Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Rao, P. Srinivasa , Kalyani, S. , Reddy, K. V. N. Suresh and Krishnaiah, A.(2005) 'Comparison of Biosorption of Nickel (II) and Copper (II) Ions from Aqueous Solution by *Sphaeroplea* Algae and Acid Treated *Sphaeroplea* Algae', Separation Science and Technology, 40: 15, 3149 — 3165
To link to this Article: DOI: 10.1080/01496390500385350
URL: http://dx.doi.org/10.1080/01496390500385350

Separation Science and Technology, 40: 3149–3165, 2005

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390500385350

Comparison of Biosorption of Nickel (II) and Copper (II) Ions from Aqueous Solution by *Sphaeroplea* Algae and Acid Treated *Sphaeroplea* Algae

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Abstract: Biosorption of nickel (II) and copper (II) ions from aqueous solution by dead *sphaeroplea* algae in natural and acid treated forms were studied as a function of concentration, pH, and adsorbent dose. The optimum pH for nickel (II) and copper (II) biosorption was found to be 6.0 and 4.0 respectively. The metal ion uptake increased with initial metal ion concentration studied up to 500 mg/L. Both the Freundlich and Langmuir adsorption models could fit the equilibrium data. The adsorption reasonably fitted the Lagergren kinetic model. Further the biomass was characterized by FTIR spectra. Surface area values are measured to be 0.9 and 2.1 m^2/g for natural and acid treated forms respectively. The maximum adsorption capacity was found to be 3.40, 4.15 mmol/g for nickel (II) and 2.21, 3.41 mmol/g for copper (II) in natural and acid treated forms respectively.

Keywords: Green algae, biosorption, nickel, copper, FTIR, waste water

INTRODUCTION

The increase in individual activities has intensified environmental pollution and deterioration of some ecosystems, with the accumulation of pollutants such as heavy metals, synthetic compounds, waste nuclear lipids etc (1). It

Received 2 May 2005, Accepted 25 August 2005

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is well known that the presence of heavy metals in the environment has resulted in a number of environmental problems. Nickel (II) and copper (II) were known to be commonly used heavy metals. Hence removal of these metals from waste water streams was important. Many industries, especially plating and battery, release heavy metals like nickel and copper in waste water. These metals, which find many useful applications in our life, are very harmful if they are discharged into natural water resources and may pose finally a serious health hazard (2–4). Traditional technologies for the removal of heavy metals such as ion exchange, chemical precipitation, reverse osmosis, and electro chemical processes are often ineffective and/or very expensive when used for the reduction of heavy metal ions at very low concentrations. The search for new technologies involving the removal of toxic metals from waste waters has directed attention to biosorption.

Biosorption is the process of accumulation and concentration of pollutants from aqueous solutions by the use of biological materials such as algae, fungi, and bacteria (5). The advantage of using dead biomass are

i. It can be easily regenerated
ii. Requires only minimal solid-liquid separation operation.

Algae possess a high metal binding capacity, where the cell wall plays an important role in metal ion binding (6–8). This is due to the presence of carboxyl, hydroxyl, sulfate, and amino groups in algal cell wall polysaccharides, which can act as binding sites for metals. The performance of any biosorbent also depends on biomass characteristics, physico-chemical properties of the target metals, and the solution pH.

This communication reports on nickel (II) and copper (II) biosorption on inert biomass of *Sphaeroplea* algae in natural and acid treated forms. Although there has been sufficient work on biosorption of heavy metals with green algae, *Sphaeroplea* algae is a novel adsorbent for the removal of metal ions from aqueous solutions. This was chosen as biosorbent because of its relative abundance as a waste product from local prawn ponds. On acid washing of the biosorbents microalgae *Chlamydamo reinhardtil*, *Aspergillus oryzae*, increase in adsorption capacity was observed in the literature (9, 10). In this work also *Sphaeroplea* algae was treated with acid and the adsorption capacity was compared with natural form. Further the biomass was characterized by FTIR spectral analysis and surface area values are measured to understand the mode of metal–biomass interaction. The basic objective of the study was to contribute to the understanding and modeling of the equilibria adsorption processes. For this purpose, various factors affecting on adsorption, such as time of contact, initial pH of the solution, and metal ion concentrations were investigated by the batch equilibrium technique. The experimental data are fitted to Freundlich and Langmuir adsorption isotherm models and Lagergren first order kinetic equation.

EXPERIMENTAL

Material

Analytical grade nickel ammonium sulphate and copper sulphate were purchased from S. D. Fine Chemicals, for nickel (II) and copper (II) ion sources. Hydrochloric acid and sodium hydroxide used for pH adjustment and for the treatment of algae were obtained from Aldrich Chemical Company and Chemical Drug House Ltd. Double distilled water was used in all experimental work.

Biosorbent Preparation

Green algae (*Sphaeroplea*) were collected from fresh water prawn ponds of Nellore district in Andhra Pradesh, India. It was washed several times with water to remove particles and waste adhered on the surface followed by double distilled water. It was then dried in an oven at 70°C for 2 hr. The dried material was ground mechanically and sieved to 80–100 mesh particle size. The powdered algae material was used as the adsorbent for metal removal.

Acid Treatment of the Biosorbent

The algae sample (5 g in each time) was treated with 50 mL of 0.5 N hydrochloric acid at 70°C for 30 minutes. The reacted mass was allowed to cool and sodium hydroxide solution was added till the acid is neutralized. The mass was filtered in vacuum and washed with double distilled water till the washings are free from alkalinity. The wet mass was taken in an enamel tray and dried in an oven. The lumps were crushed during the drying period and the powdered mass was used as the biosorbent.

Biosorption Studies

An adsorbate stock solution of 1000 mg/L of nickel (II) and copper (II) were prepared by dissolving 6.73 g of nickel ammonium sulphate and 3.92 g copper sulphate in double distilled water. This stock solution was diluted to required concentration for obtaining standard solution containing 50 to 500 mg/L of nickel (II) and copper (II). Batch experimental studies were carried out with known weight (100 mg) of adsorbent and 100 mL of nickel (II) and copper (II) stock solution of desired concentration at pH 4.0 and 6.0 in 100 mL stopper bottles and are agitated at 120 rpm for 70 and 90 minutes time intervals at room temperature (33°C) in a mechanical shaker. After an equilibration alga was separated by filtration and the aqueous-phase concentration of metal was analyzed with atomic absorption spectrophotometer (Perkin–Elmer 2380).

The biosorption equilibrium uptake capacity for each sample was calculated according to mass balance on the metal,

$$q_e = \left(\frac{C_i - C_e}{m}\right) \cdot v \tag{1}$$

where C_i and C_e are respectively initial and equilibrium concentrations of metal ion, m is the mass of adsorbent and v is volume of solution in liters.

Statistical Analysis

Experiments were conducted with metal ion solution in absence of adsorbent and were found that there is no metal adsorption by the walls of the container. Each experiment was repeated at least three times independently and mean values were taken. The standard deviation and error bars were indicated wherever necessary. Statistical analysis was carried out to determine standard deviation.

Effect of pH on Metal Biosorption

The effect of pH of the suspending medium on metal removal was studied by performing equilibrium sorption experiments at different pH values. Adjustments to pH were made with 0.1 N hydrochloric acid and 0.1 N sodium hydroxide solutions. The effect of pH was studied by keeping the metal concentration (100 mg/L), the amount of algae (100 mg) and the temperature (33°C) constant.

FTIR Spectra Analysis

FTIR spectra of algae in natural form and acid treated form were recorded in a Perkin–Elmer–283B FTIR spectrometer over the wave range 4000–400 cm^{-1}. The samples were prepared as KBr discs.

Surface Area Analysis

Surface area of the samples (both natural and acid treated forms) was measured by single point BET method using thermal conductivity detector (Carlo Erba Soptomatic–1800) with the range of 0.1 to 2000 m^2g^{-1}.

RESULTS AND DISCUSSION

Biomass Characterization

Green algae, containing fatty acids, lipids, and pyrenoids with cyatoplasmic imaginations, possess a high metal binding capacity. This is due to the presence of carboxyl, carbonyl, phosphate, and amino groups in algal cell wall polysaccharides, which can act as binding sites for metal ions. Generally the metal adsorption capacity increases by increasing the concentration of acid solution. In the present investigation 0.5 N HCl was used for the treatment of algae, which results in not only a physical cleaning or washing out, but also some chemical transformation, such as denaturation of the protein molecules. Treatment of biomass with HCl implies the protonation which displaces the light metal ions from the binding sites (i.e., carboxylic, sulfonic, and others). Huang et al. (11) reported that acid washing process resulted in a better metal removal capacity of *A. Oryzae mycelia* over the whole range of pH tested. According to him acid treated biomass contained a higher percentage of surface nitrogen. This indicates that acid treatment may dissolve polysaccharide compounds in the outer layer of the algal cell wall and therefore produce additional binding sites (amino groups). Acid treatment results not only in a clean-up of the surface impurities, stabilization of the surface compounds, and increases the surface area by opening the available sites for metal adsorption (10). Surface area analysis indicates the enhancement of surface area due to acid treatment. The measured values are $0.9\,m^2/g$ for natural and $2.1\,m^2/g$ for acid treated forms of algae respectively.

FTIR spectra for algae in natural, acid treated forms and both loaded with nickel (II) and copper (II) are shown in Fig. 1(a), 1(b), 1(c), 1(d), 1(e), and 1(f) respectively. In Fig. 1(a), there is a strong peak at $3419\,cm^{-1}$ representing the N–H stretching of amino group and the peak at $2918\,cm^{-1}$ indicates the presence of C–H stretching. The appearance of peaks at 1718 and $1040\,cm^{-1}$ indicate the presence of C=O stretching and C–O stretching in carbonyl and carboxyl groups, where as the peaks at 1143 and $910\,cm^{-1}$ present the characteristic peaks of P=O and P–O stretching respectively (12). Cell proteins are typically indicated by a number of amide bands. They dominate at $1613\,cm^{-1}$ (amide I), and show other distinct bands at $1548\,cm^{-1}$ (amide II), and $1225\,cm^{-1}$ (amide III) (C–N stretching). A shoulder at $1687\,cm^{-1}$ in the FTIR spectrum of green algae (natural form) can be due to C=O stretching of amides (13). During the acid treatment of algae, the main functional groups remain unchanged and disappearance of some peaks (peak at $1120\,cm^{-1}$, shoulder at 1183 and peak at $1312\,cm^{-1}$ related to polysaccharides) indicate the clean up the surface as shown in Fig. 1(b). Additional peaks found at 3696 and $2380\,cm^{-1}$(–CH stretching)in acid treated form confirm the production of additional functional groups. The FTIR spectral analysis of biomass loaded with nickel (II) and copper (II)

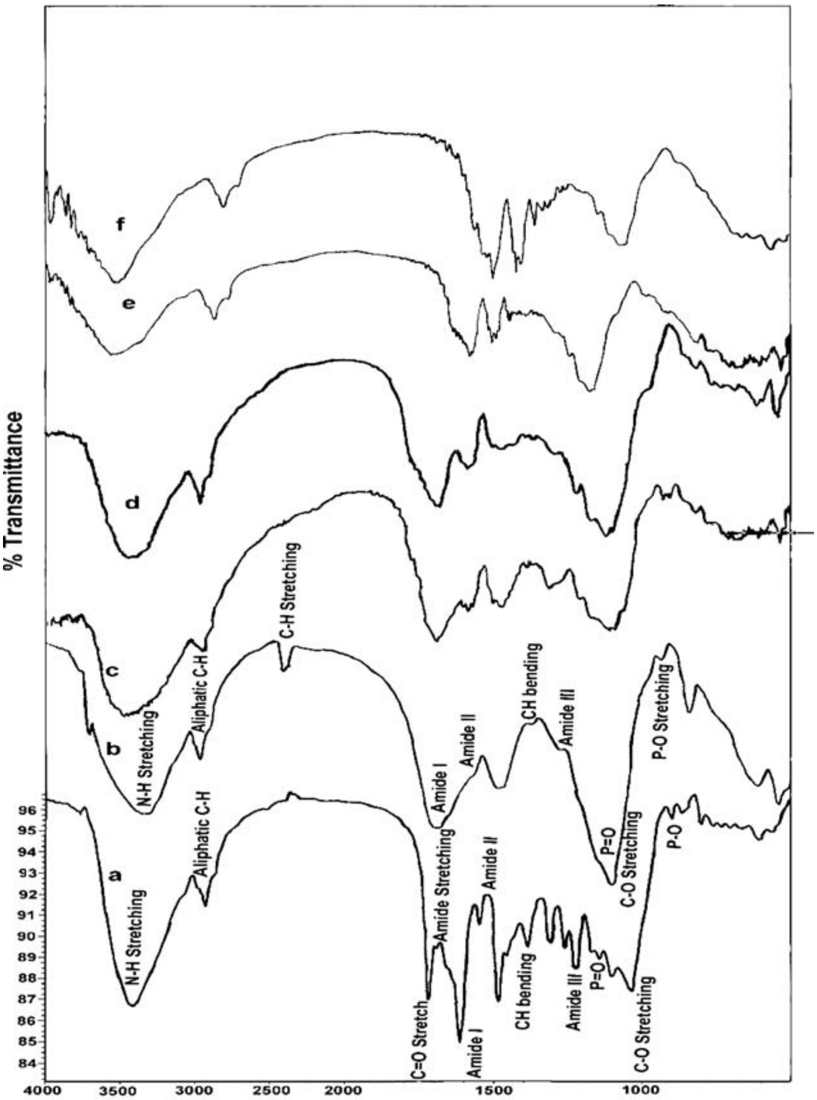

Figure 1. FTIR spectra of algae (a) natural form, (b) acid treated form, (c) natural form with nickel (II), (d) acid treated form with nickel (II), (e) natural form with copper (II), (f) acid treated form with copper (II).

(Fig. 1(c), 1(d), 1(e), 1(f)) shows elongation of these bands after nickel (II) and copper (II) adsorption indicating the role of these groups in biosorption. The IR spectra of biomass loaded with nickel (II) and copper (II) showed a similar nature, which may be due to the close proximity of such transition metals in the periodic table. A comparison of the spectra for biomass with that of metal loaded revealed a characteristic shift in –C=O groups indicating the interaction of nickel (II) and copper (II) ions with C=O groups of biomass. The disappearance of a peak at 1150 and 2410 cm^{-1} for the metal loaded biomass indicates C–C stretching and C–O–C asymmetric stretching as a consequence of sorbed metal ions with phosphate harboring compounds like oligo and polysaccharide of algal cell wall. In acid treated form, metal ion adsorption was clearly indicated by more elongation and sharpness of the peaks.

Effect of pH on Nickel (II) and Copper (II) Biosorption

Earlier studies on heavy metal biosorption have shown that pH was the single most important parameter affecting the biosorption process (14). Figure 2 shows the uptake of nickel (II) and copper (II) ions at different initial pH values using *Sphaeroplea* algae. The adsorption was increased with pH up to 6.0 and 4.0 for nickel (II) and copper (II) respectively. Nickel and copper speciation was not studied beyond the pH at 8.0 and 6.0 because of the formation metal hydroxide precipitates. The poor sorption of nickel (II) as well as copper (II) in the low pH range could be due to competition with the H$^+$ ions for metal binding sites on the algal cell, while increase in pH favors metal sorption mainly because of the elevated levels of negatively charged groups (15, 16). Friis and Myers-Keith (17) reported that metal adsorption is brought about by ionization of negative functional molecular groups, which serve as the binding sites. The decrease in recoveries at higher pH values may be attributed to the competition between ligand of

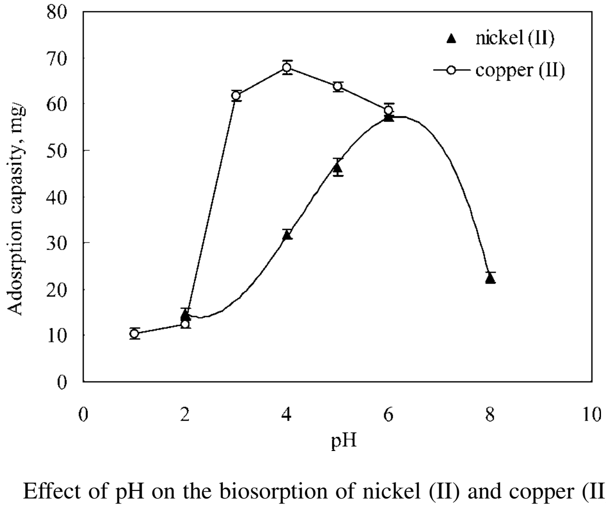

Figure 2. Effect of pH on the biosorption of nickel (II) and copper (II) on algae.

the cell wall and base. The lower uptake is also probably due to the formation of anionic hydroxide complexes at higher pH values (18). Because of this effect at higher pH values on the ligands such as carboxylate and sulfonate groups could uptake fewer metal ions.

Time Course Study on Nickel (II) and Copper (II) Biosorption

Figures 3, 4, 5, and 6 show the effect of treatment time on the adsorption of nickel (II) and copper (II) ions at various concentrations onto the biosorbent (natural and acid treated form) from aqueous solutions. It is seen that the adsorption ability of nickel (II) and copper (II) ions in both forms of algae are comparable. The adsorption efficiency increases with time and attained equilibrium for all the concentrations (100, 250, and 500 mg/L) at 70 and 60 minutes for nickel and 90 and 75 minutes for copper in case of natural and acid treated forms respectively. Noticeably, the nickel biosorption rate was relatively a little faster throughout than that of copper, which may be due to more chelation or complexation with the groups present on the algal surface. The extent of adsorption of both the metals is more on acid treated form than on natural form which may be attributed to the activation of the adsorption sites and increased surface area on acid treatment. According to Sigg (19), this cell surface consists of a mosaic of cation and anion exchange sites on the cell walls. The external surface of the biomass has a fibrous composition of proteins and carbohydrates with which metallic species can react. The amino and carboxyl groups and the nitrogen and oxygen of the peptide bond could be available for characteristic coordination bonding with metallic ions (12).

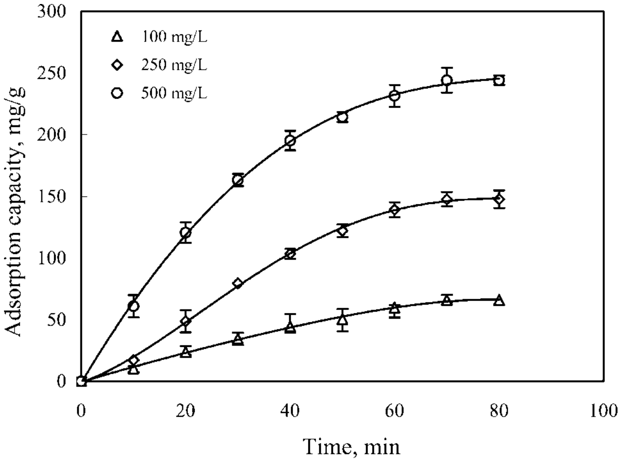

Figure 3. Effect of time on biosorption of nickel (II) on algae.

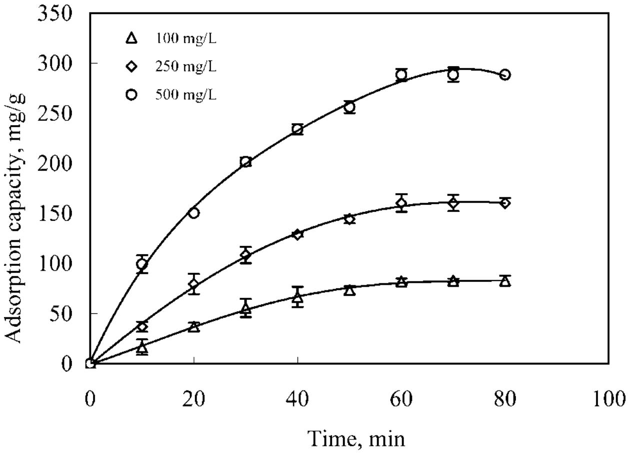

Figure 4. Effect of time on biosorption of nickel (II) on acid treated algae.

The adsorption kinetics of nickel (II) and copper (II) ions on green algae in natural and acid treated forms follows first order rate expression given by Lagergren,

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_{ad}}{2.303}\right)t \tag{2}$$

where q_e and q_t are the amount of solute adsorbed per unit weight of the adsorbent (mg/g) at equilibrium time, and at time t (minutes) and K_{ad} is the rate constant (min^{-1}). The K_{ad} values at different initial metal ion concentrations are calculated from the slopes of the linear plots and are presented

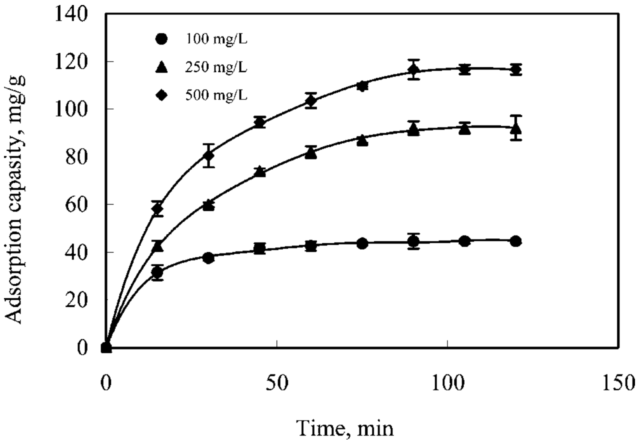

Figure 5. Effect of time on biosorption of copper (II) on algae.

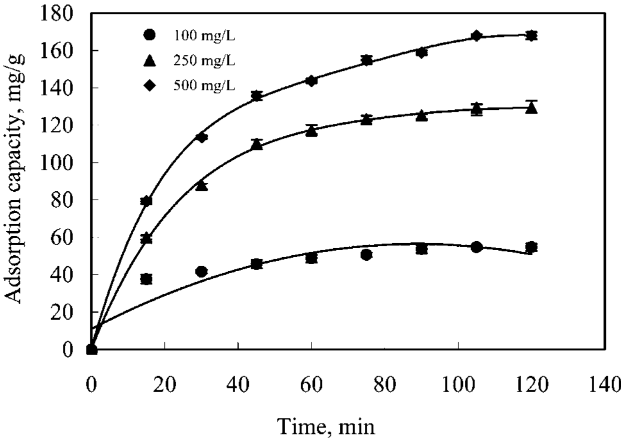

Figure 6. Effect of time on biosorption of copper (II) on acid treated algae.

in Table 1. From the results it is observed that there is no significant change in the values of K_{ad} at various concentrations of nickel and copper.

Effect of Adsorbent Dose

The effect of dead *Sphaeroplea* algae dose on the biosorption kinetics of nickel (II) and copper (II) ions were studied at a pH of 6.0 and 4.0 and 100 mg/L initial metal ion concentrations. The adsorbent dose is varied from 0.05 to 0.3 g for nickel and 0.1 to 0.5 g for copper. Adsorption efficiency increases, but adsorption capacity per unit mass decreases with increase in algae dose. The reduction in adsorption capacity with increase in the adsorbent dose is mainly due to unsaturation of adsorption sites through the adsorption reaction. Adsorption capacity decreases from 1.37 to

Table 1. Adsorption rate constants of Lagergren plot for nickel (II) and copper (II) on algae

Metal ion	Concentration of metal ion (mg/L)	Natural form		Acid treated form	
		K_{ad}	R^2	K_{ad}	R^2
Nickel (II)	100	0.041	0.995	0.049	0.995
	250	0.040	0.991	0.049	0.990
	500	0.043	0.991	0.050	0.993
Copper (II)	100	0.030	0.991	0.039	0.994
	250	0.035	0.993	0.038	0.995
	500	0.030	0.997	0.035	0.991

0.51 and 1.95 to 0.53 mmol/g for nickel (II), 0.70 to 0.19 and 0.86 to 0.25 mmol/g for copper (II) (Figs. 7 and 8) with natural and acid treated forms respectively.

Freundlich and Langmuir Adsorption Isotherms

An adsorption isotherm is characterized by certain constants, the values of which express the surface properties and affinity of the biosorbent and can also be used to compare biosorptive capacity of biomass for different metal ions. Out of several isotherm equations, two have been applied for this study, the Freundlich and Langmuir isotherms. The Langmuir equation was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surface. The Freundlich model was chosen to estimate the adsorption intensity of the sorbent towards the biomass. The linearized Freundlich and Langmuir adsorption isotherms of nickel (II) and copper (II) ions for both the forms of algae obtained at 33°C varying the concentration from 50–500 mg/L was shown in Figs. 9 and 10.

The values of K and 1/n are evaluated from the intercept and the slope of the linear plot of $\log q_e$ and $\log C_e$ based on experimaental data. The magnitude of these values showed easy uptake of nickel (II) and copper (II) from waste water with a high adsorptive capacity of *Sphaeroplea* algae.

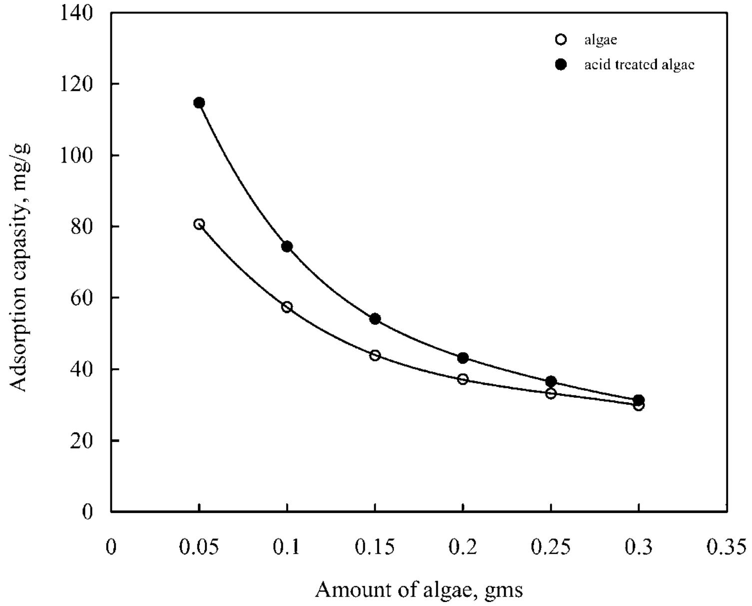

Figure 7. Effect of dose of adsorbent on biosorption of nickel (II).

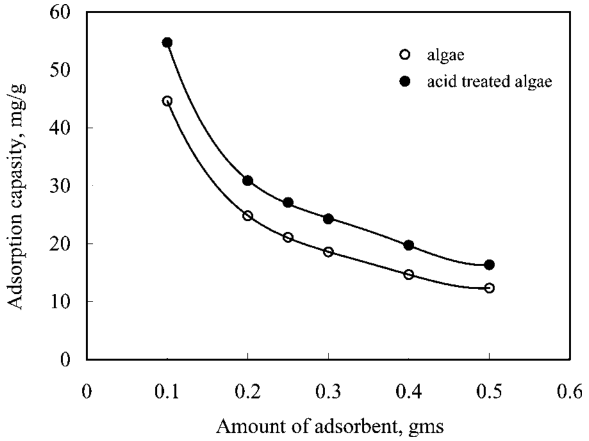

Figure 8. Effect of dose of adsorbent on biosorption of copper (II).

The K_f value is the least for copper (II). n value also follows the same trend as seen from Table 2 for both the forms of algae and metal ions.

The Q° appears to be significantly higher fornickel (II) compared with copper (II) in both forms of algae. A large value of 'b' also implied strong binding of nickel to the biomass. Langmuir parameters of *Sphaeroplea* algae also indicated a maximum adsorption capacity for nickel than for copper in both the forms. The results are depicted in Table 2. Though both the models represent the data adequately, but according to the values of correlation coefficient, Langmuir isotherm well fitted the experimental data

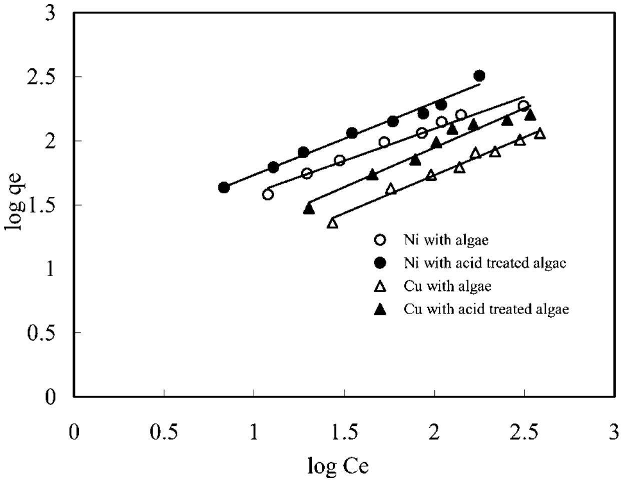

Figure 9. Freundlich isotherm for biosorption of nickel (II) and copper (II) on algae.

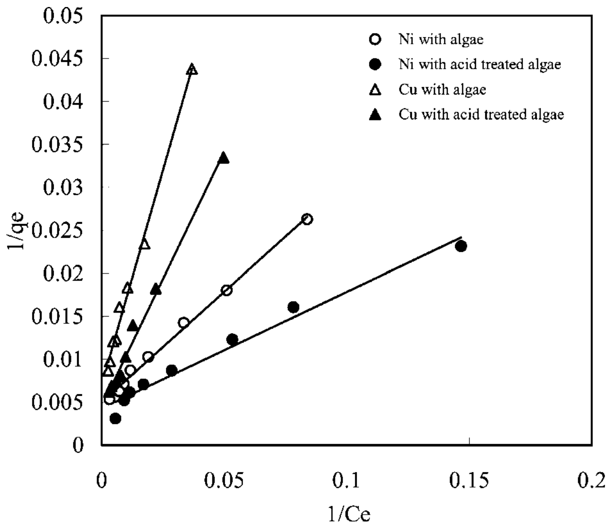

Figure 10. Langmuir isotherm for biosorption of nickel (II) and copper (II) on algae.

due to monolayer adsorption of metal ions with chemical groups preset on the biomass surface.

Table 3 shows a comparison between the results of this work and others in the literature. The values of nickel (II) specific uptake found in this work were significantly higher than reported elsewhere. *Sphaeroplea* algae is a quite good biosorbent. Its relatively high affinity to nickel (II) and copper (II) ions compared to other biosorbents might be attractive in treatment of waste water because of its capability of uptaking investigated metal ions from a diluted solution. The physical and chemical differences of different algae are as follows: seaweeds are found throughout the world's oceans are in three basic colors: brown (Phaeophyta), red (Rhodophyta), and green (Cholorophyta). Brown and red algae are almost exclusively marine, but the vast majority of green algae are fresh water and terrestrial. The brown color of Phaeophyta results from the dominance of the xanthophylls pigment fucoxanthrin which masks the other pigments while the red color of the Rhodophyta is due to the presence of the pigment phycoerythrin. The green color of the Chlorophyta comes from chlorophyll a and b. Typical algal cell walls of Phaeophyta, Rhodophyta, and Cholorophyta are comprised of a fibrillar skeleton and an amorphous embedding matrix. The most common fibrillar skeleton material is cellulose. It can be replaced by xylom in the Cholorophyta and Rhodophyta in addition to mannan in the Cholorophyta.

According to Hashim et al., red seaweeds have more cationic sites than green and brown seaweeds and thus have a relatively low affinity for positively charged metal ions compared to the green algae (20). Thus binding of metal

Table 2. Langmuir and Freundlich constants for the adsorption of nickel (II) and copper (II) on algae

	Nickel (II)						Copper (II)					
	Langmuir constants			Freundlich constants			Langmuir constants			Freundlich constants		
Algae	Q° (mmol/g)	b (L/mg)	R^2	K_F	n	R^2	Q° (mmol/g)	b (L/mg)	R^2	K_F	n	R^2
Natural form	3.40	0.019	0.995	12.43	2.00	0.972	2.21	0.0071	0.992	3.53	1.68	0.983
Acid treated form	4.15	0.026	0.990	19.13	2.09	0.990	3.41	0.0077	0.989	5.18	1.62	0.955

Table 3. Comparison of this work with different biosorbents regarding nickel (II) and copper (II) removal capacity (Langmuir model) at 25°C

	Nickel (II)		Copper (II)		Reference
Biosorbent	pH	Q° (mmol/g)	pH	Q° (mmol/g)	
Cholerella vulgaris	5.0	0.98	4.5	0.75	21
Scenedesmus obliquus	5.0	0.51	4.5	0.52	21
Synechocystis sp.	5.0	3.23	4.5	0.59	21
Pseudomonas aeruginosa	8.0	4.51	7.0	2.16	22
Streptomyces coelicolor A3(2)	8.0	7.1	5.0	1.04	23
Aspergillus niger 405	5.0	0.034	5.0	0.07	24
Streptomyces noursei (1)	5.9	0.013	5.5	0.14	25
Padina sp.	5.5	0.628	5.0	1.14	26
Sargassum sp	5.5	0.61	5.0	0.98	26
Ulva sp.	5.5	0.29	5.0	0.74	26
Gracillaria sp.	5.5	0.27	5.0	0.58	26
Chitosan	5.0	0.04	5.0	0.26	27
Epichlorohydrin crosslinked chitosan	5.6	0.012	5.6	0.37	28
Chitosan coated perlite	5.0	1.95	5.0	3.08	29
Sphaeroplea algae (natural form)	6.0	3.40	4.0	2.21	Present study
Sphaeroplea algae (acid treated form)	6.0	4.15	4.0	3.41	Present study

ions by algal biomass may depend on the species and ionic charges of metal ion, the algal organism and the chemical composition of the metal ion solution.

CONCLUSIONS

In this work we aimed to determine the biosorption ability of *Sphaeroplea* algae in the removal of nickel (II) and copper (II) ions and compared its efficiency with acid treated form of biomass. The process of removing metal ions from aqueous environment using sphaeroplea algae, as a biosorbent is cheaper than any adsorbent as the biomass is a waste byproduct from the prawn ponds. The kinetics of nickel (II) and copper (II) biosorption is fast. The adsorption equilibrium data correlate well with the Langmuir and Freundlich isotherm models. Biosorption can be accomplished with a high yield by increasing metal ion concentration from 50 to 500 mg/L. So algal biosorption can be used successfully with both low and high metal ion concentrations in waste waters. The adsorption of algae for nickel was relatively more than that of copper, which may be due to more chelation or complexation of nickel with the groups present on the algal surface. The maximum adsorption capacity of algae in both natural and acid treated forms used in this study are 3.40, 4.15 mmol/g for nickel (II) and 2.21, 3.41 mmol/g for copper (II) ions respectively. The adsorption capacity of algae in acid treated form is greater than its natural form for both the metal ions.

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