metals (Pb^{2+} and Zn^{2+}) revealed that

the maximum biosorption of Pb^{2+} occurs (82%) at pH 4, and that of Zn^{2+} (90%) was at pH 8. Similar increased percentage removal of Cr^{6+} by untreated yeast biomass occurs at pH 4.2 [33,34]. Normally, surface of the biomass contains membranes characterized with proteins, lipids, carbohydrates, and other organic molecules bear many functional groups (carboxyl, amide, hydroxyl, methyl groups, etc.). Functional groups with varied states of ionization have different degree of affinity and accessibility to metal ion(s). Functionalization or treatment of algal biomass by acids or ECH, alter the charges present on the functional group(s) and change the surface properties. Based on the kinetics and FTIR spectral analysis of control and functionalized samples, it is believed that the modification of functional groups of nucleic acids, carbohydrates, proteins, and lipids occurs. The modifications like P=O stretching, C–O–C groups, CH_2, and CH_3 bending to a larger extent are probably involved in biosorption. Groups of protein amide I and protein amide II (N–H bending, C–N, and C=O stretching) of acid-treated samples to some extent responsible for efficient uptake of Cr^{6+} and stability of biosorption. Earlier study from our laboratory showed that live *S. platensis* could be used for biosorption of Cr^{6+}, and q value was calculated to be 1.35 mg $g^{-1} \pm 0.086$ SD on the third day and 1.66 mg $g^{-1} \pm 0.18$ SD on the seventh day of incubation. However, in the present study, HCl acid-treated *S. platensis* biomass shows increased biosorption in 15 h with $q > 5$ mg g^{-1}. The uptake in acid-treated samples, particularly in HCl-treated algal biomass was found to be increased by more than 3-fold with reduced contact time.

In this study, growth-independent non-living biomass was used as a biosorbent, which does not require expensive nutrients for growth. Adsorption or biosorption is not governed by physiological constraint of live algae, while the algal biomass behaved as an anion exchanger. The biosorption process is rapid, requires few hours, with wide range of pH [49]. However, biosorption process using modified algal biomass suffers from early saturation, and that needs to be addressed. The studies are in progress for metal recovery, regeneration of biosorbent, and immobilization of modified *S. platensis* for industrial applications.

5. Conclusion

Contamination of water bodies by the discharge of industrial wastes without proper treatment is the major threat to environment. Our main concern is heavy metal contamination, particularly by Cr^{6+}. This led us to carry out biosorption experiments on the removal of Cr^{6+} from aqueous solution. Earlier study from our laboratory suggested that the *S. platensis* could be used as a biosorbent in the industrial wastewater treatment. However, to reduce the time, and to increase the efficiency of Cr^{6+} uptakes and further to make the process more cost effective, *S. platensis* algal biomass was subjected to chemical treatment. Dried algal biomass was treated with acid HCl/HNO_3/H_2SO_4 or ECH to modify the groups present on the surface. The results of our study show that all the different acid-treated samples efficiently remove Cr^{6+}- and HCl-treated sample that requires less contact time. Further, HCl is less hazardous compared with other acids. The order of efficiency of biosorption of Cr^{6+} of acid-treated *S. platensis* samples was found to be $HCl > HNO_3 > H_2SO_4$. The studies are in progress to immobilize the HCl-treated *S. platensis* algal biomass for the industrial applications. Identification, characterization, and purification of the biomolecules/proteins involved in biosorption of Cr^{6+} from *S. platensis* would be an additional objective of our future work.

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