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Evaluation of Cr(VI) Exposed and Unexposed Plant Parts of *Tradescantia pallida* (Rose) D. R. Hunt. for Cr Removal from Wastewater by Biosorption

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Phytoremediation is an efficient method for the removal of heavy metals from contaminated systems. A productive disposal of metal accumulating plants is a major concern in current scenario. In this work, Cr(VI) accumulating *Tradescantia pallida* plant parts were investigated for its reuse as a biosorbent for the removal of Cr(VI) ions. The effect of pH, contact time, sorbent dosage, Cr(VI) concentration and temperature was examined to optimize these process parameters. Results showed that Cr(VI) exposed/unexposed *T. pallida* leaf biomass could remove 94% of chromium with a sorption capacity of 64.672 mg g^{-1}. Whereas the kinetics of Cr(VI) biosorption was well explained by the pseudo second-order kinetic model, the Langmuir model better described the data on Cr(VI) sorption isotherm compared with the Freundlich model. The changes in the free energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°) were found to be -5.276 kJ mol^{-1}, 0.391 kJ mol^{-1} K^{-1} and 11.346 kJ mol^{-1}, respectively, which indicated the process to be spontaneous, feasible and endothermic in nature. FTIR spectra of *T. pallida* leaf biomass revealed the active participation of ligands, such as $-NH$, amide, hydroxyl and sulphonate groups present in the biomass for Cr(VI) binding, SEM analysis revealed a porous structure of the biosorbent for an easy uptake of Cr(VI).

Keywords: chromium(VI) removal, *Tradescantia pallida*, pseudo second-order kinetics, Langmuir isotherm, thermodynamics, FTIR

Introduction

Pollution due to heavy metals is a major environmental concern owing to their toxicity, non-biodegradability and bioaccumulation potential (Mishra *et al.* 2014). Chromium (Cr) is one of the high priority heavy metal pollutants in surface water and groundwater. Owing to its widespread use in various industries and its technological importance, it is used extensively in leather tanning, dyeing, wood preservation, chromium plating, metal cleaning and processing, and alloy preparation industries (Lokeshwari and Joshi 2009). Among the different oxidative states of chromium, hexavalent and trivalent species of chromium are the most stable and prevalent in industrial effluents. However, the hexavalent form has been considered most hazardous for most organisms due to its mutagenic and carcinogenic properties.

Cr(VI) mainly originates from anthropogenic sources and maximally occurs in the aqueous environment as $HCrO^-_4$, $Cr_2O^-_2$, $Cr_2O_7^{2-}$ and CrO_4^{2-} that are highly mobile (Mohanty *et al.* 2006; Chen *et al.* 2011). Unregulated and untreated industrial discharge of chromate (CrO_4^{2-}) can cause an impending danger to flora and fauna disturbing biological processes. To save the aquatic ecosystem it is, therefore, essential to treat effluent from industries to acceptable level of Cr prior to its discharge into the environment.

Chemical and physical treatment methods, such as precipitation, oxidation-reduction, electrochemical treatment, evaporation recovery, reverse osmosis, membrane technologies and ion exchange have been tested for the removal of Cr from industrial wastewater (Liu *et al.* 2007). Major concerns with these treatment methods are cost, incomplete metal removal, large reagent and energy demand, and release of toxic sludge (Gupta and Babu 2009). Management of large amount of this detrimental sludge further poses disposal problems which limit the techno-economic feasibility of these treatment processes. Under this scenario, particularly considering the economic and environmental prospectives, biosorption has emerged as a very promising method for treatment of heavy metal containing industrial effluents.

Biosorption involves passive uptake mechanism and depends mainly on the "affinity" between a biosorbent and sorbate which can result from complexation, metal chelation, ion exchange, adsorption and microprecipitation (Sud *et al.* 2008). Performance of an adsorbent depends on many factors, such

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as pH, the ionic form of the metal to be removed and competition from other organic or inorganic ions for the available binding sites on the adsorbent (Anwar *et al.* 2009). Different types of biomass have been studied for the removal of Cr(VI), which includes agricultural wastes, plant biomass, and industrial by-products (Pakshirajan *et al.* 2013). Some heavy metal hyperaccumulator plants have the ability to take up the heavy metal in its parts (Unamuno *et al.* 2007). Following bioaccumulation, however, proper waste disposal management of such plants is needed. One viable solution to this problem could be their reuse as biosorbent for removal of the same metal, which has not been reported so far in the literature. This way waste plant biomass can serve as a material source as well as reduce the cost of waste disposal.

Therefore, this study evaluated the potential of different plant parts, namely roots, shoots and leaves of Cr(VI) unexposed and exposed *T. pallida* plants for the removal of Cr(VI) from aqueous solution. *T. pallida* is a trailing perennial plant belonging to the Commelinaceae family, and is a rapidly growing plant with low maintenance and high biomass yield. This plant was previously investigated for the uptake of Cr(VI), and was found to bioaccumulate a substantial amount of chromium in its different parts (Sinha *et al*. 2014). Phytochemical analysis of the leaf extract revealed the presence of biologically active compounds, such as alkaloids, saponins, flavonoids, steroids, glycoside, terpenoids, tannin and phenolic compounds and oil (Muthukrishnan and Subramaniyan 2012). Presence of several functional groups further enables its use in the metal biosorption process.

Materials and Methods

Reagents

All chemicals used in this study were of analytical reagent grade and procured from Merck India Ltd. Stock solution of hexavalent chromium (1000 mg L^{-1}) was prepared by dissolving 0.283 g of potassium dichromate (Merck, India) in 100 ml de-ionized water. The stock solution was suitably diluted to achieve a desired working initial Cr(VI) concentration in the experiments. For adjusting the pH of Cr(VI) containing solution of desired concentration,1 N HCl /1 N NaOH was used.

Source and Preparation of T. pallida Plant Biomass for Cr(VI) Biosorption

T. pallida plants were initially collected from North Guwahati, India, and were grown under hydroponic conditions for 60 days with or without supplementation with 10 mg L^{-1} Cr(VI), as described by Sinha *et al.* (2014). These Cr(VI) exposed and unexposed plants were collected and subsequently separated into different parts (roots, shoots and leaves). These plant parts were washed extensively with water and then with de-ionized water to remove any adhering dirt and particulate material from its surface, followed by drying in an oven for 2 days at 343 K. The dried plant parts were finally ground to a desired size and stored until further use in Cr(VI) biosorption experiments.

T. pallida Biomass Characterization

Characterization of the *T. pallida* (exposed/unexposed) leaf biomass was carried out by scanning electron microscope (SEM) and Fourier transform infrared (FTIR) spectroscopy analysis. The surface morphology of *T. pallida* Cr(VI) loaded leaf biomass was elucidated using SEM (500× and 10 K X) (LEO, 1430 vp, Germany). In order to determine the functional groups in the plant biomass for Cr(VI) binding, biomass samples taken before (control) and after Cr(VI) biosorption (loaded) with 50 mg L^{-1} initial Cr(VI) solution (pH = 2) were analysed using FTIR (IR Affinity, Shimadzu, Australia) within the range 400–4000 cm^{-1}. KBr was taken as the background material for this FTIR analysis.

Cr(VI) Biosorption Experiments

To examine the Cr(VI) removal from aqueous solution by *T. pallida* biomass (roots, shoots and leaves), batch biosorption experiments were performed in which a known dosage of the plant biomass was taken into a 250 mL conical flask with 50 mL solution of known Cr(VI) concentration. All these experiments were conducted by agitating the biosorption flasks at 250 rpm in an orbital incubator shaker till the equilibrium was established. The temperature was maintained within ±274 K of the required values during the experiments.

The effect of different process parameters, viz. solution pH, contact time, biosorbent dose, temperature and initial concentration, was first investigated by varying these parameters one-at-a-time and by maintaining the other parameters at a constant level. The following range of these parameters was tested to examine their effect: pH 2–3.5, temp. 303–323K, biosorbent dose 0.5–2 g, initial Cr(VI) conc. 50–200 mg L^{-1}.

At the end of each biosorption experiment, samples were taken from the respective test solutions to determine the residual Cr(VI) concentration. Prior to the Cr(VI) analysis, the biosorbent was separated by filtration with Whatman filter paper number 1 followed by centrifugation at 4,000 ×g for 10 min. Each biosorption experiment was conducted in triplicate, and the mean value was used for calculations. Cr(VI) removal was expressed as either% removal or mg removed per g of biosorbent (mg g^{-1}) as represented by equations (1) and (2), respectively.

$$\%\,\text{removal} = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

$$Uptake\ capacity\,(q) = \frac{C_i - C_f}{m} \times V \tag{2}$$

where C_i, and C_f are initial and final Cr(VI) concentrations (mg L^{-1}), respectively. V is the volume of the solution (L) and m is the mass of the biosorbent (g).

Cr(VI) Sorption Kinetics and Isotherm

For determining the Cr(VI) sorption kinetics, aqueous solution containing different Cr(VI) ion concentration (50–200 mg L^{-1}) was taken with 0.5 g of *T.pallida* leaf biomass (exposed) as the biosorbent. Other initial conditions were: pH 2, temperature 308 K and agitation speed 250 rpm. Samples were taken from the solution at definite time intervals until the equilibrium was achieved. The results obtained at different time intervals were fitted to the pseudo first and pseudo second-order kinetic models to estimate the kinetic parameters associated with the Cr(VI) sorption by the plant biomass. These models are briefly described further. The general form of the pseudo-first order rate model is expressed as:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \tag{3}$$

where q_e and q_t are the amount of Cr(VI) (mg g^{-1}) at equilibrium and at time t, respectively. k_1 is the pseudo first-order rate constant (min^{-1}). Integrated form of this equation is:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{4}$$

The pseudo second-order model is based on sorption capacity of the biosorbent and is written as:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{5}$$

where k_2 is the pseudo second-order rate constant (g $mg^{-1}min^{-1}$). Integrated linear form of this equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

In order to determine the Cr(VI) sorption isotherm parameters in this study, aqueous solution (pH = 2) containing different initial Cr(VI) concentration (50–200 mg L^{-1}) was added with the plant leaf biomass and incubated at a temperature in the range 303–323K. The results were fitted to the Langmuir and Freundlich isotherm models. The mathematical expression of the Langmuir isotherm is given by:

$$Q_0 = \frac{Q_0 b C_e}{1 + b C_e} \tag{7}$$

$$\frac{1}{Q_e} = \frac{1}{Q_0} + \frac{1}{b Q_0 C_e} \tag{8}$$

where $C_e$and Q_e are the equilibrium Cr(VI) concentration in solution (mg L^{-1}) and the equilibrium Cr(VI) loading on the biosorbent (mg g^{-1}), respectively. Q_0 and b are the Langmuir constants related to maximum Cr(VI) sorption capacity (mg g^{-1}), and the relative energy of sorption (L mg^{-1}), respectively.

The Freundlich isotherm model is given by:

$$Q_e = K_f (C_e)^{1/n} \tag{9}$$

$$\log Q_e = log K_f + \frac{1}{n} \log C_e \tag{10}$$

where, K_f and n are Freundlich constants related to Cr(VI) sorption capacity (L g^{-1}) and intensity, respectively. Cr(VI) biosorption thermodynamic parameters were obtained by varying the temperature over the range 303–323K and by keeping the other variables constant.

The changes in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) related with Cr(VI) sorption in this study were determined using the following equations:

$$\Delta G^\circ = -RT \ln K \tag{11}$$

where ΔG^0 is the change in free energy (kJ mol^{-1}), R is the universal gas constant (8.314 J $mol^{-1}K^{-1}$) and T is the absolute temperature (K). The equilibrium constant may be defined as:

$$K = \frac{C_{ae}}{C_e} \tag{12}$$

where C_{ae} and C_e are the equilibrium concentration (mg L^{-1}) of Cr(VI) on the biosorbent and in the solution, respectively.

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \tag{13}$$

where ΔH^0 is the change in enthalpy (kJ mol^{-1}) and ΔS^0 is the change in entropy (kJ $mol^{-1}K^{-1}$).

$$log K = \frac{\Delta S^\circ}{2.303 R} - \frac{\Delta H^\circ}{2.303 RT} \tag{14}$$

The enthalpy change, ΔH°, and the entropy change, ΔS°, for the Cr(VI) sorption process were obtained from the intercept and slope, respectively, of Eq. (14).

Analytical Methods

Chromium content in the samples was analysed following the diphenyl carbazide method (Chen *et al.* 2010) by measuring the absorbance of a colour complex formed at 540 nm using a UV visible spectrophotometer (Cary 100, Varian, Australia).

Results

Characterization of T. pallida Leaf Biomass

FTIR Spectroscopy

The FTIR spectra of *T. pallida* leaf biomass before (control) and after sorption (Cr(VI)-loaded) were analysed to reveal the vibrational frequency changes in the functional groups in the

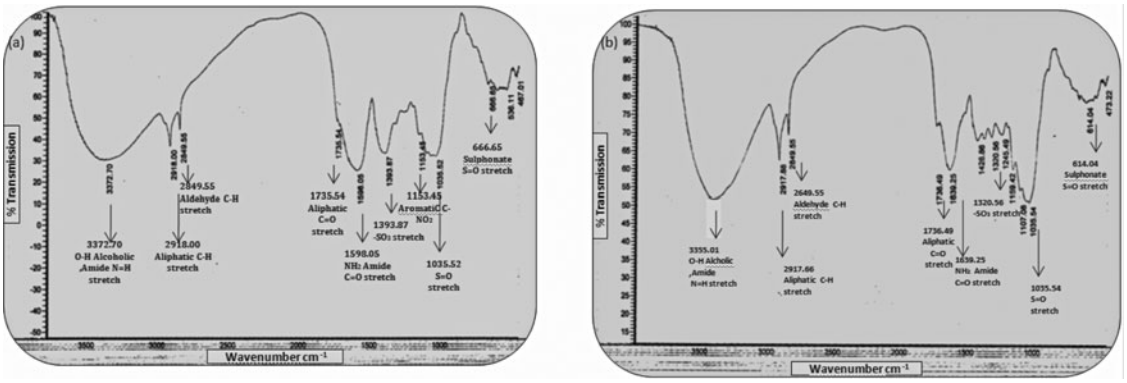

Fig. 1. FTIR spectra of Cr(VI) exposed *T. pallida* leaf biomass : (a) control and (b) Cr(VI)-loaded.

leaf biomass, which showed better Cr(VI) removal than the other plant parts. In the spectra obtained using the Cr(VI)-loaded biomass (Fig. 1b), a band shift to 3355 cm^{-1} from 3372 cm^{-1} along with a substantial decrease in its intensity represented the $-OH$ groups of cellulose and $-NH_2$ asymmetric stretching due to amines of proteins present in the biomass (Shroff and Vaidya 2012). This broad shift indicates overlapped stretch of hydroxyl and amines groups on the leaf surface. The major peak shift from 2849 cm^{-1} to 2649 cm^{-1} observed in the Cr(VI)-loaded biomass can be attributed to stretching vibration of the C−H group (Barbu *et al.* 2010). The band ranging from 1500 cm^{-1} to 1650 cm^{-1} represents amide I and amide II bands of peptide bonds and ammonium salts of carboxylic acid compounds (Li *et al.* 2011). A clear shift in the band position to 1320 cm^{-1} from 1393 cm^{-1} represents $-SO_3$ stretching, which indicates binding of Cr(VI) mostly with $-SO_3$ groups in the leaf biomass (Murphy *et al.* 2009). The additional peak shift at 666 cm^{-1} can be assigned to the bending due to aromatic compounds present in the biosorbent (Bansal *et al* 2009). These shift in wavelength of the peaks and their intensity following Cr(VI) biosorption suggest the presence of functional groups mainly −NH, amide, hydroxyl and sulphonate groups for Cr(VI) binding on the *T. pallida* leaf biomass (Table 1).

Table 1. IR absorption bands and corresponding possible functional groups

Frequency (cm^{-1})	Functional group	*T. pallida* leaf biomass (control)	Cr(VI) loaded *T. pallida* leaf biomass
3300–3450	−OH, −NH stretching	3372	3415
2910–2920	−CH stretching	2918,2849	2917,2649
1730–1740	C=O stretching	1735	1736
1600–1640	−COO, C=O stretching	1598	1639
1300–1450	Amide or sulfamide bond	1393	1320
1270	−C−O stretching	1153	1159
1030–1070	S=O stretching	1035,666	1035,614

Scanning Electron Microscopy

Figure 2 shows the scanning electron micrographs of Cr(VI) biosorbed *T. pallida* leaf biomass which shows irregular and porous surface with the complexed Cr(VI) ions. These SEM images provided direct evidence of Cr(VI) binding to the pores of the leaf biomass.

Effect of Process Parameters on Cr(VI) Biosorption

The effect of pH, contact time, temperature and sorbent dose on Cr(VI) sorption by the different plant parts are shown in Fig. 3. The optimum pH for the Cr(VI) biosorption was found to be 2, and used for all further experiments (Fig. 3a).

Biosorption increased with an increase in the contact time (Fig. 3b). Profiles shown in this figure show an initial curved portion followed by a linear profile and a plateau depicting that the equilibrium was achieved within the initial 5 hours. After this time period the removal was slower and remained nearly the same.

To examine the temperature effect on Cr(VI) biosorption, experiments were performed at four different temperatures (303, 308, 313, 323 K). The results indicate an increase in Cr(VI) sorption with a raise in the temperature (Fig. 3c).

Cr(VI) removal efficiency increased with an increase in the biosorbent dose (Fig. 3d). However at 2g biosorbent dose, the maximum removal was 94% as compared with 92% at 1g, biomass dosage, which indicates saturation of available sites in the biomass for Cr(VI) binding above 1g. Thus, a maximal removal efficiency of 94% was obtained using *T. pallida* leaf biomass with a Cr(VI) initial concentration of 100 mg L^{-1} and at a 323K temperature. In all these batch experiments, no significant difference in Cr(VI) removal efficiency was observed between the treated and control *T. pallida* leaf biomass. As both the control and Cr(VI) exposed leaf biomass showed the best and an equal Cr(VI) removal efficiency, only the Cr(VI) treated leaf biomass was further examined for its Cr(VI) sorption kinetics, isotherm and thermodynamics.

Cr(VI) Sorption Kinetics and Isotherm

Table 2 presents the results of fitting the Cr(VI) sorption kinetics to pseudo first and second-order kinetic models. The plot of t/q_t versus t showed that Cr(VI) sorption kinetics in

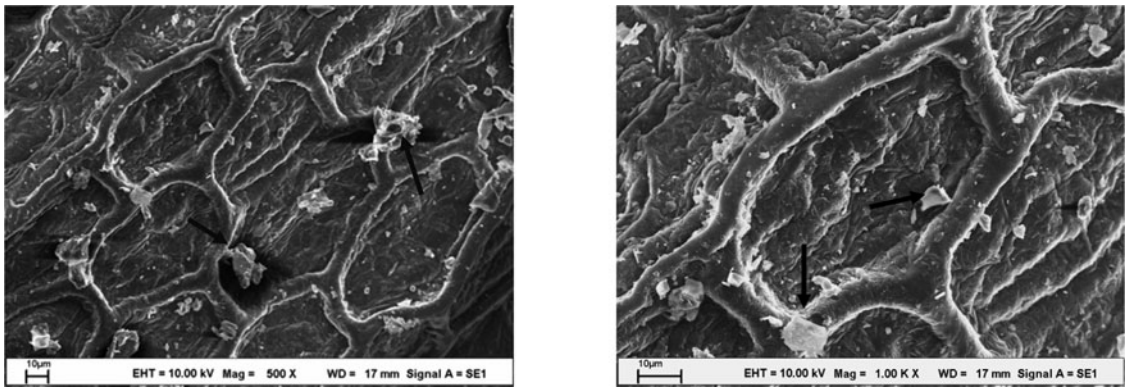

Fig. 2. SEM images of Cr(VI) biosorbed *T. pallida* leaf biomass showing multiple well developed pores (a) 500x magnification and (b) 1000X magnification (Arrows inside these two figures indicate sorbed Cr(VI) species).

the study followed the pseudo second-order rate expression more accurately than the pseudo first-order kinetics in which case the R^2 value was 0.999. Using this model, the amount of Cr(VI) sorbed at equilibrium (q_e) was estimated to be 2.299 g $mg^{-1}min^{-1}$.

Table 3 presents the Langmuir and Freundlich isotherm model parameters for Cr(VI) sorption in the study (Pehlivan *et al.* 2008). The equilibrium data fitted well with the Langmuir sorption isotherm with a Q_o value 64.672 mg g^{-1}, and an equilibrium constant (b) value of 0.328 L mg^{-1}. These values of the Langmuir isotherm parameters suggest a very high capacity of the biosorbent for Cr binding and a strong affinity of Cr ions to the biosorbent, respectively.

Cr(VI) Sorption Thermodynamics

Figure 4 shows a highly linear Van't Hoff plot obtained between ln b and 1/T for Cr(VI) sorption in this study. The negative value of ΔG° at different temperatures shows that the Cr(VI) biosorption process is spontaneous, and *T. pallida* leaf

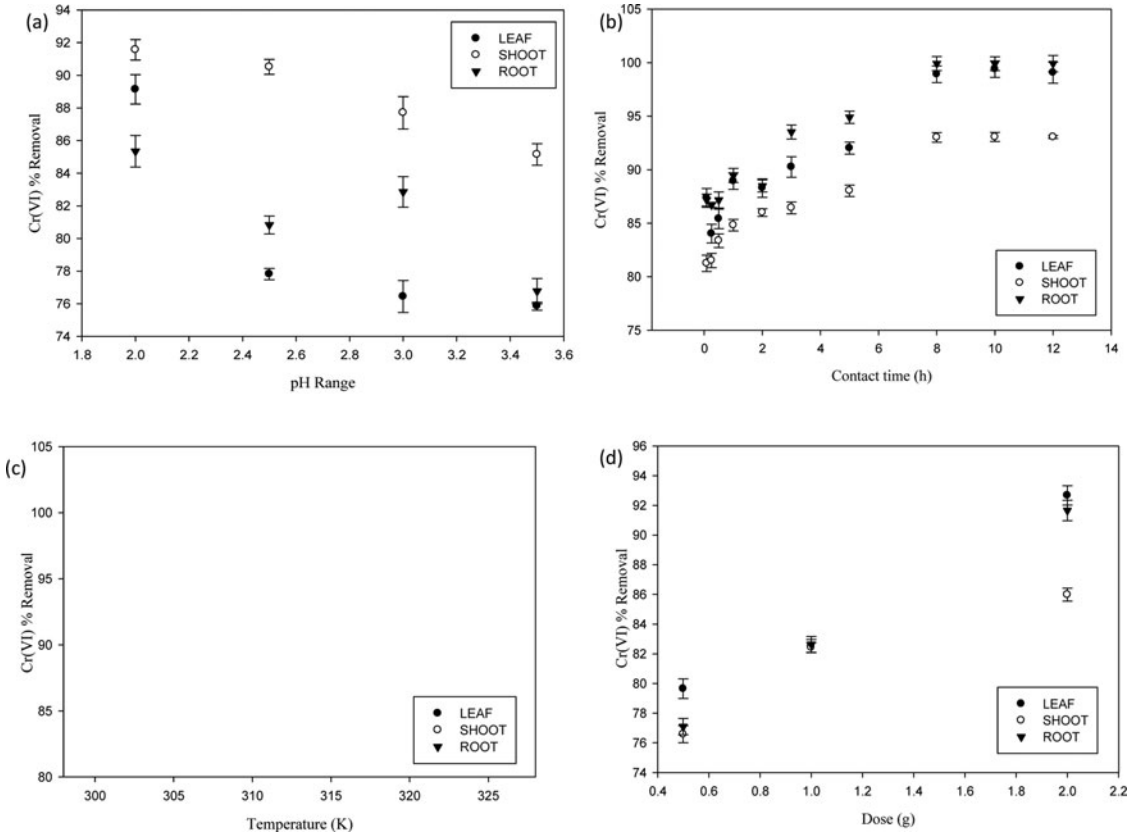

Fig. 3. Effect of different parameters on Cr(VI) biosorption by plant parts of Cr(VI) exposed *T. pallida* (a) pH (b) contact time (c) temperature (d) dose.

Table 2. Estimated kinetic parameters of Cr(VI) biosorption obtained using the pseudo first-order and second-order kinetic models.

	Cr(VI) exposed *T. pallida* biomass			*T. pallida* biomasss (unexposed)		
(a) Pseudo first-order kinetics						
	Leaf	Shoot	Root	Leaf	Shoot	Root
Coefficient of determination (R^2)	0.886	0.485	0.841	0.842	0.754	0.831
Rate Constant (k1)(min^{-1})	0.001	0.001	0.005	0.001	0.001	0.001
Equilibrium amount of metal ion (q_e) (mg g^{-1})	0.908	0.606	1.195	0.913	0.597	0.983
(a) Pseudo second-order kinetics						
Coefficient of determination (R^2)	0.998	1	0.981	0.999	0.999	0.991
Rate Constant (k2)(g $mg^{-1}min^{-1}$)	0.207	0.232	0.207	0.199	0.213	0.198
Equilibrium amount of metal ion (q_e)(mg g^{-1})	2.299	0.245	1.859	1.913	1.619	1.513

biomass has a high affinity for the metal ions at higher temperatures (Table 4). The maximum sorption capacity, Q_o, and the sorption equilibrium constant, b, increased from 53.968 to 64.678 mg g^{-1} and 0.208 to 0.328 L mg^{-1}, respectively, as the temperature was raised from 303 to 323 K. The increase in Cr(VI) sorption equilibrium constant values with temperature reveals a higher heat of sorption with increasing temperature, which clearly demonstrates that Cr(VI) sorption on to *T. pallida* biomass is an endothermic process.

The change in enthalpy (ΔH°), and entropy, (ΔS°), for Cr(VI) sorption process were obtained from the intercept and slope respectively, of Eq. (13). The value of these parameters were found to be 11.346 kJ mol^{-1} and 0.391 kJ mol^{-1} K^{-1}, respectively. The positive value of ΔH° further indicates that Cr(VI) biosorption onto the biosorbent is endothermic. The positive values of ΔS° reveal that randomness of the Cr(VI) sorption process increases at the solid–liquid interface. It also reflects the affinity of the biosorbent for chromium ions and structural changes in the biosorbent following Cr(VI) sorption.

Discussion

T. pallida leaves have been studied for heavy metal bioaccumulation, which included Ba, Ce, Co, Cr, Cs, La, Rb, Sb, Sc, Zn etc. and is also known for air pollution biomonitoring (Luccia and Thiago 2012). Hence, this plant species is a potent bioindicator of environmental pollution and can easily propagate in regions of high pollution level (Mišík *et al.* 2007; Batalha *et al.* 1999). In the previous study as well, *T. pallida* leaves were shown to bioaccumulate substantial amount of chromium (449 μg g^{-1}dw) (Sinha *et al*. 2014).

This study was carried to further examine Cr(VI) sorption capacity of the chromium accumulated *T. pallida* plant and compare its efficiency with that of the Cr(VI) unexposed plants. Comparison was also made among the different plant parts (roots, shoots and leaves) in order to define the metal binding potential of each. The results showed that the Cr(VI) removal due to either Cr(VI) exposed or unexposed plant parts was the same. However, among the different plant parts, *T. pallida* plant leaf biomass exhibited a higher Cr(VI) removal than *T. pallida* roots or shoots (exposed or unexposed). Cr(VI) sorption capacity of the *T. pallida* depended upon its porosity and chemical reactivity of the functional groups present (Table 1 and Figs. 1–2). This can be attributed mainly to the plant leaves which possess photosynthetic function with a rich content of proteins, lipids, nitrogen, organic acids and sugars (non-structural carbohydrates as well as structural carbohydrates) than woody stem tissues (Poorter and Jong 1999). These components thus provide a large number of functional groups which could bind with Cr(VI).

Table 3. Langmuir and Freundlich isotherm parameters estimated for Cr(VI) sorption obtained using the Cr(VI) exposed *T. pallida* leaf biomass

	Langmuir constants			Freundlich constants		
Temperature (K)	Q_o (mg g^{-1})	b (L mg^{-1})	R^2	n	k_f (L g^{-1})	R^2
303	53.968	0.208	0.997	1.0	1.648	0.935
308	54.032	0.334	0.997	1.2	1.613	0.934
313	59.098	0.330	0.998	1.0	1.656	0.954
323	64.672	0.328	0.999	1.4	1.572	0.854

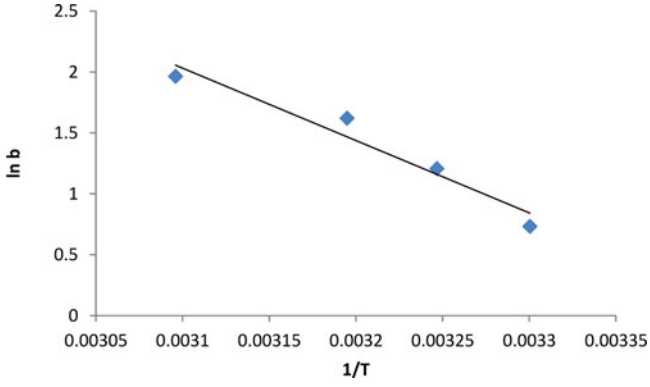

Fig. 4. Van't Hoff plot (temperature = 308–323 K, pH = 2, Cr(VI) conc. = 50 mg L^{-1}, biomass dose 0.5 g).

Table 4. Thermodynamic parameters of Cr(VI) sorption obtained using the Cr(VI) exposed *T. pallida* leaf biomass

Temperature (K)	Equilibrium constant K	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ $mol^{-1}K^{-1}$)
303	16.39774	−1.84814	11.346	0.391
308	28.07096	−3.09003		
313	42.85714	−4.21988		
323	77.88162	−5.27626		

FTIR analysis results of the *T. pallida* leaf biomass, following Cr(VI) sorption revealed the involvement of −NH, amide, hydroxyl and sulphonate as the major functional groups for chromium binding by the plant biomass. These functional groups are mainly part of the protein and sugar content of the leaf biomass, which strongly interacted with Cr(VI) ions for binding (Poorter and Jong 1999).

The Cr(VI) sorption onto *T. pallida* leaf biomass was further elucidated from the results of kinetics, isotherm and thermodynamic analyses (Tables 2–4). Pseudo second-order kinetic model fitting of the data revealed intraparticle diffusion of Cr(VI) ion as the rate controlling step. Estimated Cr(VI) sorption isotherm parameters due to the Langmuir model yielded significant details of the biosorbent properties and its affinity to Cr(VI) (Table 3). A better fit of the isotherm data to this model further suggested that Cr(VI) sorption was restricted to monolayer on the biomass surface with a finite number of identical sites (homogenous). A large q_{max} value along with a high b value for Cr(VI) binding further indicated respectively, a very high binding capacity and good affinity of the leaf biomass for Cr(VI), (Table 3). Thermodynamic parameter revealed a feasible and endothermic nature of the Cr(VI) sorption process in the study.

Among the different process parameters examined for their effect on Cr(VI) biosorption by *T. pallida* leaf biomass, pH was found to be the most significant (Fig. 3a). This is mainly because not only the metal speciation depends on solution pH, but also the dissociation of active functional sites on the biosorbent (Yu *et al*. 2003). $HCrO^{4-}$ and $Cr_2O_7^{2-}$ are the predominant species in the pH range 0–6.5 and CrO_4^{2-} ions dominates at pH above 6.5 (Levankumar *et al*. 2009; Blázquez *et al*. 2009). With a decrease in solution pH, functional groups such as carboxyl (−COOH) and amino ($-NH_2$) gets protonated. Due to the positively charged biomass surface at a low solution pH, its coordination with the anionic Cr(VI) species is highly enhanced. Thus a lower pH favored Cr(VI) biosorption by the leaf biomass than did the higher pH (Moussavi and Barikbin 2010).

The high Cr(VI) removal efficiency obtained using either treated or untreated *T. pallida* plant biomass demonstrates its potential for use in treating Cr(VI) contaminated wastewaters by both hyperaccumulation and by biosorption even after it has ceased to grow. This result suggest that Cr(VI) biosorption by *T. pallida* is unaffected because of prior exposure of the plant to the metal although it has been reported that when grown in presence of the metal, the plant accumulates Cr into its cells following initial and quick binding of the metal onto the cell surface (Sinha *et al.* 2014). In the case of Cr bioaccumulation by plants, the binding takes place inside the cytoplasm involving various ligands, such as phytochelatin, metallothioneins, metal binding proteins, etc. or in the vacuole by tonoplast-located transporters or both (Yang *et al*. 2005). On the contrary, biosorption is a metabolism-independent process in which Cr binding takes place only on the plant cell surface involving functions groups, such as carboxyl, amide, etc. Thus, it could be well said that even if *T. pallida* was grown in the presence of Cr(VI), its cell surface functional groups responsible for Cr binding were still available for the metal biosorption.

Cr(VI) can also be recovered from the loaded biomass by desorption using suitable agents, which however needs to be investigated further. Moreover, investigations aimed at continuous column sorption using the *T. pallida* leaf biomass and desorption of bound Cr(VI) need to be carried out to further establish its application potential. Usage of such plant systems would reduce the costs for waste disposal and at the same time serve as a productive material resource.

Conclusions

This study showed that Cr(VI) exposed *T. pallida* leaf biomass can be used as an efficient biosorbent to remove Cr(VI) from aqueous solution. Among the different parameters examined for Cr(VI) biosorption, solution pH was the main influential parameter. Whereas Cr(VI) biosorption followed the pseudo second-order kinetics with intra particle diffusion of Cr(VI) as the rate controlling step, the FTIR study revealed that −NH, amide, hydroxyl and sulphonate groups were mainly involved in the binding of Cr(VI). Thermodynamics of Cr(VI) sorption in this study revealed that the process is highly spontaneous and therefore highly feasible for the removal of Cr(VI) from contaminated water..

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