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Single and binary chromium(VI) and Remazol Black B biosorption properties of *Phormidium* sp.

Zümriye Aksu[a,*], Sevgi Ertuğrul[b], Gönül Dönmez[b]

[a] *Department of Chemical Engineering, Hacettepe University, 06532 Beytepe, Ankara, Turkey*
[b] *Department of Biology, Ankara University, 06100 Ankara, Turkey*

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ABSTRACT

Wastewaters of textile and leather dying industries may contain significant quantities of chromium(VI) ions besides anionic and water-soluble dyes. Moreover the temperature of these wastewaters may be a controlling parameter affecting the biosorption efficiency. In this study biosorption of chromium(VI) and Remazol Black B reactive dye by dried *Phormidium* sp., a thermophilic cyanobacterium, was studied as a function of initial chromium(VI) concentration and temperature in no dye and 100 mg l^{-1} dye-containing media at an initial pH value of 2.0 at which the biomass exhibited the maximum chromium(VI) and dye uptakes. The decrease of both metal and dye uptakes with temperature indicated that the uptakes were exothermic in nature. Equilibrium uptake of chromium(VI) enhanced considerably with both chromium(VI) and 100 mg l^{-1} dye concentrations. Moreover the presence of chromium(VI) also increased the uptake of dye. At 25 °C, 22.8 mg g^{-1} chromium(VI) and 91.3 mg g^{-1} dye were sorbed by the biomass in binary 100 mg l^{-1} chromium(VI) and 100 mg l^{-1} dye-containing medium. The Langmuir was the best suitable adsorption model for describing the biosorption of chromium(VI) individually and in dye-containing medium. The pseudo-second-order kinetic model described both the chromium(VI) and dye biosorptions kinetics accurately.

1. Introduction

Synthetic dyes, used for dyeing of textile and leather; heavy metals such as chromium(VI); reducing agents and sulfate salts, used as dye bath additives are some of the potentially problematic compounds found in textile and tannery effluents. Water-soluble reactive dyes with azo-based chromophores combined with different types of reactive groups, e.g., vinyl sulfone, are the largest group of synthetic dyes known, and also the most common group of pollutants released into environment [1–3]. Soluble hexavalent chromium is extremely toxic and exhibits carcinogenic effects on biological systems due to their strong oxidizing nature among heavy metals. In such aqueous wastes, chromium(VI) is present as either dichromate ($Cr_2O_7^{-2}$) in acidic environments or as chromate (CrO_4^{-2}) in alkaline environments [4]. Since many synthetic dyestuffs are resistant to biological degradation due to their complex aromatic molecular structures and heavy metals cannot be biodegraded, colour and heavy metal removals by traditional biological processes are difficult and not complete [1–5]. In recent years many physical and chemical treatment methods including adsorption, chemical coagulation, precipitation, filtration, electrodialysis, membrane separation and oxidation have been used for the treatment of dye and heavy metal containing effluents. Some of these techniques have been shown to be effective, although they have limitations [3,5–8].

Biosorption can be defined as sequestering of organic and inorganic species including metals, dyes and odour causing substances from aqueous solutions using live or dead biomass or their derivatives. This biomass may be bacteria, fungi, algae, sludge from biological wastewater treatment plants, by-products from fermentation industries or seaweeds. Microbial cell surfaces carry various types of functional groups, which are responsible for the sequestration of hazardous materials from industrial effluents. The main attractions of biosorption are high selectivity and efficiency, cost effectiveness, good removal performance, possible regeneration at low cost and availability of known process equipment. The use of dead microbial cells in biosorption is more advantageous for water treatment in that dead organisms are not affected by toxic wastes, they do not require a continuous supply of nutrients and they can be regenerated and reused for many cycles [9–22].

Although individual heavy metal or dye uptake from liquid media can provide useful data about the sorption capacity of microorganisms, they do not exactly reflect the real situation of wastewaters containing heavy metal ions and dyes together. The examining the effects of metal ions and dyes in various combinations is more representative of the actual environmental problems

* Corresponding author. Tel.: +90 312 2977401; fax: +90 312 2992124.
E-mail address: zaksu@hacettepe.edu.tr (Z. Aksu).

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faced by living organisms. In these systems, the biosorption of the species of interest not only depends on the biomass surface properties and physical–chemical parameters of a solution such as pH and temperature, but also depends on the number of species and their concentrations. Binary mixture studies may provide additional information on the nature of sorption process, such as the fraction of adsorption sites being shared with each species, their relative affinities toward these sites, and the lateral interaction between the adsorbed species [23–30]. Therefore, it is critically important to understand the altered adsorption properties caused by competitive or cooperative effects and the underlying mechanisms of the processes to accurately predict the adsorption behaviours of contaminants in mixture systems. Moreover various textile and other dye effluents are produced at changing temperatures, therefore, temperature can be an effective removal capacity determinant for the real application of biosorption.

Among the microorganisms tested, microalgae (including prokaryotic photosynthetic microorganisms such as cyanobacteria), which are the primary biomass producers of the aquatic food chains have been suggested as ideal biosorbents for wastewater treatment systems. Cyanobacteria are suggested to have some added advantages over other microorganisms because of their large surface area and greater mucilage volume with high binding affinity [19,35]. Additionally, they can grow under high pH conditions, which can prevent contamination by other organisms. Cyanobacteria can be cultivated in large-scale at low cost due to their simple nutrient requirements. Although cyanobacteria have been successfully used as biosorbents for wastewater treatment systems, very few have been investigated to determine their heavy metal and dye removal abilities [19,31–38]. Moreover the uptake of multi-ions by microalgae has not been extensively investigated [23,27,29,39]. So this article extended the treatment to cover the combined effects of the heavy metal (chromium(VI)) and textile dye (Remazol Black B) components together on the thermophilic cyanobacterium *Phormidium* sp.

2. Materials and methods

2.1. Microorganism and growth conditions

A strain of filamentous cyanobacterium *Phormidium* sp. was isolated from hot spring located in Ayas, Ankara, Turkey, as described in the previous report [39]. The microorganism was cultivated in BG 11 medium using the shake flask method. The pH of the medium was adjusted to 8.5 with dilute H_2SO_4 and NaOH solutions before autoclaving. Once inoculated, unshaken flasks were incubated under continuous illumination at 2400 lx light intensity provided by cool white fluorescent lamps for 14 days at 45 °C in a plant growth chamber (Lab-line Biotronette).

2.2. Preparation of the biosorbent, chromium(VI) and Remazol Black B dye solutions for biosorption

After the growth period, the biomass was harvested from the medium and washed twice with distilled water, and then dried at 60 °C for 24 h. For the biosorption studies, a weighed amount of dried biomass was suspended in 100 ml of double-distilled water and homogenized in a homogenizer (Janke and Kunkel, IKA-Labortechnick, Ultra Turrax T25, Germany) at 8000 rpm for 20 min and then stored in the refrigerator. At the beginning of biosorption, 10 ml of dried biomass suspension was contacted with 90 ml of solution containing a known concentration of chromium(VI) or dye or chromium(VI) and dye together in an Erlenmeyer flask at the desired temperature and pH. All the final solutions contained 1.0 g l^{-1} of biosorbent.

Stock solution of chromium(VI) was prepared by dissolving the exact quantity of potassium dichromate (Merck) in double-distilled water and diluting to a concentration of 10 g l^{-1}. The chromium(VI) concentration tested varied between 10 and 100 mg l^{-1} in both single chromium(VI) and chromium(VI) and dye mixture containing media. Remazol Black B (C.I. Reactive Black 5; empirical formula $C_{26}H_{21}O_{19}N_5S_6Na_4$; molecular weight = 991.8), a commercial diazo reactive dye containing two vinyl sulfone as reactive groups, was kindly supplied from AYTEMIZLER Textile Co., Turkey. The dye stock solution was prepared by dissolving the powdered dyestuff in distilled water to a concentration of 2% (w/v). The dye concentration was selected as 100 mg l^{-1} both in single dye and in chromium(VI)–dye binary mixture containing media. The liquid media containing desired combinations of dye and chromium(VI) were prepared by diluting stock solutions of dye and chromium(VI) and mixing them in aqueous media. The initial pH value of each solution was adjusted to the required value with diluted or concentrated H_2SO_4 and NaOH solutions before contacting the biosorbent and no buffer was used in biosorption medium.

2.3. Biosorption experiments

Sorption studies were conducted in a routine manner by the batch technique in 250 ml Erlenmeyer flasks containing 100 ml of chromium(VI) or chromium(VI)–dye mixture bearing synthetic solutions at the desired level of each component. The flasks were agitated on a shaker at a 100-rpm constant shaking rate for 1 day to ensure the equilibrium was reached. Samples (5 ml) were taken before mixing the biosorbent and the chromium(VI) or chromium(VI)–dye mixture bearing solution at definite time intervals. Before analysis the samples were centrifuged at 4000 rpm for 3 min and the supernatant fractions were analyzed for the remaining chromium(VI) and/or dye ions. All the biosorption experiments were repeated twice to confirm the results. The data were the mean values of two replicate determinations. The flasks containing the dye and chromium(VI) together at desired levels only were used as control samples to observe any reaction between the dye and chromium(VI) ions.

The uptake of each component by unit mass of sorbent at any time (q_i, mg g^{-1}) was determined from Eq. (1):

$$q_i = \frac{C_{o,i} - C_{res,i}}{X} \quad (1)$$

where $C_{o,i}$ is the initial chromium(VI) or dye concentration (mg l^{-1}), $C_{res,i}$ is the residual (unadsorbed) chromium(VI) or dye concentration at any time (mg l^{-1}), and X is the sorbent concentration (g l^{-1}). $C_{res,i}$ is equal to $C_{eq,i}$ and q_i is equal to $q_{eq,i}$ at equilibrium.

2.4. Analytical methods

The concentration of chromium(VI) ions in the supernatant was determined spectrophotometrically by using diphenyl carbazide as the complexing agent in acid solution [40]. The absorbance of the purple coloured solution was read at 540 nm, where the maximum absorption peak existed, using a Shimadzu UV 2001 model double beam spectrophotometer. The concentration of residual dye in the biosorption medium was also determined spectrophotometrically. The absorbance of dye solution was read at 590 nm. Glass cells with 1 cm light path were used for the analysis. Other pollutant did not interfere with chromium or dye determination.

3. Results and discussion

3.1. Effect of initial pH on equilibrium chromium(VI) and Remazol Black B uptakes

The pH of metal and/or dye solution plays an important role in the whole biosorption process and particularly in the adsorption capacity, influencing the surface charge of the biosorbent, the

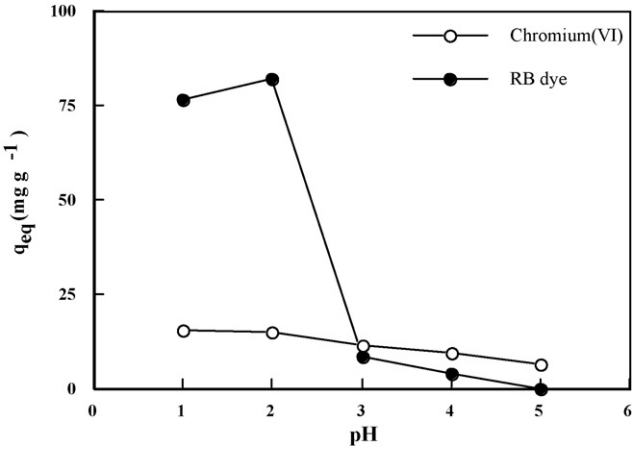

Fig. 1. Effect of initial pH on equilibrium uptake capacity of *Phormidium* sp. for single chromium(VI) and single Remazol Black B biosorptions ($C_{o,Cr}$: 100 mg l^{-1}; $C_{o,RB}$: 100 mg l^{-1}; *T*: 25 °C; *X*: 1.0 g l^{-1}; agitation rate: 100 rpm).

degree of ionization of the species present in the solution and the dissociation of functional groups on the active sites of biosorbent, and the solution metal and dye chemistries. In order to find a suitable pH for the effective binary dye and chromium(VI) biosorption by thermophilic cyanobacteria, experiments were performed at five different initial pH values ranging from 1.0 to 6.0 in single 100 mg l^{-1} chromium(VI) and in single 100 mg l^{-1} dye-containing media. As seen in Fig. 1, pH significantly affected the extent of adsorption of both components. The highest uptake values were found at pH 2.0 for both situations tested and biosorption of dye decreased sharply while chromium(VI) uptake lessened gradually with further increase in pH. Since both components showed the highest sorption at pH 2.0, all further biosorption studies were carried out at this pH.

The interaction between sorbates and sorbent is affected by the pH of an aqueous medium in two ways. Firstly, since dyes are complex aromatic organic compounds having different functional groups and unsaturated bonds, they have different ionization potentials at different pH, resulting in the pH dependent net charge on dye molecules. Reactive dyes are known to ionize to a high degree in aqueous solutions to form coloured anions due to the sulfonate group(s) in their structures. At lower pH values, two sulfonate ($-SO_3^-$) groups of Remazol Black B dye are easily dissociated and have negative charges in the aquatic environment. Besides dyes, chromium(VI) ions also behave as an oxo-anion in aqueous solution with an overall negative charge. In acidic environments chromium(VI) is present as mainly $HCrO_4^-$ and $Cr_2O_7^{-2}$ anions. Secondly, the surface of sorbent includes many functional groups, so the net charge on sorbent, which could be measured in the form of zeta potential or isoelectric point, is also pH dependent. Therefore, the interaction between dye or chromium(VI) and sorbent is basically a combined result of charges on molecules and the surface of sorbent. Carbohydrates, hexosamines, and phycobiliproteins are the major cell wall constituents of cyanobacteria [19,35,36]. At pH values below the isoelectric point (<4.0), the biomass will have a net positive charge due to protonation of nitrogen-containing functional groups. It is expected that positively charged functional groups on the sorbent surface will favour the adsorption of negatively charged dye anions and chromate ions due to electrostatic attraction which could be the primary mechanism [4,10,12–14,16,19–21,23,35,36,38]. Reduction in the biosorption of both components at pH value higher than 2.0 is probably due to the change in the overall surface charge on the cells and the competitiveness between the chromium and dye anionic species and OH^- ions in the bulk for the adsorption on active sites of the sorbent.

3.2. Effect of temperature on equilibrium chromium(VI) and Remazol Black B uptakes

Temperature is well known to play an important role in both biosorption rate and equilibrium uptake of metal and dye ions by microorganisms. Effect of temperature on the adsorption of chromium(VI) and dye has been studied over a range of 25–45 °C. The results revealed that both the sorptions of chromium(VI) and dye by dried *Phormidium* sp. were temperature dependent and increase in temperature from 25 to 45 °C decreased the uptakes of both components (Tables 1 and 2). For 100 mg l^{-1} initial chromium(VI) concentration, 15.2 and 22.8 mg chromium(VI) per gram of dried *Phormidium* sp. were adsorbed at equilibrium at 25 °C in the absence and in the presence of 100 mg l^{-1} initial dye concentration, respectively. With raising the temperature to 45 °C, equilibrium uptake capacity of biosorbent *Phormidium* sp. decreased to 11.5 and 15.0 mg g^{-1} in no dye and 100 mg l^{-1} dye-containing media resulted in 24.3% and 34.2% decrements in biosorption capacity. At 25 °C, for 100 mg l^{-1} chromium(VI) containing medium, dried algal biomass exhibited the highest Remazol Black B uptake capacity of 91.3 mg g^{-1}. However with increasing the temperature up to 45 °C, biosorption capacity of the biomass for

Table 1
Comparison of the pseudo-second-order kinetic constants of chromium(VI) biosorption at different initial chromium(VI) concentrations with respect to temperature in the absence and in the presence of 100 mg l^{-1} Remazol Black B concentration (initial pH: 2.0; *X*: 1.0 g l^{-1}; agitation rate: 100 rpm).

Temperature (°C)	No dye-containing medium					100 mg l^{-1} dye-containing medium				
	$C_{o,Cr}$ (mg l^{-1})	$q_{eqCr,exp}$ (mg g^{-1})	k_{Cr} ($\times 10^2$ g mg^{-1} min^{-1})	$q_{eqCr,cal}$ (mg g^{-1})	R^2	$C_{o,Cr}$ (mg l^{-1})	$q_{eqCr,exp}$ (mg g^{-1})	k_{Cr} ($\times 10^2$ g mg^{-1} min^{-1})	$q_{eqCr,cal}$ (mg g^{-1})	R^2 (mg g^{-1})
25	11.6	3.5	5.30	3.6	0.999	11.3	5.1	5.96	5.3	0.999
	23.2	6.2	2.49	6.3	0.999	24.7	10.4	2.85	10.5	0.998
	52.6	11.4	1.36	11.8	1.000	49.7	16.5	1.58	17.1	0.999
	74.1	13.7	1.21	13.9	1.000	76.9	20.5	1.41	21.4	0.999
	98.0	15.2	1.12	15.8	0.999	99.1	22.8	1.27	23.3	0.999
35	10.5	2.8	4.68	2.9	0.999	10.4	4.1	5.57	4.3	0.998
	26.5	5.9	2.05	6.2	1.000	24.5	8.4	2.58	8.9	0.998
	52.2	9.8	1.07	9.8	0.999	52.1	14.2	1.40	15.4	0.999
	74.2	11.9	0.94	12.3	0.999	76.6	17.2	1.23	18.4	0.999
	97.7	13.2	0.85	13.8	0.999	102.3	19.5	1.25	20.3	0.999
45	10.6	2.4	4.18	2.5	0.999	10.2	3.1	4.96	3.4	0.999
	25.6	4.9	1.85	5.2	1.000	26.4	6.8	2.29	7.4	0.999
	51.9	8.3	0.88	8.7	1.000	53.0	10.8	1.15	11.1	1.000
	76.5	10.3	0.74	10.9	1.000	75.6	13.3	1.00	14.0	0.999
	98.7	11.5	0.73	11.8	1.000	98.0	15.0	0.88	15.5	0.999

Table 2
Comparison of the pseudo-second-order kinetic constants of 100 mg l^{-1} Remazol Black B biosorption at different initial chromium(VI) concentrations with respect to temperature (initial pH: 2.0; *X*: 1.0 g l^{-1}; agitation rate: 100 rpm).

Temperature (°C)	$C_{o,Cr}$ (mg l^{-1})	$C_{o,RB}$ (mg l^{-1})	$q_{eqRB,exp}$ (mg g^{-1})	k_{RB} ($\times 10^2$ g mg^{-1} min^{-1})	$q_{eqRB,cal}$ (mg g^{-1})	R^2
25	11.6	101.5	84.1	8.85	84.1	1.000
	23.2	100.2	86.5	9.27	86.8	1.000
	52.6	99.4	87.9	9.57	88.5	1.000
	74.1	101.7	88.9	10.11	89.0	0.999
	98.0	100.8	91.3	10.45	92.2	0.999
35	10.5	99.8	82.7	8.32	82.9	1.000
	26.5	100.9	84.4	8.72	84.9	0.999
	52.2	101.2	85.9	8.93	86.5	0.999
	74.2	101.9	87.1	9.23	88.0	1.000
	97.7	100.2	88.5	9.52	88.9	1.000
45	10.6	102.4	78.2	7.11	78.3	0.999
	25.6	101.9	79.9	7.40	80.8	0.999
	51.9	100.3	81.5	7.78	82.3	1.000
	76.5	100.3	83.6	8.33	84.3	1.000
	98.7	101.5	84.9	8.65	85.4	1.000

the dye lessened to 84.9 mg g^{-1} showing 7.0% reduction in uptake capacity (Table 2). These results indicate the exothermic character of both sorptions. Since sorption is an exothermic process, this is an expected result due to weakened physical bonding between the chromium(VI) and/or dye ions and active sites of biosorbent with increasing temperature. Therefore, the decline in sorption capacity with increasing the temperature may be attributed to the physical adsorption.

3.3. Effect of initial chromium(VI) concentration on single chromium(VI) and binary chromium(VI) and dye uptakes

As demonstrated in Table 1, the equilibrium uptake of chromium(VI) by the biomass *Phormidium* sp. was strongly dependent on the initial chromium(VI) concentration, and metal uptake enhanced notably with increasing the initial chromium(VI) concentration tending to saturation at higher metal ion concentrations in both single chromium(VI) and binary chromium(VI) and 100 mg l^{-1} dye containing situations at all temperatures studied. At 25 °C, on changing the initial chromium(VI) concentration from 10 to 100 mg l^{-1}, the amount of biosorbed chromium(VI) increased from 3.5 to 15.2 mg g^{-1} and from 5.1 to 22.8 mg g^{-1} in the absence and in the presence of 100 mg l^{-1} dye, respectively, due to the increase in the number of ions competing for the available binding sites on the biomass surface and the increase in the driving force of the concentration gradient with the higher initial chromium(VI) concentration. The initial chromium(VI) concentration also remarkably influenced the chromium(VI) removal yield as shown in Fig. 2 in both single chromium(VI) and binary chromium(VI)–dye-containing media. Percent metal ion removal decreased with increasing chromium(VI) concentration due to nearly complete coverage of the binding sites of biosorbent at high chromium(VI) concentrations. Chromium(VI) removal efficiency was higher for low chromium(VI) concentrations because of availability of unoccupied binding sites on the biosorbent.

For the biosorption media including 100 mg l^{-1} of fixed dye concentration, the effect of initial chromium(VI) concentration on the dye removal was also significant. Both the amount of dye adsorbed onto *Phormidium* sp. and the dye removal efficiency increased with increasing the initial chromium(VI) concentration at all temperature values studied (Table 2 and Fig. 2). At 25 °C Remazol Black B biosorption capacity and removal efficiency of dried algal biomass enhanced from 84.1 to 91.3 mg g^{-1}, and 83.7–90.6%, respectively, with changing initial chromium(VI) concentration from 10 to 100 mg l^{-1}.

3.4. Effect of 100 mg l^{-1} initial Remazol Black B concentration on equilibrium chromium(VI) uptake

Table 1 and Fig. 2 also illustrated the effect of 100 mg l^{-1} of Remazol Black B dye concentration on the removal of chromium(VI) by dried *Phormidium* sp. biomass at different initial chromium(VI) concentrations with respect to temperature. The results clearly demonstrate that the existence of 100 mg l^{-1} dye led to a notable enhancement in the amount of chromium(VI) removed from aqueous solution and percent chromium(VI) removal efficiency at all temperatures studied. At 25 °C, when studied with 25 and 100 mg l^{-1} chromium(VI) concentrations, as the dye concentration changed from 0 to 100 mg l^{-1}, the amount of chromium(VI) adsorbed onto dried biosorbent at equilibrium increased from 3.5 to 5.1 mg g^{-1} (31.3% increase) and from 15.2 to 22.8 mg g^{-1} (33.3% increase), respectively, whereas the percent removal efficiency increased from 26.7% to 42.1%, and 15.5% to 23.0%, respectively.

3.5. Biosorption kinetics of single and binary chromium(VI) and dye uptakes

The kinetics of chromium(VI) and Remazol Black B removals both individually (at a representative concentration of 100 mg l^{-1}) and in 100 mg l^{-1} other component containing media has been carried out to understand the chromium(VI) and dye adsorption behaviours of the biosorbent. Fig. 3 shows the variation of chromium(VI) and Remazol Black B uptakes in single and binary systems and the biosorption selectivity of each species in binary system with time. As seen from figure, typical kinetic curves were obtained for the biosorption of both pollutants for each case and the presence of one species in solution did not influence the dynamic uptake process of other species. Both the extent of chromium(VI) and dye removals enhanced with increasing contact time and they remained constant after a contact time of about 120 min for chromium(VI) and 360 min for Remazol Black B (i.e., the equilibrium time) in the absence and in the presence of 100 mg l^{-1} co-component. For all cases studied, initial sorption of each component occurred much more rapidly and the majority of uptake took place within the first 30 min of contact due to vacant sites available at the initial stage for biosorption. For 100 mg l^{-1} initial chromium(VI) concentration, in the absence of dye, the amount of chromium(VI) adsorbed on the sorbent was 14.5 mg g^{-1} (95.4% of total adsorbed amount) at an initial adsorption time of 30 min. When 100 mg l^{-1} dye was added to the 100-mg l^{-1} chromium(VI) containing medium, in a similar initial time period, the equilibrium

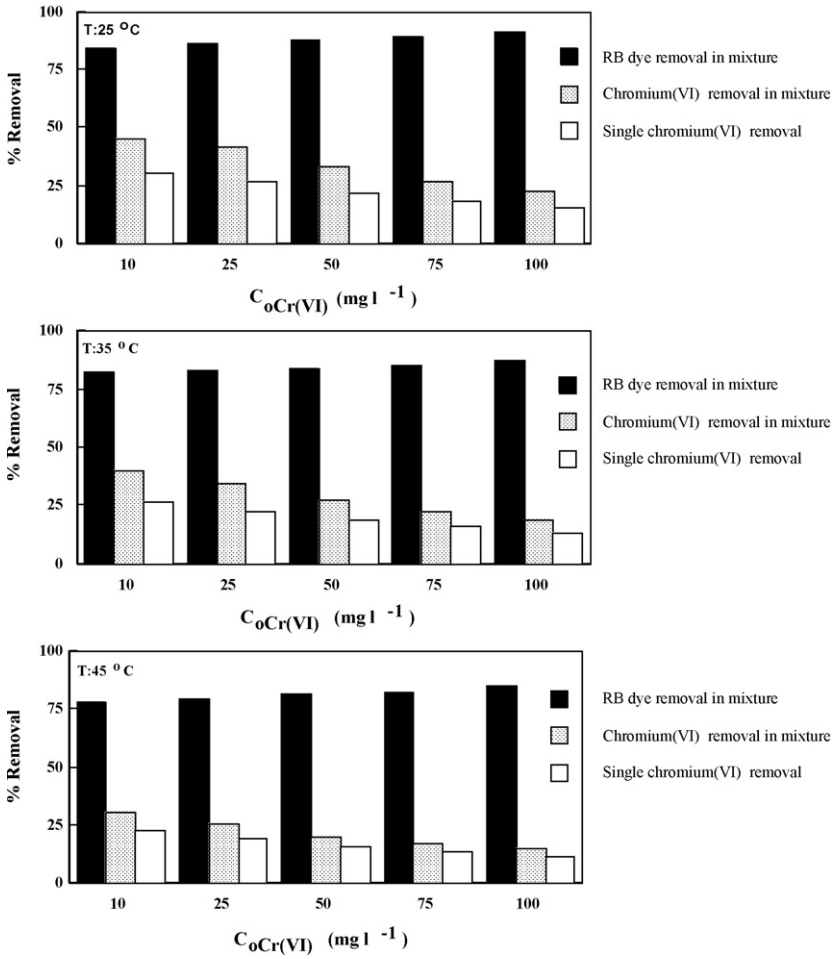

Fig. 2. Effects of temperature and initial chromium(VI) concentration on the single and binary chromium(VI) and Remazol Black B biosorption efficiencies ($C_{o,RB}$: 100 mg l^{-1}; X: 1.0 g l^{-1}; agitation rate: 100 rpm).

uptake of chromium(VI) by dried biomass raised to 21.0 mg g^{-1} (92.1% of total adsorbed amount). Results from the biosorption experiments with 100 mg l^{-1} dye indicated that 77.6 mg g^{-1} (94.6% of total adsorbed amount) was removed in 30 min. When 100 mg l^{-1} chromium(VI) added to 100 mg l^{-1} dye-containing medium, the level of colour removal achieved after 30 min of treatment was 78.8 mg g^{-1} (88.9% of total adsorbed amount). Such a rapid uptake of either or both chromium(VI) and dye ions by *Phormidium* sp. indicates that this biosorbent has an affinity for both anions pointing towards physical adsorption and that the uptake of each species occurs predominantly by surface binding.

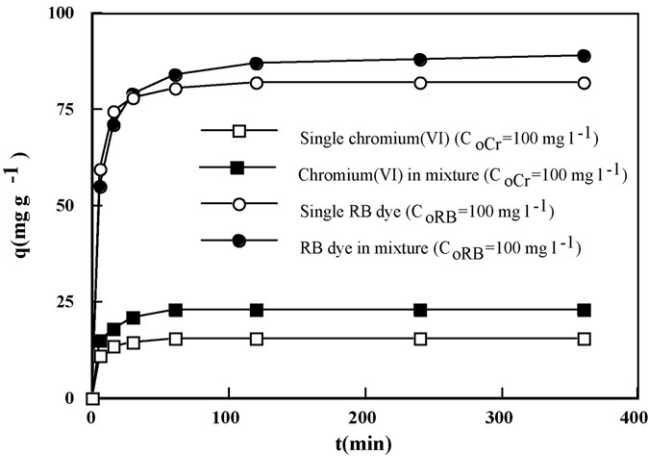

Fig. 3. Biosorption curves of 100 mg l^{-1} chromium(VI) and 100 mg l^{-1} Remazol Black B in the absence and in the presence of 100 mg l^{-1} other component (initial pH: 2.0; T: 25 °C; X: 1.0 g l^{-1}; agitation rate: 100 rpm).

From these results it is evident that Remazol Black B was adsorbed to a greater extent than chromium(VI) ions from both individual and mixed solutions. Higher uptake of dye was related to the strong affinity of the dye for the biosorbent. For the binary chromium(VI)–dye mixture biosorption studies, the presence of one species enhanced the uptake of other species so the total adsorption capacity of biosorbent increased. This suggests that the combination of species in solution had the effect of increasing the affinity of the microalgal surface for adsorption. This is known as cooperative adsorption. Although the synergistic adsorption mechanism is not very clear to us, an alteration of the overall charge within the system or changing the chemical characteristics of the adsorbent surface or the reorientation of adsorbed molecules or binding to the same sites on biosorbent surface may be occurred. The hydrogen adsorbed may form some new "hydrogen-bonding adsorption sites" for both components, which can also help to increase the total adsorption capacity. Molecular wedging effects may be responsible for the creation of new adsorption sites on the biosorbent surface. Alternatively, the sorption of components on the biomass with the highest affinity may induce a modification of

the specific binding sites for the components with the lowest affinity, increasing their sorption capability. Another mechanism may be that metal ion and dye may form a complex structure and then binds to the cell surface [30,41–44].

3.6. Application of equilibrium models to chromium(VI) biosorption data in the absence and in the presence of 100 mg l^{-1} Remazol Black B concentration

Within the literature, Freundlich and Langmuir are the most frequently used mono-component two-parameter models describing the sorption of metal ions on the biomass from the single metal solution. Insofar as metal sorption from two-component solution is concerned, an analysis of the literature revealed that both these mono-component and binary isotherm models have frequently been used to predict the behaviour of metal ion in a binary mixture [21,23–25,27,29,43,45–48]. The mono-component two-parameter models are usually preferred since they are simple, well-established, recharacterized by a limited number of adjustable parameters and easily linearized. They give a good description of experimental behaviour in a large range of operating conditions and have a physical meaning. In order to discover the sorption capacity of dried *Phormidium* sp. for chromium(VI) in the absence and in the presence of 100 mg l^{-1} Remazol Black B dye, the equilibrium adsorption data are correlated by the mono-component Freundlich and Langmuir isotherm equations. The major assumption here was that chromium(VI) indicated an ideal sorption behaviour (equilibrium model constants do not depend on the presence of other ionic species in solution). The empirical mono-component Langmuir equation is given by Eq. (2):

$$q_{eq} = \frac{Q^o b C_{eq}}{1 + bC_{eq}} \quad (2)$$

where parameters Q^o and b are the Langmuir constants related to maximum adsorption capacity and bonding energy of adsorption, respectively.

The empirical mono-component Freundlich isotherm is expressed by the following equation:

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

where K_F and n are the Freundlich constants characteristic on the system.

The corresponding Langmuir and Freundlich parameters for chromium(VI) sorption from single chromium(VI) and binary chromium(VI)-100 mg l^{-1} dye-containing solutions are listed in Table 3 with respect to temperature. The applicability of the models was established from the regression correlation, R^2 and fitted

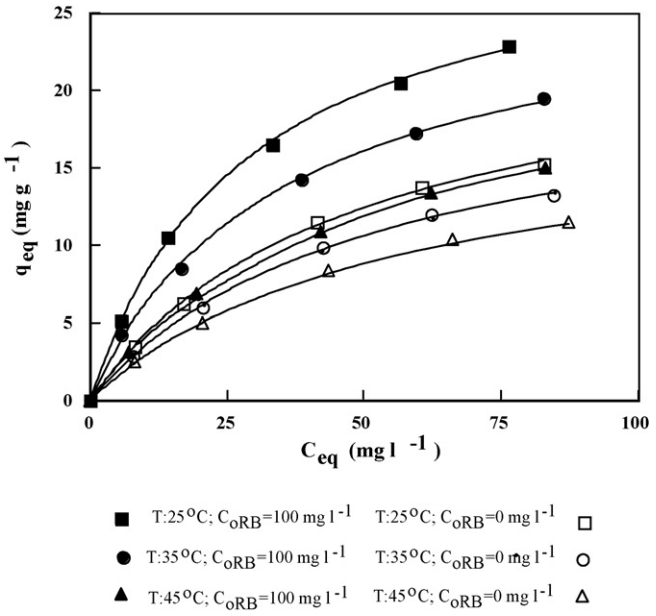

Fig. 4. Langmuir adsorption isotherms of chromium(VI) obtained at different temperatures in the absence and in the presence of 100 mg l^{-1} Remazol Black B dye (X: 1.0 g l^{-1}, agitation rate: 100 rpm) (symbols show experimental points and curves show model fittings).

curves. The results showed that the regression correlations for the Langmuir model are between 0.996 and 1.000 while those of the Freundlich model are between 0.981 and 0.992. This suggests a greater fit by the Langmuir model in comparison to the Freundlich model. Using the model parameters, equilibrium uptake values of chromium(VI) for each case were predicted from the related formulae at all temperature values studied and plotted. The non-linearized adsorption isotherms of chromium(VI) ions in the absence and in the presence of 100 mg l^{-1} dye are shown in Figs. 4 and 5 together with experimental points at three temperatures studied. The isotherms showed the saturation of cell-binding sites at higher chromium(VI) concentrations. The plots also indicated that the equilibrium uptake of chromium(VI) diminished regularly with raising the temperature and enhanced apparently by the presence of 100 mg l^{-1} dye. The data in Figs. 4 and 5 also confirmed that the Langmuir model closely predicted the equilibrium data, as evident from the overlapping of its model curves.

The Freundlich constant n is an empirical parameter that varies with the level of heterogeneity indicating the degree of non-

Table 3
Effect of temperature on the Freundlich and Langmuir adsorption constants of chromium(VI) biosorption in the absence and in the presence of 100 mg l^{-1} Remazol Black B dye (initial pH: 2.0; X: 1.0 g l^{-1}; agitation rate: 100 rpm).

Temperature (°C)	Freundlich model					
	No dye-containing medium			100 mg l^{-1} dye-containing medium		
	K_F [(mg g^{-1})(mg l^{-1})$^{-1/n}$]	n	R^2	K_F [(mg g^{-1})(mg l^{-1})$^{-1/n}$]	n	R^2
25	0.96	1.55	0.988	2.08	1.75	0.981
35	0.76	1.51	0.989	1.51	1.68	0.992
45	0.61	1.49	0.992	0.92	1.55	0.991
Temperature (°C)	Langmuir model					
	No dye-containing medium			100 mg l^{-1} dye-containing medium		
	Q^o (mg g^{-1})	b (l mg^{-1})	R^2	Q^o (mg g^{-1})	b (l mg^{-1})	R^2
25	24.3	0.0207	0.998	31.2	0.0345	1.000
35	21.7	0.0189	0.997	27.6	0.0278	0.996
45	18.9	0.0172	0.997	23.5	0.0210	0.998

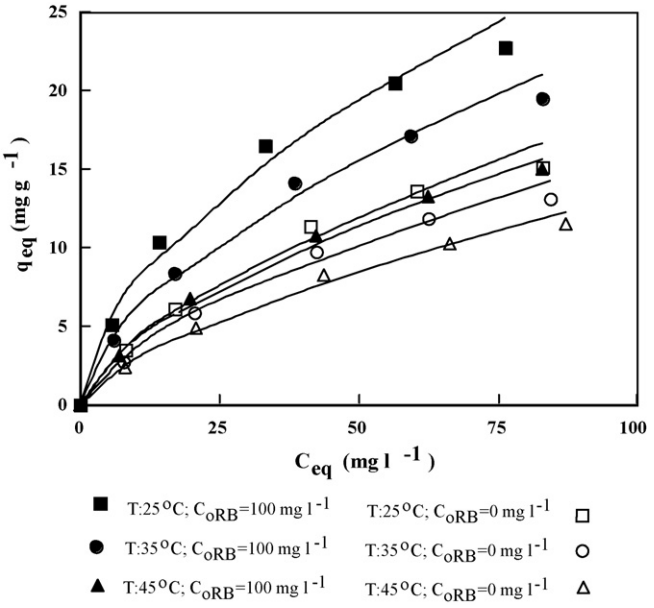

Fig. 5. Freundlich adsorption isotherms of chromium(VI) obtained at different temperatures in the absence and in the presence of 100 mg l^{-1} Remazol Black B dye (X: 1.0 g l^{-1}; agitation rate: 100 rpm) (symbols show experimental points, curves show model fittings).

linearity between chromium(VI) uptake capacity and unadsorbed chromium(VI) concentration and is related to the distribution of bonded ions on the sorbent surface. In general $n > 1$ illustrates that adsorbate is favourably adsorbed on an adsorbent, corresponds to a normal an L-type Langmuir isotherm, and the higher the n value the stronger the adsorption intensity. In particular, the value of n, which is significantly higher than unity, indicated that chromium(VI) ions are favourably adsorbed by *Phormidium* sp. at all the temperatures studied. The values of n also indicated that the chromium(VI) biosorption intensity was positively affected by the 100-mg l^{-1} dye added into biosorption medium. The constant K_F, related to biosorption capacity, can be defined as a sorption coefficient which represents the quantity of adsorbed chromium(VI) for a unit equilibrium concentration (i.e., $C_{eq} = 1$). From table it was seen the value of K_F decreased with the rise in temperature. The co-existence of dye at its initial concentration also increased the K_F constant significantly. The highest K_F value was 0.96 in the absence of dye and the value increased to 2.08 with the addition of 100 mg l^{-1} dye at 25 °C, which was consistent with the experimental observation.

Table 3 also indicates that Langmuir model parameters (Q^o and b) of chromium(VI) biosorption were also largely dependent on the Remazol Black B dye added and the temperature. While the Freundlich model does not describe the saturation behaviour of the biosorbent, Q^o represents the monolayer saturation at equilibrium or the total capacity of biosorbent for chromium(VI) metal ion. High Q^o values show a desirable high capacity of chromium(VI) binding. As seen from Table 3, dried *Phormidium* sp. exhibited the maximum biosorption capacity (Q^o) at 25 °C and at 100 mg l^{-1} dye-containing medium. The addition of 100 mg l^{-1} dye enhanced the maximum chromium(VI) uptake capacity of biomass from 24.3 to 31.2 mg g^{-1} compared to the single metal conditions. A high value of the other Langmuir parameter, b, indicates a steep desirable beginning of the isotherm which reflects the high affinity of the biosorbent for the sorbate(s). Its value is the reciprocal of the chromium(VI) concentration at which half of the saturation of the biosorbent is attained. The highest b value obtained at 25 °C also increased with the addition of dye indicating its positive effect on chromium(VI) biosorption.

3.7. Application of pseudo-second-order kinetic model for chromium(VI) and dye biosorptions

The pseudo-second-order model was used to test the individual biosorption kinetics of chromium(VI) and Remazol Black B dye in the mixture. Contrary to other well-established kinetic models, pseudo-second-order model predicts the adsorption behaviour over the whole range of adsorption period and it is in agreement with the chemisorption mechanism being the rate-controlling step. Chemisorption (ion-exchange and electrostatic attractions) is commonly cited as the main mechanism for the adsorption of anionic species in acidic conditions [49]. The pseudo-second-order equation is based on the sorption capacity of the solid phase and is expressed for each species as

$$\frac{dq_i}{dt} = k_i(q_{eq,i} - q_i)^2 \quad (4)$$

where k_i is the rate constant of second-order biosorption of each component. After integration and applying the boundary conditions of $t = 0$ to $t = t$ and $q_i = 0$ to $q_i = q_{eq,i}$; the integrated form of Eq. (4) becomes a linear function and model parameters of $q_{eq,i}$ and k_i can be estimated from the slope and intercept of the t/q_i against T plot.

The values of rate constant (k_i) and equilibrium uptake ($q_{eq,Cr}$) were determined from the plots of linearized form of the pseudo-second-order model at all chromium(VI) concentrations at 0 and 100 mg l^{-1} dye levels with respect to temperature (data not shown) and are presented in Table 1 along with the corresponding linear regression coefficients. The results indicated that the second-order rate constants were affected by the initial chromium(VI) concentration, 100 mg l^{-1} dye concentration added and temperature. The rate constants, diminished notably with both increasing chromium(VI) concentration and temperature, may be attributed to dominant surface adsorption. The rate constants of chromium(VI) biosorption increased in 100 mg l^{-1} dye-containing medium when compared with its single-solute adsorption. The correlation coefficients obtained greater than 0.999 and the adequate fitting of theoretical and experimental $q_{eq,Cr}$ values for all combinations suggest the applicability of second-order kinetic model in explaining the kinetics of chromium(VI) biosorption.

For the biosorption of 100 mg l^{-1} Remazol Black B dye at the three different temperatures in the presence of increasing chromium(VI) concentrations from 10 to 100 mg l^{-1}, pseudo-second-order rate constants and $q_{eq,RB}$ values determined from the plots of linearized form of the pseudo-second-order model (data not shown) are presented in Table 2 along with the corresponding linear regression coefficients. The results indicated that the rate constants of dye biosorption were also affected by the initial chromium(VI) concentration and temperature; they diminished slightly with increasing temperature and increased regularly with chromium(VI) concentration. The values of predicted equilibrium sorption capacities showed reasonably good agreement with the experimental equilibrium dye uptake values. Moreover the correlation coefficients were close to 1.0 for all cases.

3.8. Thermodynamic modelling of chromium(VI) and dye biosorptions

Thermodynamic parameters reflect the feasibility and spontaneous nature of the process. Thermodynamic parameters of free energy, enthalpy and entropy changes can be estimated using equilibrium constants varying with temperature. Both the sorptions of chromium(VI) and dye anions can be summarized by the following reversible process which represents a heterogeneous equilibrium.

$$\text{Ionic species in solution} \leftrightarrow \text{Ionic speices} - \text{Biosorbent} \quad (5)$$

The apparent equilibrium constant ($K'_{c,i}$) of the biosorption of each component is defined as

$$K'_{c,i} = \frac{C_{ad,eqi}}{C_{eq,i}} \quad (6)$$

where $C_{ad,eqi}$ is the concentration of each ionic species on the biosorbent at equilibrium. When 1 g l^{-1} of sorbent is used, the value of $C_{ad,eqi}$ will give the value of $q_{eq,i}$ and the apparent equilibrium constant ($K'_{c,i}$) will be equal to:

$$K'_{c,i} = \frac{q_{eq,i}}{C_{eq,i}} \quad (7)$$

For the biosorption of chromium(VI) in the presence of 100 mg l^{-1} Remazol Black B dye, the standard thermodynamic equilibrium constant (K_c^o) of the chromium(VI) sorption system can be obtained by calculating the apparent equilibrium constants ($K'_{c,Cr}$) at different initial concentrations of chromium(VI) and extrapolating to zero at 25 °C. This value will be also equal to the opposite of intercept value of $C_{eq,Cr}/q_{eq,Cr}$ vs. $C_{eq,Cr}$ plot ($K_c^o = bQ^o$) which shows the linearized form of the Langmuir model. The K_c^o value is used in the following equation to determine the free energy change of the chromium(VI) adsorption reaction (Gibbs free energy) (ΔG^o) at 25 °C:

$$\Delta G^o = -RT \ln K_c^o \quad (8)$$

The free energy change indicates the degree of spontaneity of the chromium(VI) sorption process and the higher negative value reflects a more energetically favourable adsorption. The equilibrium constant may be expressed in terms of enthalpy change of sorption (ΔH^o) and entropy change of sorption (ΔS^o) as a function of temperature. The relationship between the K_c^o and temperature is given by the van't Hoff equation:

$$\ln K_c^o = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (9)$$

ΔH^o and ΔS^o can be obtained from the slope and intercept of a van't Hoff plot of $\ln K_c^o$ vs.1/T.

The value of K_c^o evaluated from $q_{eq,Cr}/C_{eq,Cr}$ vs. $C_{eq,Cr}$ plot as 1.076 (data not shown) at 25 °C was used to find the ΔG^o value of chromium(VI) biosorption in 100 mg l^{-1} dye-containing medium. Using Eq. (8), the value of standard Gibbs free energy change was calculated as −0.18 kJ mol^{-1}. The negative value of ΔG^o found here indicates that the adsorption process is thermodynamically feasible at room temperature. The standard enthalpy and entropy changes of the biosorption process were determined from the $\ln K_c^o$ vs. 1/T plot (R^2 = 0.989). The negative ΔH^o value of −387.24 kJ mol^{-1} confirmed the exothermic nature of chromium(VI) biosorption on dried *Phormidium* sp. while negative ΔS^o value of −1.32 kJ mol^{-1} K^{-1} revealed the decreased randomness at the solid/solution interface.

For the biosorption of 100 mg l^{-1} Remazol Black B dye in the presence of increasing chromium(VI) concentrations, an average apparent equilibrium constant ($K_{c,RB}$) of the sorption system was obtained as 7.02 at 25 °C. Using Eq. (8), the value of standard Gibbs free energy was determined as −48.3 kJ mol^{-1}. The higher negative value of ΔG^o confirms the feasibility and spontaneous nature of Remazol Black B biosorption process in chromium(VI) containing medium at 25 °C with a high degree of affinity of the dye ions for the biosorbent surface. From the van't Hoff plot (R^2 = 0.998), the negative value of ΔH^o for Remazol Black B biosorption (−279.06 kJ mol^{-1}) also suggested the exothermic nature of dye adsorption process favourable at lower temperatures and possible strong bonding between dye and the sorbent. Again the negative value of ΔS^o (−0.78 kJ mol^{-1} K^{-1}) explained the decreased randomness at the interface and no structural modification in biosorbent.

The enthalpy and entropy values can give some idea about the mechanism of bonding. Generally, the change of free energy for physical adsorption is smaller than that of chemisorption. The change in adsorption enthalpy for physisorption is between 20 and 40 kJ mol^{-1}, but chemisorption is in the range of 80–400 kJ mol^{-1}. The values of the change in enthalpy indicated that each adsorption process is chemical in nature.

4. Conclusion

In this study, thermophilic cyanobacterium *Phormidium* sp. was used and evaluated as a possible biosorbent for the single chromium(VI) and binary chromium(VI) and Remazol Black B dye treatment. In the binary system, changing concentrations of chromium(VI) and 100 mg l^{-1} Remazol Black B added into biosorption medium exhibited a cooperative (synergistic) adsorption on the biosorbent. The results showed that although the microalgae has a reasonable uptake capacity for chromium(VI), it exhibited a considerable potential for the removal of Remazol Black B reactive dye. This work can provide a useful data for both the rapid bioremovals of chromium(VI) and Remazol Black B anions from the solutions containing 100 mg l^{-1} dye and chromium(VI) at changing levels by the cyanobacterium *Phormidium* sp.

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