Biosorption of chromate anions from aqueous solution by a cationic surfactant-modified lichen (*Cladonia rangiformis* (L.))

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ABSTRACT

Biosorption has been appearing as a useful alternative to conventional treatment systems for the removal of toxic metals from aqueous stream. The batch removal of chromate anions (CrO_4^{2-}) from wastewater under different experimental conditions using a cationic surfactant-modified lichen (*Cladonia rangiformis* (L.)) was investigated in this study. Cetyl trimethyl ammonium bromide (CTAB) was used for biomass modification. The results of the experiments showed that biomass modification substantially improved the biosorption efficiency. Effects of pH, biosorption time, initial CrO_4^{2-} concentration, biosorbent dosage, and the existence of the surfactant on the biosorption of CrO_4^{2-} anions were studied. Studies up to date have shown that the biosorption efficiency of chromium increased as the pH of the solution decreased. In the present study, the removal of chromate anions from aqueous solutions at high pH values with surfactant-modified lichen was investigated. From the results of the experiments it was seen that the removal of chromate anions by modified lichen was 61% at the solution natural pH (pH 5.11) but at the same pH value the removal of chromate anions by unmodified lichen was 6%. Also concentrations ranging from 30 to 150 mg/L Cr(IV) were tested and the biosorptive removal efficiency of the metal ions from aqueous solution at high pH was achieved more than 98%.

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1. Introduction

Wastewater produced in many industrial processes often contains toxic and heavy metals that are not amenable to direct treatment systems. Although such wastewaters may be treated by the conventional physical–chemical methods like reverse osmosis, ion exchange, chemical precipitation or lime coagulation these processes require either high energy consumptions or expensive synthetic resins and chemicals. Moreover, these methods are ineffective at lower concentrations of metal ions and also generate large quantity of toxic sludge, which is to be disposed in further steps [1,2].

Therefore, there is an urgent need for development of innovative but low-cost processes, where metal ions can be removed economically [3]. The uptake of metal ions by dead cells could simply be defined as biosorption [4]. Biosorption of heavy metals by microbial biomass has been suggested as a potential alternative to the existing physico-chemical technologies for detoxification and recovery of toxic and valuable metals from wastewaters [5]. The biomass

employed is often byproducts of food, beverage, or pharmaceutical production, and may be a viable alternative for the development of an inexpensive biosorption process [6].

The uptake of heavy metal ions by microorganisms is classified into three categories as; cell surface binding, intercellular accumulation, and extracellular accumulation [7]. In the biosorption process a physico-chemical reaction occurs between metal species and cell components of live and dead cell material [8]. Bioaccumulation is the preferred term in the case that living organisms are used. The uptake of metal ions by dead cells also can be defined as biosorption. Several investigators have reported the potential use of living and dead microbial biomass or plants to adsorb heavy metal ions from aqueous solutions [7,9]. The nonliving biomass of bacteria [10], fungi [1,8], yeast [11,12], algae [13,14], lichen [15–17], and plant material [18] has been reported as a method of effective and economical removal of a variety of toxic heavy metals from wastewater.

The cell walls of biomass contain many potential sites for the sorption ions, and it is unlikely that only one type of molecule or functional group would be responsible for the adsorption of the metals [19]. The chemical structures, the hydrophobic and polar characters of the microbial cells, are the most important [20]. The groups including carboxlylate, hydroxyl, sulfate, phosphate, amide,

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and amino groups on the biomass surface are found to be responsible for metal sorption [1,6,21].

Most researchers using native biomass have reported unsatisfactory performance due to their poor mechanical strength and low sorption capacity (less then 30 mg/g). In order to increase the sorption capacity of biomass for metal ions, some researchers investigated the surface modification of the biomass [6,20,22,23]. The effect of physical and chemical pre-treatment processes appeared to enhance the metal (usually cations) biosorption capacity. Physical methods commonly include heat treatment, autoclaving, and freeze drying or boiling, whereas chemical methods include contact with acids, alkali or organic chemicals [22]. There are some biosorption researches to remediate various metals with special modified biomass up to date. Loukidou et al. [22], studied removal of arsenates with surfactant and a cationic polyelectrolyte modified *P. chrysogenum* biomass. Bai and Abraham [1] investigated the biosorption of Cr(VI) by chemically modified biomass of *Rhizopus nigricans*. Bayramoğlu et al. [20], searched hexavalent chromium biosorption onto the untreated and heat-, acid- and alkali treated *Lentinus sajor-caju* mycelia from aqueous solution. Tiemann et al. [23] tried to remove lead(II) by chemically modified alfafta biomass. Park et al. [21] achieved the biosorption of hexavalent chromium by chemically treated biomass of *Eclonia* sp. All of these studies showed that biomass modification substantially improved the biosorption efficiency.

Lichens are usually slow-growing organisms consisting of a fungus and an alga or cyanobacterium which combine in a symbiotic relationship with several unique physiological and morphological characteristics [24]. Lichens do not have a complex root system, waxy cuticle or stoma, and hence they obtain most of their nutrients from the atmosphere through wet and dry deposition [25]. Lichens have been widely used as air pollution monitors because of their ability to strongly bind and accumulate metals [26,27]. The metal-ion binding properties of lichens have been found that nonliving lichen biomass is able to bond metal-ions to a greater degree than living lichens [27] because the living plasma membrane excludes metals from entering the cell [28]. The mechanism cation uptake by lichen is generally regarded as an abiotic process governed by surface complexation of cations with exposed functional groups on the lichen surface [29]. Carboxylic, hydrocarboxlic acids and chitin heave been suggested as metal binding ligands in lichen [28]. There are some studies related the use of lichens as biosorbent in the literature. Uluozlu et al. tried to remove Pb(II) and Cr(III) by *Parmelina tiliaceae* [17], Sari et al. also studied biosorption of Ni(II) and Pb(II) by *Cladonia furcata* [16], Pipiska et al. removed Co^{2+} by *Hypogymnia physodes* [29], Dogan et al. [30] and Turhan et al. [31] used *Cetraria islandica* (L.) and *Usnea longissima* for Au(III) and Cu(II) uptake and Ates et al. removed Ni(II) and Cu(II) by *Pseudevernia furfuracea* (L.) [24] from aqueous solutions.

The terricolous fruiticosa *Cladonia rangiformis* [32] is the most common lichen type found in a wide range of habitats including heaths, dunes, coastal plains, lichen woodlands, bogs and tundra [31]. Its appearance is bush-like; its color is grey if it is dry. Its colour changes to green when it gets wet [33]. Individuals of this type accumulate high amounts of heavy metals [34]. Chettri et al. studied uptake of Pb, Cu and Zn by living and dead *C. rangiformis* [28] and Ekmekyapar et al. achieved to remove 76.5% of Pb(II) by *C. rangiformis* [15] from aqueous solutions.

Chromium is commonly used in industrial applications, such as in tanning processes, electroplating, pigmentation, textile dyeing, or as a catalyst for corrosion inhibitors and wood preservatives [1,21]. All of these industrial processes exceed the permissible limit of 0.05 mg/L in drinking water. Over-exposure of chrome workers to chromium dusts and mists has been related to irritation and corrosion of the skin and the respiratory tract, and to lung carcinoma.

Ingestion may cause epigastric pain, nausea, vomiting, severe diarrhea, and haemorrhage [35]. Chromium exists in several oxidation states. The most stable and common forms are the trivalent Cr(III) and the hexavalent Cr(VI) species, which display quite different chemical properties. Cr(VI), considered the most toxic form of Cr, is usually associated with oxygen as chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) ions. The hexavalent form is considered to be a group 'A' human carcinogen because of its mutagenic and carcinogenic properties [1].

2. Methods

2.1. Preparation of Cr(VI) solution

$K_2Cr_2O_7$ was obtained from Merck (Darmstadt, Germany). A stock solution (1000 mg/L) of Cr(VI) was prepared by dissolving required quantity of $K_2Cr_2O_7$ in deionized distilled water. For biosorption experiments, Cr solution having 30–150 mg/L was prepared and used.

2.2. Preparation of biomass

The lichen biomass of *C. rangiformis* was used as a biosorbent for the biosorption of CrO_4^{2-} anions. Samples of the lichen were collected from the East Black Sea region of Turkey in July and August of 2003. They were washed with deionized water and inactivated by heating in an oven at 80 °C for 48 h. The inactivated dried lichen biomass was grounded and sieved through the following sizes: 75–180, 180–300, 300–425, 425–600 μm. 180–300 μm fraction was used in all experiments.

2.3. Modification of the biomass

Cetyl trimethyl ammonium bromide (CTAB) was obtained from Sigma Corp. (St. Louis, MO, USA) and used as received. CTAB sorption isotherms were developed in a batch reactor. 0.5 g/L of lichen and 350 mg/L of CTAB was mixed in a 250 mL of flasks and stirred at 150 rpm for 2 h. Preliminary experiments showed that the equilibrium between CTAB and yeast cells was reached in less than 2 h. After 2 h, some liquid was transferred to a centrifuge tube, and then solid and liquid were separated at 5000 rpm. Supernatant was analyzed for CTAB. CTAB sorption isotherms were developed in a batch reactor.

2.4. Biosorption studies

The biosorption experiments were also conducted using 250 mL of Erlenmeyer flasks. The stock solutions of CrO_4^{2-}, CTAB and lichen were added to the flasks at prescribed amounts and then the volume of the solution was adjusted to 100 mL by adding DI water. The flasks were stirred at constant speed (150 rpm) for 2 h at 20 °C. The samples were filtered through a cellulose acetate membrane with pore sizes small enough to block the passage of the biomass and adsorbed ions.

2.5. Analysis of Cr(VI) ions

The analyses of Cr(VI) in aqueous samples were determined using a spectrophotometer (UV-160A SHIMADZU) at 540 nm after complexation with 1,5-diphenylcarbazide [2]. The zeta potential of the microorganism cells was measured using the Zeta-Meter (ZETA-METER 3+).
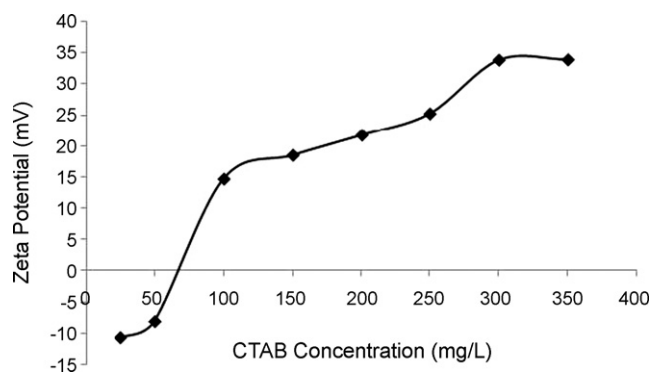
Fig. 1. Effect of CTAB concentration on the zeta potential lichen (lichen concentration = 5 g/L, pH 5.11, T = 20 °C, t = 2 h).

Fig. 2. Cr(VI) biosorption at various pH (initial Cr(VI) (C_o) (100 mg/L, biomass concentration (m) = 5 g/L, CTAB concentration (C_{CTAB}) = 350 mg/L, T = 20 °C, t = 2 h).

3. Results and discussion

3.1. Effect of CTAB concentration on the zeta potential of lichen

The effect of CTAB dosage on the zeta potential of lichen is shown in Fig. 1. The zeta potential of 0.5 g/L of lichen modified with different concentrations of CTAB ranging from 25 to 350 mg/L were studied. The sorption of CTAB to lichen cells changes the surface characteristics of lichen cells. The nonpolar portion of CTAB has most likely interacted with the cell surface and the polar charged head groups pointed towards the bulk solution making the surface potential positive. Similar results for highly hydrophobic surfaces were reported in a recent study in which atomic force microscopy results were presented. It was suggested that at low concentrations, cationic surfactant monomers lie flat to the surface similar to nonionic surfactants [36]. It was also reported that CTAB sorption to activated carbon surface was predominantly hydrophobic forces at the concentrations above 0.3 mg/L (approximately 0.01 mM) [37].

3.2. Effect of pH on CrO_4^{2-} removal

Biosorption of heavy metal ions onto biomass is affected by several factors, including the specific surface properties of the biomass cell wall and the physico-chemical properties of the adsorption medium such as metal ion concentration, temperature, pH, and the amount of biosorbents [38,39]. Earlier studies on metal biosorption have showed that pH was an important parameter affecting the biosorption process [38,40–42]. The optimum pH not only changes for different metals but also varies from one kind of biomass to the others [36]. The pH of the aqueous solution affects the solubility of the metal ions, concentration of the counter ions on the functional groups of biosorbent, and the degree of ionization of the biosorbate during reaction.

The biosorption characteristics of CrO_4^{2-} anions with various pH in the range of 2–10 were studied at initial concentration of 100 mg/L, using 0.5 g/L modified and unmodified lichen as shown in Fig. 2. Temperature and agitation speed were kept at 20 °C and 150 rpm, respectively. The highest biosorption efficiency (19.57%) was obtained at pH 2.0 for unmodified lichen and the efficiency decreased with the increase in pH. This may be attributed to the chemical interactions of metal with the functional groups of biomass cell surface [40,41]. At high pH values, the overall surface charge becomes negative and biosorption is interrupted due to the competition between CrO_4^{2-} anions and OH^- for the same sites. Similar results have been shown by other researchers [18,38,40–44,8]. Earlier studies focused on the adsorption of Cr(VI) under strongly acidic conditions (pH 1–3) because the adsorption amount of Cr(VI) onto these biomaterials steeply decreased
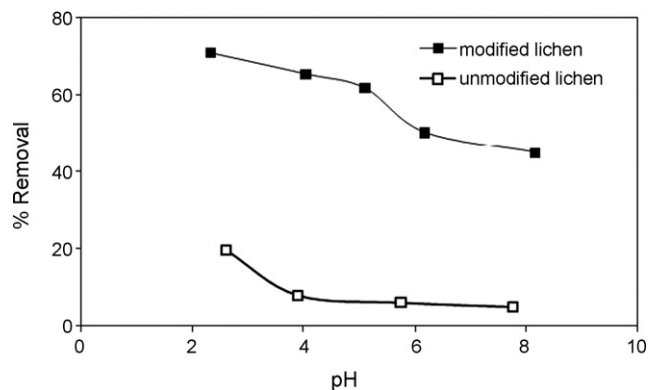
above pH 3. Although it may be possible to control the water's pH in the industrial wastewater treatment process; it is impossible to control the natural water's pH in the environmental remediation process [42]. The removal efficiency of CrO_4^{2-} anions with surfactant-modified lichen at all pH values was bigger than 45% and the removal efficiency was found 61% at the natural pH of the solution (pH 5.11). This was ten times greater than the result (5.98%) obtained with unmodified lichen at the same pH. Higher CrO_4^{2-} removal efficiencies can be attributed to the change of surface characteristics of cells as a result of the sorption of CTAB to the lichen cells.

The effect of pH on the zeta potential of lichen biomass and surfactant-modified lichen without metal ions is illustrated Fig. 3. The zeta potential values could not be measured due to the high ionic strength at pH 2.0, but it was considered that these values of lichen biomass were slightly positive. It can be seen from the figure that the zeta potential of modified cells were all positive. The higher CrO_4^{2-} removal can be attributed to this positive charge of cell wall.

3.3. Biosorption time

The effect of contact time on the biosorption of CrO_4^{2-} anions was studied with 50 mg/L CrO_4^{2-}, 350 mg/L CTAB and 0.5 g/L lichen at natural pH. The mixture of the metal/CTAB solution and dried lichen were continuously stirred in the shaker at 150 rpm for 3 h. The metal uptake was very rapid and the equilibrium was reached within 10 min (Fig. 4). After this equilibrium period, the amount of adsorbed CrO_4^{2-} anions did not significantly change with time.
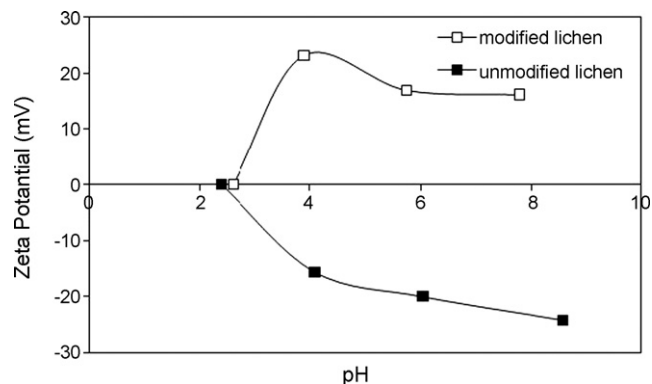

Fig. 3. Relation between zeta potential and pH (m = 0.5 g/L, C_{CTAB} = 350 mg/L, pH 5.11, T = 20 °C, t = 2 h).
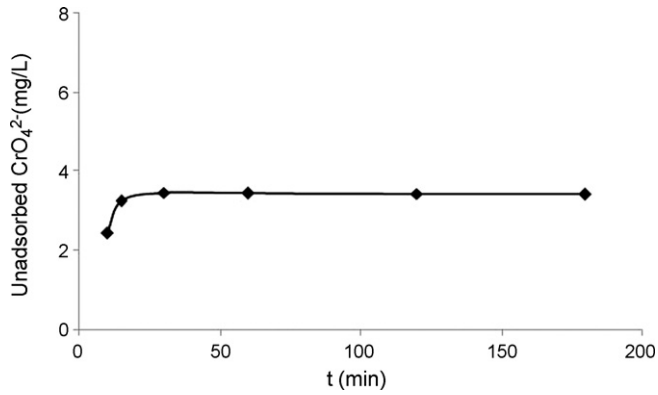
Fig. 4. Effect of stirring time on biosorption ($C_o = 50$ mg/L, $C_{CTAB} = 350$ mg/L, $m = 0.5$ g/L, pH 5.11).

3.4. Effect of initial CrO_4^{2-} concentration on biosorption

The initial metal concentration plays an important role in the process of biosorption. In order to show the effect of the concentration of CrO_4^{2-} anion on the biosorption, sorption experiments were carried out at different initial Cr ion concentration which varied from 30 to 150 mg/L (Fig. 5). The biosorption efficiency decreased with the increase in the initial concentration of the metal ions. At low initial concentrations (<30 mg/L), CrO_4^{2-} anions in the solution interacted with the binding sites and thus facilitated 99% adsorption. At higher concentrations, more CrO_4^{2-} anions have been left un-adsorbed in solution due to the saturation of binding sites.

3.5. Equilibrium models

Two well-known equilibrium models, Langmiur and Freundlich, were applied for the analysis of sorption data obtained at different initial concentrations, keeping the sorbent concentration and CTAB concentration constant at 0.5 g/L and 350 mg/L, respectively. The Langmiur equation [8], valid for a monolayer sorption onto a surface of a finite number of identical sites, can be represented as

$$\frac{1}{q_e} = \frac{1}{Q_{max}} + \frac{1}{bQ_{max}C_e} \qquad (1)$$

where C_e is the residual CrO_4^{2-} concentration (mg/L), q_e is the amount of metal adsorbed (mg/g), Q_{max}(mg/g) and b (L/mg) are the Langmiur constants showing the maximum amount of metal ion adsorbed per unit weight of lichen biomass to form a complete mono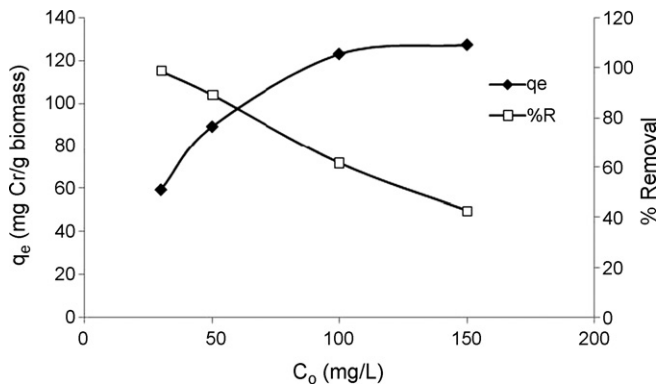layer on the surface bound at high equilibrium metal ion concentration and the energy of the adsorption, respectively. Langmiur isotherm showed linear plot and values of Langmiur constant (Q_{max} and b) calculated from the slope and the intercept of the plot (Fig. 6) are presented in Table 1.

Adsorption capacity was found to be very high for the lichen ($Q_{max} = 125$ mg/g). The essential characteristics of Langmiur isotherm model can be explained in terms of a dimensionless constant separation factor or equilibrium parameter R_L which is defined as

$$R_L = \frac{1}{1 + bC_o} \qquad (2)$$

where b is the Langmiur constant (L/mg) and C_o is the initial concentration (mg/L) [45]. The dimensionless constant separation factor is used to determine if the adsorption favorable or not.

Values (R_L)	Types of isotherm
$R > 1$	Unfavorable
$R = 1$	Linear
$0 < R < 1$	Favorable
$R < 0$	Irreversible

The values of R_L for the present biosorbent was in the range of 0–1, and also the shape of curve (Fig. 7) confirm favorable uptake of CrO_4^{2-} anions by lichen.

The empirical Freundlich adsorption isotherm [46] is obtained on the assumption that the sorption takes place on a heterogeneous adsorbent surface where the sorption energy distribution decreases exponentially. This equation is also applicable to multilayer adsorption and can be expressed as

$$\log q_e = \frac{1}{n(\log C_e)} + \log K_f \qquad (3)$$

where K_f and n are the Freundlich constants which represent the adsorption capacity and the adsorption intensity of the sorbent, respectively.

Freundlich isotherm showed linear plot and values of Freundlich constant (K_f and n) calculated from the slope and the intercept of the plot (Fig. 8) are presented in Table 1. The high values of K_f and n demonstrate high probability of adsorption.

Fig. 6. Langmiur adsorption isotherms for the adsorption of Cr ions onto modified lichen.

Fig. 5. Effect of varying initial concentration of Cr(VI) ions (C_o) on Cr uptake ($q =$ mg Cr/g biomass) and the removal of Cr ions ($m = 0.5$ g/L, $C_{CTAB} = 350$ mg/L, pH 5.11, $T = 20$ °C).
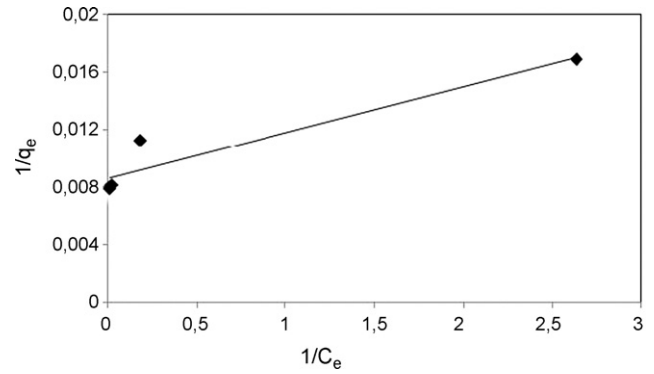
Table 1
Freundlich and Langmiur isotherms regression constants

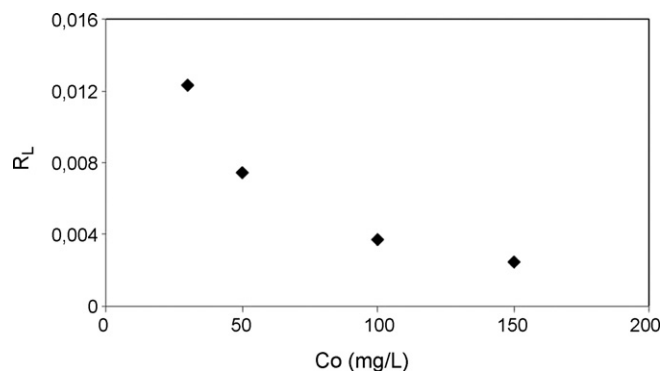| Freundlich isotherm			Langmuir isotherm		
R^2	K_f	$1/n$	R^2	Q_{max}	b
0.96	71.78	0.135	0.91	125	2.67

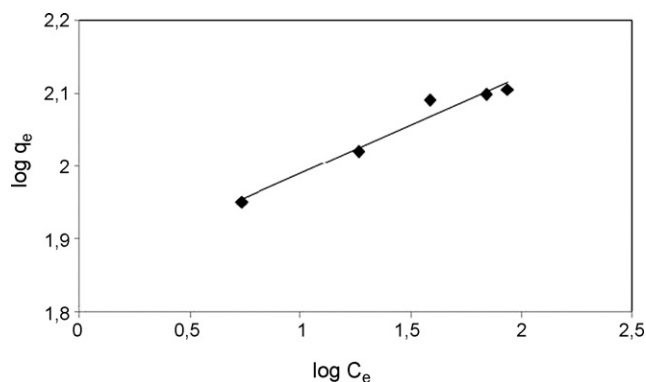**Fig. 7.** Separation factor for the adsorption of Cr ions onto lichen.

Fig. 8. Freundlich adsorption isotherms for the adsorption of Cr ions onto modified lichen.

3.6. Effect of biomass dosage on CrO_4^{2-} removal

The percentage removal of CrO_4^{2-} was studied by altering the biosorbent dose between 0.5 and 10 g/L at a CrO_4^{2-} concentration of 150 mg/L. The lichen/CTAB ratio was stabled as per 0.5 g/L lichen was modified with 350 mg/CTAB. The percentage of CrO_4^{2-} uptake steeply increased with the biomass loading up to 2 g/L (Fig. 9). This may be due to the higher number of available binding sites that interacts with CrO_4^{2-} anions of the solution [2,15,38,40]. Further increase in sorbent concentration did not cause improvement in adsorption. However, Cr uptake values showed a reverse trend. q_e
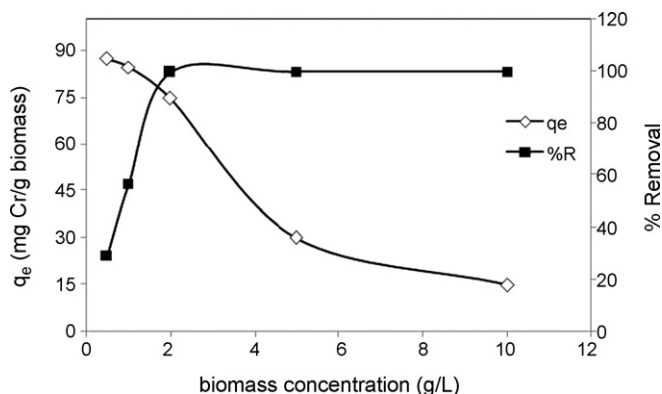

Fig. 9. Effect of biosorbent concentration on Cr uptake and the removal of Cr ions (C_o = 150 mg/L, C_{CTAB} = 350 mg/L, pH 5.11, T = 20 °C).

is the measure of the amount of chromate anions bound by unit weight of biomass and its magnitude decreased with increment in biomass concentration.

4. Conclusion

The batch removal of chromate anions (CrO_4^{2-}) from wastewater under different experimental conditions using a cationic surfactant-modified lichen (*C. rangiformis* (L.)) was investigated in this study. Cetyl trimethyl ammonium bromide (CTAB) was used for biomass modification. The results of the experiments showed that biomass modification substantially improved the biosorption efficiency. The highest biosorption efficiency (19.57%) was obtained at pH 2.0 for unmodified lichen and the efficiency decreased with the increase in pH. The removal efficiency of CrO_4^{2-} anions with surfactant-modified lichen at all pH values was bigger than 45% and the most important result of this study is the removal efficiency (61%) at the natural pH of the solution (pH 5.11). This is 10 times greater than the result (5.98%) obtained with unmodified lichen at the same pH. The adsorption data of modified biomass have been found to be fitting to both Langmiur and Freundlich isotherms.

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