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Studies of chromium removal from tannery wastewaters by algae biosorbents, *Spirogyra condensata* and *Rhizoclonium hieroglyphicum*

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Abstract

Chromium in the effluent is a major concern for tanning industry. Chemical precipitation methods are commonly employed for the removal of chromium but this leads to formation of chrome-bearing solid waste, plus it is uneconomical when the concentration of chromium in the effluent is low. Ion exchange and membrane separation methods are relatively expensive. In this study, two algae namely, *Spirogyra condensata* and *Rhizoclonium hieroglyphicum* have been employed to remove chromium from tannery effluent. The effect of pH and chromium concentration showed *S. condensata* to exhibit maximum uptake of about 14 mg Cr(III)/g of algae at optimum pH of 5.0 whereas *R. hieroglyphicum* had 11.81 mg of Cr(III)/g of algae at pH of 4.0. Langmuir and Freundlich models were applied. Increase of initial concentration of Cr resulted to a decrease in adsorption efficiency. Dilute sulphuric acid (0.1 M) showed good desorption efficiency (>75%). Interference from cations negatively impacted on biosorption of chromium. Immobilized algae on Amberlite XAD-8 in a glass column, gave better recovery of chromium in tannery effluent compared to a batch method with unimmobilized algae. Fourier transform infra red (FT-IR) analysis of the two algae revealed the presence of carboxyl groups as possible binding sites.

Keywords: Chromium; Algae; Biosorption; Tannery; Wastewater

1. Introduction

"Biosorption" is a process in which materials of natural origin, such as micro-organisms (living or dead) are employed for sequestration of heavy metals from an aqueous environment [1,2]. Metal ions in solution interact with the biosorbent and hence are sequestered. The mechanism of metal ions uptake from solution can be due to physical sorption, complexation with microbial cell surface groups or bioaccumulation [2]. Biosorption could occur through interactions between metal ions and functional groups of the cell wall biopolymers of living and dead organisms. The major functional groups on biopolymers which act as binding sites include carboxylate ($–COO^-$), amide ($–NH_2$), thiols (–SH), phosphate (PO_4^{3-}) and hydroxide (–OH) [3,4].

Heavy metals are widespread pollutants of great concern as they are non-degradable and thus persistent. Pollution of the environment by toxic heavy metals is largely as a result of industrial activities such as mining, electroplating, leather tanning, etc. The effective removal of heavy metals from aqueous wastes is among the most important issues in the world today [5–7]. A number of methods exist for the removal of heavy metal pollutants from liquid wastes when they are present in high concentrations. These methods which include chemical precipitation, evaporation, electroplating, ion-exchange and membrane processes, are otherwise suitable at high concentration but ineffective and cost prohibitive when applied to dilute solutions or lead to secondary pollution [2,5,6,8]. This limitation has led to a growing interest in application of biosorption technology for the removal of toxic metal from dilute aqueous solution. Biosorption is technically feasible, economical and eco-friendly [1,4,9]. Several biological materials have been investigated for the removal of heavy metals and include bacteria, algae, yeast and fungi [3,4,6]. Metal binding by living or dead algae offers promise

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in the treatment of low-grade industrial waste streams and in remediation of environmental metal pollution.

Chromium has found extensive use in tanning industry mainly because of the good quality of leather obtained. When the wastewaters containing chromium are discharged into the environment, they pose a serious problem to the quality of the latter. Removal of chromium from wastewaters is obligatory in order to avoid water pollution. Legislation by different governments, demands the concentration of Cr in discharges be less than 0.5 mg L^{-1} irrespective of its oxidation state [9]. This has lead to removal of chromium from wastewaters before discharge. However the current methods being employed such as chemical precipitation are not feasible to reduce the concentration to the desired levels of 0.5 mg L^{-1} Cr (WHO). Using various micro-organisms as biosorbents for chromium removal, offers a potential alternative to existing methods for its recovery from industrial wastewaters and is subject to extensive studies [10,11]. The objective of this study was to investigate the biosorption of chromium by *Spirogyra condensata* and *Rhizoclonium hieroglyphicum* from aqueous media and its recovery (desorption) from the biosorbents using dilute acids.

2. Materials and methods

2.1. Biosorbents

The algae, *S. condensata* was obtained from a fresh water pond at Egerton University, Njoro, Kenya while *R. hieroglyphicum* was obtained from a fresh water pond at the University of Botswana, Gaborone, Botswana. The sampling sites were chosen because of minimal heavy metal pollution. The algae were each collected from the pond with a beaker and then rinsed with distilled deionized water to remove attached particulate materials. Upon arrival in the laboratory the algae samples were first soaked in 0.5 M HCl for 2 h and rinsed three times with distilled water. The algae were oven dried at 80 °C and then ground into powder (particle size, 450 μm) before use.

2.2. Tannery wastewaters

Two types of tannery effluents were used in this study, namely the treated effluent and the sludge. The treated effluent was used without further treatment except filtration through a 0.45 μm while the sludge was treated as follows: 0.5 g of oven dried sludge was mixed with 10 mL concentrated nitric acid and 10 mL perchloric acid. The sludge–acid mixture was heated at about 120 °C and the liquid evaporated to incipient dryness. Ten milliliters of 0.1 M HCl was added to the residue and the mixture stirred thoroughly, cooled and then filtered through 0.45 μm. The filtrate was placed in 100 mL flask and made to the mark with distilled–deionized water. The chromium content was determined by FAAS.

2.3. Reagents

All chemicals used were of analytical grade unless otherwise stated. Chromium stock solution (1000 mg L^{-1}) was prepared by dissolving $CrCl_3 \cdot 6H_2O$ in distilled–deionized water. Acetate buffer solution was prepared by addition of 0.2 M acetic acid solution to 0.2 M sodium acetate until the desired pH (range 3–6) was attained. Other reagents and materials used include, HCl (0.1 M, 0.5 M), H_2SO_4 (0.1 M), $CaCl_2$ (0.1 M), Amberlite XAD-8. All aqueous solutions were prepared in distilled–deionized water.

2.4. Instrumentation

The Cr content in solution was determined by a Varian flame atomic absorption spectrometer (FAAS) model Spectra AA 220 FS. Fourier transform infra red (FT-IR) spectrophotometer (System 200 FT-IR) was used for functional group analysis.

2.5. Procedures

2.5.1. Effect of pH on chromium binding

The biosorption of chromium was studied in batch equilibrium experiments. The effect of pH in batch equilibrium was investigated as follows: 0.1 g of algae was mixed with 10 mL of 10 mg L^{-1} Cr(III) and the solution buffered with 10 mL of sodium acetate buffer at different pH values of 3, 4, 5 and 6. The mixtures were equilibrated in conical flasks for 2 h. After equilibration the mixtures were filtered and final concentration of chromium in filtrate was determined by FAAS. The same procedure was applied to tannery effluent at optimum pH.

2.5.2. Adsorption isotherm and effect of metal ion concentration

Batch sorption isotherm was determined in 100 mL conical flasks. The amount of chromium ions taken up (q_{eq}) as a function of metal concentration was determined as follows: 0.1 g of finely ground algae was mixed with 10 mL of buffer at pH 4.0 and 5.0 for *R. hieroglyphicum* and *S. condensata*, respectively, and 10 mL Cr(III) of solution in the concentration range, 4–500 mg L^{-1}. Each mixture was agitated for 2 h. The resulting mixture was centrifuged and the concentration of Cr(III) ions (C_{eq}) of the supernatant solution in equilibrium with solid *Spirogyra* spp. determined by FAAS. The same procedure was adopted to determine the concentration in tannery waste.

2.5.3. Adsorption kinetics

Rate of chromium adsorption by *S. condensata* and *R. hieroglyphicum* was studied as follows: approximately 0.1 g of algae was mixed with 10 mL of 10 mg L^{-1} Cr(III) solution and 10 mL acetate buffer at pH 4.0 and 5.0 for *R. hieroglyphicum* and *S. condensata*, respectively. The mixtures were equilibrated in conical flasks. At predetermined time intervals of 10 min, 2 mL of solution was drawn using a syringe fitted with membrane filter and Cr concentration was determined.

2.5.4. Effect of selected metal ions on Cr(III) adsorption

The metal ion solutions of Ca^{2+}, Mg^{2+}, Cu^{2+}, Fe^{3+} and Pb^{2+} were prepared from their nitrate salts namely $Ca(NO_3)_2$, $Mg(NO_3)_2$, $CuSO_4$, $Fe(NO_3)_3$ and $Pb(NO_3)_2$, respectively. The effects of competing metal ions were investigated as follows:

10 mL of 10 mg L^{-1} of Cr(III) solution was mixed with 10 mL of 10 mg L^{-1} of the competing cation and with 0.1 g of algae, at pH 4.0 and 5.0 for *R. hieroglyphicum* and *S. condensata*, respectively. The solution was equilibrated for 2 h, filtered and concentration of Cr in the filtrate was determined by FAAS. Blank sample without competing ions was used as control.

2.5.5. Chromium recovery: desorption agents

Recovery of adsorbed Cr was done using the following desorbing agents: 0.1 M HCl, 0.1 M $CaCl_2$ (in 0.1 M HCl), 0.1 M H_2SO_4 and 0.1 M Na_2CO_3. The agents were investigated in batch equilibration experiments as follows: 0.1 g of algae was mixed with 10 mL of 10 mg L^{-1} Cr(III) and 10 mL of buffer at optimum pH. The mixture was equilibrated in conical flasks for 2 h. The mixture was filtered and Cr concentration determined in the filtrate. A desorption agent (20 mL) was mixed with the residue and equilibrated for 1 h, the resulting mixture was filtered and the filtrate analyzed for Cr(III) concentration. The same procedure was repeated for both tannery wastewater treated effluent and sludge.

2.5.6. Biosorbent immobilization using Amberlite XAD-8

Column studies were carried out by the following method reported by Turker and Baytak [8] with some modifications. Amberlite XAD-8 was washed with methanol, 0.1 M HCl and distilled water to remove any contaminants. Immobilization of algae on XAD-8 was done as follows: 0.3 g of Amberlite XAD-8 was mixed with 15.0 g algae. The mixture was wetted with 2 mL of distilled water and thoroughly mixed. The resulting paste was heated in the oven at 105 °C until it dried. The dry mixture was ground into powder before packing into the column. One gram of Amberlite–algae mixture was packed in a glass column (1 cm i.d. and 20 cm long). The pH of the adsorbent in the column was adjusted to optimum value (4 or 5 depending on the type of algae). Conditioning of Column pH was achieved by passing the acetate buffer at pH 4 or 5 through the column and monitoring the pH of the eluate coming out of the column. Once the desired pH was obtained, the column was ready for use. A standard solution of 100 mL of 10 mg L^{-1} or 100 mL of tannery effluent was passed though the column at a flow rate of 1 mL min^{-1}. A suitable eluent (e.g. 0.1 M H_2SO_4) was passed through the column to recover the adsorbed Cr which was then determined by FAAS. The regenerated algae in the column was subjected to second cycle of adsorption (or recycled).

2.5.7. FT-IR analysis of algae

FT-IR analysis of the algae was done to predict the functional groups on the walls of the biomass responsible for the adsorption process. This was done by mixing approximately 1.0 mg dried sample of algae with 300 mg KBr (1:300), ground to fine powder and pressed under vacuum to a pellet. The pellet was analysed in the range 4000–400 cm^{-1}.

2.5.8. Calculation of Cr(III) uptake by biomass

The amount of Cr(III) accumulated by biomass was calculated as the difference between the amount present in the initial solution and that in the final solution after equilibration with biomass using the following formula:

$$q_{eq} = \frac{(C_0 - C_{eq})V}{M} \quad (1)$$

where q_{eq} (mg g^{-1}) is the amount of metal adsorbed, C_0 and C_{eq} are the dissolved metal concentration in the initial and final equilibrium solutions, respectively, V (in litre) is the volume of solution and M (g) is the mass of biomass.

3. Results and discussion

3.1. Effect of pH on Cr(III) accumulation

It is well documented that pH is an important parameter affecting biosorption of heavy metals [8,12]. The effect of pH on Cr(III) biosorption was studied in the range 3–6. This range was chosen based on studies reported in the literature [7,8]. Chromium(III) ions were found to bind more strongly as the pH was increased from 3 to 5. The pH dependence occurs when metal ions and protons compete for the same active metal binding sites such as carboxylate or amine groups on the algae surface [5,6,15]. The functional groups act as binding sites for the metal ions. The results of the effect of solution pH on Cr(III) adsorption are shown in Fig. 1. The biosorption capacity increased as pH increased from 3 to 5 for *S. condensata*. Above pH 5 a decrease in adsorption capacity was observed. For *Rhizoclonium hieroglyphicum*, adsorption capacity increased from pH 3 to 4 but decreased above pH 4. The highest adsorption capacity values were observed at pH 4 and 5 for *Rhizoclonium hieroglyphicum* and *S. condensata*, respectively, and these pH values were used in subsequent experiments.

The pH affects the availability of metal ions in solution. In explaining the pH dependence of algal biosorbents in heavy metal adsorption, it is important to consider the ionic states of cell wall, functional groups as well the heavy metal solution chemistry at various pH values. Cr(III) exists in solution

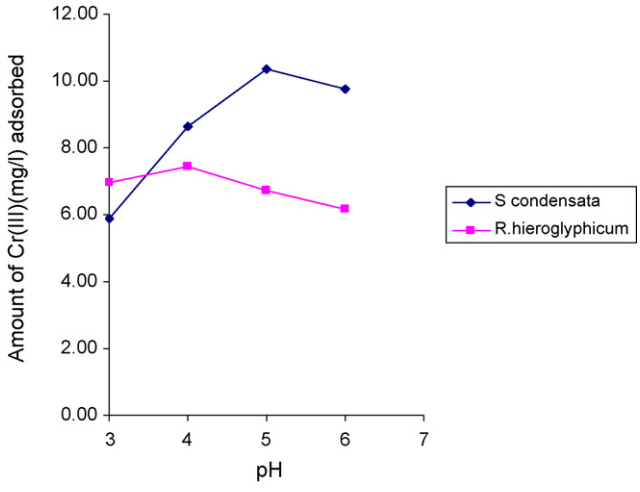

Fig. 1. Effect of pH on Cr(III) adsorption by *Spirogyra condensata* and *Rhizoclonium hieroglyphicum*.

as $Cr(OH)^{2+}$ in the pH range 4–6 [5,6], this implies that its biosorption depends on protonation and deprotonation of the cell wall polymer functional group, relative to their pK_a. The cell walls of algae are mainly composed of cellulose, alganic acid and heterogeneous fucose-containing sulphated polysaccharides as basic building blocks, all of which have ion exchange properties [5,13]. These polymers possess various functional groups which act as binding sites for metal ions. At low pH, the protonation of functional groups gives an overall positive charge to the polymer molecules unable to adsorb positively charged $Cr(OH)^{2+}$, hence reduction in adsorption capacity [6,15]. Increasing the pH reduces the electrostatic repulsion, exposing more ligands carrying negative charges hence increase in adsorption [6,8,14]. Reduction of adsorption of metal ions at high pH (>6) has been attributed to formation of hydroxylated chromium complexes of the metal rendering the latter unable to effectively bind the sorbent [8]. Also increase in pH leads to precipitation of Cr from solution. Reduced Cr adsorption capacity by the two algae at pH < 3 and precipitation of Cr at pH > 6 led us to restrict our studies to pH values between 3 and 6.

3.2. Effect of chromium concentration on biosorption

Results obtained from biosorption of Cr(III) by *S. condensata* and *Rhizoclonium heiroglyphicum* is represented in Figs. 2 and 3, respectively. The Q_{max} (in Eq. (2)) were 14.82 and 11.81 mg g^{-1} for *S. condensata* and *Rhizoclonium heiroglyphicum*, respectively. The biosorption capacity of Cr increased with increase in initial Cr concentration. This increase is attributed to competition for the available binding sites, i.e. most binding sites are unoccupied. High initial concentration provides an important driving force to overcome mass transfer resistance of metal ion between the aqueous and solid phases [14]. Hence a higher initial concentration of chromium(III) should increase the biosorption. Such an effect was clearly demonstrated in Figs. 2 and 3.

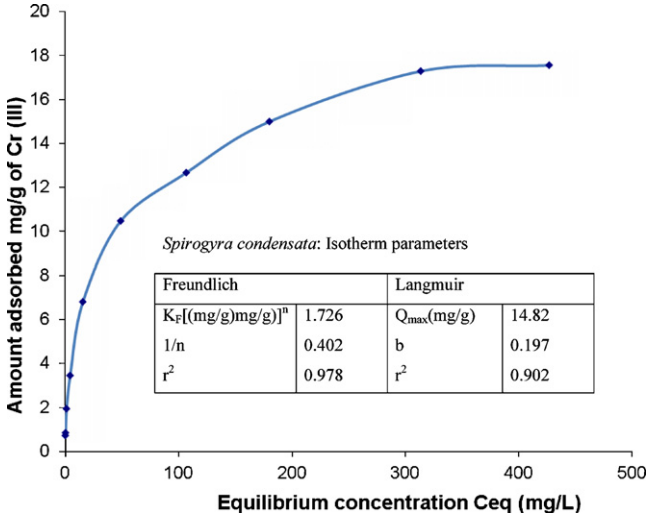

Fig. 2. Effect of Cr(III) concentration on sorbent adsorption by *Spirogyra condensata* at pH 5.

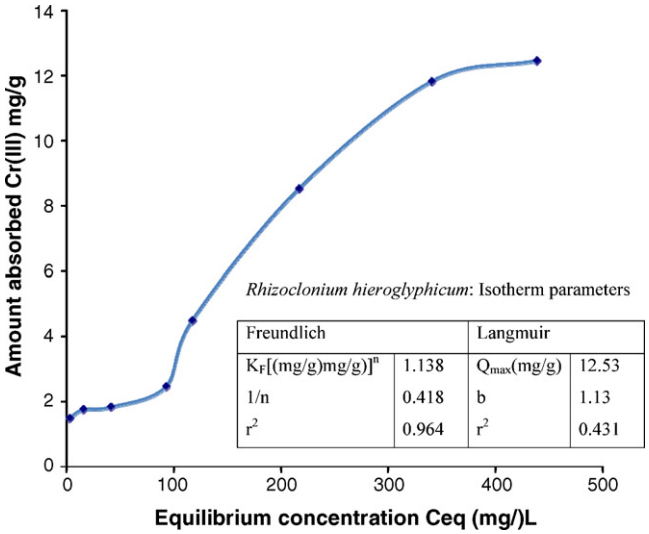

Fig. 3. Effect of Cr(III) concentration on sorbent adsorption by *Rhizoclonium heiroglyphicum* at pH 4.

Chromium(III) removal yield was high (>75%) at low concentration for both algae due to high cell density than at higher concentration of Cr(III), making more binding sites available for adsorption. Low percentage of adsorbed Cr(III) may be due to the fact that the available sites on surfaces of algal cell get saturated, therefore further adsorption of metal ions is prevented [7]. Differences in the amounts adsorbed by the different biomasses can be attributed to difference in functional groups or different cell composition of the two species.

3.3. Adsorption isotherm

Classical adsorption models such as Langmuir and Freundlich have been extensively used to describe the equilibrium established between adsorbed metal ions on the biomass (q_{eq}) and the metal concentration remaining in solution (C_{eq}) at a constant temperature. The Langmuir equation refers to a monolayer sorption into a surface containing a finite number of accessible sites:

$$q_{eq} = \frac{bQ_{max}C_{eq}}{1 + bC_{eq}} \quad (2)$$

where Q_{max} is the maximum quantity of metal ions per unit weight of biomass to form a complete monolayer on the surface (mg g^{-1}), where b is a constant related to the affinity of binding sites with the metal ions. Q_{max} represents a practical limiting adsorption capacity corresponding to the surface of sorbent fully covered by metal ions [15]. The empirical Freundlich equation accounts for sorption on heterogeneous surfaces:

$$q_{eq} = K_F C_{eq}^{1/n} \quad (3)$$

In Eq. (3), K_F is an indicator of adsorption capacity and n indicates the effect of concentration on the adsorption capacity and represents the adsorption intensity [10,15]. All the other symbols have the same meaning as in Eq. (2). Experimental adsorption isotherm parameters (for Freundlich and Langmuir) and corre-

lation coefficient (R^2) data for Cr(III) obtained at optimum pH values, are given as table insets in Figs. 2 and 3 for *S. condensata* and *R. hieroglyphicum*, respectively.

The adsorption isotherms obtained for Cr(III) ions uptake by *R. hieroglyphicum* and *S. condensata* were found to fit well with the Freundlich prediction within the studied metal concentration range (5–500 mg L^{-1}). This observation implies heterogeneous conditions were predominant under the applied experimental conditions. This implies that the biosorption of chromium by the two algae proceed via more than one mechanism and that more than one binding site on the biosorbent may be available.

Other adsorption isotherms fitted include Redlich-Peterson and Dubinin-Radushkevich. Both models did not fit well to experimental data (plots not shown). This implies that the Freundlich isotherm best fits the experimental data (based on the correlation coefficient R^2 values obtained for all the isotherms).

3.4. Sorption kinetics of chromium(III)

Kinetics of sorption describes the rate of solute uptake which in turn governs the residence time of sorption reaction that defines efficiency of sorption [3]. The kinetics of removal of Cr(III) by *S. condensata* and *R. hieroglyphicum* was carried out to study the behavior of the two algae. Biosorption was plotted as a function of time and the result is as shown in Fig. 4. The two curves had similar shapes.

The rate of metal uptake was rather fast and 90% of the total uptake occurred within 40 min. After 40 min, there was a slower uptake rate approaching steady state where no significant adsorption was noted with time. The initial rapid phase within the first 10 min may involve physical adsorption or ion exchange at cell surface and the subsequent slower phase may involve other mechanisms such as complexation, micro-precipitation or saturation of binding sites. Two kinetic models were used to determine the rate of adsorption process of Cr(III) on *S. condensata* and *R. hieroglyphicum*; namely the pseudo-first order and pseudo-second order kinetic models. A series of contact time experiments were carried out with constant initial Cr(III) concentration of 10 mg L^{-1} and constant algae amount of 0.1 g at 298 K. The linear functions of the pseudo-first and pseudo-second-order models used in this study are given in Eq. (4) and (5), respectively [16].

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

q_e and q_t are amount of metal adsorbed at equilibrium and time, t, respectively. k_1 and k_2 are rate constants for pseudo-first order and pseudo-second order models, respectively.

Kinetic equations were solved by the help of MATLAB program and the parameters of the models were determined. The plots of $\log(q_e - q_t)$ against t for the pseudo-first-order equation give a linear relationship and k_1 and q_e values can be

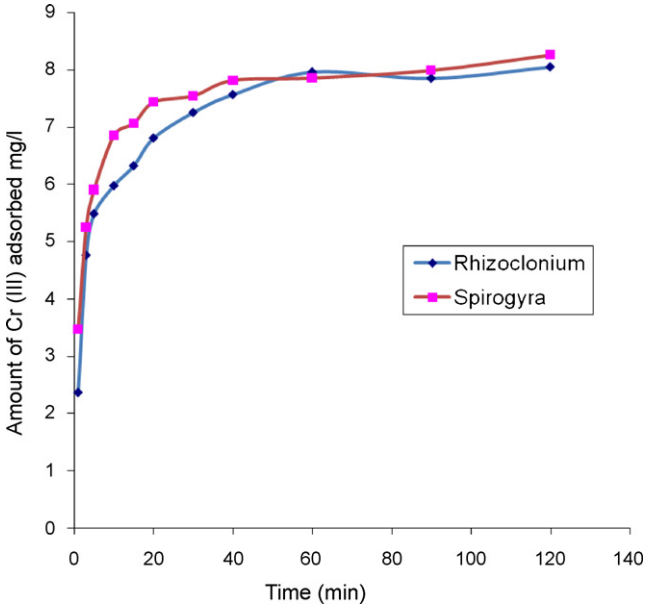

Fig. 4. Kinetics of chromium adsorption by *Spirogyra condensata* and *Rhizoclonium hieroglyphicum*.

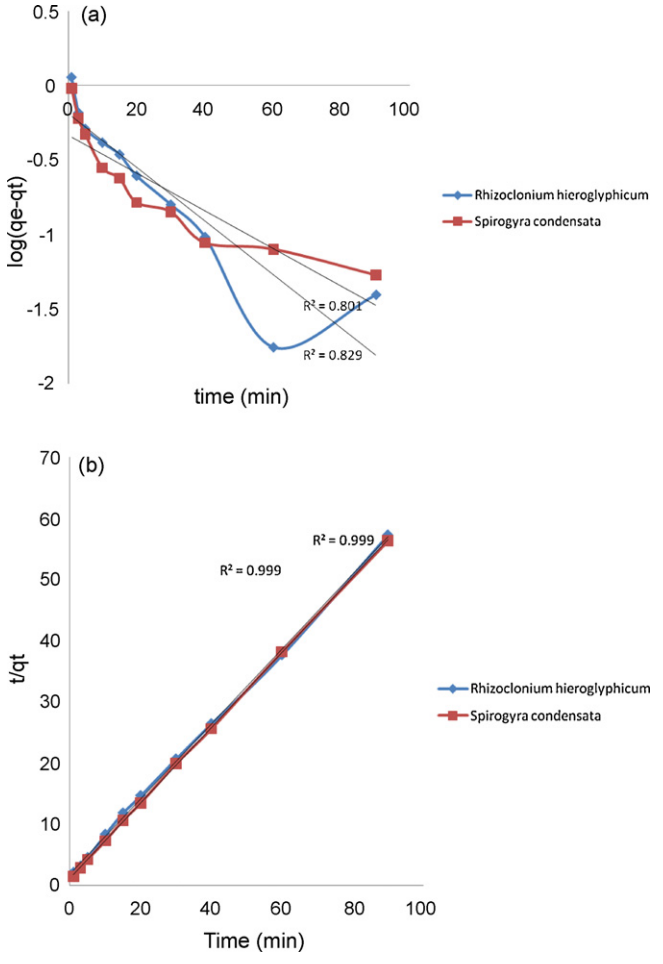

Fig. 5. Plots for the adsorption of Cr(III) on *Spirogyra condensata* and *Rhizoclonium hieroglyphicum* at 298 K: (a) pseudo-first-order kinetics and (b) pseudo-second-order kinetics.

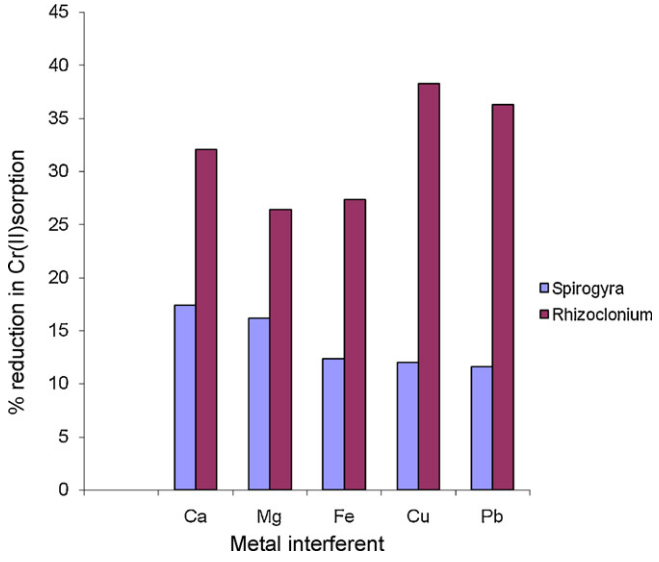

Fig. 6. Effect of different metal ions on adsorption of Cr(III) by *Rhizoclonium*.

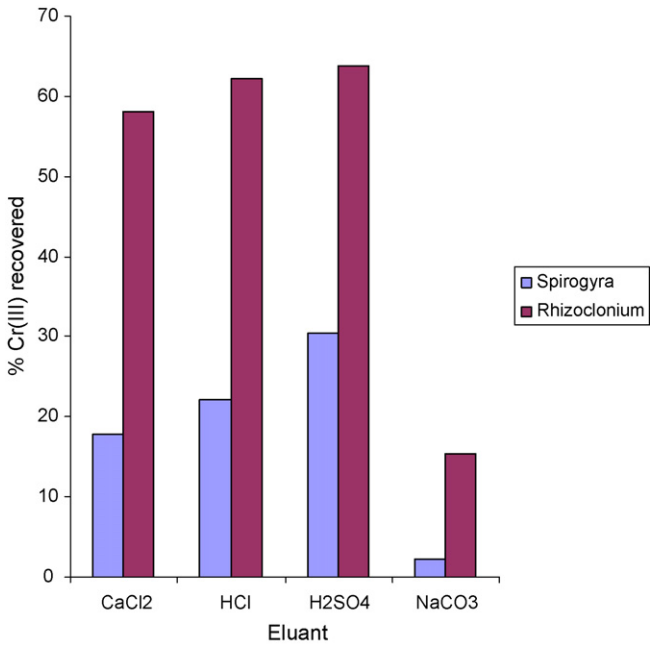

Fig. 7. Percentage recovery efficiency of different desorbing agents.

determined from the slope and the intercept of this equation, respectively. Fig. 5(a) shows the plots of the linear functions of the pseudo-first-order equation. As can be seen from Fig. 5(a), the correlation coefficients (R^2) for the first-order kinetic model obtained at 298 K are 0.801 and 0.823 for *S. condensata* and *R. hieroglyphicum*, respectively. The correlation coefficients are not high, so the adsorption of Cr(III) on *S. condensata* and *R. hieroglyphicum* do not fit pseudo first-order equation. The q_e and k_2 values of the pseudo-second-order kinetic model can be determined from the slope and the intercept of the plots of t/q_t versus t, respectively. Fig. 5(b) gives the results of the linear form of the pseudo-second-order kinetic model. The calculated q_e values for pseudo-second-order kinetic model are closer to the experimental data than the calculated values of pseudo-first-order model. Further the correlation coefficients for pseudo-second-order model are quite high (>0.999). Therefore, the adsorption of Cr(III) can be approximated more favorably by the pseudo-second-order model. The pseudo-second-order model is based on the assumption that the rate-limiting step may be a chemical sorption involving valance forces through sharing or exchange of electrons between adsorbent and adsorbate [16].

3.5. Effect of selected metal ions on Cr(III) adsorption

Fig. 6 illustrates the effect of some cations on the biosorption of chromium(III) ions by *S. condensata* and *R. hieroglyphicum*. The results clearly demonstrate that presence of various cations lead to a significant decrease in the amount of Cr removed from solution by the two algae. Between the two algae, *R. hieroglyphicum* is more affected than *S. condensata*, as Cu and Pb reduce its biosorption by 38% and 36%, respectively. In general, presence of other metal ions decreases the concentration of adsorbed chromium(III). This may be due to competition for the available binding sites. Another reason for the decrease in biosorption could be attributed to ionic strength of the aqueous phase. The presence of cations in the sample will result in increased ionic strength since cations are charged species. Adsorption decreases with increasing ionic strength of aqueous phase. This change may be ascribed to changes in metal activity of the electrical double layer [3]. According to surface chemistry theory, when two phases in aqueous solution are in contact, they are bound to become surrounded by an electrical double layer owing to electrostatic interaction. If the adsorption mechanism is significantly dependent on the electrostatic attraction, adsorption decreases with increase in ionic strength [17]. This observation is in agreement with those obtained by other investigators regarding the ability of biosorbents to bind heavy metal in the presence of competing cations [5,6,18].

3.6. Chromium recovery

The result of metal desorption by different desorbing agents is shown in Fig. 7. For the two types of biosorbents, the desorption efficiency was $H_2SO_4 > HCl > CaCl$ (in HCl) $> Na_2CO_3$. In general, the dilute acids and $CaCl_2$ in HCl had reasonably good recovery efficiency (>55%). Recovery of chromium from *S. condensata* gave a relatively low yield (<40%) compared to *R. hieroglyphicum*. The reason for the low yield could not be established. From this experiment, 0.1 M H_2SO_4 was taken to be the most efficient desorbing agent and therefore was used in subsequent experiments for chromium recovery. Complete recovery (100%) was not achieved possibly implying that mechanism other than ion exchange may be responsible for chromium(III) adsorption.

3.7. Tannery effluent studies

Chromium concentration in tannery effluents: treated effluent (TE) and sludge are $8.26 \pm 0.06\,mg\,L^{-1}$ and $3356.70 \pm 0.25\,mg\,L^{-1}$, respectively. It is noted that both

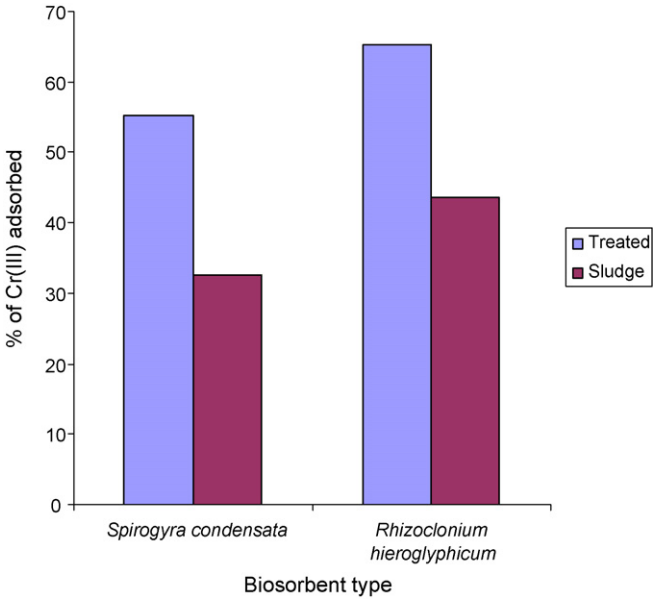

Fig. 8. Percentage adsorbed Cr(III) from tannery effluents by *Rhizoclonium heiroglyphicum* and *Spirogyra condensata*.

treated effluent and sludge contain high concentration of Cr, with the sludge showing significantly higher concentration than the treated effluent. Furthermore, the level of sludge is significantly higher than the world health organization (WHO) limit of 0.5 mg L^{-1}.

3.8. Biosorption of chromium from tannery effluents

The result of adsorption and desorption of chromium are as shown in Figs. 8 and 9, respectively. *R. hieroglyphicum* showed higher adsorption (Fig. 8) for chromium in the treated effluent than *S. condensata*. The adsorbed amount in treated effluent was 55% and 65% for *S. condensata* and *R. hieroglyphicum*, respectively. Percentage adsorptions of Cr in the sludge were 32% and 43% for *S. condensata* and *R. hieroglyphicum*, respectively. These adsorption percentages were low compared to those obtained with synthetic solutions.

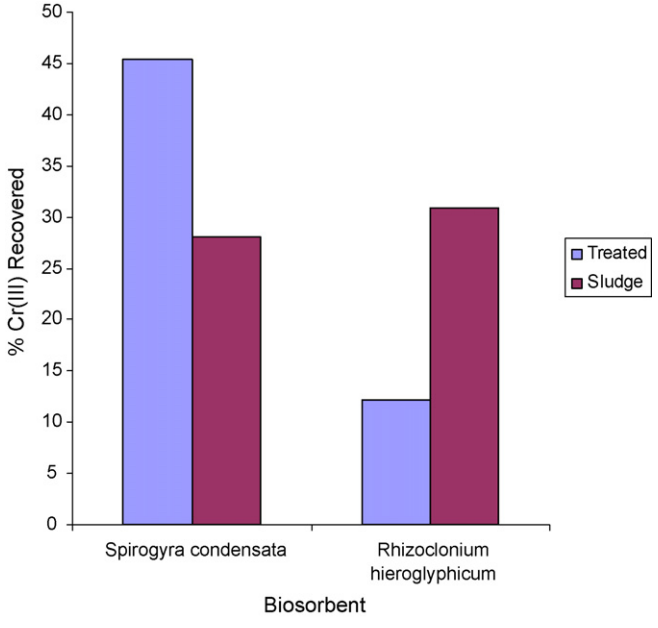

Fig. 9. Percentage recovery of Cr(III) initially adsorbed from treated effluent and sludge for both *Spirogyra condensata* and *Rhizoclonium heiroglyphicum*.

Table 1
Comparison of Cr(III) uptake by different biosorbents (mg g^{-1}): studied in this work vs. literature reports [22–23]

Biosorbent	Adsorption capacity	Reference
Spirogyra condensata	14.82 mg/g	This study
Rhizoclonium heiroglyphicum	11.81 mg/g	This study
Solanum elaeagnifolium	2.78	[19]
Sargassum sp.	41.02	[20]
Padina sp.	43.67	[20]
Sargassum sp.	67.60	[21]

Comparison of adsorption capacities between the two algae studied in the present work, shows that *S. condensata* has slightly higher adsorption capacity (14.82 mg g^{-1}) than that of *Rhizoclonium heiroglyphicum* (11.81 mg g^{-1}). However, when these adsorption capacities are compared against those of other biosorbents reported in the literature [19–21], the two algae in this work have relatively lower values than those in the literature as shown in Table 1, except for *Solanum elaeagnifolium* with 2.78 mg g^{-1} [19].

The low adsorption capacity could be attributed to presence of interfering matrices in the effluents such as cations which compete with chromium for the binding sites. Analysis of the samples (treated effluent and sludge) showed Ca and Mg concentration (data not shown) to be in the range of 40 mg L^{-1}. However, other cations such as Fe^{3+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, etc. expected to be present, were not detected. From previous studies on the same tannery effluent by [22], the composition of tannery effluent was shown to have mainly Cr, Ca and Mg as well as organic substances of animal origin. Levels of other metals were insignificant.

Low levels of adsorption may also be attributed to presence of other binding materials such as ligands capable of binding chromium more strongly than the algae therefore making the metal unavailable for adsorption by the algae. The concentration of chromium recovered during desorption (Fig. 9) was low for both of the algae (<45%). Low recovery may be attributed to presence of interfering cations which may be given desorption preference over Cr(III).

3.9. Biosorbent immobilization by Amberlite XAD-8

The batch experiments have demonstrated the ability of the algae (biomasses) to bind chromium from solution. However, it is not feasible to apply batch system to the treatment of wastewater because of the tedious procedure required for separating the analyte from the sorbent by filtration. A practical approach to removing metal ions from wastewaters with biomass would be to pass the effluent through a column con-

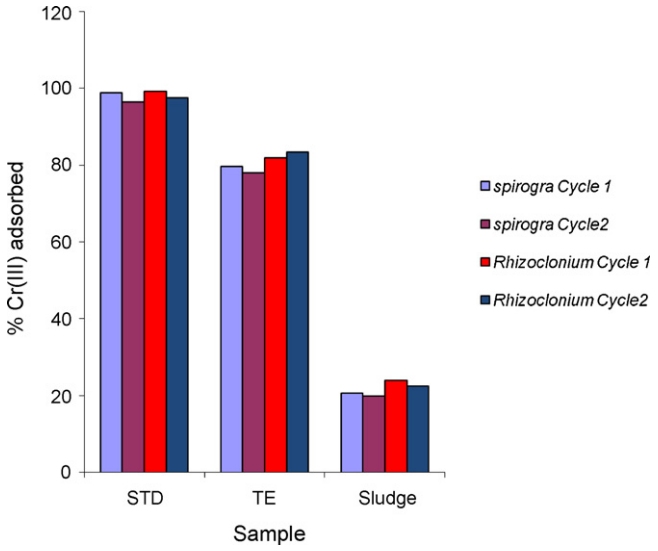

Fig. 10. Performance of Amberlite XAD-8 immobilized *Spirogyra condensata* and *Rhizoclonium hieroglyphicum* in percentage chromium(III) adsorption.

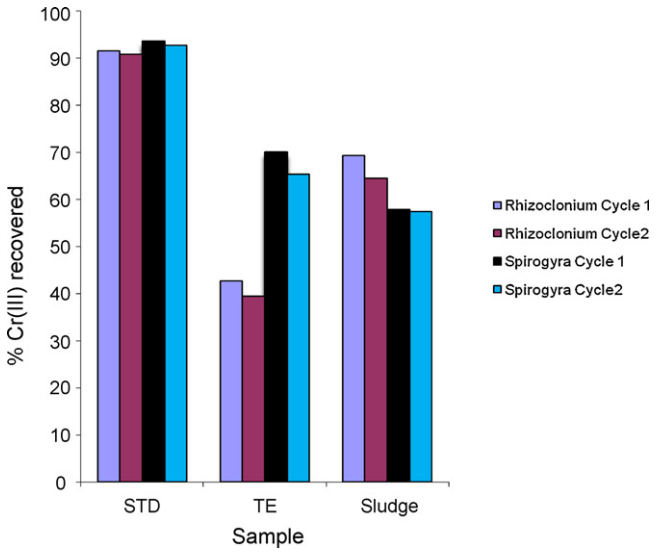

Fig. 11. Percentage recovery of Cr(III) by Amberlite immobilized *Spirogyra condensata* and *Rhizoclonium hieroglyphicum* biomasses with 0.1 M H_2SO_4.

taining the biomass. In this study, the algae were immobilized on Amberlite XAD-8 packed in a glass column. Amberlite XAD-8 was investigated for Cr(III) adsorption prior to use for immobilization of algae. It did not show any Cr(III) adsorption activity hence making it suitable for algae immobilization. Results (Fig. 10) showed the algae in column studies to have relatively higher efficiency for chromium recovery than batch (unimmobilized algae) experiments. A possible explanation for improved biosorption when the algae is immobilized on XAD-8 as a support, could be that immobilization results in a relatively larger surface area of algae binding sites, than when it is not immobilized.

Fig. 10 shows the percentage Cr(III) adsorbed in the column in replicate runs for synthetic solution and real samples. A relatively higher percentage of adsorbed Cr was observed in the synthetic solution (STD) than for the tannery effluents (treated effluent, TE and sludge). The high sorption in the synthetic solution could be due to lack of competing cations as opposed to the real sample matrix that may contain other cations such as Ca^{2+} and Mg^{2+}. The low adsorption in the tannery samples could be attributed to the presence of interfering cations competing with chromium for the available binding sites as well as ligands competing with algae functional groups, for chromium. Comparing treated effluent and sludge, better adsorption of Cr(III) was observed in treated effluent than in the sludge. A possible reason for high adsorption capacity in the treated effluent could be the relatively low Cr(III) concentration in the treated effluent. If this explanation holds, it would then imply that both *R. hieroglyphicum* and *S. condensata* are suitable for low Cr(III) concentrations. Another possible explanation is that since sludge has complex sample matrix, it is possible a fraction of Cr is either in precipitated form or highly complexed by the protein substances of animal origin present in the sludge, a characteristic of tannery effluents [22].

The results of replicate analyses indicate that biosorption capacity for consecutive runs is not significantly different based on statistical *t*-test ($p = 0.05$). This implies that the biosorbent could be recycled.

The results for chromium recovery by immobilized algae on Amberlite XAD-8 are shown in Fig. 11. The recovery of adsorbed chromium is high for synthetic solution (>90%) compared to that of tannery effluents (<75%). The low recovery results for tannery effluents are consistent with those obtained in batch experiments. Similar explanation as that given for batch experiment applies to column studies. In addition, since algae is expected to have different binding sites for holding different types of interfering cations with varying strengths, it is possible that during recovery the loosely held cations may be eluted first with Cr being among the last of the cations to be eluted due to, possibly its relatively high affinity for the algae binding sites [5].

Table 2
Characteristic FT-IR absorption wavenumbers for (A) *Spirogyra condensata* and (B) *Rhizoclonium hieroglyphicum*

Wave number (cm^{-1})	Band assignment
A	
3622	–OH monomeric alcohols, phenols, N–H amine stretches
3341	–OH hydrogen bonded alcohol
2925	–C–H alkane stretches
2360	–CC– triple bond (alkynes)
1656	–C═O aldehydes, ketones, carboxylic acid
1038	–C—O stretches. Alcohols, ethers, carboxylic acid, esters.
B	
3341	–OH hydrogen bonded alcohol
2924	–C–H alkane stretches
2360	–CC triple bond (alkynes)
1659	–C═O aldehydes, ketones, carboxylic acid
1540	–N–H amine bends
1242	–C–N amine stretches
1057	–C–O stretches. Alcohols, ethers, carboxylic acid, esters

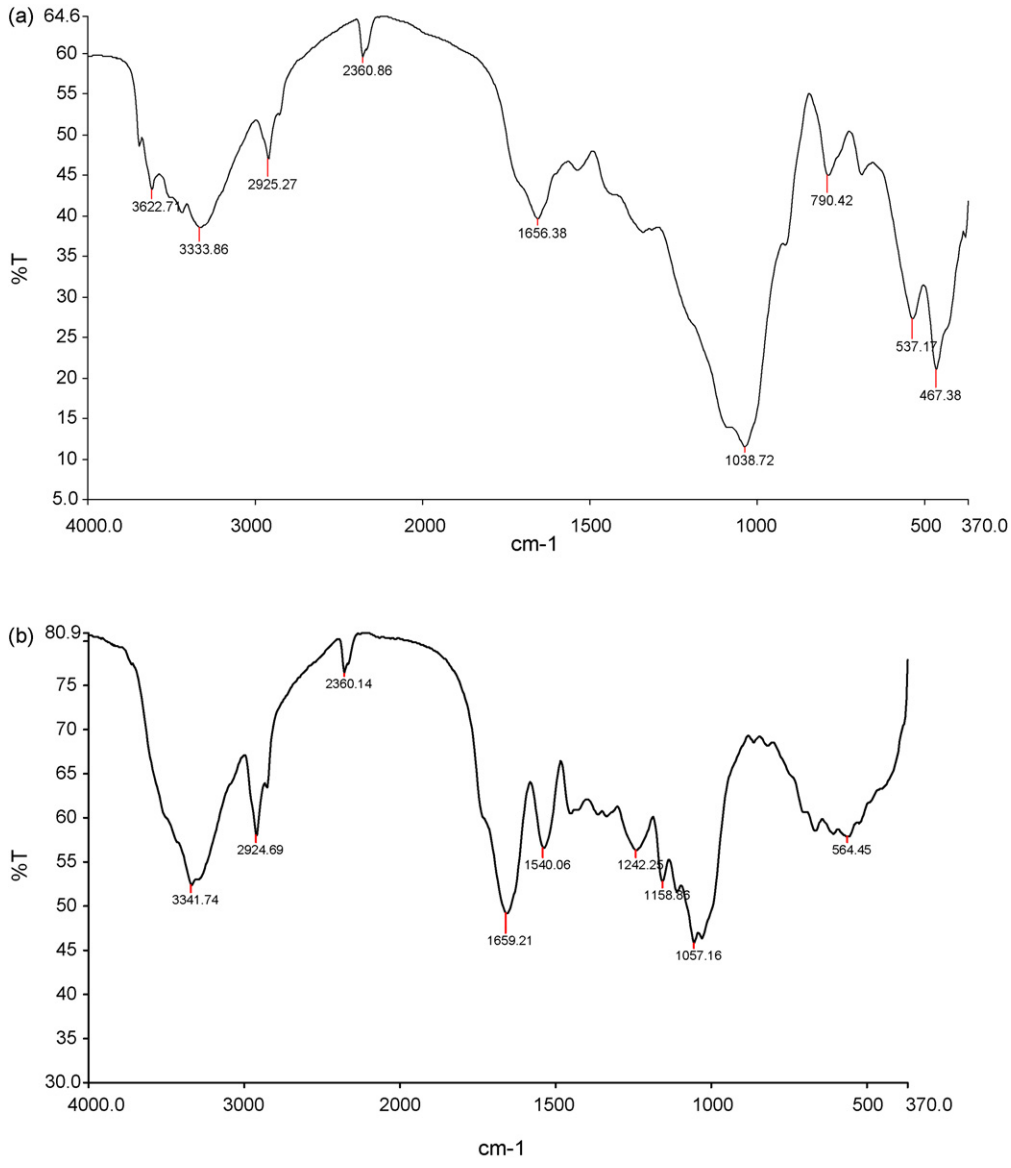

Fig. 12. Infra-red (FT-IR) spectra of (a) *Spirogyra condensata* and (b) *Rhizoclonium hieroglyphicum*.

3.10. FT-IR analysis of S. condensata and R. hieroglyphicum

The profiles by FT-IR spectroscopy for *S. condensata* and *R. hieroglyphicum* are as shown in Fig. 12(a) and (b), respectively. The functional groups suggested here agree with those reported in other studies on infrared spectra of biomass [3,18]. FT-IR spectra of both algae showed the presence of characteristic absorption bands of hydroxyl groups (–OH), amines ($–NH_2$), alkyl (–C–C), carbonyl (–C=O), carboxylic acids (–COOH) and esters (–COOR). *Rhizoclonium hierogyphicum* showed extra peaks in addition to those observed for *S. condensata*. A complete list of absorption peaks and band assignment is given in Table 2(A) and (B). The carboxylate group is believed to be the main binding site via ion-exchange mechanism [4,23]. Co-ordination of chromium may also be taking place via the oxygen of the carbonyl group, C=O. This may further explain why the optimum pH for adsorption in the two algae, is between 4 and 5 because the pK_a of carboxylic acid lies in the same range.

4. Conclusions

Spirogyra condensata and *R. hieroglyphicum* demonstrated good capacity for chromium biosorption when the concentration was less than 100 mg L^{-1}. The study also demonstrated that pH has a strong effect on biosorption capacity of the two algae. The optimum pH was 4.0 for *R. hieroglyphicum* and 5.0 for *S. condensata*. The Freundlich and Langmuir adsorption models were fitted and it conformed well to the former predicting the presence of more than one binding sites. FT-IR analysis revealed the presence of carboxyl and amine groups that may act as binding sites. The result obtained here showed that both species are good as adsorbing media for synthetic solutions of Cr(III) hence

can yield high adsorption values for wastewaters containing Cr(III) with low interference. Thus the presence of competing cations affected Cr(III) uptake negatively. The biosorption of chromium was rapid (>90% Cr in the initial solution) within 40 min. Recovery studies showed the treated effluent to have relatively good yield (65%) with dilute sulphuric acid (0.1 M) being the best desorbing agent. Column studies with immobilized algae on Amberlite XAD-8 showed better results than in the batch process without Amberlite XAD-8. In general the two algae immobilized on XAD-8 showed relatively better performance of Cr removal particularly from the treated effluent (65–70%) by *S. condensata*. The performance of the algae in sludge was relatively lower (55–65%). This was predicted to be due to the highly complex matrix of the tannery effluent which contains largely organic substances of animal origin that pose interference for the algae, to effectively bind and hence remove Cr.

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References

[1] E. Romera, F. Gonzalez, A. Ballester, M.L. Blázquez, J.A. Muñoz, Comparative study of biosorption of heavy metals using different types of algae, Bioresour. Technol. 98 (2007) 3344–3353.
[2] B. Preetha, T. Virithagiri, Biosorption of zinc(II) by *Rhizopus arrhizus*: equilibrium and kinetic modeling, Afr. J. Biotechnol. 6 (2005) 506–508.
[3] G. Naja, C. Mustin, B. Volesky, J. Berthelin, A high-resolution titrator: a new approach to studying binding sites of microbial biosorbents, Water Res. 39 (2005) 579–588.
[4] H.L. Ehrlich, C.L. Brierley, Microbial Mineral Recovery, McGraw-Hill, New York, 1990.
[5] M. Loukidou, A. Zouboulis, T. Karapantsios, K. Matis, Equilibrium and kinetic modeling of chromium(VI) biosorption by *Aeromonas caviae*, Coll. Surf. A: Physcicochem. Eng. Asp. 242 (2004) 93–104.
[6] J.T. Matheickal, Q. Yu, Biosorption of lead(II) from aqueous solutions by pre-treated biomass of Australian marine algae, Bioresour. Technol. 69 (1999) 223–229.
[7] J.P.V. Vilar, M.S. Cidália, A.R. Boaventura, Influence of pH, ionic strength and temperature on lead biosorption by Gelidium and agar extraction algal waste, Process Biochem. 40 (2005) 3267–3275.
[8] J.L. Zhou, P.L. Haung, R.G. Lin, Sorption and desorption of Cu and Cd by macroalgae and microalgae, Environ. Poll. 101 (1998) 67–75.
[9] N. Bishnoi, R. Kumar, S. Kumar, S. Rani, Biosorption of Cr(III) from aqueous solution using algal biomass *spirogyra* spp, J. Hazard. Mater. 145 (2007) 142–147.
[10] M. Horsfall, A. Abia, A. Spiff, Removal of Cu(II) and Zn(II) ions from wastewater by cassava (*Manihot esculenta*) waste biomass, Afr. J. Biotechnol. 10 (2003) 360–364.
[11] X. Hana, Y.S. Wong, M.H. Wong, N.F.Y. Tama, Biosorption and bioreduction of Cr(VI) by a microalgal isolate, *Chlorella miniata*, J. Hazard. Mater. 146 (2007) 65–72.
[12] Z.Y. Lia, S.Y. Guo, L. Li, Study on the process, thermodynamical isotherm and mechanism of Cr(III) uptake by *Spirulina platensis*, J. Food Eng. 75 (2006) 129–136.
[13] A. Turker, S. Baytak, Use of *Escherichia coli* immobilized on Amberlite XAD-4 as a solid phase extractor for metal preconcentration and determination by atomic absorption spectroscopy, Jpn. Soc. Anal. Chem. 20 (2004) 329–334.
[14] S. Ilhan, M. Nourbakhsh, S. Kilicarslan, H. Ozdag, Removal of chromium, lead and copper from industrial waste by *Staphylococcus saprophyticus*, Turk. Electron. J. Biotechnol. 2 (2004) 50–57.
[15] G. Domnez, Z. Aksu, Removal of chromium from saline wastewater by *Dunaliella* species, Process Biochem. 38 (2002) 751–762.
[16] D. Mohan, K.P. Singh, V.K. Singh, Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth, J. Hazard. Mater. B135 (2006) 280–295.
[17] Y. Goksungur, S. Uren, U. Guvenc, Biosorption of copper ions by caustic treated waste baker's yeast biomass, Turk. J. Biotechnol. 27 (2003) 23–29.
[18] J.Z. Xie, H. Chang, J.J. Kilbane II, Removal and recovery of metal ions from wastewater using biosorbents and chemically modified biosorbents, Bioresour. Technol. 57 (1996) 127–136.
[19] T.H. Baig, A.E. Garcia, K.J. Tiemann, J.L. Gardea-Torresdey, Proceedings of the 1999 Conference on Hazardous Waste Research, pp. 131–137.
[20] P.X. Sheng, L.H. Tan, J.P. Chen, Y.P. Ting, Biosorption performance of two brown marine algae for removal of chromium and cadmium, J. Disper. Sci. Technol. 25 (5) (2004) 681–688.
[21] E.A. Silva, E.S. Cossich, C.G. Tavares, L.C. Filho, R. Guirardello, Biosorption of binary mixtures of Cr(III) and Cu(II) ions by *Sargassum* sp. Braz. J. Chem. Eng. 20(3) (2003) 283–289 (cited in http://www.scielo.br/scielo.php, 04 February 2005).
[22] J.K. Kiptoo, J.C. Ngila, Voltammetric evaluation of binding abilities of tannery effluents by competing ligand exchange method using synthetic solutions of Cr(VI), Ni(II), Cu(II) and Pb(II), Chem. Spec. Bioavail. 17 (3) (2005) 103–108.
[23] V. Murphy, H. Hughes, P. McLoughlin, Cu(II) binding by dried biomass of red, green and brown macroalgae, Water Res. 41 (2007) 731–740.