# Effects of anion species and concentration on the removal of Cr(VI) by a microalgal isolate, *Chlorella miniata*

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## Abstract

The presence of nitrate, chloride and sulfate anions on the removal of Cr(VI) by *Chlorella miniata* was investigated. Results of kinetic studies indicated that the equilibrium time in each anion system increased with increases of the initial salt concentration, and the inhibitory order was $NO_3^- > Cl^- > SO_4^{2-}$ for Cr(VI) removal and was $SO_4^{2-} > Cl^- \approx NO_3^-$ for the biosorption of the bioreduced Cr(III). The inhibitory effect caused by different anions was attributed to biosorption mechanism and metal speciation. Since both biosorption and bioreduction were involved in Cr(VI) removal, the presence of anions could compete with Cr(VI) for the adsorption sites, and the affinity of anions to the algal biomass followed the order of $NO_3^- > Cl^- > SO_4^{2-}$, which was consistent with their inhibitory order on Cr(VI) removal. Speciation results also indicated that the formation of $CrO_3SO_4^{2-}$ in the sulfate system made it easier to be adsorbed on the biomass than $HCrO_4^-$. The biosorption–bioreduction model further suggested that the bioreduction rate constant $k$ decreased with increases of anion concentrations ranging from 0 to 0.5 M, and followed the order of $SO_4^{2-} > Cl^- > NO_3^-$. The biosorption constant $b$ also decreased with anion concentrations in the range of 0–0.2 M, suggesting that this parameter was more sensitive to anion effects than the $k$ values. The higher $b$ values in the sulfate than in the nitrate and chloride systems indicated that Cr(VI) in the sulfate system was more easily adsorbed on the algal biomass. These findings demonstrated that the presence of anions significantly affected the removal of Cr(VI) by *C. miniata*. Since chloride, nitrate and sulfate ions are commonly found in industrial wastewater, it may be necessary to eliminate these ions prior to chromium removal.
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## 1. Introduction

Hexavalent chromium, Cr(VI), is a pollutant commonly found in wastewater produced from leather tanning, dye, wood preservation and electroplating industries and their concentrations can range from tens to hundreds of mg L$^{-1}$ [1]. Cr(VI) is more toxic than Cr(III) due to its carcinogenic and mutagenic effects. A variety of diseases such as bronchogenic carcinoma, asthma, pneumonitis and dermatitis have been reported to be associated with occupational Cr(VI) exposure [2]. Therefore Cr(VI) should be removed from wastewater prior to discharge.

In recent years, biosorption has been widely studied for the removal of metal ions, especially at the concentrations rang-

ing from 1 to 100 mg L$^{-1}$, due to its lower cost and higher effectiveness than the conventional methods such as chemical precipitation and ion exchange [3]. However, biosorption of target metal ions might be hindered under the presence of different anions [4], and the effect of anion species on biosorption was always neglected. The inhibition among different anions such as nitrate, chloride and sulfate varied, dependent on different metal cations used in the experiments [4–8]. Metal speciation and chemical complexation with anions in solution seemed to be a possible reason for the decreases of metal cation biosorption in the presence of various anions [7,9–11]. Kapoor and Viraraghavan [3] believed that if the stability constants of metal–anion complexes were greater than those of metal–biosorption sites on the cell-wall surface, the biosorption could be expected to be reduced considerably. Cr(VI) is an anion that mainly exists as an oxy-anion in the aqueous phase in the form of $CrO_4^{2-}$, $HCrO_4^-$ or $Cr_2O_7^{2-}$, dependent on pH of the solution. The

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presence of anions could compete with the adsorption sites if the ion exchange was the dominant mechanism [12,13]. However, the removal of Cr(VI) by biosorbents like seaweed, yeast and green microalgae was mainly due to biosorption along with bioreduction, but not ion exchange [14–16], and the effect of the presence of anions on each step of Cr(VI) removal may be different.

*Chlorella miniata* is a green microalgal species (spherical cells with a diameter of 2–3 μm) isolated from a municipal sewage treatment plant in Hong Kong SAR by the present research team. This isolate has been reported for its high biosorption capacity to Ni(II), Zn(II), Cr(III) and Cr(VI) ions [14,17–20]. Our recent study further demonstrated that the algal isolate could be mass cultured in domestic wastewater and the removal of Cr(VI) and Cr(III) ions by this biomass had no significant difference from that in commercial medium, indicating that the algal mass could be cheaply produced thus reducing the treatment cost [21]. The present study aims to (i) evaluate and compare the performance of *C. miniata* in the removal of Cr(VI) in the presence of different anion systems, including Cl⁻, NO₃⁻ and SO₄²⁻ (in the form of sodium salts), which are commonly found in industrial wastewater and whose concentrations are very high in some chromium-contained wastewater [22,23]; (ii) explore the effect of anion species and its concentration on Cr(VI) removal on the basis of metal speciation and removal mechanisms.

## 2. Materials and methods

### 2.1. Mass culture of microalgae and preparation of biosorbent

*C. miniata* was cultivated in 10 L Bristol medium in a transparent acrylic column, and the culture was illuminated by cool fluorescent light with an average light intensity 4.2 klx in 16/8 h light/dark cycle at room temperature $25 \pm 1\,^{\circ}$C. The algae were harvested at the stationary phase and centrifuged at 5000 rpm for 15 min, washed with deionized water twice to remove any residues adsorbed on the cell walls. The washed cells were then freeze dried prior to use. The daily yield was around 10 g freeze-dried algal biomass in 10 L medium.

### 2.2. Cr(VI) removal experiments

K₂Cr₂O₇ was selected as the Cr(VI) salt in Cr(VI) removal experiments. In kinetic studies, Cr(VI) removal in the presence of 0–1.0 M NaCl, NaNO₃ or Na₂SO₄ was determined under the conditions of an initial Cr(VI) concentration of 100 mg L⁻¹, working volume of 150 mL and biomass concentration of 5.0 g L⁻¹. Liquid solution samples (2 mL from each flask) were collected at regular intervals and analyzed for the residual concentration of Cr(VI) and total Cr. The set-up without any salt addition at the beginning of the experiment was used as the control. In all experiments, pH was fixed at 2.0, since this value was proven to an optimal pH for Cr(VI) removal [14]. pH values were maintained by regularly adjustment using 0.5 M NaOH or the respective acid, i.e., HNO₃, HCl and H₂SO₄ were
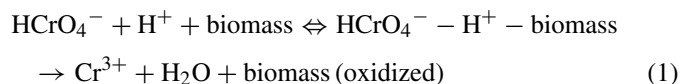
used in the nitrate, chloride and sulfate systems, respectively. In all experiments, samples were agitated on a shaker at 160 rpm at room temperature ($25 \pm 1\,^{\circ}$C).

The speciation of Cr(VI) was calculated using the software Mineql⁺, which was developed by Schecher and McAvoy [24]. Cr(VI) in water was measured according to the standard method described by Clesceri et al. [25] and Kratochvil et al. [26]. The absorbance of the purple complex formed from reacting Cr(VI) with 1,5-diphenylcarbohydrazide at $\lambda = 540$ nm was measured by a UV spectrophotometer (Shimadzu, UV-1201). Total Cr including Cr(VI) and Cr(III) was determined by flame atomic absorption spectroscopy (AAS) (Shimadzu, AA-6501) and the Cr(III) content in liquid solution was obtained by subtracting the content of Cr(VI) from that of total chromium.

In Cr(VI) removal experiments, a parametric two-way analysis of variance (ANOVA) was used to test any difference in Cr(VI) as well as the produced Cr(III) concentrations with anion species and reaction time as the two factors. A multiple comparison test of Tukey was employed when the ANOVA result showed a significant difference among treatments at $p \leq 0.05$. All statistical tests were carried out by software SPSS Version 11 from SPSS Inc. (USA).

### 2.3. Biosorption–bioreduction kinetic model

Both biosorption and bioreduction have been demonstrated to be involved in Cr(VI) removal by *C. miniata* [14], and in order to analyze the effect of anion species and concentration on each step, the biosorption–bioreduction model proposed in our previous study [14] was used. The chemical equation of the Cr(VI) removal by *C. miniata* could be described:

$$HCrO_4^- + H^+ + biomass \Leftrightarrow HCrO_4^- - H^+ - biomass$$
$$\rightarrow Cr^{3+} + H_2O + biomass\ (oxidized) \tag{1}$$

Since $HCrO_4^-$ biosorption on biomass was a fast step compared with bioreduction, the reaction rate was determined by the bioreduction step. If bioreduction of Cr(VI) on the biomass was thought to be a pseudo first order reaction, it could be defined

$$\frac{dq}{dt} = -kq \tag{2}$$

where $k$ was the bioreduction rate constant and $q$ was the Cr(VI) adsorbed on biomass.

If Cr(VI) biosorption equilibrium was thought to be present during the whole process, $q$ could be expressed by Langmuir isotherm

$$q = \frac{QbC}{bC+1} \tag{3}$$

where $Q$ was the maximum sorption capacity, $b$ was the biosorption constant of Cr(VI) and $C$ was the concentration of Cr(VI) in solution. By combining Eqs. (2) and (3), the following equation was obtained:

$$\frac{dC}{dt} = -kC(bC+1) \tag{4}$$

with the initial conditions: $t = 0$, $C = C_0$, $C_0$ was the initial concentration of Cr(VI), we could get

$$kt = \ln \left( \frac{C_0}{bC_0 + 1} \right) - \ln \left( \frac{C}{bC + 1} \right) \qquad (5)$$

The parameters $k$ and $b$ in Eq. (5) could be estimated by a nonlinear regression using the Sigmaplot 8.0 software.

## 3. Results

### 3.1. Kinetics of Cr(VI) removal

Fig. 1a shows that there was no significant difference in Cr(VI) removal ($p > 0.05$) among the three systems in the control, and equilibrium was reached after 69 h with a complete removal of Cr(VI), suggesting that the small amount of anions that came from the respective acids used for pH adjustments had no effect on Cr(VI) removal. As to Cr(III) produced in the control, the sulfate system had significantly higher concentrations than those of the nitrate and chloride systems (Fig. 1b), indicating that the anion effect of the additional acid for pH adjustment could not be neglected.

In initial anion concentration of 0.5 M (in sodium salts), a significant difference in Cr(VI) removal was found, with sulfate having the lowest inhibition, followed by chloride and nitrate
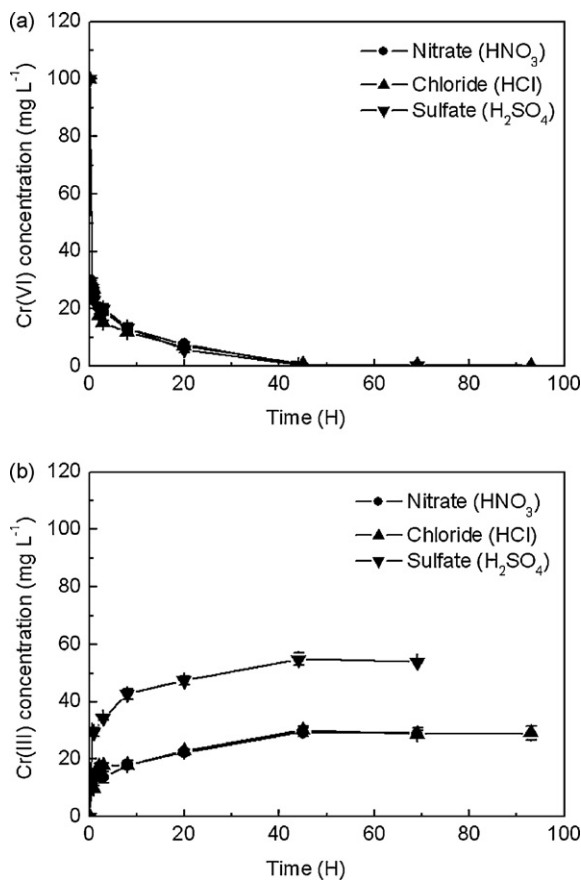


Fig. 1. Kinetic study of Cr(VI) removal in the control using different acids for pH adjustment: (a) Cr(VI) concentration; (b) Cr(III) concentration. Mean and standard deviation values of three replicates are shown.
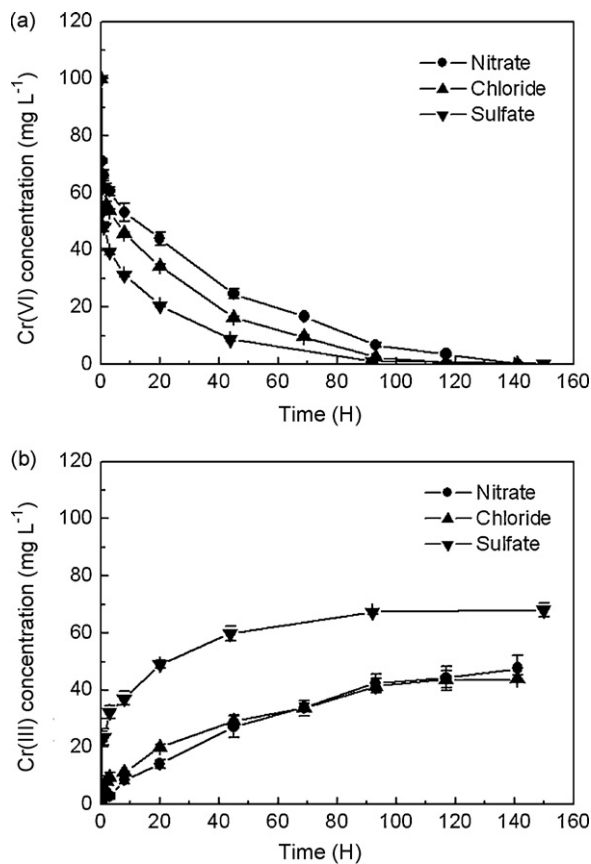


Fig. 2. Kinetic study of Cr(VI) removal under different anion systems at initial anion concentration (in sodium salt) of 0.5 M: (a) Cr(VI) concentration; (b) Cr(III) concentration. Mean and standard deviation values of three replicates are shown.

(Fig. 2a). Similar patterns were found when initial anion concentrations were at 0.1, 0.2 and 1.0 M (Supporting Figs. 1a, 2a and 3a). Equilibrium time in each anion system increased with the increase of initial anion concentrations (Supporting Table 1). As to the concentration of Cr(III) produced from Cr(VI) bioreduction, the trend was similar to that in the control, the biosorption of the reduced Cr(III) was significantly inhibited in the sulfate system, while Cr(III) concentration in the chloride system was comparable to that in the nitrate system (Fig. 2b). Similar patterns were also found when initial anion concentrations were at 0.1, 0.2 and 1.0 M (Supporting Figs. 1b, 2b and 3b). In this experiment, the amount of anions from the acids added to adjust the pH to 2.0 varied from 0.04 to 0.07 M in the nitrate and the chloride systems, and about 0.02–0.06 M in the sulfate system.

### 3.2. Speciation of Cr(VI)

The relative abundance of different species of Cr(VI) under different anion systems was shown in Fig. 3. Similar speciation was observed in both nitrate and chloride systems (Fig. 3a and b), and $HCrO_4^-$ and $Cr_2O_7^{2-}$ were the two dominant species. Other species, such as $CrO_3Cl^-$ in the chloride system, were not analyzed due to negligible amounts (less than 5%). With the increase of anion concentrations from 0 to 1.0 M, the abundance
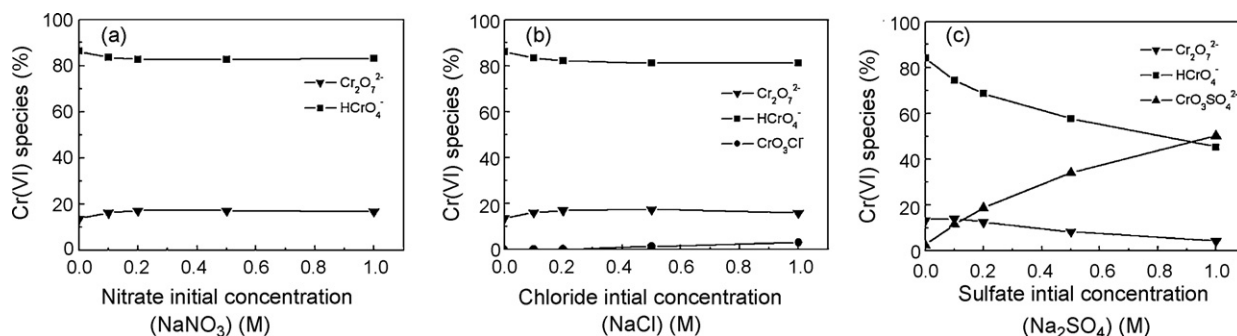
Fig. 3. Cr(VI) speciation under different anion systems (initial sodium salt concentration 0–1.0 M) in the experiment with 100 mg L$^{-1}$ Cr(VI) and pH kept at 2.0 with the respective acid. (a) Nitrate system; (b) chloride system; (c) sulfate system. Percentages of each species were calculated using the software Mineql$^+$.

of HCrO$_4^-$ and Cr$_2$O$_7^{2-}$ in both nitrate and chloride systems was the same, with less than 5% changes.

In contrast, percentages of HCrO$_4^-$ and Cr$_2$O$_7^{2-}$ decreased significantly in the sulfate system, while CrO$_3$SO$_4^{2-}$ increased from 2.4 to 52.0% with increases of sulfate concentrations (Fig. 3c). As for the other species such as CrO$_4^{2-}$, H$_2$CrO$_4$ aq., KCrO$_4^-$ and NaCrO$_4^-$, their relative amounts were small (total amounts <2%), and were not included in the figures.

## 4. Discussion

The presence of anions could affect metal cation biosorption, and their inhibition differed among the biomass employed and the metals needing to be removed. Kuyucak and Volesky [8] found that nitrate significantly inhibited Co$^{2+}$ biosorption by dead marine brown algae (*Ascophylum nodosum*), while phosphate and sulfate had no effect. The effect of anion on Mn(II) biosorption by extracellular polymeric substance (EPS) from *Rhizobium etli* followed the order of Cl$^-$ > NO$_3^-$ > SO$_4^{2-}$ [4], while the inhibitory order of anion on Zn$^{2+}$ biosorption by *Oscillatoria anguistissima* was SO$_4^{2-}$ > Cl$^-$ > NO$_3^-$ [6]. However, the presence of anions on the removal of metal anions was paid little attention so far.

It is generally believed that the addition of salts in solution can increase the ionic strength of the solution, which has a negative effect on target metal removal [12,13,27]. Niu and Volesky [13] have reported that the removal percentage of Au(CN)$_2^-$, SeO$_4^{2-}$, CrO$_4^{2-}$ and VO$_4^{3-}$ decreased with the increase of ionic strength. The present study showed that under the same initial anion concentration (in sodium salt), although ionic strength of Na$_2$SO$_4$ was three times of NaCl or NaNO$_3$, the fastest Cr(VI) removal was found in the sulfate system while the lowest was in the nitrate system (Figs. 1a and 2a). These results indicated that the difference in Cr(VI) removal by *C. miniata* was mainly due to the presence of anion species but not ionic strength.

Both biosorption and bioreduction processes were demonstrated to be involved in Cr(VI) removal by *C. miniata* [14]. Previous studies suggested that the presence of anions could compete with Cr(VI) biosorption, and Cr(VI) removal decreased with the increase of anion concentrations [13,28,29]. The hydration energy of anions in solution differed among anion species in the order of ΔG$_{Sulfate}$(−1103 kJ mol$^{-1}$) > ΔG$_{Chloride}$(−

338 kJ mol$^{-1}$) > ΔG$_{Nitrate}$(−314 kJ mol$^{-1}$), and anion with low ΔG was more easily adsorbed on the sorbents [30]. The affinity order of these three anions to the resins Purolite A-520E and Aliquat 336 was found to be NO$_3^-$ > Cl$^-$ > SO$_4^{2-}$ [31,32] and the adsorption site in the anion exchange resins was the protonated amine group [31,33]. Since the protonated amine group on *C. miniata* was also proved to be the main site for HCrO$_4^-$ biosorption [14], the affinity of anions to the protonated amine sites on the algal biomass should follow the same order of NO$_3^-$ > Cl$^-$ > SO$_4^{2-}$, which indicated that NO$_3^-$ had the strongest competition effect with Cr(VI) biosorption while SO$_4^{2-}$ had the weakest, and explained the order of Cr(VI) removal as shown in Figs. 1a and 2a.

Metal speciation in the presence of different anions is another important factor that may affect the removal of Cr(VI) and the produced Cr(III). In the present study, HCrO$_4^-$ was found to be the dominant Cr(VI) species in nitrate and chloride systems. In the presence of sulfate, a new species CrO$_3$SO$_4^{2-}$, with two negative charges, was formed, which made it easier to be adsorbed on the biomass than HCrO$_4^-$. This was another reason why a higher Cr(VI) biosorption rate was found in sulfate than that in the nitrate and chloride systems. Zachara et al. [34] also showed that excess sulfate seemed to enhance sorption of chromate by kaolinite. In the present study, biosorption of the produced Cr(III) from bioreduction of Cr(VI) was inhibited by the sulfate system, even in the control where sulfate was only added from H$_2$SO$_4$ for maintaining reaction pH at a fixed value. Our previous study indicated that the formation of the neutral-charged Cr(OH)SO$_4$ aq., which was not easily adsorbed on the algal biomass, and the decrease of Cr(OH)$^{2+}$ and Cr$^{3+}$ in the sulfate system were the reasons why SO$_4^{2-}$, even at a low concentration, had the strongest inhibitory effect on Cr(III) biosorption on the *C. miniata* biomass [35]. These results suggested that sulfuric acid should be avoided in the adjustment of pH in Cr(VI) removal.

The biosorption–bioreduction kinetic model, which proved to be the best fit mechanism involved in Cr(VI) removal by *C. miniata* [14], was used to quantitatively explore the inhibitory effects of anions on Cr(VI) biosorption and bioreduction in this study. The higher values of correlation coefficients $R^2$ shown in Supporting Table 2 indicated that this model could well describe Cr(VI) removal in the presence of different anions at concentrations ranging from 0 to 1.0 M. Supporting Table 2 also describes
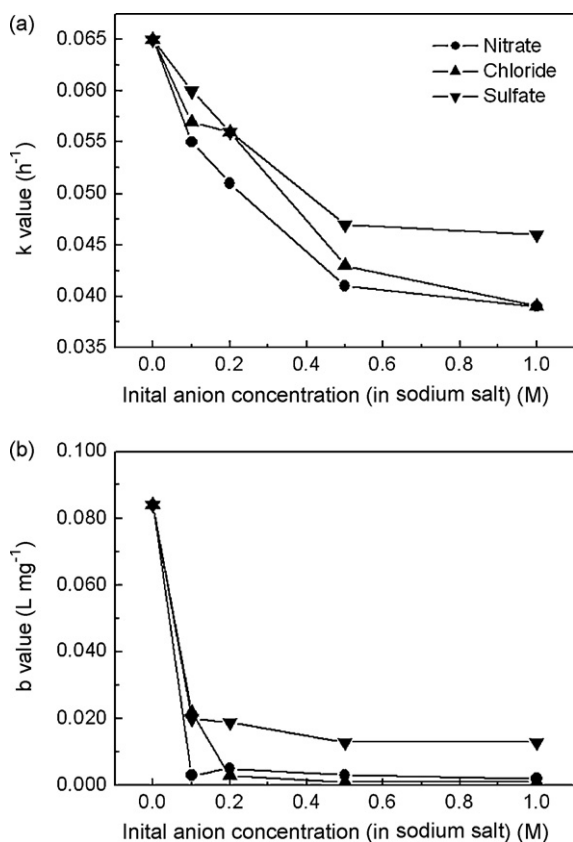
Fig. 4. Parameters of the biosorption–bioreduction model under different anion systems. *k* and *b* were plotted against initial anion concentrations (in sodium salts): (a) *k*-value; (b) *b*-value.

the effect of anions on the bioreduction rate constant ($k$), and the biosorption constant ($b$) of Cr(VI) on biomass. The relationships between $k$, $b$ values and initial anion concentrations (in sodium salt) were plotted (Fig. 4). It is obvious that $k$ values decreased with the increase of initial concentrations and began to level off if the concentration was higher than 0.5 M (Fig. 4a). Sulfate had the least inhibitory effect on Cr(VI) bioreduction, followed by chloride, and the presence of nitrate had the highest decreases of $k$ values. The adsorption constant $b$ values were more sensitive to anion than the $k$ values. A rapid decrease of $b$ value was found with the addition of anion in the range of 0–0.2 M. This is probably due to the competition of similar anions with increases of salt concentrations as reported by Niu and Volesky [13]. The higher $b$ values in the sulfate than in the nitrate and chloride systems further confirmed that Cr(VI) in the sulfate system was more easily adsorbed on the algal biomass.

## 5. Conclusions

The present study showed that anions had inhibitory effects on the Cr(VI) removal by the biomass of *C. miniata*, and $NO_3^-$ had the highest inhibitory effect, followed by that of $Cl^-$, and $SO_4^{2-}$ had the lowest inhibition. The biosorption of the Cr(III) produced from Cr(VI) bioreduction followed the order of $SO_4^{2-} > Cl^- \approx NO_3^-$. The inhibitory order for Cr(VI) removal could be explained by the biosorption–bioreduction

mechanism. The presence of anions could compete with Cr(VI) for the same adsorption sites; since the affinity of anions to the biomass was $NO_3^- > Cl^- > SO_4^{2-}$, biosorption of Cr(VI) was, therefore, least affected by sulfate. Also, the formation of $CrO_3SO_4^{2-}$ in the sulfate system was easier to be adsorbed on the biomass than $HCrO_4^-$. The biosorption–bioreduction model further suggested the bioreduction rate constant $k$ values reduced in the order of $SO_4^{2-} > Cl^- > NO_3^-$, and were more sensitive in the initial anion concentrations ranging from 0 to 0.5 M, while the adsorption constant $b$ was more sensitive in the lower range, 0–0.2 M.

## Acknowledgements

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2008.02.024.

## References

[1] E. Dermou, A. Velissariou, D. Xenos, D. Vayenas, Biological chromium(VI) reduction using a trickling filter, J. Hazard. Mater. 126 (2005) 78–85.

[2] J. Kotas, Z. Stasicka, Chromium occurrence in the environment and methods of its speciation, Environ. Pollut. 107 (2000) 263–283.

[3] A. Kapoor, T. Viraraghavan, Fungal biosorption—an alternative treatment option for heavy metal bearing wastewaters: a review, Bioresour. Technol. 53 (1995) 195–206.

[4] W. Pulsawat, N. Leksawasdi, P.L. Rogers, L.J.R. Foster, Anions effects on biosorption of Mn(II) by extracellular polymeric substance (EPS) from *Rhizobium etli*, Biotechnol. Lett. 25 (2003) 1267–1270.

[5] P. Ahuja, R. Gupta, R.K. Saxena, Sorption and desorption of cobalt by *Oscillatoria anguistissima*, Curr. Microbiol. 39 (1999) 49–52.

[6] P. Ahuja, R. Gupta, R.K. Saxena, Zn$^{2+}$ biosorption by *Oscillatoria anguistissima*, Process Biochem. 34 (1999) 77–85.

[7] V. Diniz, B. Volesky, Effect of counterions on lanthanum biosorption by *Sargassum polycystum*, Water Res. 39 (2005) 2229–2236.

[8] N. Kuyucak, B. Volesky, Accumulation of cobalt by marine alga, Biotechnol. Bioeng. 33 (1989) 809–814.

[9] R. Herrero, P. Lodeiro, C. Rey-Castro, T. Vilarino, M.E.S. de Vicente, Removal of inorganic mercury from aqueous solutions by biomass of the marine macroalga *Cystoseira baccata*, Water Res. 39 (2005) 3199–3210.

[10] J.T. Trevors, G.W. Stratton, G.M. Gadd, Cadmium transport, resistance, and toxicity in bacteria, algae, and fungi, Can. J. Microbiol. 32 (1986) 447–464.

[11] M. Tsezos, E. Remoudaki, V. Angelatou, A study of the effects of competing ions on the biosorption of metals, Int. Biodeterior. Biodegrad. 38 (1996) 19–29.

[12] H. Niu, B. Volesky, Characteristics of gold biosorption from cyanide solution, J. Chem. Technol. Biotechnol. 74 (1999) 778–784.

[13] H. Niu, B. Volesky, Characteristics of anionic metal species biosorption with waste crab shells, Hydrometallurgy 71 (2003) 209–215.

[14] X. Han, Y.S. Wong, M.H. Wong, N.F.Y. Tam, Biosorption and bioreduction of Cr(VI) by a microalgal isolate, *Chlorella miniata*, J. Hazard. Mater. 146 (2007) 65–72.

[15] D. Park, Y.S. Yun, J.H. Jo, J.M. Park, Mechanism of hexavalent chromium removal by dead fungal biomass of *Aspergillus niger*, Water Res. 39 (2005) 533–540.

[16] M. Zhao, J.R. Duncan, Batch removal of sexivalent chromium by *Azolla filiculoides*, Biotechnol. Appl. Biochem. 26 (1997) 179–182.

[17] A.M.Y. Chong, Y.S. Wong, N.F.Y. Tam, Performance of different microalgal species in removing nickel and zinc from industrial wastewater, Chemosphere 41 (2000) 251–257.

[18] X. Han, Y.S. Wong, N.F.Y. Tam, Surface complexation mechanism and modeling in Cr(III) biosorption by a microalgal isolate, *Chlorella miniata*, J. Colloid Interface Sci. 303 (2006) 365–371.

[19] J.P.K. Wong, Y.S. Wong, N.F.Y. Tam, Nickel biosorption by two Chlorella species, *C. vulgaris* (a commercial species) and *C. miniata* (a local isolate), Bioresour. Technol. 73 (2000) 133–137.

[20] N.F.Y. Tam, J.P.K. Wong, Y.S. Wong, Repeated use of two Chlorella species, *C. vulgaris* and WW1 for cyclic nickel biosorption, Environ. Pollut. 114 (2001) 85–92.

[21] X. Han, Y.S. Wong, M.H. Wong, N.F.Y. Tam, Feasibility of using microalgal biomass cultured in domestic wastewater for the removal of Cr pollutants, Water Environ. Res., in press.

[22] N.F. Fahim, B.N. Barsoum, A.E. Eid, M.S. Khalil, Removal of chromium(III) from tannery wastewater using activated carbon from sugar industrial waste, J. Hazard. Mater. 136 (2006) 303–309.

[23] S. Suteerapataranon, M. Bouby, H. Geckeis, T. Fanghanel, K. Grudpan, Interaction of trace elements in acid mine drainage solution with humic acid, Water Res. 40 (2006) 2044–2054.

[24] W.D. Schecher, D.C. McAvoy, Comput. Environ. Urban Syst. 16 (1992) 65–76.

[25] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, DC, 1998, pp. 366–368.

[26] D. Kratochvil, P. Pimentel, B. Volesky, Removal of trivalent and hexavalent chromium by seaweed biosorbent, Environ. Sci. Technol. 32 (1998) 2693–2698.

[27] S. Schiewer, M.H. Wong, Ionic strength effects in biosorption of metals by marine algae, Chemosphere 41 (2000) 271–282.

[28] G.S. Agarwal, H.K. Bhuptawat, S. Chaudhari, Biosorption of aqueous chromium(VI) by *Tamarindus indica* seeds, Bioresour. Technol. 97 (2006) 949–956.

[29] Z.H. Li, Influence of solution pH and ionic strength on chromate uptake by surfactant-modified zeolite, J. Environ. Eng. – Asce 130 (2004) 205–208.

[30] G.M. Brown, P.V. Bonnesen, B.A. Moyer, B.H. Gu, S.D. Alexandratos, V. Patel, R. Ober, The design of selective resins for the removal of pertechnetate and perchlorate from groundwater, in: E.T. Urbansky (Ed.), Perchlorate in the Environment, Kluwer Academic/Plenum Publishers, New York, 2000, pp. 155–165.

[31] B.H. Gu, Y.K. Ku, P.M. Jardine, Sorption and binary exchange of nitrate, sulfate, and uranium on an anion-exchange resin, Environ. Sci. Technol. 38 (2004) 3184–3188.

[32] S.L. Lo, S.F. Shiue, Recovery of Cr(VI) by quaternary ammonium compounds, Water Res. 32 (1998) 174–178.

[33] B.H. Gu, Y.K. Ku, G.M. Brown, Sorption and desorption of perchlorate and U(VI) by strong-base anion-exchange resins, Environ. Sci. Technol. 39 (2005) 901–907.

[34] J.M. Zachara, C.E. Cowan, R.L. Schmidt, C.C. Ainsworth, Chromate adsorption by kaolinite, Clays Clay Miner. 36 (1988) 317–326.

[35] X. Han, Ph.D. Thesis, City University of Hong Kong, Hong Kong, 2007, pp. 107–134.