

Removal of Hexavalent Chromium from Aqueous Media using Mediterranean *Posidonia oceanica* biomass : Adsorption Studies and salt Competition Investigation

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Received 2 July 2011;

Revised 2 May 2012;

Accepted 14 May 2012

ABSTRACT: The biosorption of hexavalent chromium from saline solutions by *Posidonia oceanica*, a marine biomass, was studied as a function of pH, initial chromium (VI) and salt (NaCl) concentrations in batch system. The sorbent exhibited the maximal chromium (VI) uptake at pH 2 regardless of the presence of increasing salt concentration. Equilibrium uptake increased with chromium (VI) concentration up to 250 mg/l and decreased slightly in the presence of increasing salt concentrations of salt up to 50 g/l. The biomass adsorbed 14.48 mg of metal per gram of biomass at 100 mg/l initial chromium concentration in the absence of salt. When 50 g/l salt concentration was added to the solution, the value diminished to 11.49 mg/g under the same conditions (i.e. a 20.6% decrease in the biosorption capacity). The equilibrium sorption data were analyzed using Freundlich, Langmuir and Redlich-Peterson models. The Langmuir equation was the most suitable adsorption model for describing the biosorption equilibrium data of chromium (VI) both in salt free and loaded media. The pseudo-second-order type kinetic model depicted the biosorption kinetics accurately at all chromium concentrations in absence and presence of increasing concentrations of salt.

Key words: Chromium, Biosorption, *Posidonia*, Salt, Modeling

INTRODUCTION

Heavy metal pollution is one of the most serious environmental problems of this century (Park *et al.*, 2006; Nasrabadi *et al.*, 2010; Ghaderi *et al.*, 2012; Okuku and Peter, 2012; Ashraf *et al.*, 2012; Divis *et al.*, 2012). Chromium, which is present in effluents of industries like leather tanning, electroplating, textile dyeing and metal finishing (Alves *et al.*, 1993) exists in hexavalent and trivalent forms. However, the hexavalent form is more toxic and is reported to cause cancer in the digestive tract and lungs of human beings (Kaufman, 1970).

Conventional physical and chemical methods for the removal of chromium (VI) from wastewaters, including ion-exchange resins, reverse osmosis, reduction and precipitation and coagulation, are highly expensive and also ineffective at lower concentration of metal ions. Moreover, these methods also generate large quantity of toxic sludge (Bai and Abraham, 2001). There is, therefore, a need for some alternative techniques, which is efficient and cost-effective.

Biosorption has been cited as a promising alternative (Ekmekyapar *et al.*, 2012; . The concept of biosorption is based on the use of alternative materials: bacteria (Bueno *et al.*, 2008; Zhou *et al.*, 2007), alga (Lodeiro *et al.*, 2005; Hansen *et al.*, 2006), yeast (Seki *et al.*, 2005; Göksungur *et al.*, 2005), fungi (Pal *et al.*, 2006; Tunali *et al.*, 2005), but also agro-industrial by-products (Han *et al.*, 2005; Demirbas *et al.*, 2008), biopolymers (Khotimchenko *et al.*, 2008; Kobak *et al.*, 1996; Nagh and Fatinathan, 2010). These renewable resources have been evaluated with the aim of identifying highly efficient metal removal biosorbent. Marine biomass represents an important resource for biosorption processes. They are efficient biosorbents with the ability to bind various metals from aqueous effluents (Davis *et al.*, 2003; Tsui *et al.*, 2006). The main metal binding mechanisms include ion-exchange and complex formation (Davis *et al.*, 2003) but these may differ according to biomass type, origin and the processing to which it has been subjected (Murphy, 2008).

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We are interested in one of the most abundant marine seagrass; *Posidonia oceanica*, an endemic Mediterranean magnoliophyta found in the Mediterranean Sea. The valorisation of this available and renewable lignocellulosic biomass can be considered as a suitable solution for this problem.

The ability of *P. oceanica* as an adsorbent for chromium (VI) has been recognized and studied to a certain degree for its biosorption capability (Ncibi *et al.*, 2008). However, the roles of salts on metal biosorption by this biomass have not been investigated. Besides, industrial wastewaters generally contain different kinds of chemical compounds, which may significantly affect metal biosorption including soluble salts such as sodium chloride. Thus, the effect of NaCl salt concentration on the biosorption equilibrium and kinetics of chromium (VI) to *P. oceanica* was studied and compared to single component situation.

MATERIALS & METHODS

A Shimadzu (6101) spectrophotometer UV-VIS was used for determining chromium (VI) concentrations. A WTW (270) pH meter was used for pH measurements. A mechanical shaker (Macro Scientific Works) was used for agitating the samples. SEM Analyses were performed using an environmental scanning electron microscopy (Quanta 200). Elemental analyses were performed with elemental analyzer (EA 1100). X-ray diffractometer (D8-ADVANCE) with CuK α_1 radiation source was used to record the X-ray measurements of the adsorbent. For BET specific surface area estimation, a porosimeter (ASAP 2010) was used. Fourier transform infrared spectrometry (Shimadzu 8400 s) was used to analyze the functional groups in the adsorbent. The transmission spectrum was acquired at a 64 scans with 4 cm⁻¹ resolution and the spectrum was corrected for a KBr background.

Synthetic stock solutions of chromium (1 g/l) and salt (100 g/l) were prepared by dissolving weighted amount of potassium dichromate and NaCl in distilled water, separately. For single chromium (VI) and binary chromium-salt mixture studies, desired combinations of chromium (VI) and salt were obtained by diluting stock solutions of these components and mixing them in the test medium. Before mixing with biosorbent solution, the pH of each test solution was adjusted to the required value with H₂SO₄ and NaOH solutions. The ranges of initial concentrations of chromium (VI) and salt prepared from stock solutions varied from 20 to 250 mg/l and 0 to 50 g/l, respectively. The dead leaves of *P. oceanica* were collected from the coast of Jijel (East of Algeria) in December 2010. The material was first washed with tap water to remove salt and

epiphytes, then they were washed with distilled water. The material was dried at 60°C for 24 h. Dried materials were ground using a crusher machine. Ground dead leaves of *P. oceanica* were sieved for used in the experiments with particle size of 0.3 - 0.5 mm

Biosorption experiments were carried out using batch technique in 250ml Erlenmeyer flasks containing 100 ml of chromium (VI) or chromium-salt mixture. Synthetic solutions at desired level of each component were adjusted at pH 2. The flasks were agitated at 150 rpm constant shaking rate for 4 h to ensure that equilibrium was reached. The contents were filtered, and the metal ion or metal-salt mixture bearing solution were analyzed for the remaining chromium (VI) ions. Studies were performed at a constant temperature of 25±1°C.

All the biosorption experiments were repeated twice to confirm the results. The data were the mean values of the duplicates.

The chromium (VI) uptake by biomass quantity, q (mg/g) was determined according to the following equation:

$$q_t = \frac{(C_0 - C_{res}) \cdot V}{m} \quad (1)$$

where C_0 is the initial chromium (VI) concentration (mg/l), C_{res} is the residual chromium (VI) concentration at any time (mg/l), V is the volume of solution (l) and m is the mass of the sorbent (g). At equilibrium, C_{res} is equal to C_{eq} and q is equal to q_{eq} .

RESULTS & DISCUSSION

The physical characteristics along with the percentage of carbon, oxygen, hydrogen, nitrogen and sulphur of *P. oceanica* are presented in Table 1.

Table 1. Characteristics of *P. oceanica* leaves

Parameters	Values
Specific surface area (m ² /g)	3.30
Ash (%)	1.20
Moisture (%)	6.43
Apparent density (g/dm ³)	345.7
Water-holding capacity	83.9
Particle size (mm)	0.3-0.5
C (%)	40.95
O (%)	32.63
H (%)	5.56
N(%)	1.22
S (%)	2.98

The FTIR spectrum and X-ray diffraction pattern of *P. oceanica* are shown in Figs. 1 and 2, respectively. IR spectra of *P. oceanica* confirm the adsorbent heterogeneity and evidence the presence of different characteristic peaks. Several intense bands can be attributed to functional groups present in cellulose, hemicellulose and lignin which are the major components of *P. oceanica*.

The first part of the spectra (4000 – 2000 cm^{-1}) is poorly resolved: the broad absorption peak around 3394 cm^{-1} is indicative of the existence of O-H and N-H stretching, thus showing the presence of hydroxyl and amine groups on the adsorbent (Elangovan *et al.*, 2008). Two small peaks at 2926 cm^{-1} and 2860 cm^{-1} correspond

to symmetric $-\text{CH}_2$ valence vibration and $-\text{CH}$ stretching vibration, respectively (Schwanninger *et al.*, 2004) where as bands at 2362 cm^{-1} and 2341 cm^{-1} are indicative of amine and amide groups (Williams and Fleming, 1995). It is generally difficult finding useful information from this wavenumber range and spectrum analysis is generally focused on the 2000–600 cm^{-1} region. The peaks at 1635 cm^{-1} and 1429 cm^{-1} represent the carboxylate salt COO-M , where M denotes to the metal cations such as Na^+ , K^+ , Ca^{2+} and Mg^{2+} that may naturally exist in the biomass. The brand around 1249 cm^{-1} could be stretch of $-\text{SO}_3$ (Sheng *et al.*, 2004). The bands around 1041 cm^{-1} are due to $-\text{C-O}$ stretching of alcoholic groups (Yang and Chen, 2008). The X-ray

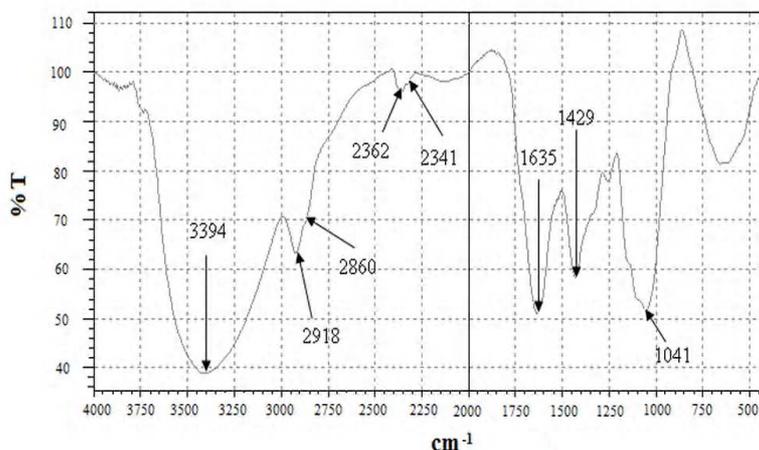


Fig. 1. FTIR spectrum of *P. oceanica* leaves

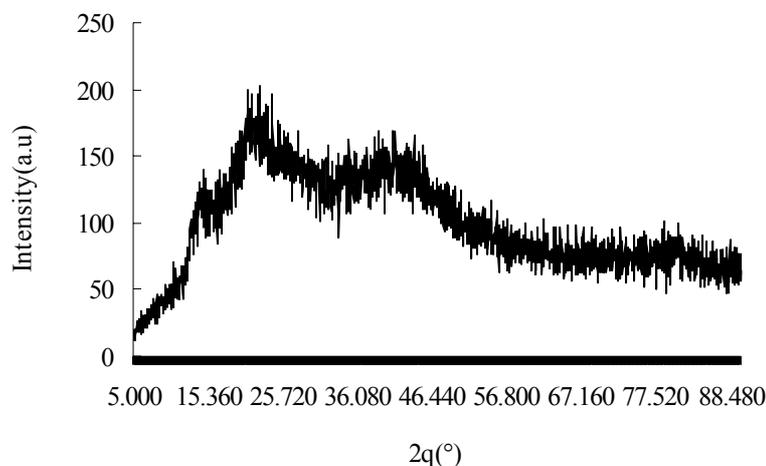


Fig. 2. X-ray diffraction of *P. oceanica* leaves

diffraction spectra of *P. oceanica* show an amorphous nature of the biomass.

Scanning electron microscopic photographs of *P. oceanica* shown in Fig. 3(A-B) reveal the surface morphology of the biomass. This is a very structured lignocellulosic material characterized by a fibrous aspect. This is confirmed by Fig. 3(C) that shows the presence of lamellar structures in the external layers, while the central part of the ribbon-like material is characterized by a less structured aspect.

The most important single parameter influencing the sorption capacity is the pH of adsorption medium (Goyal *et al.*, 2003). The initial pH of adsorption medium is related to the adsorption mechanisms onto the adsorbent surface from water and reflects the nature

of the physicochemical interaction of the species in solution and the adsorptive sites of adsorbents (Aksu *et al.*, 2002). To find the suitable pH for the effective biosorption of chromium (VI) ions by *P. oceanica* in single and salt containing media, experiments were performed at different initial pH values (2.0–6.0) and at different initial NaCl concentrations (0–50 g/l). The variation of equilibrium chromium (VI) uptake with initial pH is given in Fig. 4 at about 100 mg/l initial metal ion concentration. As seen from the figure, the pH of the media affected the adsorption by the sorbent. The optimum uptake values were found at pH 2, and the biosorption of chromium (VI) decreased significantly with further increase in pH for all tested NaCl concentrations.

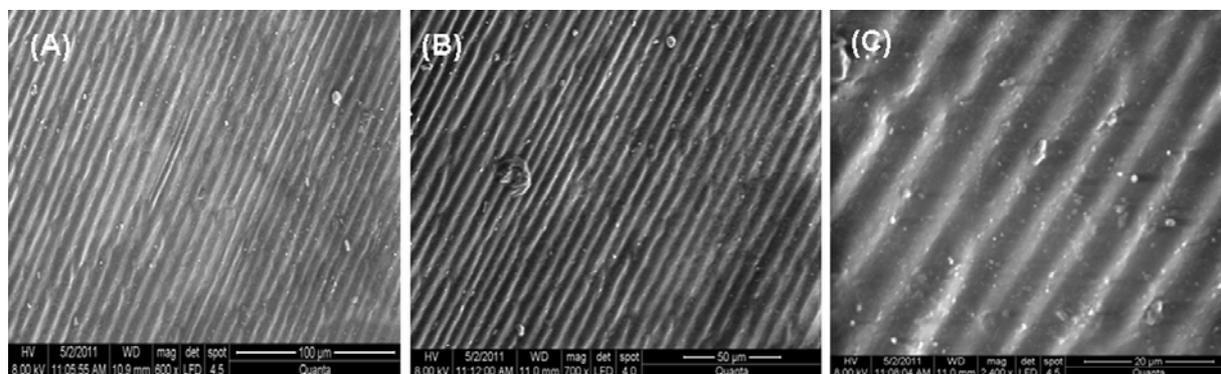


Fig. 3. SEM photographs of *P. oceanica* leaf surface [scale bar: 100μm(A), 50μm(B), 20μm(C)]

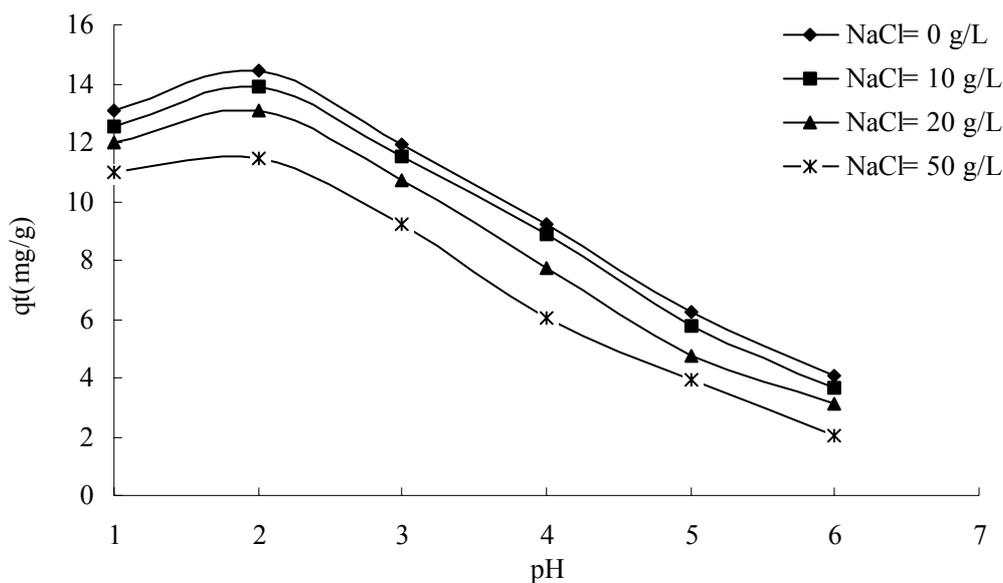


Fig. 4. Effect of pH and increasing salt concentration on equilibrium chromium(VI) sorption capacity of *P. oceanica* (C_0 : 100 mg/L, biomass quantity : 0.5 g, temperature : $25\pm 1^\circ\text{C}$, agitation rate : 150 rpm)

Several other authors have also found that adsorption of chromium (VI) on biomass increased with lowering of pH and is highest at pH value of 2.0 (Donmez *et al.*, 1999; Prakasham *et al.*, 1999; Bai and Abraham, 2001). Chromium (VI) occurs in the form of oxy anion as HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, $\text{Cr}_4\text{O}_{13}^{2-}$, $\text{Cr}_3\text{O}_{10}^{2-}$ (Aksu *et al.*, 2002; Tobin and Roux, 1998; Gardea-Torresdey *et al.*, 2000; Cimino *et al.*, 2000). The lowering of pH causes the surface of the sorbent to be protonated to a higher extent. This results in a stronger attraction for negatively charged chromium Cr (VI) complex ions in the solution. Hence, the sorption increases with the increase in the acidity of the solution. But as the pH rises, the concentration of OH^- ions increases and overall charge on the sorbent surface becomes negative which causes hindrance in the sorption of negatively charged chromium (VI) ions like $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , etc., resulting in the decreased sorption of chromium (VI) at higher pH (Ebner *et al.*, 2002). At pH 2.0, the negatively charged chromate ions would interact more strongly with the positively charged functional groups of the biomass resulting in high chromium (VI) uptake. It is known (Donmez and Aksu, 2002) that the dominant form of chromium (VI) at pH 1.0 is the acid chromate ion species (HCrO_4^-) and increasing pH shifts the concentration of HCrO_4^- to other forms, CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$. Since there is an increase in sorption of chromium (VI) as pH increased to 2.0 so it may be suggested that probably the CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ are the active forms of chromium (VI), which are being sorbed by the biomass (Neetu Tewari *et al.*, 2005). Reduction in the biosorption of chromium (VI) at pH value lower than 2.0 is probably due to the change in the chemical nature of the biomass due to hydrolytic activity of the acid at high concentration. This might change the surface characteristics of *P. oceanica* including surface area availability Salt concentration is proportional to the ionic strength of aqueous solution directly. Ionic

strength, besides pH, is also one of the important factors that influence the equilibrium uptake. Although the ionic strength or the salinity did not affect the optimum pH, adsorption decreased slightly with increasing ionic strength of the aqueous solution at all pH values studied as shown in Fig. 4. At pH 2.0, the removal of chromium (VI) decreased only from 14.4 to 13.9 mg/g at 10 g/l salt containing medium resulted in 3.5% reduction in biosorption capacity. However, chromium (VI) uptake capacity of *P. oceanica* decreased from 14.4 to 11.5 mg/g with increasing salt concentration up to 50 g/l resulted in 20.1% decrease in biosorption. This behaviour may be due to the inhibition effect of salt on the permeability of cell membrane for chromium (VI) ions and relative competition between chloride and chromium (VI) anions on the active sites of the biomass (Agarwal *et al.*, 2006).

The biosorption of chromium (VI) ions was carried out at different initial metal ion concentrations ranging from 20 to 250 mg/l and various concentrations of NaCl (0-50 g/l) at pH 2.0, at 150 rpm with 4h of contact time using *P. oceanica*. The initial concentration provides an important driving force to overcome all mass transfer resistance of metal ion between the aqueous and solid phases (Donmez and Aksu, 2002). Hence, a higher initial concentration of chromium (VI) will increase the biosorption capacity as shown in Table 2. The equilibrium sorption capacity of *P. oceanica* increased with increasing initial chromium (VI) concentration in both single chromium (VI) and salt containing situations. When the initial chromium (VI) concentration increased from 20 to 250 mg/l approximately in the absence of salt, the loading increased from 3.9 mg/g to 21.5 mg/g due to the increase in the number of ions competing for the available binding sites in the biomass.

Table 2. Equilibrium uptakes and percentage removal of chromium(VI) at different metal ions and salt concentrations

$C_{0\text{Cr(VI)}}$	$C_{0\text{NaCl}} = 0 \text{ g/L}$		$C_{0\text{NaCl}} = 10 \text{ g/L}$		$C_{0\text{NaCl}} = 20 \text{ g/L}$		$C_{0\text{NaCl}} = 50 \text{ g/L}$	
	q_{eq}	%	q_{eq}	%	q_{eq}	%	q_{eq}	%
	(mg/L)	removal	(mg/L)	removal	(mg/L)	removal	(mg/L)	removal
20	3.9	97.5	3.7	92.5	3.45	86.3	2.89	72.25
50	8.89	88.9	7.59	82.2	5.89	77.6	3.98	65.8
100	14.48	72.4	13.9	69.35	13.06	65.3	11.49	55.3
150	19.38	64.6	18.56	61.86	17.47	58.23	14.94	49.8
200	20.3	50.75	19.44	48.6	18.23	45.57	15.94	39.85
250	21.5	43.00	20.3	40.02	18.82	37.64	16.53	33.26

The uptake of chromium (VI) reached a plateau at 200-250 mg/l showing the saturation of binding sites at higher concentration levels. The initial chromium (VI) concentration also influenced the biosorption yield significantly as shown in Table 2 in both single chromium (VI) and salt containing situations. Chromium (VI) removal yield was the maximum at the 20 mg/l initial chromium (VI) concentration due to higher cell density attained than at higher concentrations of chromium (VI) (Mashkani *et al.*, 2009). Such decrease in unit biosorption of metal ion with the enhanced metal concentration indicates that the biosorbent is effective in dilute metal solutions.

These results may be explained by the fact that, at low chromium (VI) concentrations, the ratio of sorptive surface of *P. oceanica* biomass to total chromium (VI) availability is high; hence, all chromium (VI) ions may be interacted with biosorbent and removed. Same pattern was observed for chromium (VI)-salt combinations, indicating suitability of the present biomass for treating wastewaters containing up to 20 mg/l chromium (VI) with various salt concentrations.

Table 2 also illustrates the effect of salt concentration on the removal of chromium (VI) ions by *P. oceanica* at different initial chromium (VI) concentrations. When salt concentration was increased up to 50 g/l there was a slight decrease of the amount of metal removed from aqueous solution indicating a little antagonistic effect of salts on chromium (VI) biosorption. When studied with 20 and 250 mg/l initial chromium (VI) concentrations, as salt concentration increased from 0 to 10 g/l, equilibrium chromium (VI) uptakes lessened only from 3.9 to 3.7 mg/g and only from 21.5 to 20.3 mg/g, respectively. The uptakes of chromium (VI) varied by less than 5.1% and 5.5% for 20 and 250 mg/l initial chromium (VI) concentrations, respectively. However, as the concentration of salt changed from 0 to 50 g/l, the uptake of chromium (VI) adsorbed by *P. oceanica* and percent removal efficiency lessened from 3.9 to 2.89 mg/g and from 97.5 to 72.25% for 20 mg/l initial chromium (VI) concentration, respectively. When studied with 250 mg/l chromium (VI) uptake diminished from 21.5 to 16.53 mg/g, while the removal yield decreased from 43% to 33.26% with increasing salt concentration from 0 to 50 g/l.

The decrease in biosorption ability of *P. oceanica* with increasing salt concentration may be a result of biosorption mechanisms. Salt concentration could markedly influence the biosorption presumably due to the competition between chloride ions (present in salt used to change the ionic strength of solution) and chromium (VI) ions for the same binding sites in the biosorbent surface (Diniz and Volesky, 2005; Niu *et al.*,

2007). Another reason is that ionic strength increases, the activity of biosorbent (active sites) and metal activity decreases, so the adsorptive capacity of biosorbent decreases. According to surface chemistry theory, when two phases, e.g. marine seaweed particles and metal species in aqueous solution, are in contact, they are bound to be surrounded by an electrical double layer owing to electrostatic interaction (Donmez and aksu, 2002). If the adsorption mechanism is significantly related to the electrostatic attraction, variations in electrolyte concentration would remarkably influence the sorbent-sorbate interactions involving the electrostatic interaction and adsorption decreases with increase in ionic strength. Some inorganic anions existing in the solution such as chloride may also form complexes with metal ions, and therefore, affect the adsorption process adversely (Agarwal *et al.*, 2006; Niu *et al.*, 2007; Maurya *et al.*, 2006).

Kinetics of sorption describing the pollutant(s) uptake rate is useful for defining the efficiency of sorption and feasibility of adsorbent for its use in water pollution control (Aksu and Balibek, 2010). Hence, the kinetics of chromium (VI) removal both individually and in salt containing medium has been carried out to understand the chromium (VI) adsorption behaviour of the marine sea grass *P. oceanica* with respect to initial chromium (VI) and salt concentrations. The suitability of pseudo-first-order and pseudo-second-order type kinetic models for the sorption of chromium (VI) ions onto *P. oceanica* for all situations was also discussed. For this purpose, biosorption capacity (q) with initial chromium (VI) concentration of about 100 mg/l was plotted as a function of time at varying salt levels (Fig. 5). The time and salt concentration dependent, similar shaped biosorption curves were obtained. The presence of salt in solution did not influence the dynamic uptake process of chromium (VI). The extent of chromium (VI) removal enhanced with increasing contact time at all salt concentrations studied. However, the rise in salt concentration resulted in a decrease in metal uptake. For chromium (VI) and salt concentrations studied, initial sorption of chromium (VI) occurred much more rapidly and the majority of chromium (VI) uptake took place within the first 60 min of contact due to vacant sites available at the initial stage of biosorption and thereafter it proceeded at a slower rate and finally attained saturation called the equilibrium time. For the initial chromium (VI) concentration studied, in the absence of salt, the amount of metal adsorbed was 9.3 mg/g at an initial adsorption time of 30 min. However, as salt concentration rose to 50 g/l, in a similar initial time period (30 min), the equilibrium uptake of chromium (VI) by the biomass was 7.5 mg/g the metal removal

decreased by 19.3%. The data in Fig. 5 indicated that the contact time required to reach equilibrium was very short and the first 3h of adsorption was sufficient to achieve equilibrium for all cases. Such a rapid uptake of chromium (VI) by *P. oceanica* indicates that this biosorbent has an affinity for the metal ions pointing towards physical adsorption and that the uptake of chromium (VI) occurs predominantly by surface binding and that available sites on the sorbent are the limiting factor for the sorption. The equilibrium time was also found to be independent of salt concentration. Thus, the contact time was fixed at 4 h for the rest of the batch experiments to make sure that equilibrium was reached.

Adsorption is a time dependent process. In the removal of metal ions from wastewater, it is necessary to know the rate of adsorption for process design, operation control and adsorbent evaluation. For this purpose, two simplified kinetic models including pseudo-first-order (Lagergren, 1898) and pseudo-second-order (Ho and McKay, 1999) were used to test the biosorption kinetics of chromium (VI) in the absence and in the presence of increasing concentration of salt. The pseudo-first-order rate expression based on solid capacity is generally expressed as:

$$\frac{dq}{dt} = k_1 \cdot (q_{eq} - q) \quad (2)$$

where q_{eq} and q are the amounts of adsorbed metal ions on the biosorbent at equilibrium and at time t , respectively (mg/g) and k_1 is the rate constant of first-order biosorption (min^{-1}). After integration and applying boundary conditions, $t=0$ to $t=t$ and $q=0$ to $q=q_{eq}$; the integrated form of Eq. (02) becomes a linear function and model parameters of q_{eq} and k_1 were obtained from $\log (q_{eq}-q)$ versus t plot.

The pseudo-second-order equation is also based on the sorption capacity of the solid phase and on the assumption that the sorption process involves chemisorption mechanism and for chromium (VI) both singly and in the mixture is expressed as:

$$\frac{dq}{dt} = k_2 \cdot (q_{eq} - q)^2 \quad (3)$$

where k_2 is the rate constant of second-order biosorption (g/mg min^{-1}). For the same boundary conditions, the integrated form of Eq(03) gives a linear relationship. The values of q_{eq} and k_2 can be estimated from the slope and intercept of the t/q against t plot. For the application of this model there is no need to know any parameter beforehand.

Kinetic experiments were performed by varying the initial chromium (VI) concentration between 20 and 250 mg/l and keeping the salt concentration constant

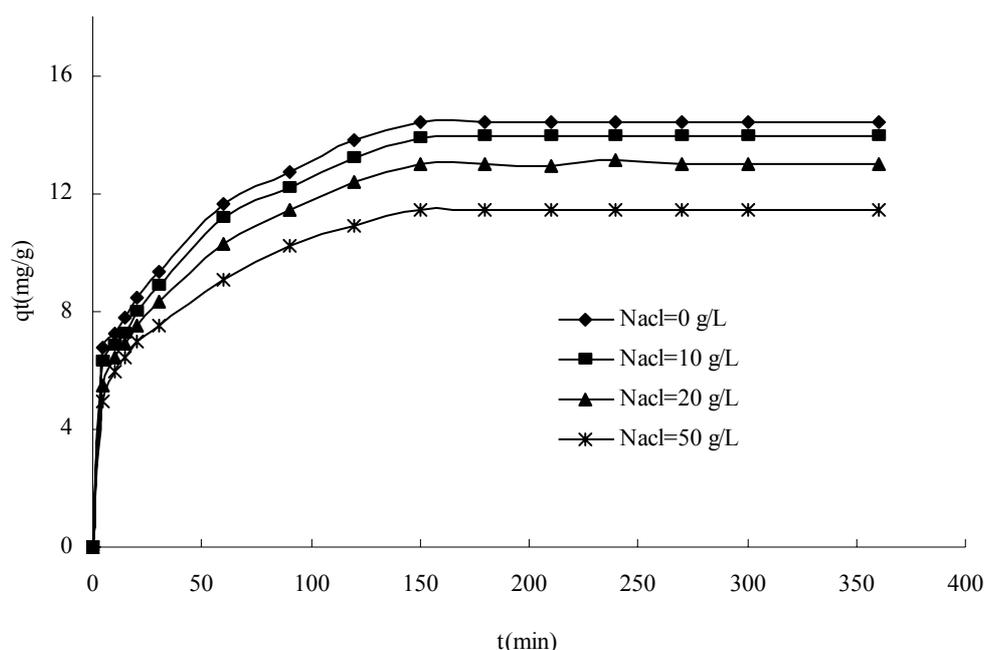


Fig. 5. Biosorption kinetics of chromium(VI) under increasing salt concentration ($C_0=100\text{mg/L}$, $m=0.5\text{g}$, Temperature: $25\pm 1^\circ\text{C}$, agitation rate= 150rpm)

between 0 and 50 g/l for each experimental set. The best-fit model was selected by comparing the linear regression correlation coefficients (R^2), and moreover, by searching the equal or close values of q_{eq} from the experiment and the predicted model as well.

The first-order rate constant (k_1) and q_{eq} values were determined from the plots of linearized form of the pseudo-first-order model (Eq. (02)) at all chromium (VI) and salt concentrations studied (data not shown) and are presented in Table 3 along with the corresponding linear regression coefficients. The changes in both the metal and salt concentrations affected the kinetic constants insignificantly. The first-order rate constants decreased slightly with increasing the initial chromium (VI) concentration and increased a little bit with increasing the salt concentration. The correlation coefficients were found to be above 0.9 but the calculated values of q_{eq} obtained from Lagergren plots were not equal to the experimental q_{eq} values, suggesting the insufficiency of the model to fit the kinetic data for all cases examined. The reason for these differences in the q_{eq} values may be due to a time lag, possibly as a result of a boundary layer or an external resistance controlling the beginning of the sorption process. In most cases in the literatures, the pseudo-first-order model does not fit the kinetic data well over the entire contact time range; therefore, generally underestimate the q_{eq} values (Aksu and Balibek, 2010).

Using Eq. (03), second-order adsorption rate constants (k_2) and equilibrium uptake values (q_{eq}) were determined from the slope and intercept of the t/q against t plots (data not shown). The values of the parameters k_2 and q_{eq} and of corresponding correlation coefficients are also presented in Table 3. The correlation coefficients obtained greater than 0.997 and the adequate fitting of theoretical and experimental q_{eq} values for all chromium (VI)–salt combinations suggest the applicability of second-order kinetic model based on the assumption that the rate limiting step may be the chemisorption in explaining the kinetics of biosorption for the entire sorption period. This indicated that pseudo-second-order kinetic model describes the kinetics adequately in the concentration ranges studied. Similar result was reported by (Kiran *et al.*, 2007) for the biosorption of chromium (VI) onto *Lyngbya putealis* (HH-15).

Biosorption data are most commonly represented by an equilibrium isotherm, which is a plot of the quantity of sorbate retained on biosorbent q_{eq} (solid phase concentration of the sorbate at equilibrium) as a function of the concentration of the sorbate in the liquid phase C_{eq} (liquid phase concentration of the sorbate at equilibrium). A dynamic equilibrium is established in the concentration of sorbate between

two phases (Maurya *et al.*, 2006). The equilibrium isotherm is of fundamental importance for the design and optimization of the adsorption system for the removal of metal ions from aqueous solution. One of the difficulties in describing the adsorption equilibrium of metal ions from waste streams is that wastewaters contain not one, but many components. If mono-component adsorption models could describe the equilibrium of metal ion in the presence of other components, such as salt, the individual isotherm parameters changed due to the level of salt can be related to initial salt concentration and these expressions may be useful to define the equilibrium data in salt-containing solutions. In order to determine the sorption capacity of *P. oceanica* for chromium (VI) in the absence and in the presence of changing concentrations of salt, the experimental data were fitted to the Langmuir, Freundlich (two-parameter models) and Redlich-Peterson (three-parameter models) empirical models which are the most frequently used equations in the literature describing the non-linear equilibrium between adsorbed metal and metal ion in solution at a constant temperature.

The Langmuir equation which is valid for monolayer sorption onto a surface a finite number of identical sites and is given by Eq(04) (Langmuir, 1918):

$$q_{eq} = \frac{Q^{\circ} b C_{eq}}{1 + b C_{eq}} \quad (4)$$

where q_{eq} is the amount of metal ion bound per gram of dried biomass at equilibrium (mg/g) and C_{eq} is the residual (equilibrium) metal concentration left in solution after binding (mg/l). The parameters Q° and b are Langmuir constants related to maximum adsorption capacity and bonding energy of adsorption, respectively, which are functions of the characteristics of the system as well as time.

The empirical Freundlich equation based on sorption on a heterogeneous surface is given below by Eq(05) (Freundlich, 1906):

$$q_{eq} = K_F \cdot C_{eq}^{\frac{1}{n}} \quad (5)$$

where K_F and n are the mono-component Freundlich constants characteristic of the system. K_F and n are indicators of biosorption capacity and biosorption intensity, respectively.

The three-parameter Redlich–Peterson model incorporated the features of the Langmuir and Freundlich isotherms into a single equation and presented a general isotherm equation as follows (Redlich and Peterson, 1959):

Table 3. Pseudo-first and pseudo-second-order kinetic constants at different chromium(VI) and salt concentrations at pH 2 and 25±1°C

Salt concentration	C ₀	q _{eq,exp.}	First-order			Second-order		
			k ₁	q _{eq, cal}	R ²	k ₂	q _{eq, cal}	R ²
0 g/L	20	3.98	0.046	3.04	0.9695	0.090	4.03	0.9999
	50	8.59	0.022	7.89	0.9619	0.0075	8.56	0.9971
	100	14.48	0.020	12.04	0.9796	0.0052	15.03	0.9972
	150	19.38	0.015	15.73	0.9657	0.0049	19.01	0.9974
	200	20.36	0.012	17.30	0.9809	0.0037	20.01	0.9999
	250	21.05	0.008	18.32	0.9767	0.0033	21.69	0.9989
10g/L	20	3.18	0.058	2.87	0.9579	0.140	3.21	0.9999
	50	7.59	0.028	6.94	0.9602	0.0091	7.98	0.9972
	100	13.87	0.022	11.99	0.9741	0.0053	13.72	0.9965
	150	18.56	0.018	14.59	0.9483	0.0047	18.37	0.9982
	200	19.44	0.015	16.63	0.9715	0.0038	19.96	0.9999
	250	20.03	0.010	18.05	0.9651	0.0031	20.61	0.9989
20g/L	20	2.09	0.071	1.4	0.9601	0.16	2.14	0.9999
	50	5.89	0.033	4.98	0.9726	0.01	6.04	0.9971
	100	13.06	0.023	10.79	0.9448	0.0050	14.20	0.9989
	150	17.47	0.020	13.32	0.9596	0.0020	17.19	0.9978
	200	18.23	0.016	15.34	0.9654	0.0040	18.92	0.9999
	250	18.82	0.012	16.45	0.9726	0.0047	19.45	0.9987
50g/L	20	1.09	0.096	0.75	0.9786	0.260	1.092	0.9999
	50	3.98	0.036	2.87	0.9628	0.015	4.18	0.9971
	100	11.26	0.025	9.53	0.970	0.0049	11.13	0.9979
	150	14.94	0.022	11.63	0.9533	0.0037	15.74	0.9982
	200	15.94	0.020	14.68	0.9720	0.0062	16.39	0.9999
	250	16.53	0.015	13.08	0.9661	0.0064	16.92	0.9989

$$q_{eq} = \frac{K_{RP}C_{eq}}{1 + a_{RP}C_{eq}^{\beta}} \quad (6)$$

where K_{RP} is the Redlich–Peterson model isotherm constant (l/g), a_{RP} the Redlich–Peterson model constant (l/mg); β the Redlich–Peterson model exponent. The exponent, β , lies between 0 and 1. Fig. 6 shows the experimental data fitted to Langmuir, Freundlich and Redlich–Peterson models.

It was revealed that equilibrium chromium (VI) uptake increased with increasing initial metal concentration up to 250 mg/l for all cases studied. The curvilinear relationship between the amount of chromium (VI) adsorbed per unit weight of biomass and the residual chromium (VI) concentration at equilibrium suggests that saturation of cell-binding sites occurred at the higher concentrations of this metal

ion. The equilibrium removal of chromium (VI) decreased slightly with increasing salt concentration. For the examination of salt effect on chromium (VI) biosorption, the Langmuir, Freundlich and Redlich–Peterson equations were applied to the equilibrium data obtained in both single chromium (VI) and chromium (VI)–salt binary systems.

The corresponding Langmuir, Freundlich and Redlich–Peterson parameters at different salt levels estimated by non-linear regression analysis were listed in Table 4 along with the average percentage errors and linear regression coefficients. The magnitude of average percentage errors and linear regression coefficients were the criteria for the selection of the most suitable isotherm model. The average percentage error was calculated by using Eq. (07), the subscripts ‘exp’ and ‘calc’ show the experimental and calculated values and N the number of measurements.

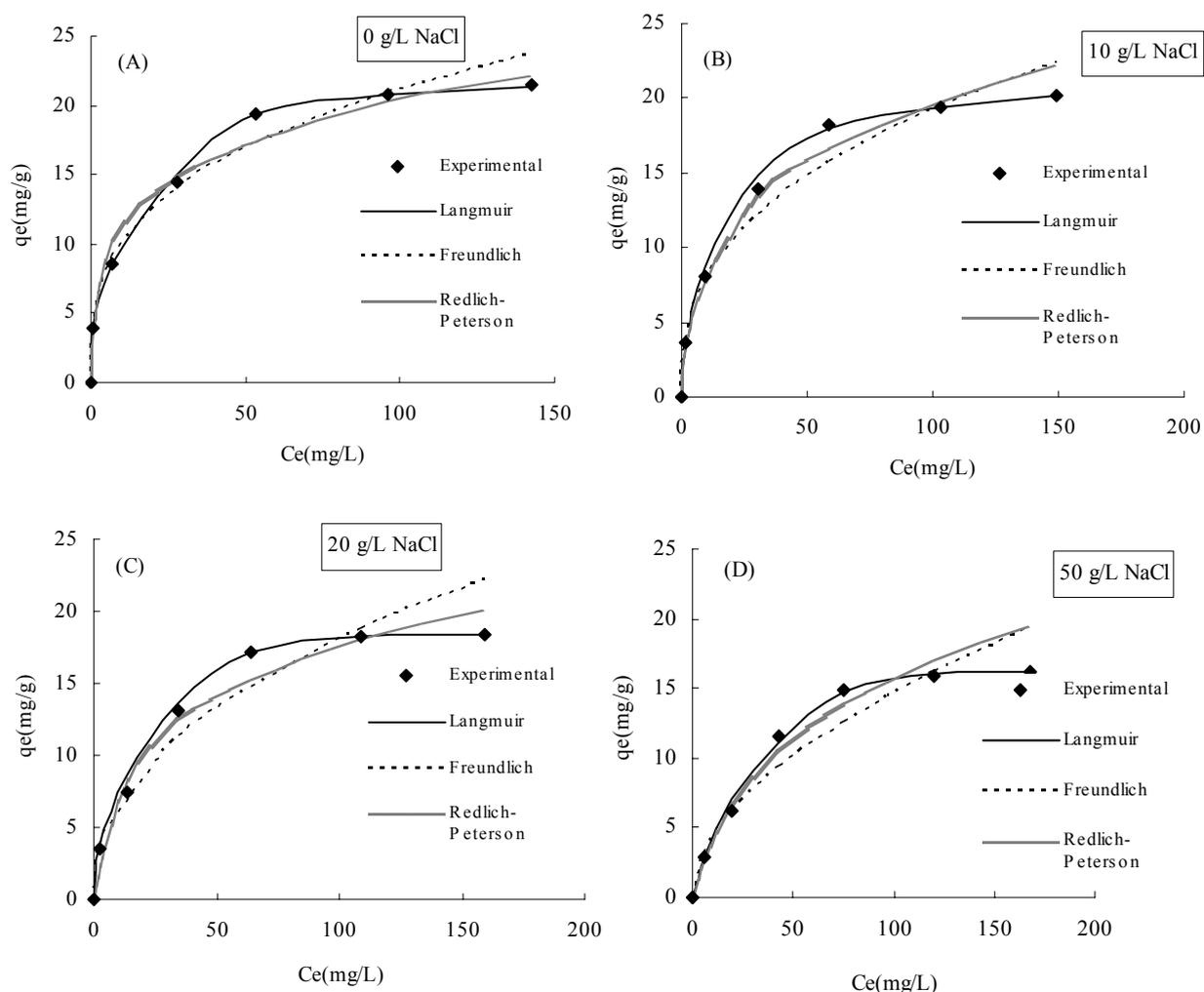


Fig. 6. Isotherms of chromium(VI) ions adsorption by *P. oceanica* as a function of NaCl concentration [(A): 0g/L, (B): 10g/L, (C): 20g/L and (D): 50g/L] at pH 2 and 25±1°C

Table 4. Effect of salt concentration on the Freundlich, Langmuir and Redlich-Peterson adsorption constants of chromium(VI) biosorption (pH : 2, biomass quantity : 0.5 g, temperature : 25±1 °C, agitation rate : 150 rpm)

Models	Salt Concentration (mg/L)			
	0	10	20	50
<u>Langmuir :</u>				
Q° (mg/g)	22.77	21.9	20.7	19.9
b	0.106	0.076	0.056	0.030
ϵ (%)	1.12	4.30	3.70	3.30
R^2	0.9939	0.9960	0.9948	0.9919
<u>Freundlich :</u>				
$K_F [(mg/g)(L/mg)^{(1/n)}]$	4.86	3.35	2.38	1.28
n	3.14	2.59	2.27	1.88
ϵ (%)	5.06	7.30	11.00	10.30
R^2	0.9882	0.9638	0.9776	0.9539
<u>Redlich-Peterson:</u>				
$a_{RP} [(L/g)^{\beta}]$	3.39	1.18	0.33	0.125
K_{RP} (L/g)	23.1	6.30	2.10	1.70
β	0.76	0.71	0.76	0.72
ϵ (%)	6.71	6.62	11.5	9.33
R^2	0.9961	0.9957	0.9907	0.9931

$$\epsilon(\%) = \frac{\sum_{i=1}^N |q_{eq,i,exp} - q_{eq,i,calc}|}{N} / q_{eq,i,exp} * 100 \quad (7)$$

On the basis of average percentage errors and linear regression coefficients (Table 4), the Langmuir model best described the chromium (VI) sorption isotherm data when compared to other models examined. The model fitted the experimental data with a lower average percentage error and a higher linear regression coefficient. The relatively higher percentage errors indicated that both Freundlich and Redlich-Peterson models were not very suitable for describing the biosorption equilibrium of chromium (VI) by the biomass in all cases.

The estimated coefficients of Freundlich model (K_F and n) for chromium (VI) sorption in both single and binary systems are listed in Table 4. K_F and n are dependent on environmental factors and are therefore indicators of the adsorption capacity and adsorption intensity, respectively (Volesky, 2003). The magnitude of K_F and n , the Freundlich constants, indicates relatively easy separation of chromium (VI)

ions from solution. The constant K_F , related to biosorption capacity, can be defined as a sorption coefficient which represents the quantity of adsorbed metal ions for a unit equilibrium concentration. From the table the magnitude of K_F showed a relatively easy uptake of chromium (VI) ions from aqueous solution in both single and binary systems. The co-existence of salt at all concentrations studied decreased K_F constant insignificantly. The maximum K_F value was 4.8 in the absence of salt and the value of K_F decreased to 1.28 with the addition of 50 g/l salt which was consistent with the experimental observation. The n is an empirical parameter that varies with the degree of heterogeneity 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. In particular the value of n , which is significantly higher than unity, indicated that chromium (VI) ions are favourably adsorbed under all the experimental conditions examined. The values of n at different salt concentrations also indicated that the salt added into biosorption medium affected the chromium (VI) biosorption quantity contrarily.

Table 4 also indicates the Langmuir model parameters (Q^0 and b). Q^0 represents the maximum capacity of the adsorbent for chromium (VI) or the monolayer saturation at equilibrium. From Table 4, *P. oceanica* exhibited the maximum biosorption capacity (Q^0) for single chromium (VI) biosorption. The addition of salt decreased the Q^0 value of chromium (VI) biosorption insignificantly. The presence of 50 g/l salt decreased the maximum chromium (VI) removal capacity of biomass from 22.77 mg/g to 19.9 mg/g compared to the monometal 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. The highest b value obtained for monometal conditions also decreased with the addition of salt indicating its negative effect on chromium (VI) biosorption.

Related biosorption parameters were also calculated according to the three-parameter isotherm of Redlich–Peterson using non-linear regression method for chromium (VI) biosorption at different salt levels and are tabulated in Table 4. Redlich–Peterson constant K_{RP} indicated that the adsorption capacity of biosorbent also increased with increasing salt concentration. It is noted that β normally lies between 0 and 1, indicating favourable biosorption in the absence and in the presence of salt.

The results showed that the Langmuir (two parameter) model fitted the biosorption isotherm data much better than other models for all cases with low percentage error values and high regression coefficients. In addition, the Langmuir model parameters changed with respect to the amount of salt. Such behaviour could be used to predict the chromium (VI) adsorption behaviour in aqueous solution as the salt concentrations fluctuate. When isotherm constants were plotted against the salt concentration, it was seen that the functional relationship between isotherm constants and salt concentration are not linear for the entire range of salt concentration (data not shown). After the regression the corresponding nonlinear plots, each isotherm parameter of Langmuir model was expressed as a function of salt concentration and presented in the following equations (Eq 8 and 9).

Thus, as expressed in Eq8 and Eq9, Langmuir parameters decreased following a second-order polynomial function of salt concentration with high linear regression coefficients of determination.

Finally, equilibrium uptake (q_{eq}) considering the variation of the salt concentration could be expressed with Langmuir model as described in Eq(10):

$$Q^0 = 0.002 (C_{0NaCl})^2 - 0.2496 (C_{0NaCl}) + 28.165 \quad \text{with } R^2 = 0.997 \quad (8)$$

$$b = 0.000008 (C_{0NaCl})^2 - 0.0009 (C_{0NaCl}) + 0.033 \quad \text{with } R^2 = 0.996 \quad (9)$$

$$q_{eq} = \frac{[0.002(C_{0NaCl})^2 - 0.249(C_{0NaCl}) + 28.165] \cdot [0.000008(C_{0NaCl})^2 - 0.0009(C_{0NaCl}) + 0.033] \cdot C_{eq}}{1 + [0.000008(C_{0NaCl})^2 - 0.0009(C_{0NaCl}) + 0.033] \cdot C_{eq}} \quad (10)$$

CONCLUSION

The aim of the present study was to find out the adsorption capacity of *P. oceanica* for chromium (VI) in the presence of mixed salts keeping in view the dual problems encountered in industrial effluent treatment. Experiments were performed as a function of pH, initial chromium (VI) and salt concentrations. Changes in these variables have an effect on chromium (VI) removal. Increasing salinity up to 50 g/l lead to a slight decrease of biosorption yield; biosorption at lower pH increased the efficiency of biosorption process and initial chromium (VI) concentration also had an increasing effect on biosorption capacity. It was decided that pseudo-second-order equation, which fits the data well showed that there is good correlation between experimental and calculated value of q_{eq}

explaining the biosorption kinetics based on the assumption that biomass biosorption of the metal is the rate limiting step. The Freundlich, Langmuir and Redlich-Peterson adsorption models were used for the mathematical description of the biosorption equilibrium of chromium (VI) ions by *P. oceanica* both singly and in salt containing medium and the isotherm constants were evaluated. Finally, Langmuir equilibrium parameters were expressed as a function of salt concentration in order to define the equilibrium of chromium (VI) biosorption in an aqueous solution at any salt concentration.

The results showed that the adsorption equilibrium data fitted very well to Langmuir model. Langmuir parameters obtained were compared to

observe the chromium (VI) biosorptive capacity of the biomass in the presence and absence of salt. It was found that chromium (VI) uptake capacity of this biomass is higher in the absence of salt ($Q^0=22.77$ mg/g) than in the presence of 50 g/L salt ($Q^0=19.9$ mg/g). Thus, presence of salt slightly reduced the chromium (VI) uptake. Thus, this marine plant has the potential for effective use in treatment of metal-contaminated saline wastewaters.

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