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Sorption sites of microalgae possess metal binding ability towards Cr(VI) from tannery effluents—a kinetic and characterization study

Sundaramoorthy Balaji[a], Thiagarajan Kalaivani[a,1], Mohan Shalini[a]
Mohan Gopalakrishnan[b], Mubarak Ali Rashith Muhammad[b],
Chandrasekaran Rajasekaran[a,*,1]

[a]*School of Bio Sciences and Technology, VIT University, Vellore, India, emails: msmbalaji@gmail.com (S. Balaji), tkvani72@gmail.com (T. Kalaivani), shalu.sowmi@gmail.com (M. Shalini), Tel: +91 416 2202542, +91 9442994888; Fax: +91 416 2243092; email: drcrs70@gmail.com (C. Rajasekaran)*
[b]*School of Advanced Sciences, VIT University, Vellore, India, emails: mgkrishna87@gmail.com (M. Gopalakrishnan), email: rashithmd@gmail.com (M.A. Rashith Muhammad)*

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ABSTRACT

Prominent microalgal species, namely *Anabaena*, *Oscillatoria*, *Phormidium*, and *Spirogyra*, were isolated from estuaries polluted with tannery effluents and studied to determine their Cr (VI) bio-sorption potential. The bio-sorption potential was determined by studying the effect of growth, biomass, reduction of Cr(VI) levels, and Cr(VI) absorption by the microalgal species. The respective values for *Anabaena*, *Oscillatora*, *Phormidium*, and *Spirogyra* compared with the control were as follows: growth in BG 11 medium containing tannery effluent was 53.99, 60.03, 55.76, and 55.85%; the biomass was 60.65, 77.61, 67.16, and 76.01%; the Cr(VI) reduction potential was 70.96, 80.64, 76.12, and 74.83%; and the bio-sorption potential was 75.48, 80.64, 79.35, and 77.41%. The removal of heavy metals by microalgal biomass involves bio-reduction and bio-sorption. Fourier-transform infrared spectroscopy and nuclear magnetic resonance results revealed the presence of microalgal sorption sites. All four species showed maximum removal through bio-sorption, which was achieved at the end of the stationary phase. Kinetic models such as pseudo-first-order and pseudo-second-order models were tested, and the experimental data were in agreement with the kinetic model. The results of this study suggest that the microalgal species employed could be used as effective bio-sorbents for Cr(VI) removal from tannery effluents.

Keywords: Bio-sorption; Microalgae; Cr(VI); Effluent; Kinetic models

1. Introduction

In India, during the past few decades, the discharge of heavy metals from tanneries into the environment has become a matter of concern [1]. Tannery pollutants introduced into the environment mainly by the leather processing units are the by-products of chrome tanning of leather using chromium [2,3]. Chromium exists in several oxidation states, but the most stable and

*Corresponding author.

[1]Contributed equally.

common forms are Cr^{3+} and Cr^{6+}, of which Cr^{6+} is more toxic [4–6]. Hexavalent chromium compounds are genotoxic carcinogens, and their accumulation in the food chain leads to serious ecological and health problems [7,8]. Ingestion of Cr(VI) can increase the risk of lung cancer, in addition to causing irritation or ulcers in the stomach and intestines of humans [9,10].

Conventional methods, such as chemical precipitation, membrane filtration, solvent extraction, and ion exchange, have been commonly employed for stripping toxic metals from wastewaters [11,12]. All conventional treatment methods have several disadvantages such as high cost and generation of toxic sludge [13,14]. Furthermore, these processes might become ineffective or extremely expensive when metal concentration in wastewater becomes very low.

Metal uptake capacity of microalgal biomass is higher than that of chemical sorbents employed in conventional techniques [15,16]. Among the various forms of algae, microalgae such as *Arthrospira* have been found to possess higher metal uptake capacities [17]. This is due to the presence of polysaccharides, proteins and lipids containing functional groups such as amino, hydroxyl, carboxyl, and sulfate on the surface of their cell walls, which can act as binding sites for metals [18]. Microalgae also exhibit eco-friendly characteristics and high uptake capacity apart from involving low cost, lack of toxicity constraints, and less sludge production. Microalgae are also effective in treating wastewater with all levels of contamination [19]. The mechanism of interaction of heavy metals, particularly chromium, with biological systems is very different and complex [20,21]. The kinetics of bio-sorption comprise an important design parameter that describes how the adsorbate interacts with the bio-sorbent [22–24]. The bio-sorption was investigated by fitting of the experimental data to the pseudo-first-order and pseudo-second-order kinetic models [25,26].

To the best of our knowledge, no in-depth study has been carried out on the removal of Cr(VI) using biomass of freshwater microalgae, such as *Anabaena, Oscillatoria, Phormidium,* and *Spirogyra*. Therefore, the objective of this study was to analyze the Cr(VI) bio-sorption capacity of the microalgal species isolated from an estuary of tannery effluent-polluted Palar River near Vaniyambadi, in Tamil Nadu, India. It is well known that Vellore district of Tamil Nadu state, particularly Vaniyambadi and Ambur (an industrial area), has several tanneries and associated industries, which release heavy metals and cause huge environmental problems. This study aimed to evaluate the adsorption capacities of the microalgae; in addition, Fourier-transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) studies determined the sorption sites, and kinetic models were used to determine the sorption rates.

2. Materials and methods

2.1. Sampling site of microalgae

The microalgae *Anabaena, Oscillatoria, Phormidium,* and *Spirogyra* were used as bio-sorbents for the bio-sorption of heavy metals in tannery effluents. Microalgal samples were collected from the estuaries of the Palar River near Vaniyambadi, Vellore district, Tamil Nadu, India. The collected microalgal species were identified by Prof. V. Krishnamurthy, (late) Director, Krishnamurthy Institute of Algology, Chennai, Tamil Nadu, India, with reference to the monograph of T.V. Desikachary [27].

2.2. Collection of tannery effluent

Tannery effluent was collected from the Ambur taluk of Vellore district, Tamil Nadu, India. The presence of chromium was analyzed by atomic absorption spectroscopy (AAS), and it was found to be 155 mg/L in 100% effluent [28,34].

2.3. Growth of the microalgae

Growth rate of *Anabaena, Oscillatoria, Phormidium,* and *Spirogyra* was monitored turbidimetrically at 560 nm, and their doubling time and specific growth rate were calculated. The formula used for calculating the doubling time (*td*) was 2.303 * (log day 2−log day 1)/(day 2−day 1), and specific growth rate (μ) was determined as $\mu = 0.693/td$ [29].

2.4. Biomass estimation

Biomass content of all the species was estimated using the following formula:

(Weight [g/L] = OD primary × 0.238 [empirical data, dependent on cell strain, etc.]) [30].

2.5. Physicochemical analysis of tannery effluent

The tannery effluent was analyzed for its physicochemical parameters before and after treatment according to the standard methods of American Public Health Association [28].

2.6. Chromium reduction study

Concentrations of chromium ions in the tannery effluent were analyzed using a spectrophotometer

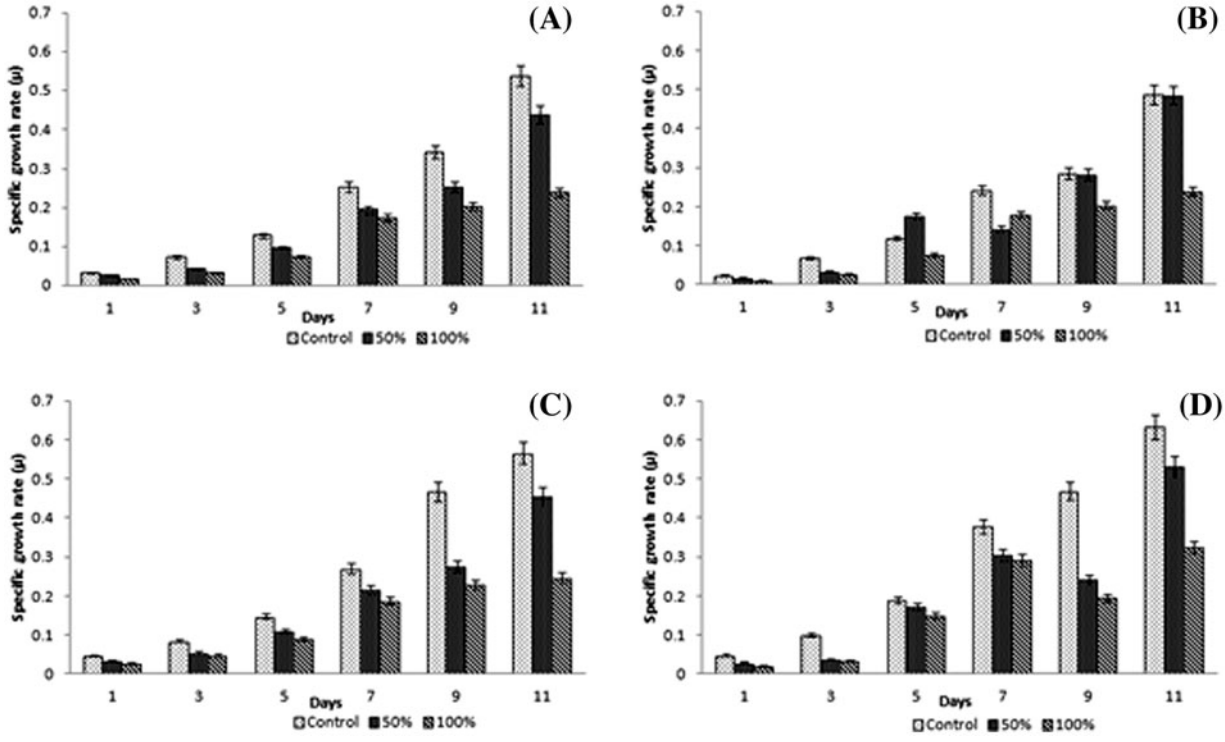

Fig. 1. Specific growth rate of (A) *Anabaena*, (B) *Oscillatoria*, (C) *Phormidium*, and (D) *Spirogyra* grown with tannery effluent.

(Gene Quant 1300 GE Lifesciences, UK) at 540 nm by complexing it with 1,5-diphenylcarbazide in an acidic medium [31].

2.7. Chromium absorption study and bio-sorption efficiency

Cell suspensions of the microalgae were analyzed for the presence of chromium by atomic absorption spectrometry (AAS) (Varian 250 model) [28]. The bio-sorption efficiency was calculated using the following formula: Sorption $(\%) = C_0 - C_e/C_0 \times 100$, where C_0 and C_e are the initial and equilibrium concentrations of Cr(VI) (mg/L) [26].

2.8. FTIR study

Dried microalgal samples were analyzed in the FTIR (Perkin–Elmer, MA, USA) for identification of the functional groups. The microalgal cell suspension was dried and finely ground with potassium bromide; these pellets were made into disks by applying pressure and used for analysis.

2.9. NMR study

Dried microalgal samples were analyzed by ^{1}H NMR (Bruker, USA) for the identification of sorption sites. The NMR spectrum was obtained using deuterated cadmium chloride solution as the solvent. Normal microalgae and microalgae with effluent were analyzed separately to determine the metal complexation on the algae sorption sites.

2.10. Kinetic modeling study

The kinetic models of the pseudo-first-order [32] and pseudo-second-order [33] adsorption rate can be determined as follows. The pseudo-first-order rate equation is $\log (q_e - q_t) = \log q_e - (k_1/2.303)\ t$, where q_e and q_t (mg/g) are the amounts of Cr(VI) sorbed onto the mass of algae at equilibrium and at time t (min), respectively, and k_1 is the rate constant of the pseudo-first-order kinetics. The pseudo-second-order kinetic model rate equation is $t/q_t = (1/k_2 q_e^2) + (1/q_e)\ t$, where q_e and q_t are the amounts of Cr(VI) sorbed onto the mass of algae at equilibrium and at time t (min), respectively, and k_2 is the rate constant for the pseudo-second-order kinetics.

2.11. Statistical analysis

All the experiments were conducted in triplicates ($n = 3$), and the data were represented as mean ±

standard error. Correlation analysis was performed between the specific growth rates of different microalgae using Pearson's correlation test using the Statistical Package for Social Sciences statistical tool (SPSS, version 16.0).

3. Results and discussion

3.1. Analysis of growth and microalgal biomass

Growth and biomass are the important parameters that are generally used in wastewater treatment studies to determine the bio-sorbent potential of an agent used for removing pollutant at a given initial concentration. This experiment was conducted with microalgae species, namely *Anabaena*, *Oscillatoria*, *Phormidium*, and *Spirogyra* inoculated in BG 11 media with tannery effluent containing Cr(VI) at room temperature, and the results are depicted in Figs. 1(A–D) and 2(A–D). The growth of microalgae in 50 and 100% effluent was 76.99 and 53.99% for *Anabaena*, 92.46 and 60.03% for *Oscillatoria*, 77.13 and 55.76% for *Phormidium*, and 72.59 and 55.85% for *Spirogyra*. Similarly, the biomass content of microalgae in 50 and 100% effluent was 74.92 and 60.65% for *Anabaena*, 87.31 and 77.61% for *Oscillatoria*, 80.40 and 67.16% for *Phormidium*, and 83.83 and 76.01% for *Spirogyra* when compared with the control. Maximum growth and biomass were observed in *Oscillatoria*, followed by *Phormidium*, *Spirogyra*, and *Anabaena*. Growth and biomass were found to be maximum at low concentrations of chromium and minimum at high concentration of chromium. It has also been reported that the growth of microalgae is a significant factor that influences the metal binding efficiency because of the presence of active sites on the algal biomass [34]. The proposed mechanism of bio-sorption is that it could be due to the presence of uronic groups in the exopolysaccharides of microalgae which bind to heavy metals [35] in addition to the presence of various polysaccharides such as cellulose and alginate in the algal cell wall [36,37]. Results indicate that the cyanobacterial microalgal species used in this study have the ability to tolerate the Cr(VI) stress and they can grow in the natural heavy metal contaminated water; this tolerance may be attributed to this capacity of bio-adsorption.

3.2. Analysis of physicochemical parameters

Physicochemical characteristics such as appearance, color, odor, total solids (TS), total dissolved solids (TDS), total suspended solids (TSS) pH, and amount of

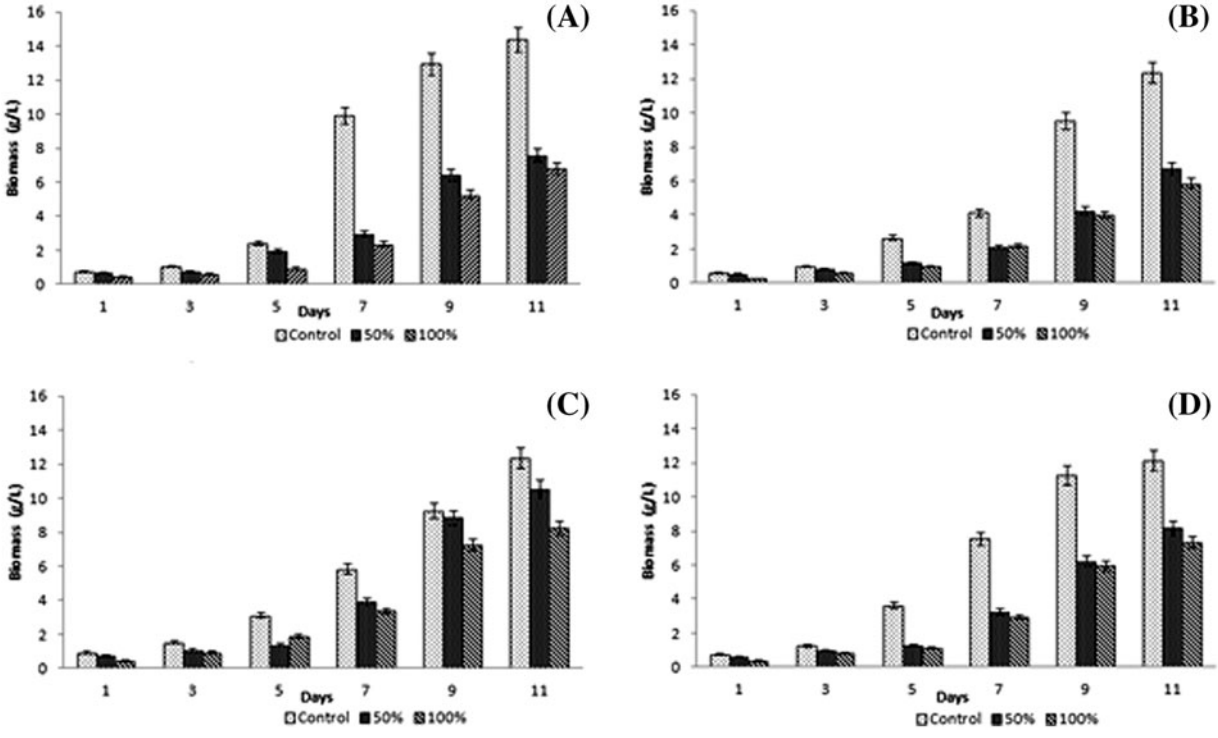

Fig. 2. Biomass accumulation of (A) *Anabaena*, (B) *Oscillatoria*, (C) *Phormidium*, and (D) *Spirogyra* grown with tannery effluent.

Table 1
Physicochemical analysis of tannery effluent before and after treatment with microalgae

S. No.	Physical examination	Effluent before treatment	Effluent after treatment with microalgae			
			Anabeana	*Oscillatoria*	*Phormidium*	*Spirogyra*
1	Appearance	Turbid	–	–	–	–
2	Color	Brown	Green	Green	Green	Green
3	Odor	Foul	None	None	None	None
4	Total solids (TS) (mg/l)	158.00 ± 0.15	149.00 ± 0.23	146.00 ± 0.16	152.00 ± 0.13	150.00 ± 0.16
5	Total dissolved solids (TDS) (mg/l)	150.00 ± 0.16	143.00 ± 0.18	141.00 ± 0.24	146.00 ± 0.16	144.00 ± 0.18
6	Total suspended solids (TSS) (mg/l)	8.00 ± 0.14	6.00 ± 0.16	5.00 ± 0.13	6.00 ± 0.16	6.00 ± 0.23
7	pH	6.4 ± 0.4	8.75 ± 0.4	8.00 ± 0.6	8.50 ± 0.6	8.50 ± 0.4
8	Chromium mg/l	155 ± 0.24	38 ± 0.16	30 ± 0.16	32 ± 0.14	35 ± 0.13

chromium present in the tannery effluent were analyzed at the end of the stationary phase (after 11 d) of the culturing of *Anabaena*, *Oscillatoria*, *Phormidium, and Spirogyra.* The growth of the microalgal species led to changes in physicochemical parameters and caused a reduction in the amount of chromium, which is shown in Table 1. After treatment with microalgae, the turbidity and foul smell of the effluent decreased and the color changed from brown to green. TS, TDS, and TSS decreased variably, and the pH also changed from acidic to alkaline after the treatment with microalgae. The reduction of physicochemical parameters could be due to the presence of polysaccharides, proteins, and other functional groups found in the microalgae [38]. The exopolysaccharides of cyanobacteria are rich in negatively charged uronic acids which can bind to cations with heavy metals [39]. Cyanobacteria species exhibit phycoremediation capacity due to the presence of reactive groups with an active binding site; these groups complex with effluents, resulting in flocculation, which reduces the TS and color of the tannery effluents [12]. Removal of chromium from the medium is due to the chelation of the chromium by exopolysaccharides or metal uptake by microalgae.

3.3. Analysis of chromium reduction

This study shows the substantial reduction of chromium level by the different microalgal species, as depicted in Fig. 3. Reduction of Cr(VI) was found to be 70.96% for *Anabaena*, 80.64% for *Oscillatoria*, 76.12% for *Phormidium*, and 74.83% for *Spirogyra,* respectively. The reduction potential is about the reduction of Cr (VI) to Cr(III); reduction of Cr(VI) is achieved by any one of the two possible mechanisms, namely accumulation of Cr(VI) inside the microalgae species or absorption of Cr(VI) on its surface [40]. Variation in the reduction of Cr(VI) levels has been reported for

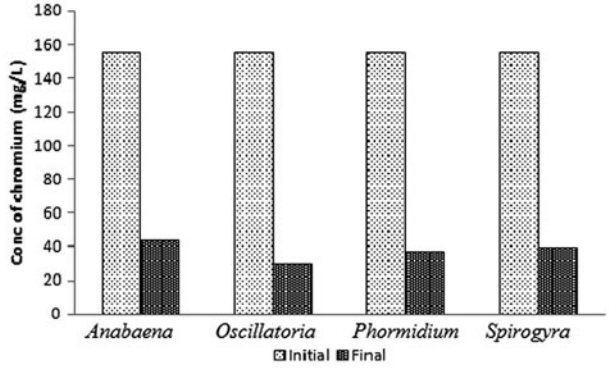

Fig. 3. Reduction of chromium(VI) in tannery effluent by microalgae species.

bio-adsorbents under varying concentrations of chromium or incubation periods [41]. Microalgae have the ability to utilize the nutrients that are already present in the tannery effluents for their growth and cause reduction in chromium levels [31,42]. Microalgal species may alleviate chromium toxicity through the synthesis of antioxidant enzymes or by producing reductants that reduce chromium by chemical redox reactions [12,43].

3.4. Analysis of chromium absorption and bio-sorption efficiency

The effect of contact time on the removal of Cr(VI) was studied with the microalgae *Anabaena, Oscillatoria, Phormidium,* and *Spirogyra* at an initial metal concentration of 155 mg/L at room temperature for 11 d (up to the stationary phase) by AAS and is depicted in Fig. 4. Removal of Cr(VI) was 75.48% in *Anabaena*, 80.64% in *Oscillatoria*, 79.35% in *Phormidium,* and 77.41% for *Spirogyra.* The increased bio-absorption capacity might be attributed to the fact that the initial

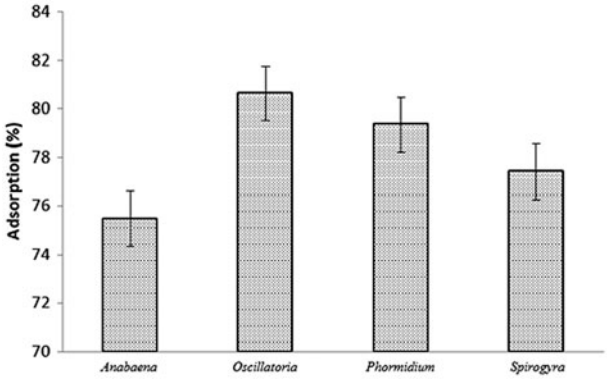

Fig. 4. Adsorption of chromium(VI) in tannery effluent by microalgae species.

metal concentration increased the adsorption probability due to contact between chromium ions and microalgae. Increased sorption capacity with increased sorbate concentration was previously reported in biosorption studies of some metals [21,44].

The bio-sorption efficiency was calculated from the formula and was found to be 90.32% for *Anabaena*, 93.53% for *Oscillatoria*, 90.96% for *Phormidium*, and 88.38% for *Spirogyra*, respectively. The initial high sorption capacity might be due to the availability of a large number of vacant surface sites in the microlagae. Subsequently, occupation of the remaining vacant surface sites becomes difficult due to repulsive forces among the Cr(VI) ions adsorbed on the algal biomasses [45]. The cell wall structure of the microalgae is composed of hydroxyproline-rich glycoproteins and the functional groups such as amino, carboxylic acid, hydroxyl, and carbonyl groups responsible for biosorption [Lesmana et al.]. Similar results were reported by other researchers in bio-sorption studies of heavy metals such as Cr(VI) [16,33].

3.5. FTIR analysis

FTIR analysis was carried out to evaluate the ability of functional groups present in the microalgae to

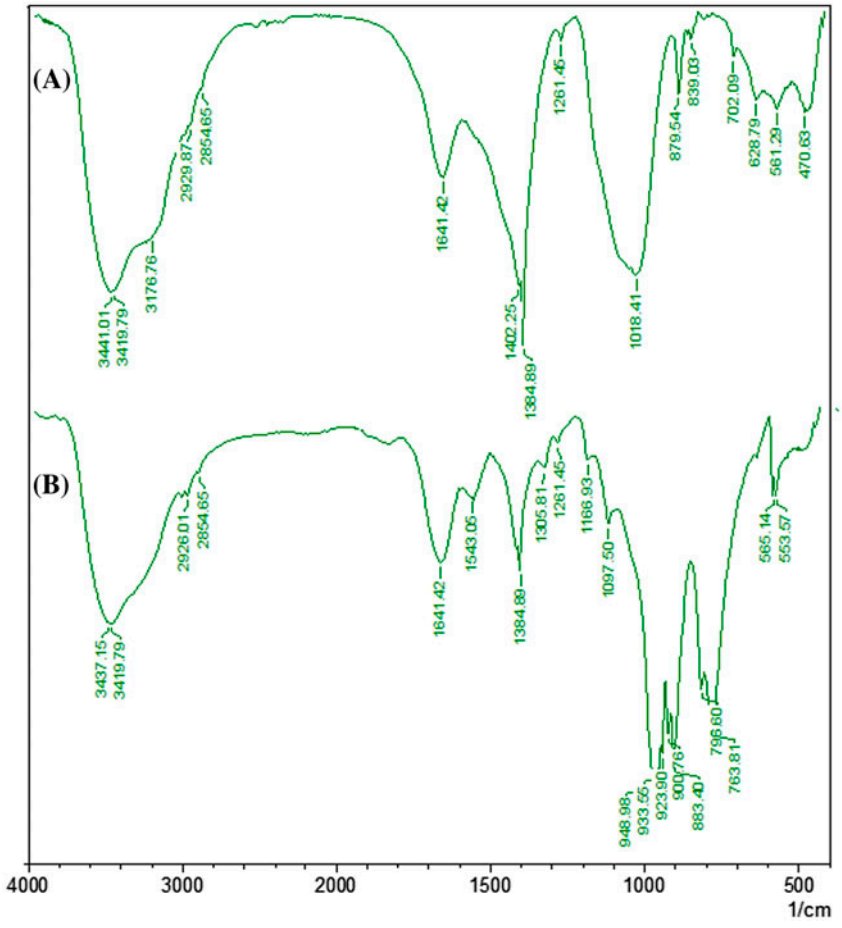

Fig. 5. FTIR spectrum of *Anabaena* grown under (A) control and (B) tannery effluent treatment.

form complexes with heavy metals. Strong affinity of microalgae for metal ions was noticed at the carboxylate, hydroxyl, and ester groups. The FTIR spectra of the microalgae *Anabaena*, *Oscillatoria*, *Phormidium*, and *Spirogyra* (Figs. 5(A), 6(A), 7(A), and 8(A)). Figs. 5(B), 6(B), 7(B), and 8(B) represent the complex formation of microalgae with heavy metals. Heavy metals are preferentially bound to the carboxylate sites on the microalgae, forming metal-acetate complex in the region 1,755–1,500 cm^{-1}. This region is characteristic of the C=O group; the stretching vibrations are in the region of 1,641.42, 1,641.42, 1,651.07, and 1,641.42 cm^{-1} and the intensity of peaks are shifted to 1,543.06, 1,633.71, 1,641.42, and 1,618.28 cm^{-1} in *Anabaena*, *Oscillatoria*, *Phormidium*, and *Spirogyra*, respectively. The bands in the region 3,500–3,000 cm^{-1} are characteristic of the N–H and O–H groups; the stretching vibrations are in the region of 3,441.01, 3,419.79, 3,444.87 and 3,419.79 cm^{-1} and the intensity of peaks are shifted to 3,437.15, 3,132.40, 3,421.72 and 3,471.87 cm^{-1} in *Anabaena*, *Oscillatoria*, *Phormidium*, and *Spirogyra*, respectively. The bands within the region 1,500–1,000 cm^{-1} are characteristic of the ester group. Several additional peaks were obtained in this region indicating the stretching vibrations. The shifting of these peaks shows that the sorption sites of microalgal species possess metal binding ability, indicating the usefulness of microalgae in treating tannery effluents containing chromium. Possible sorption mechanisms involved were functional group present in the cell wall of microalgae binds with the metal ions then transported across the cell membrane into the cytoplasm [46]. In this study, rapid stage of metal uptake process has been observed and FTIR analysis also shows the affinity of metal ion and microalgae. FTIR analysis confirms the bio-sorption and bio-reduction mechanisms of Cr(VI) ions with microalgae [47].

3.6. Metal sorption assessment by NMR spectroscopy

NMR spectroscopy provides an important avenue to investigate the involvement of the functional groups

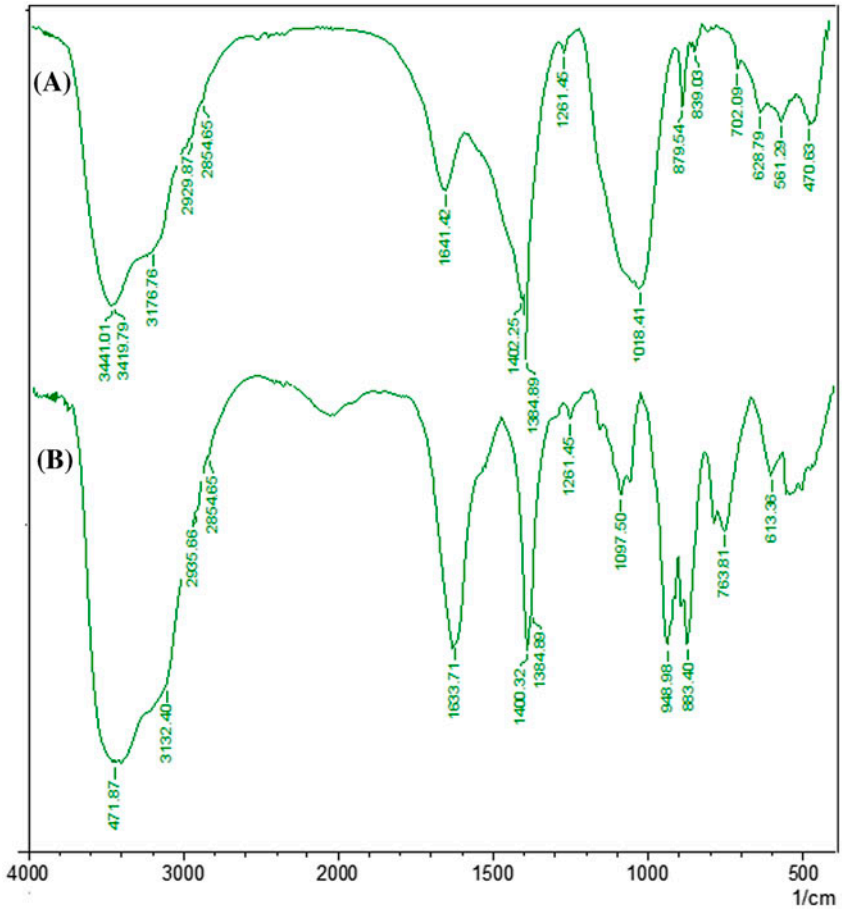

Fig. 6. FTIR spectrum of *Oscillatoria* grown under (A) control and (B) tannery effluent treatment.

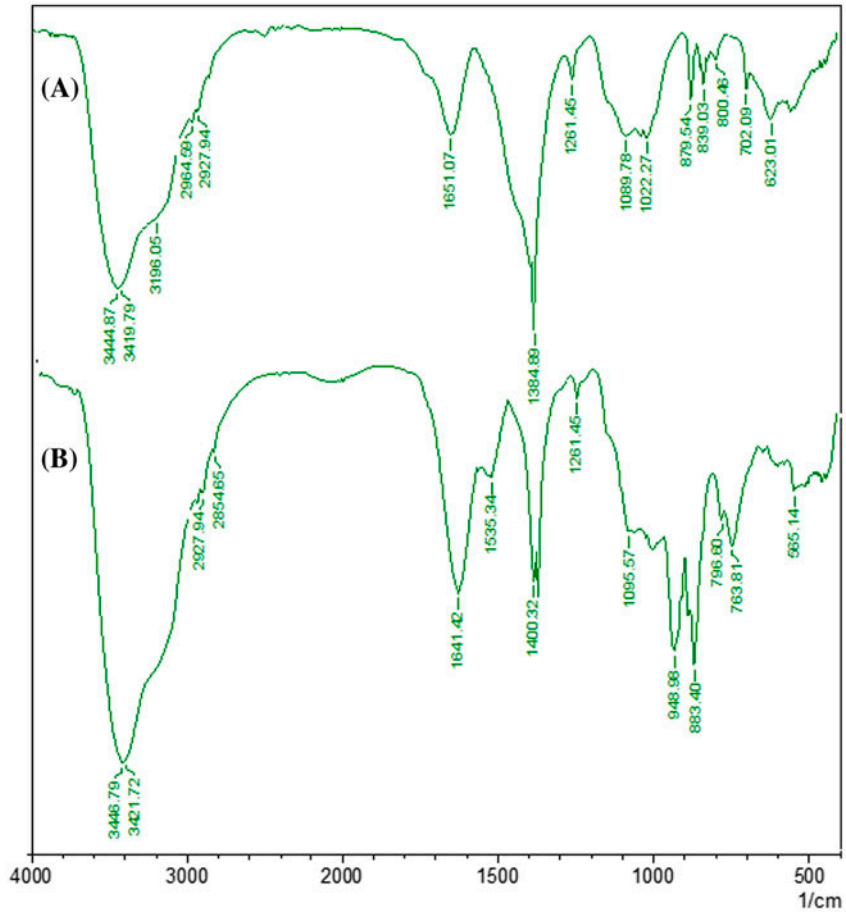

Fig. 7. FTIR spectrum of *Phormidium* grown under (A) control and (B) tannery effluent treatment.

of microalgae in metal ion binding. The ^{1}H NMR spectra of microalgae with tannery effluent were obtained to investigate the sorption of heavy metals on the microalgal sites. The microalgae *Oscillatoria* and *Phormidium* were analyzed by NMR spectroscopy because they gave maximum metal removal when compared with *Anabaena* and *Spirogyra*. The spectra obtained from microalgae with effluent and without effluent were then compared to evaluate the interaction between them. Fig. 9(A–D) show the spectra of *Oscillatoria* and *Phormidium* before and after treatment with the tannery effluent. Three main regions are observed in the spectrum; the broad resonance from 1 to 2 ppm shows the possible contribution of carbons from amino acids. The binding of the metal ions caused the carboxylate shifts between 1 and 2 ppm to become essentially one type of carboxylate, as exhibited in Fig. 9(B) and (D). This indicates the strong affinity of the carboxyl functional groups in microalgae that possess metal binding capacity [48].

The results from ^{1}H NMR studies indicate that the peak shifts in Fig. 9(B) and (D) between 1 and 2 ppm show the presence of main functional groups in the microalgae *Phormidium* and *Oscillatoria*. The compression of carbon atoms in Fig. 9(B) indicates strong affinity between metal ions and algal functional groups. This affinity may be due to the potential involvement of carbon groups in metal sorption by these microalgal species. The knowledge of chemical structures of biosorbents is important to predict their affinities for metal ions to know the complexation properties [49]. NMR study investigates chemical functionalities which is responsible for metal ion binding in the microalgae species and provides important information to support the use of particular microalgae biomass as an efficient bio-sorbent [48].

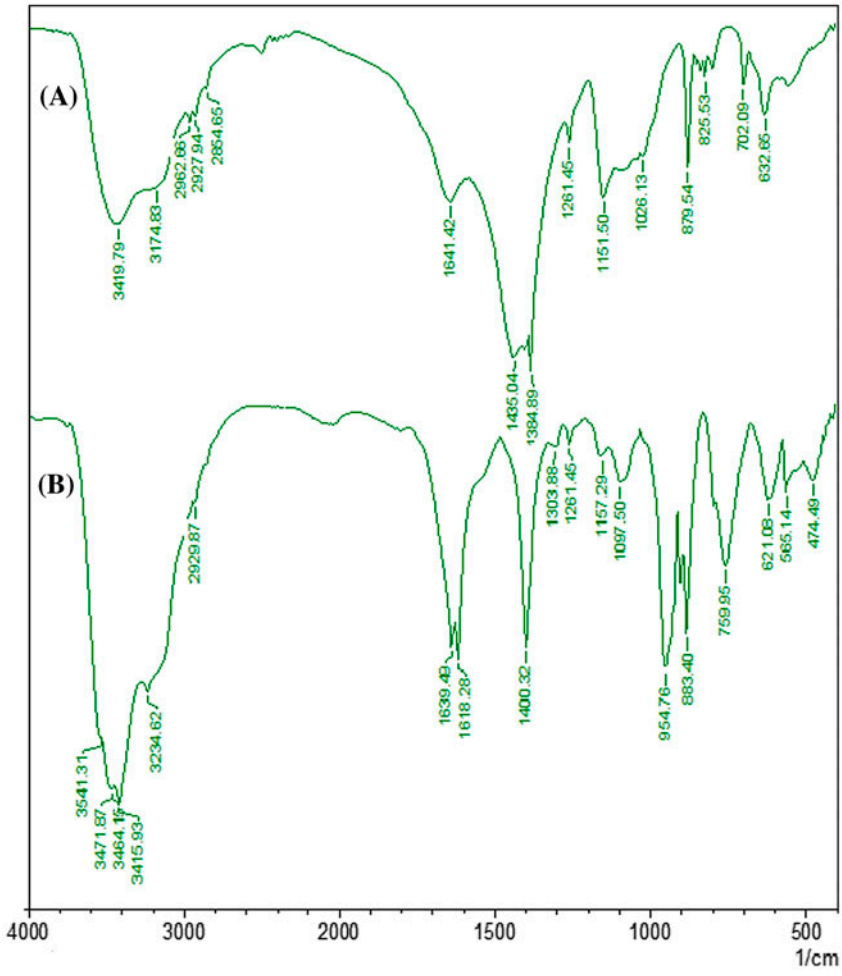

Fig. 8. FTIR spectrum of *Spirogyra* grown under (A) control and (B) tannery effluent treatment.

3.7. Kinetic modeling

For determining the kinetics of Cr(VI) bio-sorption by microalgae, kinetic models such as pseudo-first-order and pseudo-second-order models were applied, and their respective K_1 and K_2 estimated from the experimental data collected at the end of the stationary phase are presented in Table 2. In the pseudo-first-order kinetic model, the K_1 values were 1.77, 1.35, 1.45, and 1.61 for *Anabaena*, *Oscillatoria*, *Phormidium*, and *Spirogyra*, respectively. The K_2 values for pseudo-second-order model were 1.32, 0.97, 1.05, and 1.18 for *Anabaena*, *Oscillatoria*, *Phormidium*, and *Spirogyra*, respectively. The values describe the sorption kinetics of Cr(VI) onto microalgal biomasses. The uptake amounts of Cr(VI), or Cr(VI) bio-sorption, obtained from this experiment were 177, 125, 123, and 120 mg/L. These results suggest that the sorption of Cr(VI) onto microalgal biomasses was taking place through surface exchange reactions until the surface active sites were fully occupied; subsequently, Cr(VI) ions diffused into the biomass network for further interactions. However, the diffusion of metal ions within the particles was reported to be much slower. This is because of the greater mechanical obstruction to movement presented by the surface molecules or surface layers and the restraining chemical attractions between Cr(VI) and bio-sorbents [26,50,51].

3.8. Statistical analysis

The results of the specific growth rates of different microalgal species were compared and correlated; the results are represented in Table 3. Differences in the specific growth rate show the correlation among different microalgal species. *Oscillatora* showed a good correlation with *Phormidium* ($r^2 = 0.912$) and a moderate correlation with *Spirogyra* ($r^2 = 0.744$); *Phormidium* also showed a moderate correlation with *Spirogyra* ($r^2 = 0.748$). Correlation analysis indicated that the

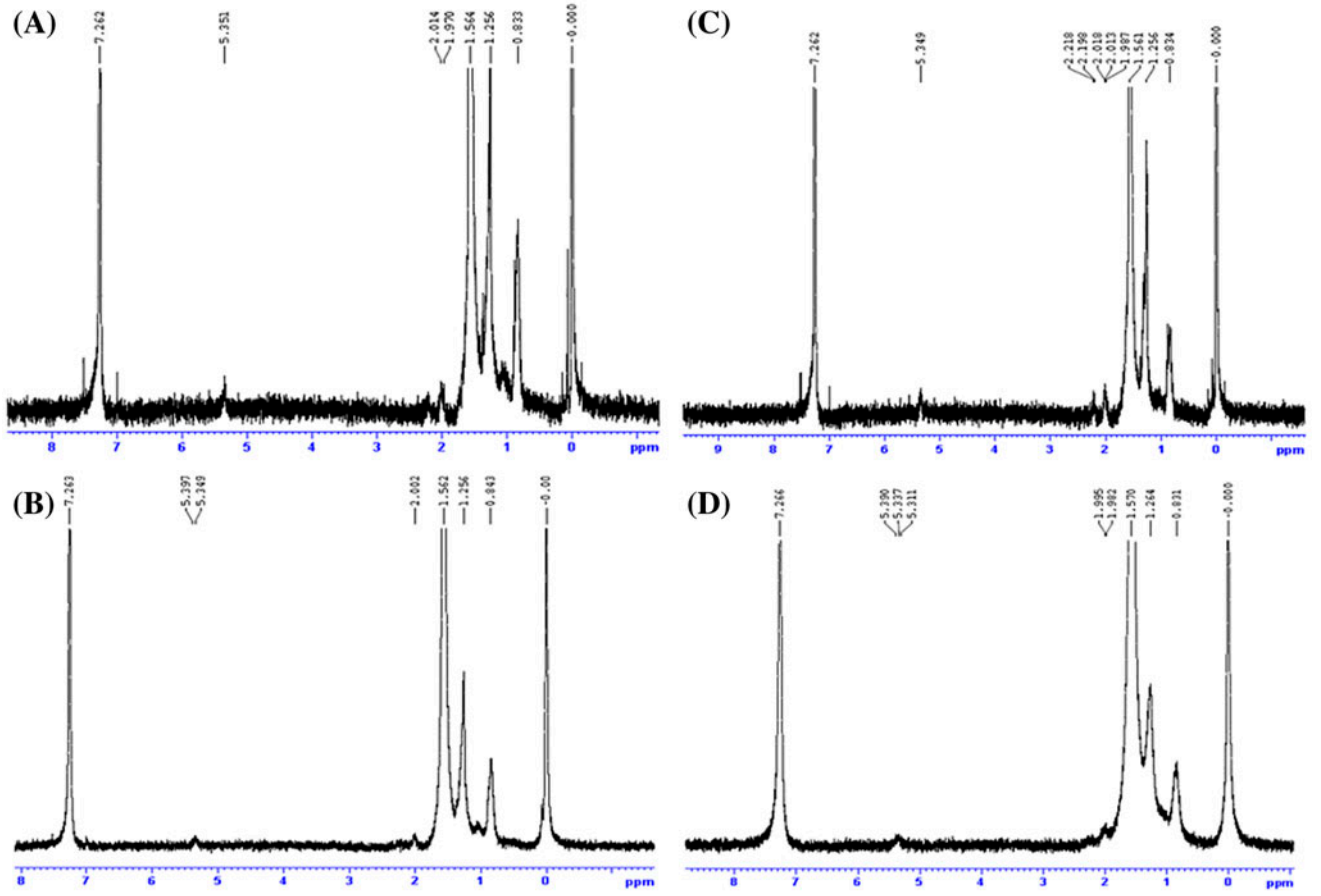

Fig. 9. ^{1}H NMR spectrum of *Oscillatoria and Phormidium* grown under (A,C) and control (B,D) tannery effluent treatment.

Table 2
Kinetic parameters obtained from pseudo-first-order and pseudo-second-order models for Cr(VI) bio-sorption by microalgae

	Pseudo-first-order			Pseudo-second-order		
Microalgae	$q_e - q_t$ (mg/L)	$K_1 \times 10^{-5}$	q_e (mg/L)	$q_e - q_t$ (mg/L)	$K_2 \times 10^{-7}$	q_e (mg/L)
Anabeana	117	1.77	155	117	1.32	155
Oscillatoria	125	1.35	155	125	0.97	155
Phormidium	123	1.45	155	123	1.05	155
Spirogyra	120	1.61	155	120	1.18	155

Note: K_1: first-order kinetic, K_2: second-order kinetic, and $q_e - q_t$: amount of Cr(VI) absorbed at time t.

Table 3
Comparison between specific growth rate of different microalgae represented by correlation coefficient (r^2)

	Anabeana	*Oscillatoria*	*Phormidium*	*Spirogyra*
Anabeana	–	0.625	0.725	0.614
Oscillatoria	0.625	–	0.912	0.744
Phormidium	0.725	0.912	–	0.748
Spirogyra	0.614	0.744	0.748	–

microalgae *Oscillatoria* and *Phormidium* show better relation when compared to other species and thus are an important for Cr(VI) metal scavenging applications.

4. Conclusion

The bio-sorption potential of microalgae such as *Anabaena*, *Oscillatoria*, *Phormidium*, and *Spirogyra* for

use in Cr(VI) removal from tannery effluents was studied. The experimental results showed that microalgal sorption sites have the maximum uptake capacity for Cr(VI). Kinetic data of the process showed that the bio-sorption of Cr(VI) onto biomass followed the pseudo-first-order and pseudo-second-order kinetic model. The bio-sorption process was found to be dependent on the biomass used and was optimized for Cr(VI) bio-sorption. The results of this study suggest that the microalgae identified in the estuaries are potentially economical and effective bio-sorbents for the removal of Cr(VI) from tannery effluents.

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