Aminopyridine modified *Spirulina platensis* biomass for chromium(VI) adsorption in aqueous solution

Gulay Bayramoglu, Aydin Akbulut and M. Yakup Arica

ABSTRACT

Chemical modification of *Spirulina platensis* biomass was realized by sequential treatment of algal surface with epichlorohydrin and aminopyridine. Adsorptive properties of Cr(VI) ions on native and aminopyridine modified algal biomass were investigated by varying pH, contact time, ionic strength, initial Cr(VI) concentration, and temperature. FTIR and analytical analysis indicated that carboxyl and amino groups were the major functional groups for Cr(VI) ions adsorption. The optimum adsorption was observed at pH 3.0 for native and modified algal biomasses. The adsorption capacity was found to be 79.6 and 158.7 mg g^{-1}, for native and modified algal biomasses, respectively. For continuous system studies, the experiments were conducted to study the effect of important design parameters such as flow rate and initial concentration of metal ions, and the maximum sorption capacity was observed at a flow rate of 50 mL h^{-1}, and Cr(VI) ions concentration 200 mg L^{-1} with modified biomass. Experimental data fitted a pseudo-second-order equation. The regeneration performance was observed to be 89.6% and 94.3% for native and modified algal biomass, respectively.

Key words | adsorption, algal biomass, aminopyridine, chromium(VI), *Spirulina platensis*, surface modification

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INTRODUCTION

Pollution of the natural water sources occurs by heavy metals through the uncontrolled discharge of the wastewater from industries such as electroplating, textile, metal finishing, leather tanning, wood preservation, nuclear power plant. These types of wastewater are generally considered to be highly toxic to the aquatic living systems, animals and humans (Bayramoglu & Arica 2005a, 2005b; Jayakumar *et al.* 2015; Ye *et al.* 2015; Yang *et al.* 2016). Among the metals, Cr(VI) ions are highly toxic, mutagenic and carcinogenic to living organisms due to their strong oxidizing properties, on the other hand, Cr(III) is relatively less toxic and considered as an essential micronutrient (Kumara *et al.* 2011; Zhang *et al.* 2013; Ren *et al.* 2014; Xu *et al.* 2015). Various methods for the removal of heavy metal ions from wastewater have been investigated such as adsorption, ion-exchange, chemical precipitation, liquid–liquid extraction, membrane filtration, and electrochemical treatment (Solisio *et al.* 2013; Lee *et al.* 2014; Chen *et al.* 2015; Sathvika *et al.* 2015; Blanesa *et al.* 2016; Ramteke & Gogate 2016; Sun *et al.* 2016; Zhou *et al.* 2016). Up to now, a large number of various adsorbents, such biological substances, clay minerals, activated carbon, synthetic polymeric resins (Tavengwa *et al.* 2013; Jayakumar *et al.* 2015) have been utilized for adsorptive removal of Cr(VI) ions. Recently, native or modified algal, fungal, and bacterial biomasses have been used as bioadsorbent in several studies (Bai *et al.* 2010; Bayramoglu *et al.* 2012, 2015; Bhatnagar *et al.* 2012; Aftab *et al.* 2014; Gautam *et al.* 2014; He *et al.* 2014; Bayramoglu & Arica 2016; Tunali-Akar *et al.* 2016). The use of modified biosorbents for the removal of metal ions provides some advantages over their native counterparts (such as enhanced adsorptive capacity and mechanical strength, and good regeneration potential) (Bayramoglu & Arica 2011a, 2011b; Aftab *et al.* 2014; He & Chen 2014). In this context, different kinds of functional groups carrying molecules such as polyamine, amino, carboxyl, amidoxime, and chlorine dioxide have been covalently immobilized onto various adsorbent surfaces to enhance the heavy metal removal capacity of the microbial biomasses (He *et al.* 2014). For example, polyethyleneimine- and amidoxime-modified *Spirulina platensis* biomass were used for removal of uranium ion in batch mode, and the maximum adsorption capacities of

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amidoxime- and PEI-modified, and native algal biomasses were found to be 366.8, 279.5, and 194.6 mg g^{-1}, respectively (Bayramoglu *et al.* 2015). The biomass of *Penicillium chrysogenum* was modified with polyethylenimine (PEI) and then cross-linked with glutaraldehyde, the adsorption capacity of the biomass for copper(II), lead(II) and nickel(II) ions increased significantly (Deng & Ting 2005).

In this study, *S. platensis* biomass surface was modified with 4-aminopyridine, and used for the removal of Cr(VI) ions from aqueous medium by using native counterpart as a control system. The impact of key operational parameters such as solution pH, sorbent dosage and contact time on Cr(VI) ions adsorption by both native and modified *S. platensis* was tested to optimize the adsorption process in a batch system. Finally, the modified *S. platensis* biomass was operated in a continuous system, and the effect of contact time and initial metal ion concentrations were discussed.

MATERIALS AND METHODS

Material

Epichlorohydrin, dimethyl sulfoxide, and 4-aminopyridine were purchased from Sigma-Aldrich Corp., St Louis, MO, USA. All reagents were of analytical purity and used without further purification, and purchased from Merck AG (Darmstadt, Germany).

Microorganism and media

The microalgae *Spirulina platensis* (*Arthrospira platensis*) was isolated from Mogan Lake in Ankara. It was grown in the nutrient medium at 28 °C having a common composition of chemicals: $NaHCO_3$, K_2HPO_4, $MgSO_4$, $CaCl_2$, citric acid, Na_2EDTA, Na_2CO_3, trace metal ion solution, and algal cell suspension were subjected to continuous illumination at a light flux: $U = 6.0 \times 10^{-3}$ J cm^{-2} s^{-1} (Chen 2011).

Preparation of 4-aminopyridine modified *S. platensis* biomass

Spirulina platensis biomass was dried in a vacuum oven at 40 °C until constant weight, then ground and sieved into fractions. The particle size fraction between 150 and 312 μm was used for crosslinking with epichlorohydrin (Luo *et al.* 2006). After the reaction, the epichlorohydrin activated biomass (about 5.0 g, dry weight) was added to water: ethanol mixture (50:50 v/v, 100 mL) containing 4-aminopyridine (1.0 g), and the reaction was carried out at room temperature for 6.0 h. The schematic presentation of the 4-aminopyridine modification reaction of the algal biomass is presented in Figure 1.

Adsorption of Cr(VI) ions on native and modified algal biomasses

Adsorption of Cr(VI) on the native, and modified algal biomass was investigated in batch and continuous systems as described previously (Bayramoglu & Arica 2011b). The concentration of the remaining Cr(VI) ions in the adsorption medium was determined spectrophotometrically at 540 nm after complexation with 1,5-diphenylcarbazide, as described previously (Arica & Bayramoglu 2005). To carry out the desorption studies, the biosorbents from adsorption experiments were gently washed with distilled water, and transferred into HCl (25 mL, 20 mmol L^{-1}) solutions for 2.0 h. The regenerated fungal biomass was washed thoroughly with acetate

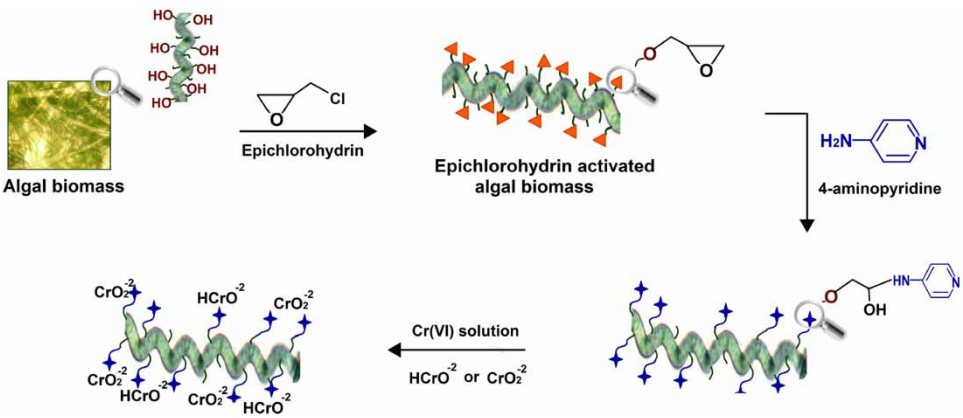


Figure 1 | Chemistry of modification reactions on the algal biomass surface with epichlorohydrin and 4-aminopyridine.

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buffer solution (50 mmol L^{-1}, pH 4.0), and then used for the next sorption–desorption cycle.

For continuous system studies, the continuous system column was made from Pyrex glass (length 10.0 cm, diameter 1.2 cm, total volume about 11.0 mL), and used for continuous mode adsorption studies. The 4-aminopyridine modified algal biomass (wet weight about 6.0 g) was packed between glass wool fillers into the glass column. The continuous system yielding a void volume was about 3.7 mL. The flow rate was regulated between 50 and 250 mL h^{-1} with a peristaltic pump (ISMATEC, IPC Model). The system was operated with 200 mg L^{-1} Cr(VI) ion concentration at 25 ± 0.2 °C and at pH 3.0 for 1.0 h. The effect of initial Cr(VI) ions concentration on the adsorption efficiency was studied between 50 and 400 mg L^{-1} in the feed solution at a flow rate of 50 mL h^{-1}. The residence time corresponding to the given flow rates is calculated by the following equation:

$$D = \frac{v_o}{\varepsilon V} \quad (1)$$

where D is the dilution rate (h^{-1}), v_o the volumetric flow rate of the Cr(VI) ions feed solution (mL h^{-1}), V the total volume of the continuous system (mL) and ε is the void fraction given as ratio of void volume to the total volume of the continuous system. Residence time (τ) is the reciprocal of dilution rate.

$$\tau = \frac{1}{D} \quad (2)$$

In order to investigate the regeneration potential of algal biomass in the continuous flow mode, the system was eluted with 20 mmol L^{-1} HCl and then the packed algal biomass was washed with deionized water.

Characterization of the algal biomasses

The chemical structures of the native and modified algal biomasses were studied using an attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) spectrometer (Nicolet IS 5, Thermo Electron Scientific Instruments, WI, USA). The amounts of the available amino groups of the native and modified algal biomasses were determined by potentiometric titration, as described previously (Bayramoglu *et al.* 2015).

The specific surface areas of the native and modified algal biomasses were determined by N_2 adsorption isotherm and application of the Brunauer–Emmer–Teller (BET) method.

Contact angles to different test liquids (i.e. water, formamide and diiodomethane (DIM) of the native and modified algal biomass film preparations were measured by sessile drop method at 25 °C using a digital optical contact angle meter (Phoenix 150 contact angle analyzer, Suwon city, Kyunggido, Korea), as described previously (Bayramoglu & Arica 2005a, 2005b). The results were analyzed according to van Oss, Good and Chaudury's acid–base method (van Oss *et al.* 1988). The average diameter of the algal biomass particles was determined by dynamic light scattering (DLS) with a Zeta-sizer NanoZS (Malvern Instruments Ltd, Malvern, UK).

RESULTS AND DISCUSSION

Characterization of native and modified algal biomasses

The average specific surface areas of the native, and 4-aminopyridine modified algal biomass were measured by BET method, and found to be 1.81 and 2.84 m^2 g^{-1}, respectively. The measured surface area of the modified algal biomass was higher by 1.57-fold than that of the native counterpart.

The spectra of the native and 4-aminopyridine modified biomass and their Cr(VI) adsorbed counterpart biomasses were measured by an ATR-FTIR spectrometer (Figure 2(a)–2(d), respectively). The peaks at 3,275, 2,919, 1,640, 1,393, 1,046, and 593 cm^{-1} are observed in the spectrum of the native algal biomass (Figure 2(a)). Additionally, the broad spectrum of native algal biomass between 3,400 and 3,200 cm^{-1} could be attributed to the overlapping of the –OH and –NH stretching vibration bands. The bands at 1,194 and 1,046 cm^{-1} exhibited correlative characteristics of C–O stretching vibrations in alcohol and amine groups on the algal biomass surface (Figure 2(a)). In a comparison of the spectra of *S. platensis* biomass with that contacted with Cr(VI) ions, some shift in peak position was observed (Figure 2(b)). These changes were due to the binding of Cr(VI) ions with amino and hydroxyl groups of the biomass. The most remarkable difference amongst these spectra is at an intensity of 3,450–3,000 cm^{-1} representing amine and hydroxyl stretching, and the band at around 1,714 cm^{-1} represents carbonyl (C-O) stretching. These peaks show the involvement of amine, hydroxyl and carboxyl groups in the binding of Cr(VI) ions. After covalent attachment of 4-aminopyridine via epichlorohydrin coupling reaction, the spectrum of the modified algal biomass exhibits some changes (Figure 2(c)). Four peaks were observed at 3,429, 3,301, 3,068 and 2,923 cm^{-1} due to the incorporation of a

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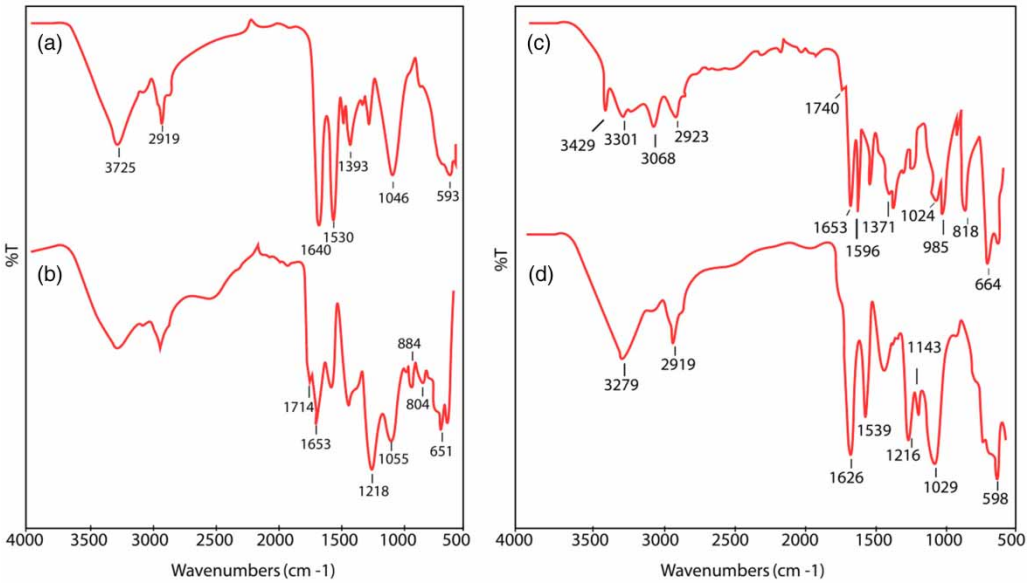


Figure 2 | FT-IR spectra: (a) native algal biomass; (b) native algal biomass after Cr(VI) adsorption; (c) modified algal biomass; (d) modified algal biomass after Cr(VI) adsorption.

large number of amine groups by the 4-aminopyridine molecules. The new peak at 1,653 cm^{-1} was attributed to the aromatic C-C, or C-N amide stretching. The peaks at 1,653 and 1,596 cm^{-1} are attributed to the -NH_2 scissoring and -C–C- stretching, respectively. After Cr(VI) adsorption by the modified algal biomass (Figure 2(d)), a significant difference in spectrum and a shift in bands were observed compared with the modified algal biomass. The most remarkable shifts are observed at around 4,500–2,700 cm^{-1}, and in the fingerprint region at around 1,500–500 cm^{-1}. FTIR spectra of the native and modified algal biomasses also revealed that the surface functional groups (such as –COOH, –NH_2, and –OH) on the biomass surface are involved in Cr(VI) adsorption.

The total available surface amino group content of the native and 4-aminopyridine modified algal biomass were found to be 0.23 and 2.87 mmol g^{-1} dry algal biomass. After 4-aminopyridine modification, the available amine group content of the algal biomass increased about 12.5-folds compared to the native counterpart.

Zeta potential studies

To investigate the change of *S. platensis* biomass surface charge before and after the surface modification protocols, the zeta potentials as a function of solution pH (i.e. between 2.0 and 11.0) were measured (Bayramoglu & Arica 2011a, 2011b). The change in the zeta potential values of the native, and modified algal biomass as a function of suspension medium pH are presented in Figure 3. As observed in this figure, the zeta potential values for native and modified algal biomass decrease with increasing solution pH. The zero zeta potential point value for native algal biomass was found to be at around pH 4.0; on the other hand, the zero potential values for 4-aminopyridine modified algal biomass were observed at around pH 9.0. The positive charge density on the 4-aminopyridine modified biomass surface significantly decreased with increasing medium pH due to the deprotonation of the amine groups on the ligand molecules. The charge density in this pH range changed from −29.8 to 6.9 mV for native algal biomass. On the other hand, for 4-aminopyridine modified algal preparation, it changed from −14.8 to 32.7 mV.

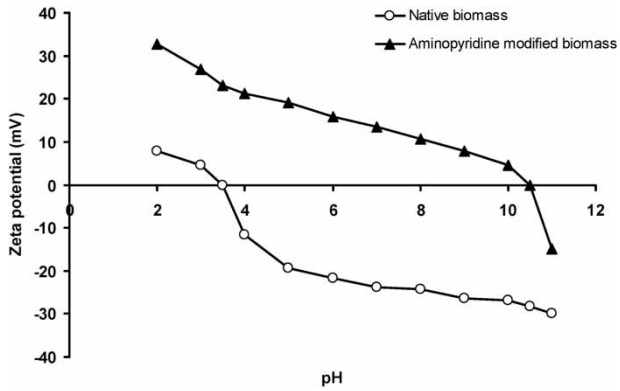


Figure 3 | pH versus zeta potential plots for the native and aminopyridine modified algal preparations.

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Thus, the medium pH is an important parameter to control in the adsorption of Cr(VI) ions.

Contact angle studies with algal biomass preparations

Contact angle data with three different test liquids (i.e. water, formamide and DIM) for the native and 4-aminopyridine modified algal biomass, and their Cr(VI)-adsorbed counterpart biomass are presented in Table 1. All the algal preparations gave different contact angle values depending on the surface properties. Covalent modification of the algal biomass with 4-aminopyridine resulted in a decrease in the surface hydrophilic characters compared to the native counterpart. The same trend was observed for both Cr(VI) biosorbed native and modified algal preparations compared to their chromium-free counterparts. It should be stated that the increase in contact angle value of the native algal biomass surface after 4-aminopyridine decoration should be caused by the incorporated relatively less hydrophilic 4-aminopyridine molecule. Both native and modified algal cell surface components were used as active components for Cr(VI) ions capture by charge interactions. The positive charges on the 4-aminopyridine molecules can attract the opposite charges of the negatively charged chromium ion species, and this causes enhancement of adsorption of chromium ions on the modified algal biomass surface compared to the native one (Bayramoglu & Arica 2005a, 2005b). The surface physicochemical properties of the native and modified algal biomass before and after contacting with Cr(VI) ions were determined using the van Oss method. The contact angle values for water, formamide and diiodomethane on the native, modified and their Cr(VI) adsorbed counterparts are presented in Table 1. The variation of the contact angle values after 4-aminopyridine modification and Cr(VI) coverage show that the hydrophilicity of the algal preparations is decreased with respect to the native form. The decrease hydrophilicity of the algal biomass surface should be caused by the incorporated 4-aminopyridine molecules on the algal biomass surfaces and that was used as a ligand for Cr(VI) ions capture by charge interactions. The determined overall surface free energy (γ^{Total}) calculated using the acid–base method of van Oss consisting of the sum of the Lifshitz–van der Waals (γ^{LW}) and the acid–base components (γ^{AB}) applies for all investigated algal preparations at different values. For all algal preparations, the γ^{LW} component is much larger than that of the acid–base component. It should be noted that, the same trend observed for the base component (γ^-) was considerably higher than the acid component (γ^+) of the algal preparations. Chemical modification of algal biomass resulted in increase in the surface polarity and in the polar component of the surface free energy (i.e. γ^- and γ^+). As expected, the electrostatic interactions increased between the modified algal biomass and Cr(VI) ion species after decoration of the algal biomass surface with 4-aminopyridine (as seen from contact angle data and calculated surface free energy parameters of the algal preparations). Thus, the modified algal preparation yielded higher Cr(VI) ion adsorption capacity compared to the native form. It should be noted that the polarity of the native and modified algal preparations was significantly decreased after chromium coverage (Table 2).

Table 1 | Contact angles values of native and aminopyridine modified algal biomass and their Cr(VI) adsorbed counterpart with three different test liquids

Biomass form	Water θ (°)	Formamide θ (°)	DIM θ (°)
Native	42.8 ± 2.3	52.9 ± 1.4	36.7 ± 1.8
Native Cr(VI) sorbed	67.4 ± 1.6	53.8 ± 0.9	44.8 ± 2.2
Modified	64.8 ± 0.7	48.4 ± 1.8	29.4 ± 1.7
Modified Cr(VI) sorbed	71.8 ± 1.5	47.9 ± 1.4	28.9 ± 1.3

Effect of biomass dosage on the adsorption efficiency

The percentage removal of Cr(VI) ions was studied by varying the adsorbent dose between 0.2 and 2.0 g L at a constant Cr(VI) ion concentration of 200 mg L^{-1} (Figure 4). As seen

Table 2 | Surface free energy parameters (mN/m^2) of the native aminopyridine modified algal biomass and their Cr(VI) adsorbed counterpart according to the van Oss *et al.* (1988)

Biomass form	γ^{LW} (mN/m^2)	γ^{AB} (mN/m^2)	γ^+ (mN/m^2)	γ^- (mN/m^2)	γ^{Total} (mN/m^2)	Polarity (%)
Native	36.17	10.13	0.76	36.54	46.30	28.0
Native Cr(VI) sorbed	37.12	2.80	0.12	15.96	39.22	7.5
Modified	44.47	−38.49	5.42	71.98	4.98	86.5
Modified Cr(VI) sorbed	44.67	2.31	0.16	8.29	46.97	5.2

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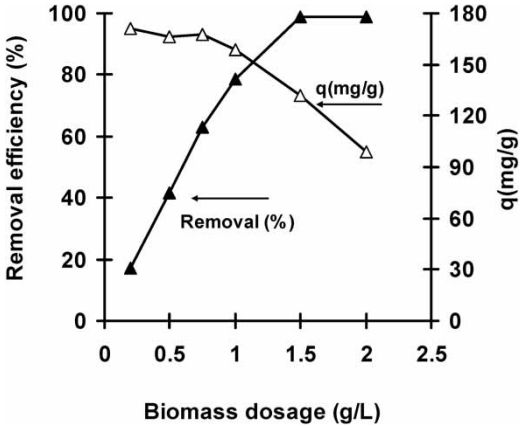


Figure 4 | Effect of sorbent dosage on the removal of Cr(VI) ions by 4-aminopyridine modified algal biomass.

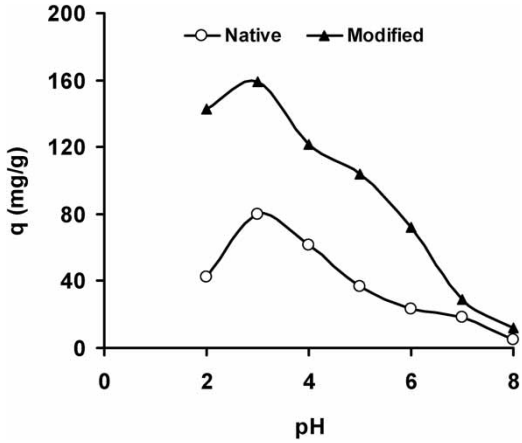


Figure 5 | Effect of pH on the removal efficiency of Cr(VI) ions by the native, aminopyridine modified algal biomass.

in this figure, when the biomass dosage increases, Cr(VI) removal efficiency also increases. On the other hand, the amount of Cr(VI) ions adsorbed decreased from 171.0 to 97.8 mg g^{-1} with increasing adsorbent dosage from 0.2 to 2.0 g and the percentage of Cr(VI) ion removal increased from 17.1 to 98.7% for the same adsorbent concentration range. At adsorbent dosages > 1.0 g, the incremental Cr(VI) ions removal becomes constant as the amount of Cr(VI) ions left in solution becomes very low. Increase in the percentage of Cr(VI) ion removal with adsorbent dosage can be attributed to increased surface area and the availability of more adsorption sites. However, with the increased amount of adsorbent the relative amount of Cr(VI) ions adsorbed (mg g^{-1}) decreases. In the rest of the study, 1.0 g adsorbent dosage in 1.0 L medium for both the native and modified algal biomasses was used.

Effect of pH on adsorption of Cr(VI) ions

It is well known that pH is a critical issue in the adsorption process, because of the influence of the formation of ionic species and the surface charge density of the adsorbent surface. The medium pH was varied between 2.0 and 8.0. The initial concentration of Cr(VI) was 200 mg L^{-1}, adsorbent dose 1.0 g L^{-1}, temperature 25 °C, and contact time about 2.0 h (Figure 5). The highest Cr(VI) ion adsorption was observed at pH 3.0 for both adsorbents. The adsorption capacity decreased significantly with increase in the medium pH above 3.0. Under high acidic conditions, amino groups of the adsorbents were protonated to form positively charged amino groups. Thus, electrostatic attraction occurred between negatively charge chromium ion species and positively charged amino groups, leading to the increase of Cr(VI) ion removal efficiency. With increasing pH, the number of protonated amino groups on the algal biomass surface decreased with the increase of the medium pH, and electrostatic interaction between the amino groups and the Cr(VI) ions reduced. This result led to the decrease in adsorption capacity of both adsorbents to Cr(VI) ions. It should be noted that the removal efficiency of 4-aminopyridine modified algal biomass was significantly improved for Cr(VI) ions. Additionally, modified algal biomass exhibited higher sensitivity to medium pH. The pH effect could be the result of the different interactions mechanisms. In aqueous media, the chromium ions mainly exist in the form of soluble oxides, including $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-} and H_2CrO_4. The ionic species depend on the medium pH and the total concentration of the chromium in the solution. When the pH is less than 2.0, the major species is H_2CrO_4 whereas when the medium pH is above 7.0, only $CrO4^{-2}$ ions exist. When the medium pH is between 2.0 and 6.0, both $HCrO^{4-}$ and $Cr_2O_7^{2-}$ ionic species dominantly exist. The algal biomass has cell walls composed mainly of polysaccharides and proteins with different functional groups such as amine, hydroxyl carboxyl, carbonyl, and phosphate groups. Thus, ion-exchange and electrostatic interactions are mainly responsible for adsorption of Cr(VI) ions to the native and modified algal biomass preparations, and the maximum adsorption at pH 3.0 can be due to the optimum combination between the functional groups on the algal biomass surface and ionic species of Cr(VI). The optimum pH for the adsorption process for both algal preparations was found to be 3.0, and the following experiments were carried out at this pH value.

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Effect of medium ionic strength on Cr(VI) ions adsorption

The presence of other competing ions in the adsorption medium can reduce the adsorption efficiency of the adsorbent for the target metal ions. The adsorbed amount of Cr(VI) ions decreased with increasing ionic strength (Figure 6). The Cr(VI) ions adsorption capacity of the native and modified algal biomass decreased by about 42% and 63%, respectively, when the NaCl concentration in the adsorption medium was 1.0 mol/L. The lower adsorption capacity at higher ionic strength may be explained by the competition between Cr(VI) ions and chloride ions (Cl^-) for the same binding sites present on the adsorbent surface. This behavior indicated that the ion exchange could be responsible for the Cr(VI) removal process. Another way to explain it is that the adverse effect of ionic strength may change the activity coefficient of chromium ion species and thus would limit their transfer to the adsorbent surface. Thus, electrostatic interactions between the adsorbents and chromium ion species could be shielded by the used anionic species (Bayramoglu & Arica 2009; Bayramoglu *et al.* 2009; Akar *et al.* 2013).

Evaluation of adsorption isotherm models

In general, the adsorption rate is greatly influenced by initial Cr(VI) ion concentration when the adsorbent dose is consistent, for which experiments should be conducted at a range of initial Cr(VI) ion concentrations. The adsorption capacity of the native and modified algal biomass increased with increasing equilibrium concentration of Cr(VI) ions, and a saturation value was achieved at Cr(VI) ion concentration of around 200 mg L^{-1}, which represents saturation of the active binding sites on the adsorbents (Figure 7). The adsorption of Cr(VI) ion onto the native and modified algal biomasses was about 79.6 and 158.7 mg g^{-1} dry biomass, respectively. The low adsorption capacity of Cr(VI) ions for native algal biomass compared to the modified counterpart can be due to the low amino group contents, and it was confirmed by analytical method, FTIR, zeta sizer, and contact angle studies. In this study, the Langmuir (1919), Freundlich (1906), and Dubinin–Radushkevich (D–R) isotherm models were applied to describe interactions between the Cr(VI) ions and native and modified algal preparations.

The Langmuir model can be described by the following linearized equation:

$$\frac{C_e}{q_e} = \left(\frac{1}{q_{max}}\right) C_e + \left(\frac{1}{q_{max} b}\right) \quad (3)$$

where q_{max} is the maximum adsorption capacity (mg g^{-1}), C_e is the equilibrium Cr(VI) ion concentration in solution (mg L^{-1}) and b is the Langmuir constant (L mg^{-1}).

The Freundlich is represented as linearized by the following equation:

$$\ln q_e = \left(\frac{1}{n}\right) \ln C_e + \ln K_F \quad (4)$$

where K_F is the Freundlich constant and n is the Freundlich exponent; $1/n$ is a measure of the surface heterogeneity ranging between 0 and 1, becoming more heterogeneous as its value gets closer to zero.

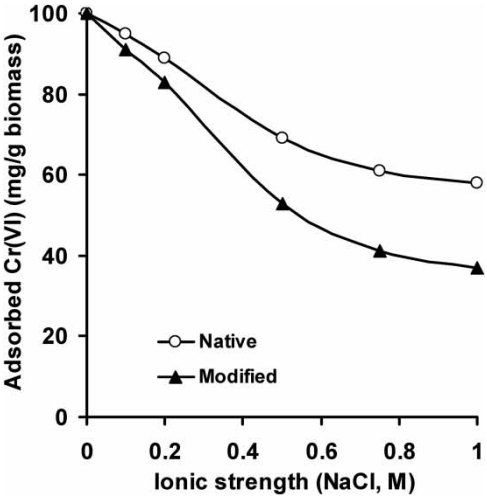


Figure 6 | Effect of ionic strength on adsorption of Cr(VI) ions by the native, aminopyridine modified algal biomass.

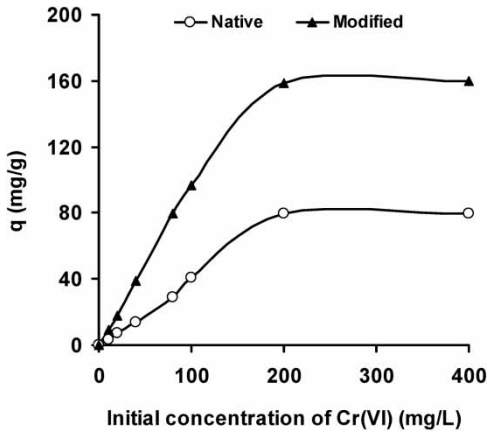


Figure 7 | Effect of initial Cr(VI) ions concentration on the adsorption efficiency of the native and 4-minopyridine modified algal biomass.

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The Dubinin–Radushkevich isotherm was chosen to estimate the apparent energy of adsorption. The linear form of the isotherm equation is as follows:

$$\ln q = \ln q_D K_D \varepsilon^2 \quad (5)$$

The q_D, the theoretical saturation capacity of the adsorbate retained (mg g^{-1}); and ε, the Polanyi potential, which is equal to $RT \ln(1 + (1/C_e))$, where R (J mol^{-1} K) is the gas constant and T (K) is the absolute temperature. The constant K is related to the mean adsorption energy, E (kJ mol^{-1}), as it is transferred to the surface of the solid from infinite distance in the solution, and this energy can be computed using the relationship $E = (2K_D)^{1/2}$.

The isotherm model parameters for the adsorption of Cr(VI) ions onto native and modified algal biomasses were calculated using above isotherm models at different temperatures (Table 3 and 4). The maximum adsorption capacity 'q_{max}' increased with increasing temperature and the maximum monolayer capacity was found to be 147.2 and 164.9 mg^{-1} at 25 °C for native and modified algal biomass, respectively. The binding affinity 'b' values were found to be 4.6×10^{-2} and 1.37×10^{-1} L mg^{-1} (or 738 and 22,468 M^{-1}) at 25 °C for native and modified algal preparations, respectively. A high 'b' value (i.e. K_a) in molar unit indicates a high affinity. The high correlation coefficient (R^2) was between 0.992 and 0.999 for the modified algal biomass at different temperatures (Table 3), indicating that the Langmuir adsorption model can be applied to the modified algal biomass. On the other hand, native biomass was not well described by the Langmuir model. The essential characteristics of the Langmuir isotherm equation can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined by Equation (6):

$$R_L = \frac{1}{(1 + bC_o)} \quad (6)$$

where C_o is the highest initial solute concentration, the values of R_L indicate the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). The values of R_L calculated for a given Cr(VI) ion concentration (400 mg L^{-1}) for the algal biomass preparations were found to be within the range of $0 < R_L < 1$, which indicated that the native and modified algal biomass preparations were suitable for adsorption of Cr(VI) ions and that the adsorption process was favorable. For native algal biomass, the Freundlich constant K_F and n were obtained as 0.781 mg g^{-1} (L $mg^{-1})^{1/n}$ and 1.13 at 25 °C, respectively, with a correlation coefficient of 0.967. The value of n values between 0 and 10 (i.e. 1.09–1.13) indicated that Cr(VI) ion adsorption onto native algal biomass was favorable at all the studied temperatures and tends to increase with increasing temperature. On the other hand, the K_F and n values were found to be 33.1 mg g^{-1} (L $mg^{-1})^{1/n}$ and 3.21 at 25 °C, respectively, for modified algal biomass; therefore, the adsorption of Cr(VI) ions on the modified algal biomass was not well described by the Freundlich model. Additionally, it has a low correlation coefficient of about 0.641 (Table 3).

For the D–R isotherm model, the values of q_D and K_D values were calculated from the intercepts and slopes of the plots, respectively (Table 4). A high q_D value indicates a higher adsorption capacity. The values of q_D from Table 4 are seen to be higher for the modified algal biomass than those of native algal biomass, showing that the modified algal biomass exhibited higher adsorption capacity than those of the native one. The electrostatic interactions between the protonated amino groups on the native and

Table 3 | Isotherm models for adsorption of Cr(VI) ions by the native and modified algal biomass from aqueous solutions at different temperatures

	Experimental		Langmuir				Freundlich		
Biomass	**T (K)**	**q_{exp} (mg/g)**	**q_{max} (mg/g)**	**$b \times 10^1$ (L/mg)**	**R^2**	**R_L^a**	**K_F**	**n**	**R^2**
Native	288	62.4	120.2	0.039	0.847	0.433	0.551	1.09	0.979
	298	79.6	147.2	0.046	0.856	0.410	0.781	1.13	0.967
	308	87.5	156.3	0.050	0.841	0.362	0.667	1.14	0.969
	318	97.1	165.0	0.058	0.872	0.391	1.122	1.15	0.971
Modified	288	124.8	138.9	0.362	0.992	0.091	7.60	1.69	0.897
	298	158.7	164.9	1.37	0.997	0.029	33.1	3.21	0.641
	308	172.3	174.2	4.34	0.999	0.010	44.8	3.33	0.729
	318	193.4	194.2	10.4	0.998	0.005	63.1	3.57	0.746

[a]Initial concentrations (C_0) of Cr(VI) ions, 400 mg/L.

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Table 4 | D-R isotherm models for adsorption of Cr(VI) ions by the native and modified algal biomass from aqueous solutions at different temperatures

Biomass	T (K)	q_D (mg/g)	$K_D \times 10^9$ (mol^2/J^2)	R^2	E (kJ/mol)
Native	288	29.4	9.6	0.984	7.2
	298	37.7	8.9	0.981	7.5
	308	40.9	8.3	0.979	7.8
	318	46.1	8.1	0.976	7.9
Modified	288	63.5	5.9	0.954	9.21
	298	59.4	2.7	0.629	13.6
	308	93.2	2.3	0.739	14.7
	318	84.8	1.4	0.641	18.9

modified algal biomass surfaces and Cr(VI) ions are reflected through the mean free energy of adsorption (7.5 and 13.6 kJ mol^{-1}) obtained from D–R isotherm model. The mean free energy and heat of adsorption values (in kJ mol^{-1}) were lower than 20 kJ mol^{-1}. This according to Atkins (1999) is characteristic for physisorption.

Adsorption kinetics

Adsorption time-dependent experiments were studied to evaluate the adsorption kinetics (Figure 8). As seen in this figure, the amount of adsorbed Cr(VI) ions increased linearly with time during the first 40 min, and then the adsorption process reached equilibrium within about 60 min. After this equilibrium period, no significant increase in the quantity of adsorbed Cr(VI) ions was observed with increase in contact time, thus, it was characterized as the optimum contact time. It should be noted that the adsorption rate of chromium ions on 4-aminopyridine modified algal biomass from the adsorption medium was much higher than that of the native biomass. The observed contact time was very short, and modified algal biomass was expected to be promising for the recovery of chromium ions from aqueous medium.

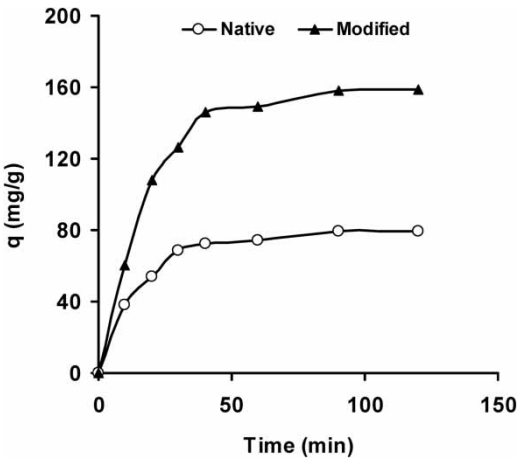


Figure 8 | Effect of contact time on the removal of Cr(VI) ions by the native and 4-minopyridine modified algal biomass.

The tested kinetic models have been used to examine the rate controlling mechanism on the adsorption process. The pseudo-first-order rate equation is given as:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (7)$$

where q_e (mg g^{-1}) is the amount of metal ion adsorbed at equilibrium, q_t (mg g^{-1}) is the amount of adsorbed metal ion adsorbed at time t, k_1 is the first-order adsorption rate constant (min^{-1}). The plot of $\log(q_e - q_t)$ versus t gives a straight line and the pseudo-first-order rate constant can be calculated from the slope value (Bayramoglu *et al.* 2006).

The pseudo-second-order equation is given as:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t \quad (8)$$

where k_2 is the second-order adsorption rate constant (g mg^{-1} min^{-1}) and q_e is the adsorption capacity calculated by the pseudo-second-order kinetic model (mg g^{-1}). The constant k_2 is used to calculate the initial sorption rate 'h' (mg (g min)$^{-1}$), at $t \to 0$ by using $h = k_2 q_e$. The application of the pseudo-second-order kinetics by plotting t/q_t versus t yields the second-order rate constant k_2.

The correlation coefficients (R^2) obtained from the pseudo-second-order model was found to be above 0.997 for all the tested temperatures, making them larger than those of the pseudo-first-order model Table 5. As seen from Table 5, the initial adsorption rate, h_0, increases with increasing temperature. The results obtained from the pseudo-second-order model were the best for describing the kinetics of Cr(VI) ionadsorption. The calculated adsorption capacities (q_{eq}) using the pseudo-second-order model agreed with the corresponding experimental adsorption capacities at different temperatures (q_{exp}). Additionally, the 4-aminopyridine modified algal biomass had a high equilibrium adsorption capacity q_{eq}, and the adsorption rates were also very fast compared to the native counterpart (Bayramoglu *et al.* 2003; Bayramoglu & Arica 2011a, 2011b).

Thermodynamic parameters

The effect of temperature on the adsorption of Cr(VI) was investigated at four different temperatures (i.e. 15, 25, 35

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Table 5 | Kinetic parameters for adsorption of Cr(VI) ions by the native and modified algal biomass from aqueous solutions at different temperatures

	Experimental		First-order kinetics			Second-order kinetics			
Biomass	T (K)	q_{exp} (mg/g)	q_{eq} (mg/g)	$k_1 \times 10^2$ (min^{-1})	R^2	q_{eq} (mg/g)	$k_2 \times 10^3$ (g/mg min)	h_0 (mg/g min)	R^2
Native	288	62.4	213.8	9.65	0.9446	62.3	1.69	6.56	0.998
	298	79.6	101.3	6.45	0.987	83.2	1.37	9.48	0.999
	308	87.5	301.6	9.90	0.899	92.5	1.26	10.8	0.997
	318	97.1	371.4	10.1	0.923	100.4	1.16	11.7	0.999
Modified	288	124.8	194.9	6.92	0.981	134.8	0.62	11.3	0.997
	298	158.7	346.8	8.01	0.978	172.1	0.51	15.1	0.998
	308	172.3	295.1	7.60	0.979	185.2	0.49	16.8	0.999
	318	193.4	397.7	8.25	0.984	199.7	0.45	17.9	0.998

and 45 °C), at pH 3.0. The adsorption of Cr(VI) ions on the native and modified algal biomass was found to be increased with the increase in temperature, indicating that the process is endothermic in nature (Table 6). The reason for an increase in Cr(VI) ions adsorption on the algal biomass at high temperatures could be attributed to increase in the interaction between Cr(VI) ions and functional groups on the algal cell surface because of an increase in the energy of the system.

The following equations have been used to determine thermodynamic parameters such as enthalpy (ΔH), Gibbs free energy (ΔG) and entropy (ΔS).

$$\Delta G = -RTln\,K_d \tag{9}$$

$$\ln K_d = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{10}$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), T represents the absolute temperature (K), and K_a ($b = K_a$) is the association coefficient which can be calculated by using the Langmuir equation (4). The values of ΔH^o and ΔS^o were determined from the slope and intercept of the van 't Hoff plot of ln K_a versus $1/T$. The values of the thermodynamic parameters are presented in Table 6. The negative values of ΔG suggested that the adsorption processes were spontaneous, and the decreasing of ΔG with the increasing of temperature indicated that the adsorption was more favorable at high temperatures. The positive values of ΔH^o confirmed the endothermic process for the adsorption of Cr (VI) ions, consistent with the increase of adsorption capacity as temperature increased. The positive value of ΔS^o suggested increasing randomness between the solid/solution interface during the adsorption process.

The activation energy (E_a) for the adsorption of an adsorbate onto a biomass surface can be determined from experimental measurements of the adsorption rate constant at different temperatures according to the Arrhenius equation. The activation energy (E_a) values for the native and modified algal biomass were found to be −7.23 and −9.29 kJ/mol, respectively (Table 6). In physical adsorption, the equilibrium is usually rapidly attained and easily reversible, because the energy requirements are small.

Table 6 | Thermodynamic parameters for adsorption of Cr(VI) ions by the native and modified algal biomass from aqueous solutions at different temperatures

		Thermodynamic parameters				
Biomass	T (K)	$q_{m(exp)}$ (mg/g)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	E_a (kJ/mol)
Native	288	62.4	1.07	99.0	0.312	− 9.29
	298	79.6	0.76			
	308	87.5	0.45			
	318	97.1	0.15			
Modified	288	124.8	−4.44	85.6	0.307	− 7.23
	298	158.7	−7.57			
	308	172.3	−10.7			
	318	193.4	−13.8			

Continuous system adsorption of Cr(VI) using modified algal biomass

The effect of flow rate on the adsorption of Cr(VI) ions by the modified algal biomass was investigated by fixing initial Cr(VI) concentration 200 mg L^{-1} and keeping flow rate between 50 and 250 mL h^{-1}. The flow rate of Cr(VI) ions containing feed solution was varied by means of a peristaltic pump (ISMATEC, IPC Model). The percent removal efficiency of Cr(VI) ions with modified algal biomass was strongly dependent on flow rate of the Cr(VI) feed solution, and significantly decreased with an increase in flow rate

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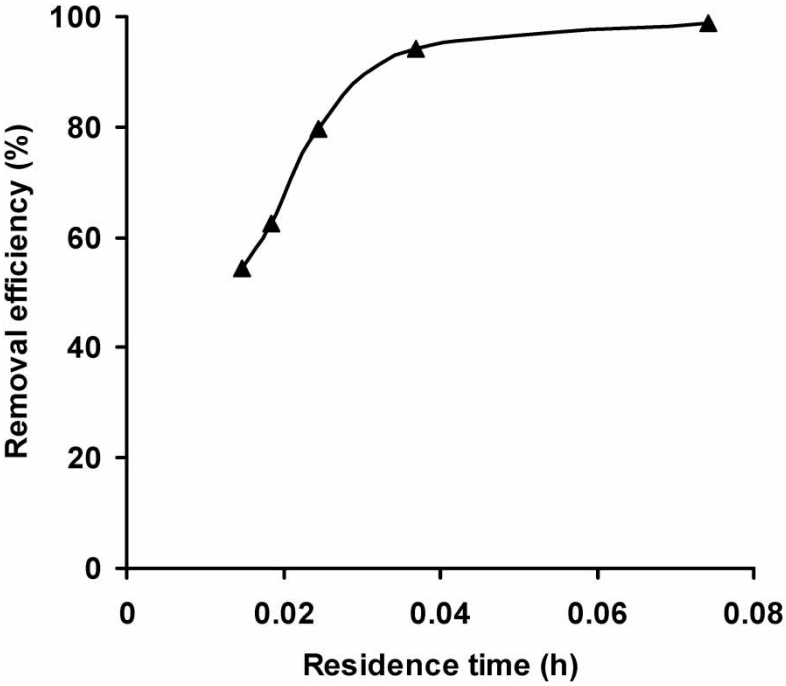


Figure 9 | Effect of residence time on the adsorption efficiency of the Cr(VI) ions for the modified algal biomass in the continuous system.

(Figure 9). The maximum removal efficiency was obtained as 98.8% at a flow rate of 50 mL h^{-1}. The results show that the adsorption of Cr(VI) ions on to the modified algal biomass was dependent on the residence time. As seen in the figure, the residence time is increased; the removal efficiency is also increased. At the highest flow rate, the lowest Cr(VI) ions removal efficiency was observed. This behavior can be due to the insufficient contact time between the Cr(VI) ions in the feed solution and the modified algal biomass.

Variation of the adsorption rate with varying Cr(VI) ion concentration in the continuous system led to a linear increase in the adsorption efficiency, which was observed up to 200 mg L^{-1} chromium(VI) concentration and after which a plateau between 200 and 400 mg L^{-1} was obtained. The residence time was calculated as 0.047 h for the continuous system at a flow rate of 50 mL h^{-1} and, this was 2.0 h for the batch system.

In the continuous system, the adsorption capacity of the modified algal biomass was determined as 202.3 mg g^{-1}. On the other hand, the adsorption capacity for this preparation was obtained as 158.7 mg g^{-1} from the batch system. In the continuous system, the adsorption capacity of the modified algal biomass was about 27% higher than that of the batch system. The observed lower adsorption capacity in the batch systems may be a result of the low equilibrium concentration of the Cr(VI) ions compared to the continuous system. In the continuous system, the concentration of Cr(VI) ions in the effluent increased gradually until the adsorptive sides of the biomass were saturated with the Cr(VI) ions. At saturation, the concentration of Cr(VI) ions in the effluent was same as the inlet Cr(VI) ions concentration in the feed solution. The driving force for adsorption is the concentration difference between the Cr(VI) ions on the adsorbent surface and the Cr(VI) ions in the solution. Thus, the high driving force due to high Cr(VI) ions concentration resulted in a better performance in the continuous system.

Desorption and reusability studies

A desorption study was carried out to determine the reversibility of the adsorption process of Cr(VI) ions. Desorption of Cr(VI) ions from the algal biomass preparations was performed in a batch system. The final Cr(VI) ion concentrations in the aqueous phases were determined as described above. When HCl is used as the elution agent, the coordination of adsorbed Cr(VI) ions is disrupted and subsequently Cr(VI) ions are released from the algal biomass surface into the desorption medium. Desorption time was found to be around 60 min. Desorption ratios were very high at about 94%.

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In order to determine the reusability of the native and modified algal biomass, consecutive adsorption–desorption cycles were repeated eight times using the same adsorbent. The adsorption behavior is stable for five cycles of use and a reduction in Cr(VI) adsorption capacities was observed after six cycles. In other words, these algal preparations can be used for up to five adsorption/desorption cycles without significant reduction in their Cr(VI) adsorption capacities (data not shown).

CONCLUSION

In this study, the native and 4-aminopyridine modified *Spirulina platensis* biomasses were used for removal of Cr(VI) ions from aqueous solutions. FTIR, zeta-sizer, contact angle and potentiometric analysis confirmed that a large number of amino groups were introduced onto the algal biomass after modification with 4-aminopyridine. The functional amino groups were essential for capturing Cr(VI) from aqueous solutions. Adsorption of chromium ion species on the modified algal biomass were dominantly realized by the electrostatic interactions between the protonated amino groups of the functional 4-aminopyridine groups on the adsorbent and the chromium anionic species. The adsorption capacities of the native and modified algal biomass were found to be 79.6 and 158.7 mg Cr(VI)/g algal biomass, respectively. The adsorption equilibrium of Cr(VI) ions on the modified algal biomass was well fitted by the Langmuir isotherm models and exhibited the highest value of regression coefficients (0.999), rather than the other studied isotherm models. On the other hand, the Freundlich model was more appropriate in describing the adsorption process with native one. The pseudo-second-order model described the adsorption processes well, indicating that the adsorption processes are mainly controlled by physico-chemical sorption. The thermodynamic data revealed the spontaneity, endothermic and irreversible natures of Cr(VI) adsorption. A series of continuous system studies revealed that flow rate and initial Cr(VI) ion concentration affected the adsorption performance of the modified algal biomass. Operational stability was evaluated over eight consecutive cycles, and a 24% reduction in the adsorption capacities was observed after eight cycles for 4-aminopyridine modified algal biomass. These results suggest that 4-aminopyridine modified algal biomass has potential application in the removal of Cr(VI) ions from aqueous solution.

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