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Biosorption of chromium(VI), nickel(II) and copper(II) ions from aqueous solutions using *Pithophora* algae

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Abstract
The biosorption of heavy metals is considered to be one of the best alternatives for the treatment of wastewater. The metal binding capacity of algae and acid-treated algae is investigated to find out the removal characteristics of Cr(VI), Ni(II) and Cu(II) ions from single metal solutions. Batch experiments are conducted and the study is extended to investigate the effect of pH, amount of adsorbent and adsorbate concentration on the extent of biosorption. The results indicate that the adsorption capacity of algae depends strongly on pH. The maximum adsorption of Cr(VI), Ni(II) and Cu(II) occurs at pH values of 2, 7 and 4.3, respectively. The adsorption process follows first-order kinetic equation. The data obtained are correlated with Freundlich and Langmuir adsorption isotherms.

Keywords: *Biosorption*, Pithophora, *heavy metals, isotherms, batch studies*

Introduction

The presence of heavy metals in water has been of great concern because of their toxicity. Some metal ions get concentrated, absorbed in the tissues of organisms causing adverse effects. Chemical precipitation, adsorption, ion exchange, etc. are some of the conventional methods used to remove heavy metals. However, high cost prevents their use by

the industry. The use of biological materials including living and non-living microorganisms to remove and possibly recover toxic metals from industrial wastewater has gained importance because of low cost and good performance [1–4]. In the process of removal of dissolved metals by biosorption, the mechanism involves several different pathways such as binding of metal cations on to cell surfaces or within the cells or with extra-cellular polymers, thus making biosorption effective in further enhancing the removal of heavy metals [5]. Biological systems such as seaweed [6], algae [7,8], fungi [9,10], bacteria [11], moss peat [12], bark [13], lignin [14], peanut hulls [15], various other non-living biomass, and plant materials [16,17] have been studied for metal binding. Among the biosorbents, an alga is used in the present study for the removal of Cr(VI), Ni(II) and Cu(II).

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems. Classical adsorption models (Langmuir and Freundlich) are used to describe the equilibrium between adsorbed metal ions on the algal cell (q_{eq}) and metal ions in solution (C_{eq}) at a constant temperature. The most widely used isotherm for modeling equilibrium is the Langmuir isotherm which is valid for monolayer sorption onto a surface with a finite number of identical sites which are homogeneously distributed over the sorbent surface. The Freundlich expression is an empirical one based on sorption on a heterogeneous surface, suggesting that binding sites are not equivalent and/or independent. Both models are developed for a single-layer adsorption. However, the Freundlich model physically provides a more realistic description of adsorption by organic matter because it accounts for different binding sites. But, in most cases, both equations fit the data set reasonably well for the experimental data over moderate ranges of concentration.

The aim of the present work is to study the biosorption of metal ions, Cr(VI), Ni(II) and Cu(II) from a single aqueous metal ion solution. As the alga *Pithophora* is a waste scrapped from the bottom of fresh water prawn ponds and is thrown out so as to clean the ponds, it is available in plenty. The adsorption characteristics of algae have been described by making use of classical adsorption models, Langmuir and Freundlich isotherms. The results indicate that this waste alga has a great potential to adsorb heavy metals from aqueous solutions at relatively low cost.

Experimental

Biomass

Alga (*Pithophora*) is collected from the bottom of the fresh water prawn pond in Nellore district, AP, India. It is washed thoroughly to remove sand and other dirt particles by deionised water followed by distilled water several times and dried in the hot air oven for 1 h at 70°C. Ten grams of the adsorbent is treated with 100 mL of 1 N HCl for half an hour and is rinsed with required volume of 1 N NaOH to neutralise the residual acid. It is again washed, and dried at 70°C for 1.5 h. The algae in natural and acid-treated forms are used as adsorbents.

Preparation of the synthetic samples

Stock solutions of Cr(VI), Ni(II) and Cu(II) are prepared in distilled water separately by taking 2.829 g of potassium dichromate, 6.7302 g of nickel ammonium sulphate and 3.929 g of copper sulphate, respectively. All the working solutions of varying concentrations are obtained by diluting the stock solutions with distilled water. The metal ions are analysed

using a flame atomic absorption spectrophotometer equipped with hollow cathode lamp (HCL) and acetylene burner (model 2380, Perkin Elmer, USA). The pH measurements are made using the digital pH meter, Systronics, model 1584, Naroda, India.

Batch adsorption studies

Adsorption studies are carried out by batch process to obtain rate and equilibrium data. By varying initial concentrations (50–200 mg L^{-1}) of Cr(VI), Ni(II) and Cu(II) with 0.1 g of algae taken constant with different time intervals namely, 10, 20, 30, 40, 50 and 60 min for each metal. The suspensions are shaken at room temperature, filtered, diluted and analysed for residual metal ions concentration. To optimise the adsorbent concentration for the removal of Cr(VI), Ni(II) and Cu(II) from solution, adsorption studies are carried out with different adsorbent doses. Samples of adsorbent ranging from 0.05 to 0.25 g are placed in 125 mL capacity Erlenmeyer Flasks. One hundred millilitres of the metal solution of 100 mg L^{-1} concentrations is added. The mixture is agitated intermittently in a rotatory shaker at 80 rpm for 60 min [Cr(VI)], 50 min [Ni(II)] and 60 min [Cu(II)] respectively. The solution is filtered, diluted and final concentration of the metal ions is determined.

The effect of pH on the adsorption of Cr(VI), Ni(II) and Cu(II) is studied by carrying out the experiment at pH values ranging from 1 to 7. The pH of the solution is adjusted to a desired pH value by adding 0.1 N HCl and 0.1 N NaOH before the addition of algae. After shaking the flasks for the required time, the solutions are filtered and analysed for residual concentrations of Cr(VI), Ni(II) and Cu(II) ions by Atomic Absorption Spectrophotometer. Adsorption of the metal ions on the walls of the glassware is negligible and is found by running blank experiments. The values reported in this article are the average of three replicate measurements.

The amount of metal ions absorbed per unit mass of adsorbent (q_e) is obtained on the basis of mass balance equation,

$$q_e = \frac{C_i - C_e}{m} * V \qquad (1)$$

where C_i and C_e are initial and equilibrium concentrations of metal ions, m is mass of algae (adsorbent) and V is the volume of solution in litres.

Fourier transform-infra red spectroscopy (FT-IR)

FT-IR spectroscopy is used to detect vibration frequency changes in the algal sorbents. The spectra collected are within the range 4000–450 cm^{-1} using a KBr window.

EDXRF studies

X-ray fluorescence spectrometer is the instrument that determines the presence of an element both qualitatively and quantitatively. It can be used to measure the energy of elements from Na to Pu in the periodic table with concentrations ranging from a few ppm to nearly 100%. The X-ray source used is usually 1–100 keV and the detector used in EDXRF must be designed to produce electrical pulses that vary with the energy of the incident X-ray. The elemental identification can be confirmed by the presence of source lines K_{α}, K_{β}, L_{α} and L_{β} for the heavy metals. EDXRF (ED 2000 model) is used for the identification of metal ions on the adsorbent.

Table I. Porosity values of untreated algae and acid-treated algae.

Biosorbent	Pore volume (cc)	Density (g cc^{-1})	Porosity (%)
Algae	0.0866	5.77	52.60
Acid-treated algae	0.1582	6.321	64.47

Porosity

Porosity is defined as the fraction of apparent volume V of the adsorbent that is attributed to the pores detected.

$$\acute{\varepsilon} = \frac{V_p}{V} \tag{2}$$

where $\acute{\varepsilon}$ is the porosity, V_p the pore volume and V the apparent volume.

   Pore volume, V_p, is the sum of volumes of all pores in 1 g of biosorbent where only internal volume inside the biosorbent particles is counted. Thus, porosity is the ratio of the total pore volume, V_p, to the apparent volume, V of the adsorbent. Porosity of the algae both in natural and acid-treated form is measured using Pycnomatic ATC, and the values are represented in Table I.

Column studies

Column studies are carried out by 1 g of the biosorbent being packed in a glass column of 5 cm in length and 1.3 cm in diameter. On either side of the column glass wool is plugged. The biosorbents are thoroughly washed with double distilled water in order to condition and clean it. Then the metal solution is passed through the column at a flow rate of 1 mL min^{-1}. The concentration of metal ion in the eluent collected at regular intervals of time is analysed using AAS.

   The metal solutions of 100 mg L^{-1} are used to investigate the column adsorption characteristics. The retention of each metal ion is examined under the optimum conditions. The flow rates of the solution are adjusted to get 1 mL min^{-1}. Samples collected at column outflow are diluted with distilled water to bring concentration within linear range of instrument. Check samples are used periodically throughout sample analysis to ensure quality control. Breakthrough curves are obtained. The concentration of the adsorbate in the effluent increases sharply and finally reaches the influent concentration. These curves followed the typical S-shaped for column operation with favourable adsorption. This indicates that the column has a high binding capacity. When the effluent coming out of the column reaches a saturation point, the regeneration of the adsorption bed to recover adsorbed materials becomes essential.

Regeneration

After column studies reach saturation point, desorption and regeneration of the adsorption bed to recover the metals becomes very important. The economic success of any adsorption process in treatment of wastewater depends on the feasibility of regenerating the adsorbent, which facilitates to use the biosorbent more than once and to recover the metal ions. Although several solvents, like mineral acids, bases and salt solutions are effective in desorbing and recovering the ions from the adsorption bed, but 0.1 M HCl is found to be

effective, non-damaging and non-polluting eluent for the desorption of metal ions from untreated and acid-treated algae. The regenerated column is used in the second cycle for the adsorption of aqueous solutions of metals. It is observed that the adsorption capacity of the regenerated column is declined after repeated adsorption–desorption recycles.

Results and discussion

Pithophora belongs to the family of filamentous green algae. Under magnification *Pithophora* is composed of irregularly branched filaments usually with numerous swollen spore-like reproductive cells known akinetes. It may range in colour from lime green to a dark greenish brown. Typical algal cell walls are comprised of a fibrillar skeleton and an emorphous embedding matrix, the most common fibrillar skeleton being cellulose material. The presence of cell wall is of greatest importance to the biosorption mechanism. Biosorption in algae has mainly attributed to the cell wall, which provides an array of ligands with several key functional groups capable of binding the majority of heavy metal ions. The difference in metal uptake capacities of the different types of algae may be related to compositional differences among the cell walls as well as binding mechanisms involved for different heavy metals.

FT-IR spectroscopy

Green algae, containing fatty acids, cellulose, and pyrenoids with cyatoplasmic imaginations, possess a high metal binding capacity. This is due to the presence of carboxylic, carbonyl, and amino groups in algal cell wall polysaccharides, which can act as binding sites for metal ions. The characteristic pattern of FT-IR spectra of untreated and treated algae *Pithophora* are shown in Figures 1 and 2. The absorption bands around $3340–3300\,cm^{-1}$ are indicative of hydrogen bonded –OH groups. These bands are absent in the treated algae; however, the bands at $3409–3348\,cm^{-1}$ in metal loaded spectra (Figures 1b, c and d and 2b, c and d) represent –OH and –NH groups. The peaks observed near $2925\,cm^{-1}$ can be assigned to –CH stretching. Cell proteins are typically indicated by amide bands. A strong asymmetrical stretch of carboxylate ion at around 1640 and $1629\,cm^{-1}$ indicate –NH deformation i.e. the presence of amides is confirmed. The bands around $1460–1428\,cm^{-1}$ are indicative of –OH deformation and strong band around $1163–1112\,cm^{-1}$ is due to C–O stretching of the carboxyl group. Shifts in the intensity in the metal loaded algae in the absorption frequencies indicate that these groups in the biomass are responsible for biosorption. Decrease in the intensity of bands is seen in the acid-treated form of the metal loaded algae. Shifts of the functional groups could correspond to the complexation and coordination of these groups with metal ions [18]. Decrease in the intensity of bands and decrease in the intensity of the peaks in the acid-treated form of the metal loaded algae indicate that the role of these functional groups increased in the adsorption of metal ions in the acid-treated biomass in the binding of metal ions.

EDXRF spectra

Elemental analysis of algae before and after biosorption is studied from the spectra of EDXRF and is shown in Figures 3 and 4. From the spectral data the presence of chromium is at 5.4 (K_{α}) and 5.95 keV (K_{β}), nickel at 7.47 (K_{α}) and 8.26 keV (K_{β}), and copper at 8.04 (K_{α}) and 8.91 keV (K_{β}), respectively. The appearance of sharp peaks in the pretreated forms indicates that the concentrations of metal ions are more, which shows that adsorption
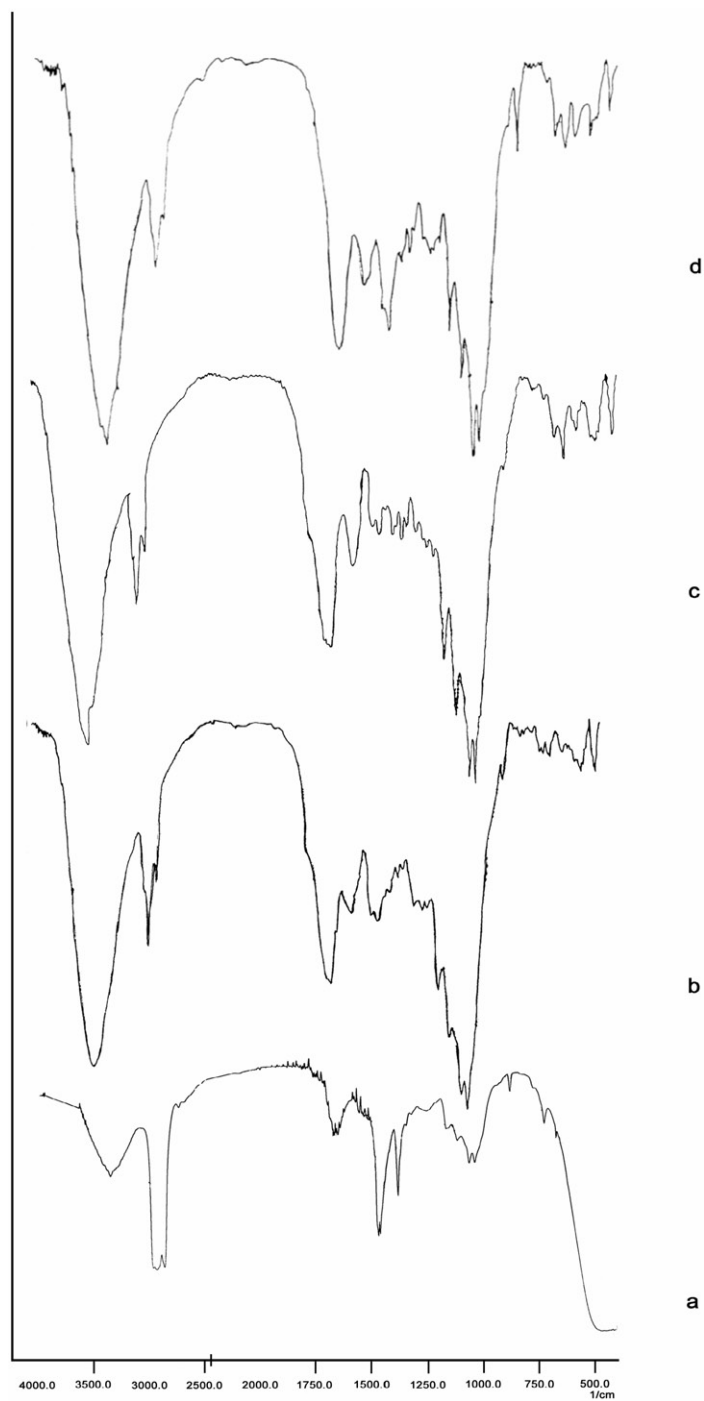
Figure 1. FT-IR spectra of untreated algae: (a) untreated, (b) chromium loaded, (c) nickel loaded and (d) copper loaded.
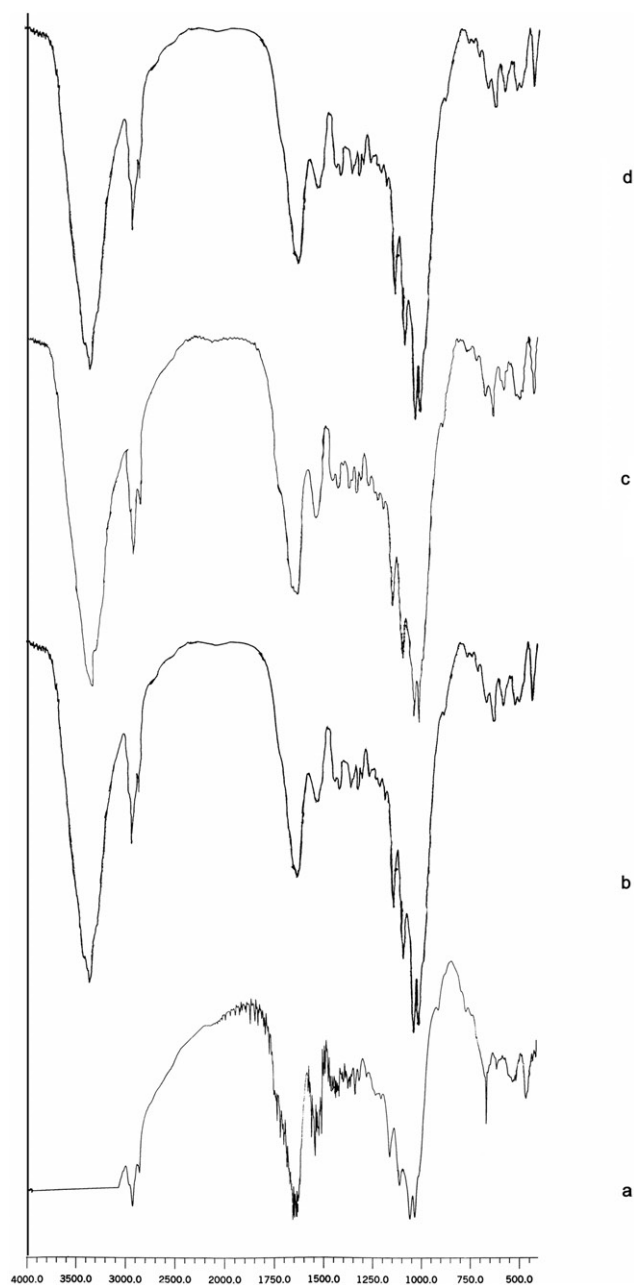
Figure 2. FT-IR spectra of acid-treated algae: (a) acid treated, (b) chromium loaded, (c) nickel loaded and (d) copper loaded.

by both the pretreated forms is greater than the crude form. The presence of iron in algae is identified only from the EDXRF spectra. The accumulation of iron in algae is from the nutrients supplied to the artificial ponds for feeding the fish and prawns [19]. The presence of iron in algae influences the removal of Cr(VI) from wastewater; permeable barriers
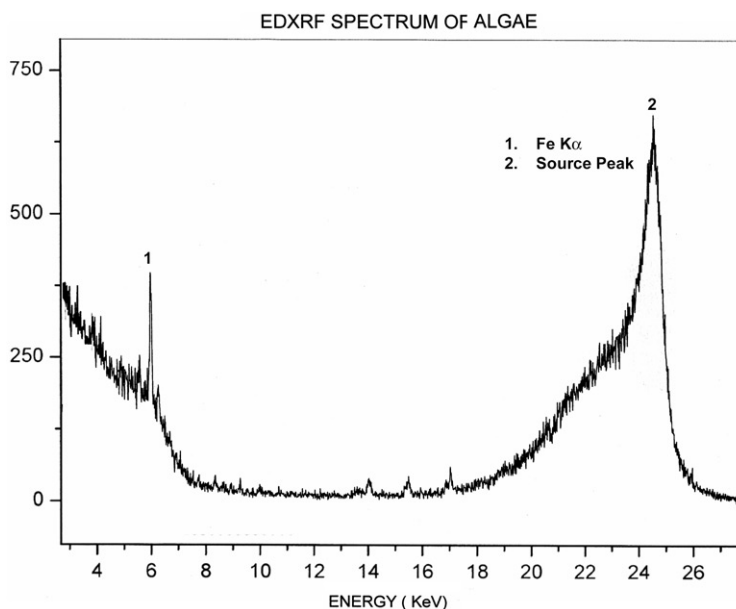
Figure 3. EDXRF spectrum of algae.

containing zerovalent iron can also reduce chromium concentrations to non-detectable levels [20–22] and this may also be another reason for the algae to adsorb chromium more than any other metal.

Porosity

It is understood from the data in Table I that the internal pores of algae have a very small volume, which may be surrounded by void particles; nevertheless, they contribute to much of the adsorption of metal ions. It is a well-known fact that the pore structure of plant and animal tissues which are of vital importance are formed fulfilling stringent conditions determined by natural processes of cell division, self organization, etc. whose processes are yet to be understood clearly.

The pretreated algae showed higher percent porosity, which means that higher pore volume as well as a higher number of pores is available for adsorption of metal ions after the pretreatment. Thus, porosity is one of the characteristics that decide the strength of the adsorbent to adsorb the metal ions from liquids. Today the control of porosity is of great industrial importance in industrial adsorbents, membranes, design of catalysts, etc.

Effect of time and kinetic studies

Equilibrium batch adsorption experiments are conducted keeping the amount of biosorbent constant (0.1 g) at different initial concentrations of metal ions. The amount adsorbed at different time intervals is determined for each concentration. The data are obtained for both untreated and treated algae. The equilibrium data in the tables indicate that adsorption is reached within a short period of 75, 50 and 60 min for Cr(VI), Ni(II) and Cu(II) respectively for all concentrations of the dissolved metal ions in the case of untreated
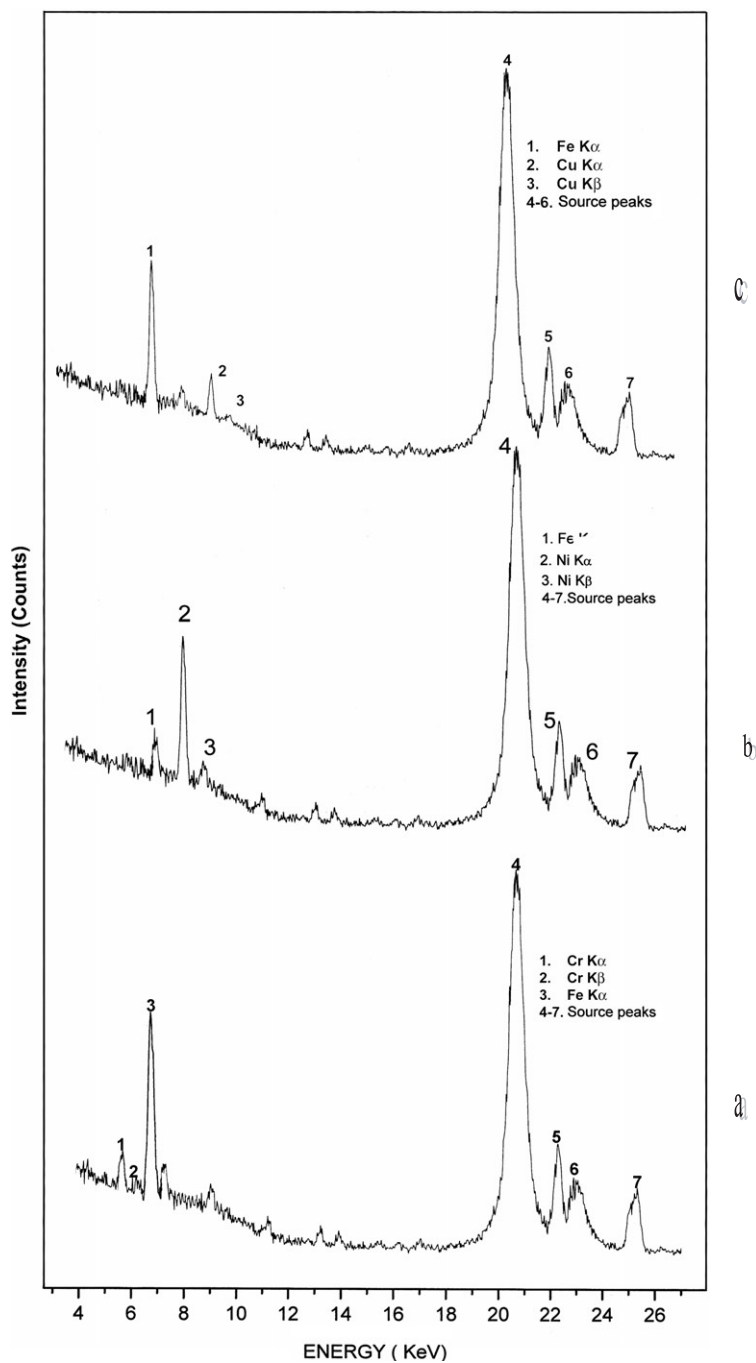
Figure 4. EDXRF spectra of metal treated algae: (a) chromium loaded, (b) nickel loaded and (c) copper loaded.
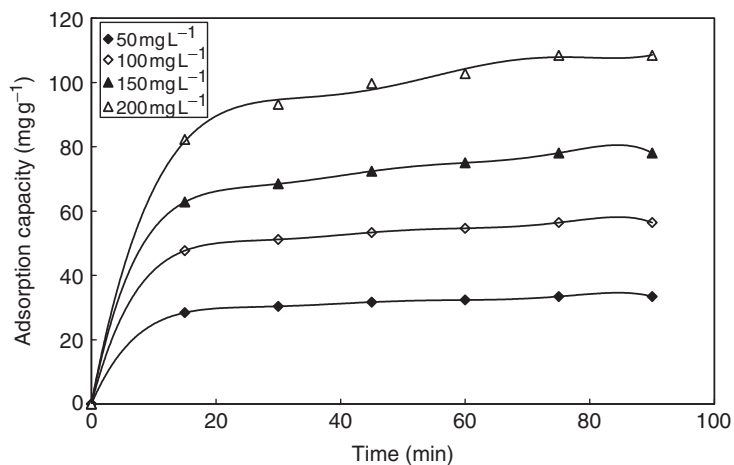
Figure 5. Effect of time on adsorption of Cr(VI) on untreated algae at different initial concentrations.
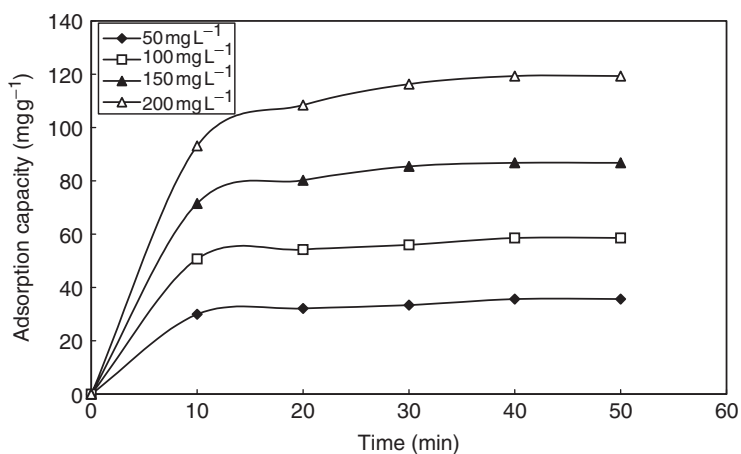

Figure 6. Effect of time on adsorption of Cr(VI) on treated algae at different initial concentrations.

algae. The solutions containing acid-treated algae, however, attained equilibrium within a still shorter period of 40, 30 and 40 min respectively for all concentrations of the dissolved metal ions. The decrease in equilibrium time in the case of acid-treated algae indicates that the rate of adsorption is faster in comparison with that of untreated algae. Therefore, the agitation time for the rest of the batch experiments was made a few minutes more than the equilibrium time for the specific metal selected. Figures 5–10 show the effect of time on removal of metal ions. The results indicate that the extent of adsorption efficiency increases sharply with time and then attained equilibrium. The results show that the increase in metal ion concentration increased the amount of metal ion uptake per unit weight of algae (mg g^{-1}).

Furthermore, it can also be stated that the biosorption efficiency of the dead biomass is greater than the live biomass. Pretreatment of the biomass and the methods employed for pretreatment give the results of biosorption. Untreated algae generally contain
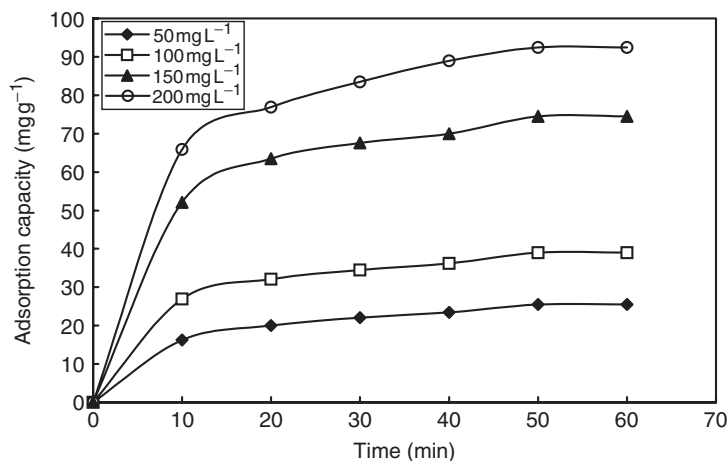
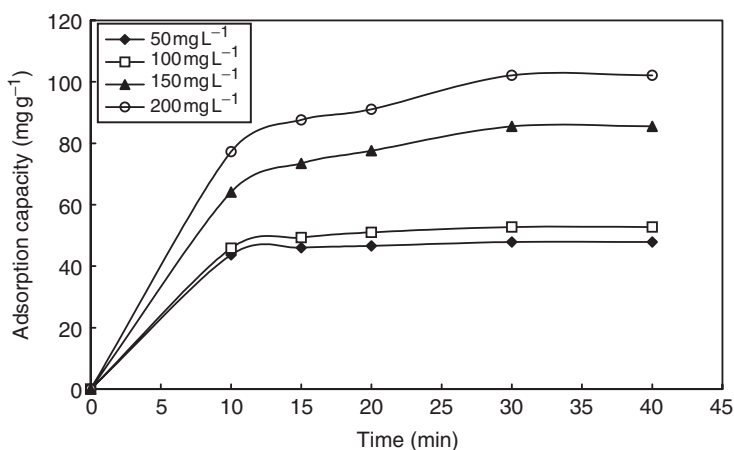Figure 7. Effect of time on adsorption of Ni(II) on untreated algae at different initial concentrations.

Figure 8. Effect of time on adsorption of Ni(II) on treated algae at different initial concentrations.

K^+, Ca^{2+}, Na^+ and Fe^{2+} bound to the acidic functional groups of algae. When this is treated with heavy metal solution, with the increase in pH there is a release of light metal ions thereby balancing the uptake of protons and heavy metals. Acid-treated algae, however, already displaces the light metal ions from the binding sites. In cases when this reacts with a single aqueous solution, the majority of the sites previously occupied by Ca^{2+}, K^+ are exchanged with the metal ions of similar size.

Two-stage kinetics of biosorption for immobilised biomass is reported. Although several models have been proposed to express the mechanism of solute molecule adsorption on to an adsorbent, a pseudo first-order kinetic model of Lagergren is taken into consideration. Further these surface reaction mechanisms take place as a result of an interaction between negatively charged groups of different functional groups present as acids and some hydroxyl groups of degraded cellulose in the alga. The adsorption dynamics of the system
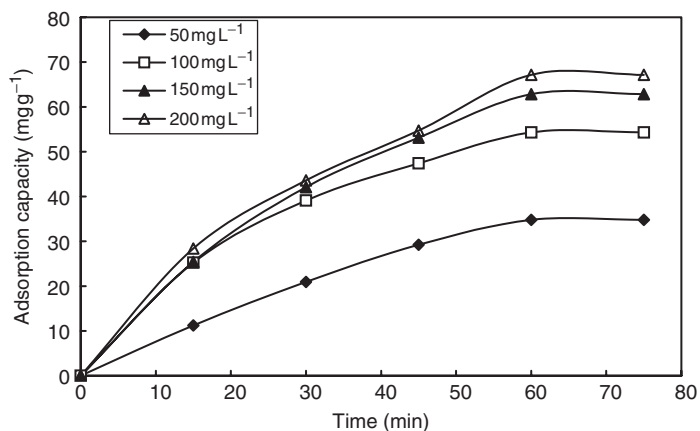
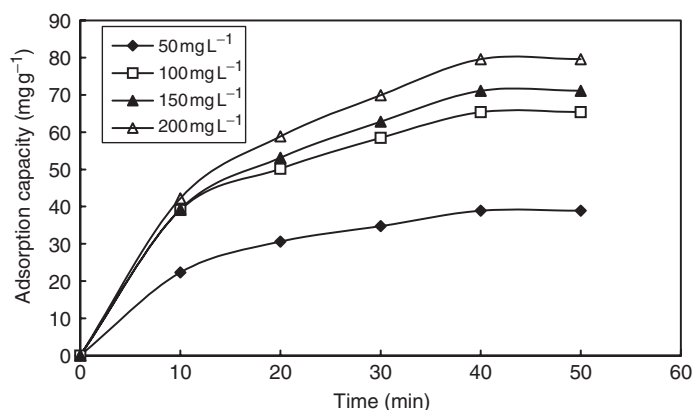Figure 9. Effect of time on adsorption of Cu(II) on untreated algae at different initial concentrations.

Figure 10. Effect of time on adsorption of Cu(II) on treated algae at different initial concentrations.

are studied according to Lagergren's equation. Ho and Mckay [23] suggested and used this equation for studying the rate constant of adsorption.

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_{ad}}{2.303}\right)t \tag{3}$$

where K_{ad} (min^{-1}) is the rate constant of adsorption, q_t and q_e are the amounts of metal ions adsorbed (mg g^{-1}) at time t and equilibrium respectively. The K_{ad} values for each system are calculated from the slope of the linear plots, are found to be constant at various concentrations and are presented in Table II. From these results, it is observed that there is no significant change in K_{ad} values for different concentrations. From the K_{ad} values of untreated and treated algae, it can be concluded that the rate of adsorption of metal ions on acid-treated algae is much faster than on the untreated algae. The order of increase of rate constant K_{ad} for the metal ions in algae is as follows:

Cu (treated) > Ni (treated) > Ni (untreated) > Cr (treated) > Cu (untreated) > Cr (untreated). This gives us an understanding of which metal ion's rate constant is fast on algae and acid-treated algae.

["

Figure 12. Effect of adsorbent dose on percentage removal of metal ions.

Depending on the pH of the solution Cr(VI) forms stable complexes such as $Cr_2O_7^{-2}$, $Cr_2O_4^{-2}$, $HCr_2O_4^-$ in solution. It suggests that negatively charged dichromate ions in solution bind through electrostatic attraction on the surface of cell walls of algae. The enhancement of the adsorption of Cr(VI) at lower pH may be due to an increase in hydronium ions, which take up the Cr(VI) ions, which are in the form of anions. It may also be due to the decrease in the forces of r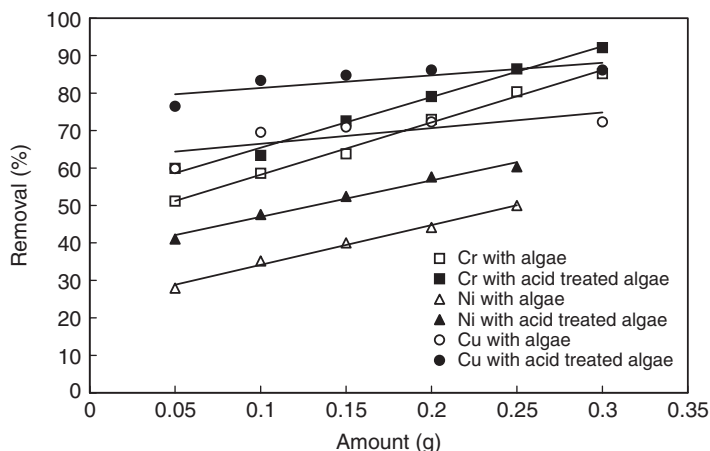epulsion between adsorbent and increase in the electrostatic forces of adsorbate and positively charged adsorbents [25].

The adsorption capacity of Ni(II), however, increases with pH and attains maximum at pH 7. Further increase in pH causes precipitation of the nickel. At pH above 3 it seems algal cell walls possess more functional groups carrying net negative charge. The pH dependency may be due to the binding of the metal through an ion exchange mechanism via functional groups or positively charged ligands with the cell walls of algae. The maximum adsorption of Cu(II) is at pH 4.3 and there seems to be a similar adsorption capacity in pH ranges between 4 and 5. Beyond pH 5, Cu gets precipitated.

Effect of adsorbent dosage

The data for the adsorption of metal ions at different algal doses are given in Figure 12. It is found that the extent of removal of metal ions increases with an increase in the amount of algae (0.05–0.300 g). The removal efficiency increases up to an optimum dose of 0.20–0.25 g of algae. This is to be expected because for a fixed initial solute concentration, increasing adsorbent doses provides greater surface area or adsorption sites. This may also be due to increase in adsorption site per unit mass with increase in their particle size, cell surface area and because more opened sites are available to bind metals [23,24]. The results clearly indicate that the percentage removal of Cr(VI) by untreated algae and acid-treated algae is 85.2 and 92.2%, of Ni(II) is 50 and 60% and of Cu(II) is 72 and 86% respectively. It can also be seen that the percentage of Cr(VI) removed by algae is much higher when compared to that of Ni(II) and Cu(II). Beyond the optimum dosage of algae, the increase in removal efficiency is negligible for a given initial metal concentration. This study is useful in establishing the optimum amount of biosorbent to be used in the metal removal.

Adsorption isotherms

Analysis of equilibrium data is important for developing a model that can be used for design purposes. Distribution of metal between the liquid phase and the adsorbent is a measure of the position of equilibrium in the adsorption process and can be expressed by two classical adsorption models such as Freundlich and Langmuir models. These two have been extensively used to describe the equilibrium established between adsorbed metal ions and metal ions remaining in solution at constant temperature.

Freundlich isothermal model,

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where n and K_F are Freundlich constants. A plot of $\log q_e$ *versus* $\log C_e$ gives a straight line where the slope and the intercept correspond to $1/n$ and $\log K_F$, respectively. The adsorption data is fitted to Freundlich isotherm and isotherm parameters are calculated. High values of K_F show higher affinity for metals and the slope $1/n$ reflects the intensity of adsorption. The adsorption capacity values indicate that a more favourable adsorption is seen in Cr(VI) than in Ni(II) and Cu(II).

Langmuir isotherm is used to describe the sorption phenomenon on homogenous surfaces and for a simple solute is given by

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \tag{5}$$

$$\frac{1}{q_e} = \frac{1}{Q_0 b C} + \frac{1}{Q^0} \tag{6}$$

where Q^0 and b represent monolayer adsorption capacity and energy of adsorption. Q^0 represents a practical liming adsorption capacity corresponding to the surface of sorbent fully covered by metal ions. This is particularly useful in the assessment of the adsorption performance [26]. The Langmuir constant, b, serves as an indicator of isotherm rise in the region of lower residual metal concentrations that reflects the strength or affinity of the sorbent for the solute [27]. The Langmuir model is based on the assumption of a single layer adsorption on a complete homogeneous surface. In spite of this, the model has been used for metal adsorption on various types of biosorbents although the metal uptake may not follow this single layer adsorption mechanism [25]. The values of Langmuir constants, correlation coefficient, R^2, separation factor, R_L and Freundlich constants along with correlation coefficients are given in Table III. R_L values less than unity indicates favourable adsorption. Figures 13 and 14 of the isotherms for Cr(VI), Ni(II) and Cu(II) on algae and acid-treated algae indicate that the two models are capable of representing the data satisfactorily. The adsorption isotherms obtained for Cr(VI), Ni(II) and Cu(II) uptake by algae and acid-treated algae follow a satisfactory Freundlich and Langmuir equation within the range of metal concentrations studied. This implies that monolayer biosorption as well as heterogeneous surface conditions may co-exist and that the overall biosorption of these metals is a complex process involving more than one mechanism such as sorption, ion exchange, surface complexation, electro statistical attraction, etc. Thus, both Freundlich and Langmuir isotherms can be used to model biosorption data from dilute aqueous solutions.

The adsorption capacities of some of the different algal species are compared with the present biosorbents and are presented in Table IV. Shang et al. [30] assess the potential of

Table III. Langmuir and Freundlich constants for the adsorption of Cr(VI), Ni(II) and Cu(II) on algae.

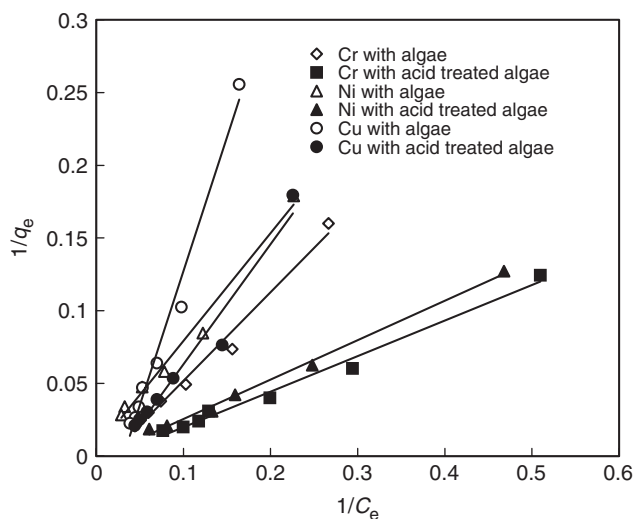| Metal ion	Algae	Langmuir constants				Freundlich constants		
		Q ($mg\,g^{-1}$)	b ($L\,mg^{-1}$)	R_L	R^2	K_F	n	R^2
Cr(VI)	Untreated form	111.1	0.015	0.40	0.98	2.12	1.01	0.99
	Acid-treated form	227.0	0.018	0.35	0.99	4.96	1.03	0.99
Ni(II)	Untreated form	100.0	0.015	0.40	0.98	1.80	1.19	0.98
	Acid-treated form	142.8	0.035	0.22	0.99	4.47	1.10	0.98
Cu(II)	Untreated form	17.6	0.031	0.20	0.98	1.94	0.98	0.99
	Acid-treated form	51.5	0.024	0.25	0.96	4.72	1.06	0.98

Figure 13. Langmuir adsorption isotherms for the removal of metal ions with untreated and treated algae.

four locally derived marine algae, namely *Sargassum* sp. and *Padina* sp. (brown macroalgae), *Ulva* sp. (a green macroalga), and *Gracillaria* sp. (a red macroalga), for the biosorption of heavy metals. The affinity sequence for *Padina* sp. and *Sargassum* sp. is Cu > Ni while the other two biosorbents *Ulva* sp. and *Gracillaria* sp. is Ni > Cu. FTIR analysis of *Sargassum* sp. and *Padina* sp. revealed the chelating character of the ion coordination to carboxyl groups. It is confirmed that carboxyl, ether, alcoholic and amino groups are responsible for the binding of the metal ions. Out of four biosorbents, *Padina* sp. shows the maximum uptake for Cu(II) ($72.96\,mg\,g^{-1}$) where as *Ulva* sp. shows the maximum uptake for Ni(II) ($48.00\,mg\,g^{-1}$). Nourbakhsh et al. [31] studied the Cr(VI) biosorption to non-living biomass of *Chlorella vulgaris*, and the biosorbent shows the maximum adsorption capacity, $24.00\,mg\,g^{-1}$. Evaluation of biosorption capacity of the algae *Spirogyra* sp. for Cr(VI) from aqueous solutions was done by Gupta et al. [32]. The adsorption capacities are evaluated from equilibrium adsorption isotherms and the results indicated that the alga is a suitable material for the development of high capacity ($14.70\,mg\,g^{-1}$) biosorbent for Cr(VI) removal. Leusch et al. [33] studied the biosorption of heavy metals (Cd, Cu, Ni, Zn and Pb) by chemically reinforced biomass of marine algae *Sargassum fluitans* and
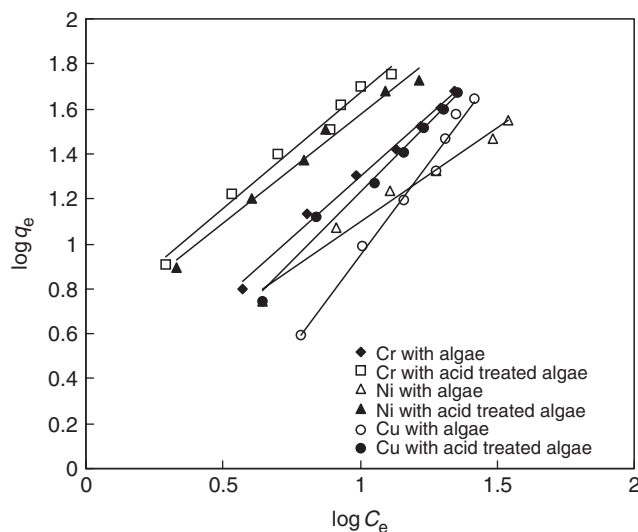
Figure 14. Freundlich adsorption isotherms for the removal metal ions with untreated and treated algae.

Table IV. Adsorption capacities $(mg\,g^{-1})$ of different algal species.

| Algal species | Q $(mg\,g^{-1})$ | | | Reference |
	Cr(VI)	Ni(II)	Cu(II)	
Padina species		37.11	72.96	[30]
Sargassam species		35.93	63.36	[30]
Ulva species		48.00	17.08	[30]
Gracillaria species		16.5	16.00	[30]
Chlorella vulgaris	24.00			[31]
Spirogyra species	14.70			[32]
Sargassum fluitans GA		80.00	100.00	[33]
Sargassum fluitans PEI		75.00	129.00	[33]
Ascophyllum nodosum PEI		113.00	87.00	[33]
Pithophora	434.10	192.00	17.66	Present study
Acid-treated *Pithophora*	666.21	625.80	51.54	Present study

Ascophyllum nodosum. The order of adsorption for *S. fluitans* biomass particles is Cu > Ni and for *A. nodosum* Ni > Cu respectively. The metal uptake for different chemical modifications shows the order GA > FA > PEI. However, the present biosorbent *Pithopora* algae showed maximum metal uptake compared with literature, i.e. $434.1\,mg\,g^{-1}$ for Cr(VI), $192.0\,mg\,g^{-1}$ for Ni(II) and $17.6\,mg\,g^{-1}$ for Cu(II) respectively, and the values were greatly increased with its acid-treated form.

Column studies

The column adsorption of metal ions Cr(VI), Ni(II) and Cu(II) from aqueous solutions on algae and acid-treated algae are investigated and are graphically represented in Figures 15–17. The results of the column experiments are used to obtain breakthrough
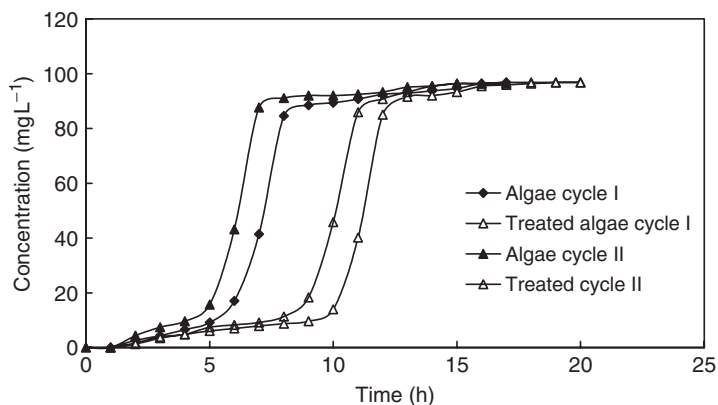
Figure 15. Breakthrough curves for Cr(VI) on untreated algae and acid-treated algae.
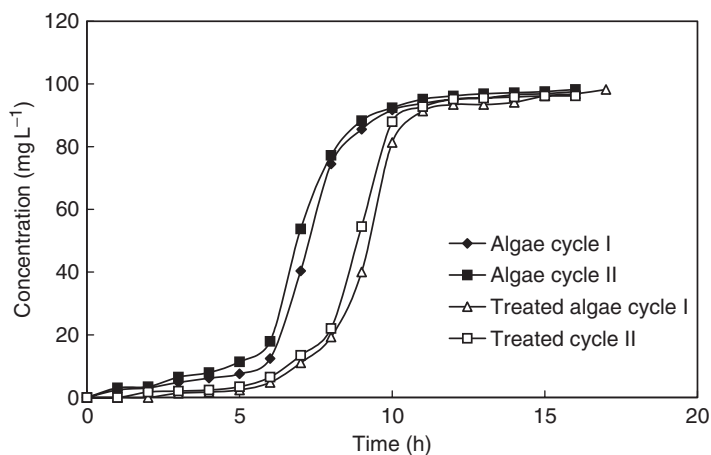

Figure 16. Breakthrough curves for Ni(II) on untreated algae and acid-treated algae.

curves by plotting time *versus* effluent concentration. Breakthrough is attained when the concentration of solute in the effluent is almost equal to influent concentration and remains unchanged. These curves are shown in Figures 15, 16 and 17.

From the graph it is apparent that the time for the primary adsorption zone to establish and move down the length of the column is smallest for untreated algae and is largest for treated algae in all the three metal ions. The time required for the movement of zone down the length of the column in algae and acid-treated algae is between 4–5 and 9–10 h for Cr(VI), 5–6 and 6–7 h for Ni(II) and 10–11 and 13–14 h for Cu(II) metal ions respectively. It is obvious that this value is less for the subsequent cycles.

From these observations, a direct relation can be developed between the length of the adsorption zone and the percentage of saturation at breakpoint as determined at $C_e/C_i = 1$. This value is kept constant to compare the results for all the metal ions. The smaller the length of the adsorption zone, higher the percentage of saturation [28]. Thus, the maximum saturation of metal ions is observed with untreated algae and the value is minimum for treated algae.
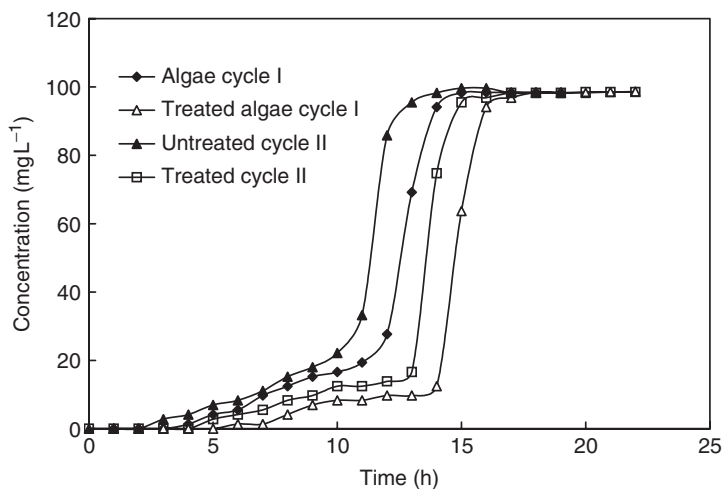
Figure 17. Breakthrough curves for Cu(II) on untreated algae and acid-treated algae.
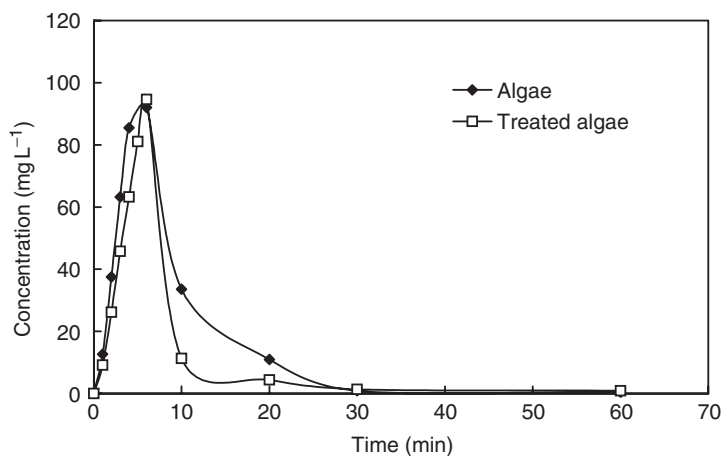

Figure 18. Desorption curves of Cr from untreated algae and treated algae.

Desorption and regeneration

The efficiency of a column is studied by regenerating the column. Therefore, the biomass, algae and acid-treated algae loaded with Cr(VI), Ni(II) and Cu(II) are eluted by various solvents like mineral acids, bases and some salt solutions. 0.1 M HCL is chosen as it is found to be effective, non-damaging, non-polluting and cheap. The biomass exposed to HCl remained the same and is suitable for subsequent cycles. Although the mineral acid released almost all the metal ions, after two cycles the original colour of the biomass algae is lost. However, it continued to biosorb metal ions to some extent. It may be said that repeated exposure to strong acid solutions could dissolve some type of polysaccharide that may contain ion-binding sites and the mineral content of the biomass algae [29]. Figures 18–20 show that the elution curves are sharp in the initial stages and decrease with higher eluant volumes. Furthermore, the percentage of desorption is higher
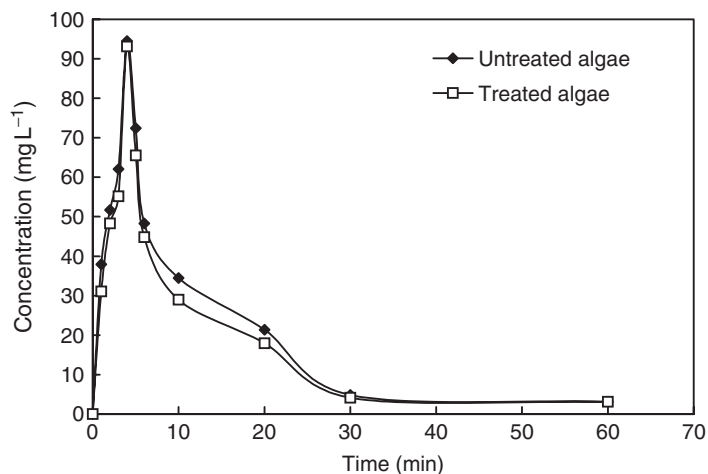
Figure 19. Desorption curves of Ni from untreated algae and treated algae.
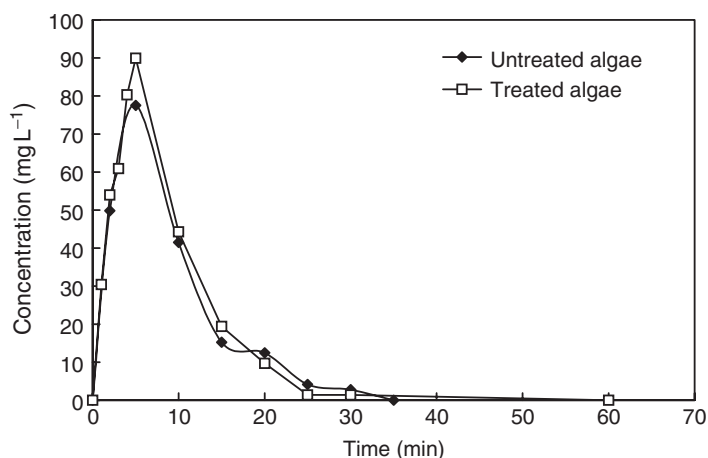
Figure 20. Desorption curves of Cu from untreated algae and treated algae.

in acid-treated algae than in untreated algae. This also supports the data that treated algae takes up more of the metal ions and, if a suitable solvent is used for desorption, releases these metal ions back into the solution.

Conclusions

It could be concluded from the data that chromium, nickel and copper are better removed from the treated algae than from untreated algae. The biosorption of algae showed greater binding capacity of Cr(VI), Ni(II) and Cu(II) and, moreover, it is even more predominant in acid-treated algae. The results showed the biosorbent is most effective at pH 2 for Cr(VI), pH 7 for Ni(II) and pH 4.3 for Cu(II). The equilibrium data conformed well to the

Langmuir and Freundlich isotherm models. The results of dynamic studies demonstrate that fixed bed operations are possible using algae but it is noted that the process is slow. However, this low cost biosorbent, algae, has the greatest potential in the removal of Cr(VI), Ni(II) and Cu(II) present in wastewaters generated from the industry. The FT-IR spectral analysis for the presence of different functional groups responsible for binding, EDXRF spectral analysis for the metal detection and porosity prove that the biosorption studies are feasible with algae. Therefore, it can be concluded that algae *Pithophora* is an efficient adsorbent for the removal of chromium, nickel and copper from single aqueous solutions.

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