Assessment of Kinetics, Thermodynamics and Equilibrium Parameters of Cr(VI) Biosorption Onto *Pinus brutia* Ten

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The aim of the present study was to investigate the sorption potential of pine bark (*Pinus brutia* Ten.) for removal of Cr(VI) ions from aqueous solutions. The biosorption characteristics of Cr(VI) ions onto bark biomass were examined with respect to the changes in initial pH of the solution, contact time, initial Cr(VI) and bark concentration, bark particle size, temperature, etc. The biosorption isotherms were described by means of Langmuir and Freundlich models and the biosorption kinetics were analysed using pseudo-first-order, pseudo-second-order and intraparticle diffusion models. The thermodynamic parameters proved that the process was feasible, spontaneous and endothermic in nature.

Keywords: biosorption, removal, pine bark, chromium, equilibrium

INTRODUCTION

The presence of heavy metals in natural waters or industrial wastewaters represents significant environmental problems even at low concentrations. Because they are non-biodegradable and, hence, are accumulated by living organisms, the most heavy metals cause a large number of diseases and disorders, in particular inducing deleterious effects on human physical and mental health.[1]

Among different heavy metal ions, chromium holds a distinct position. The most stable and common forms of chromium in the environment are Cr(III) and Cr(VI). Cr(VI), which is primarily present in the form of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), is more toxic to living organisms than Cr(III) ions due to its high oxidation potential and diffusability through cell membranes[2] Cr(VI) is considered as a powerful carcinogenic agent that modifies DNA transcription process causing important chromosomic aberrations. Furthermore, it causes cancer in the digestive tract and lungs and may cause epigastric pain, nausea, vomiting, severe diarrhoea and haemorrhage.[3,4] Chromium is released into the ecosystems from a variety of industrial activities such as electroplating, leather tanning, mining, textile dyeing, wood preserving, chromate preparation, metal finishing, etc.[5] According to the World Health Organization (WHO) drinking water guidelines, the maximum allowable limit for total chromium is 0.05 mg L^{-1}.[6] For these reasons, the removal of chromium and other toxic heavy metal ions from waters and wastewaters is an important task in terms of protection of public health and environment.

Several methods including solvent extraction, filtration, ion exchange, coagulation, reverse osmosis, chemical precipitation and chemical oxidation or reduction are commonly utilized in the treatment of Cr(VI) and other heavy metal ions contaminated effluents. However, some of these techniques have considerable disadvantages such as high reagent and energy requirements, low selectivity, high capital and operational costs, incomplete metal removal and generation of other waste products.[7] For example in chemical reduction/precipitation technique, a high amount of reducing agent is necessary for reduction of Cr(VI) to Cr(III), and a strong base must be added to the medium in order to precipitate the Cr(III) ions as hydroxides.[8] On the other hand, the development of a biosorption or adsorption technique represents a powerful alternative for removal of organic and inorganic pollutants from waters and wastewaters.[9–11] Biosorption techniques have significant advantages including high efficiency in removal of very low levels of heavy metals from dilute solutions, high selectivity, easy handling, lower operating costs and ease of the generation of the biosorbents.[12,13]

The biosorption of heavy metal ions is primarily affected by the chemistry and surface morphology of the biomass.[14,15] Although hematite,[16] glutaraldehyde cross-linked chitosan beads,[17] hydroxyapatite[18] and iron nanoparticles[19] have been used by the previous researchers, the agricultural and forestry byproducts such as brewer's yeast,[20] *Ceiba pentandra* hulls[21] and corn cobs[22] are recognized as low cost and effective biosorbents. These biosorbents contain polysaccharides and proteins having various functional groups such as carboxyl, hydroxyl and phosphates which are responsible for the binding of metal ions.[23] Among the different biosorbents, bark is one of the most abundant, effective and low cost material. From this point of view, pine (*Pinus brutia* Ten.) bark was selected as the biosorbent in this study. *P. brutia* is naturally distributed in the Mediterranean and Aegean region of Turkey, and it is an important source of timber and amenity.[24] *P. brutia* bark is an effective biosorbent for removal of Cr(VI) ions from aqueous solutions due to its high tannin content. The polyhydroxy and polyphenol groups of tannin are considered as the active species in the sorption process.[25] In literature there are several studies about the usage of pine bark in removal of both organics and inorganics pollutants.[26–32]

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The objective of the present work is to investigate the biosorption potential of *P. brutia* bark in removal of Cr(VI) ions from aqueous solutions. The effects of experimental parameters such as contact time, initial pH of the aqueous solution, initial Cr(VI) concentration, bark concentration, bark particle size, temperature etc. were studied in detail upon the biosorption process. The interferences of foreign ions were also evaluated. The biosorption mechanisms of Cr(VI) ions onto bark biomass were evaluated in terms of thermodynamics and kinetics. The biosorption isotherms were described by using Langmuir and Freundlich isotherm models.

MATERIALS AND METHODS

Preparation and Characterisation of Biosorbent

P. brutia bark was provided by the Faculty of Forestry at Karadeniz Technical University and used without any additional chemical or physical activation pretreatment except for washing and sieving to desired particle sizes. For preparation of the bark biomass for the biosorption experiments, it was washed with deionized water several times to remove any dust and other water-soluble impurities. The washed bark sample was dried in an oven at 40°C for 4 days, then ground in a blender and sieved according to the required particle size, and stored in glass containers until use for biosorption experiments.

The FTIR spectrum of the bark biomass was depicted in our previous research.[33] The surface area of the bark was determined by A Quantachrome Corporation, Autosorb-1-C/MS model specific surface area analyser. JEOL/JSM-6335F model scanning electron microscope was utilized to disclose the surface morphology of the bark. The surface acidic functional groups containing oxygen were determined according to Boehm titration[34] and other characterization parameters such as self pH value of the bark, pH of zero charge (pH_{pzc}) and moisture content were determined using standard methods.[35]

Biosorption Experiments

All chemicals were of analytical reagent grade and obtained from Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland). A stock solution containing 5000 mg L^{-1} of Cr(VI) was prepared by dissolving appropriate amount of $K_2Cr_2O_7$ in deionized water. Different concentrations of Cr(VI) solutions were prepared by diluting the stock solution. Deionized water was used for all dilutions. The pH of the solutions was adjusted to 2.0 with either HCI or NaOH solutions by using a Hanna pH-211 (HANNA instruments/Romania) digital pH meter with glass electrode. The batch biosorption tests were conducted by transferring 10 mL of Cr(VI) solution (in the concentration range of 50–1000 mg L^{-1} at initial pH 2.0) into a polyethylene centrifuge tube. Then 50 mg of bark biomass (5.0 g L^{-1}) was added to the solution, and the system was agitated on a mechanical shaker (Edmund Bühler GmbH) at 400 rpm for 4 h to reach equilibrium. Then the biosorbent was filtered through 0.45 μm nitrocellulose filter paper and the concentration of Cr(VI) ions in the filtrate was analysed by a Unicam model AA-929 Flame Atomic Absorption Spectrometer (FAAS) (Solar System ATI, Unicam Analytical Technology Inc., Cambridge, UK). All experiments were conducted in triplicate.

RESULTS AND DISCUSSION

Characterisation of Biosorbent

The bark has relatively small specific surface area since the BET surface area of the bark was found to be lower than 5.0 m^2 g^{-1}.

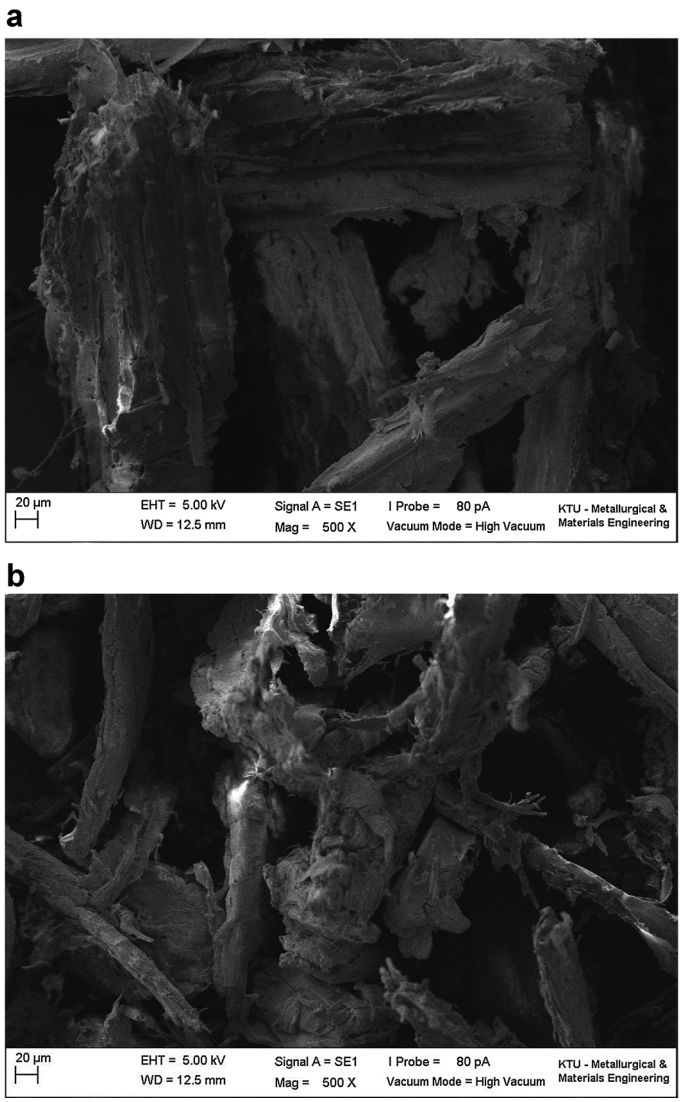

Figure 1. SEM micrographs of (a) bark (b) Cr(VI) loaded bark.

The bark surface exhibits porous structure (Figure 1a and these pores was coated with Cr(VI) ions during the biosorption process (Figure 1b). The results for the amount of surface acidic functional groups, self-pH value of the bark, pH of zero charge (pH_{pzc}) and moisture content were given in Table 1.

Effect of Initial pH and Its Optimisation

The initial pH of the aqueous solution is an important controlling parameter in the heavy metal sorption process. In order to determine the effect of initial pH on the biosorption of Cr(VI) ions onto bark biomass, the biosorption experiments were carried out with

Table 1. Characteristics of *P. brutia* bark

pH	5.18
pH_{pzc}	4.80
Moisture content (%)	7.57
Surface functional groups (mmol g^{-1})	
Carboxylic	1.73
Phenolic	2.41
Lactonic	0.34
Total acidic value	4.48

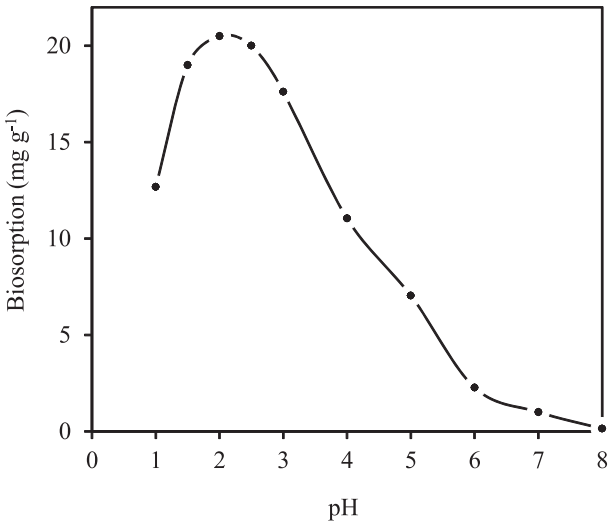

Figure 2. Effect of solution pH on Cr(VI) biosorption onto bark (initial Cr(VI) concentration: 200 mg L^{-1}; bark concentration: 5.0 g L^{-1}).

initial Cr(VI) concentration of 200 mg L^{-1} and the bark concentration of 5.0 g L^{-1} (bark particle size: 150–355 μm) by varying the initial pH values in the range of 1.0–8.0.

The bark surface has net electrical neutrality at its pH_{pzc} value. At $pH > pH_{pzc}$, the surface charge of bark is negative, whereas at $pH < pH_{pzc}$ the surface charge of bark is positive. As can be seen in Figure 2, the biosorption amount was higher at lower pH values ($pH < pH_{pzc}$). By increasing the initial pH values from 2.0 to 6.0, the amount of biosorbed Cr(VI) ions decreased from 20.50 to 2.27 mg g^{-1}. These observations can be explained by the facts that the most prevalent forms of Cr(VI) ions in aqueous solutions are acid chromates ($HCrO_4^-$), chromates (CrO_4^{2-}), dichromates ($Cr_2O_7^{2-}$) and other oxyanions. At lower pH values, acid chromate ions are the dominant species. As the initial pH of the solution was decreased, the surface of the bark biomass may get positively charged as a result of hydrogenation from hydronium ions, and, thus, the increasing electrostatic attraction between the negative chromate species and the bark surface would drive the Cr(VI) biosorption more favourable at lower pH values. In contrast, when the initial pH value was increased ($pH > pH_{pzc}$), the bark surface became more negatively charged. The competition between OH^- and chromate ions, which is the dominant species at higher pH values, and also the electrostatic repulsion between the chromate ions and the bark surface sites increased and, hence, the Cr(VI) uptake decreased at higher pH values.[36] As a result, for the biosorption of Cr(VI) onto bark biomass, the initial pH was optimised as 2.0.

Effect of Contact Time and Biosorption Kinetics

The time dependent behaviour of Cr(VI) biosorption onto bark biomass was studied by varying the contact time in the range of 1–480 min. The initial concentration of Cr(VI) was kept as 100 mg L^{-1}, while the amount of bark suspension was 5.0 g L^{-1}. The mixtures were agitated at 400 rpm. The samples were taken at predetermined time intervals and filtered immediately through 0.45 μm nitrocellulose filter paper. The supernatant was analysed for the Cr(VI) level. The data showed that the Cr(VI) biosorption amount increased rapidly at initial stages of the biosorption because of the utilization of the readily available active sorption sites on the bark surface. Thereafter it continued at a slower rate and finally reached to equilibrium as a result of saturation of bark surface sites. A larger amount of Cr(VI) was removed in the first 30 min of contact time, and the Cr(VI) uptake became almost constant after 60 min, which can be considered as equilibrium time of Cr(VI) biosorption. However, to make sure that the sufficient contact time is provided for biosorption, further experiments were carried out for 120 min of contact time.

Different kinetic models such as pseudo-first order, pseudo-second order and intraparticle diffusion models have been developed in order to understand the mechanisms of the developed biosorption process and evaluate the performance of the biosorbents for metal removal.

The pseudo-first order model is expressed as[37];

$$\frac{d_q}{d_t} = k_1(q_e - q_t) \tag{1}$$

where q_t (mg g^{-1}) is the amount of the metal ions biosorbed at time t, q_e is the amount of the metal ions biosorbed at equilibrium (mg g^{-1}), and k_1 is the rate constant of the model (min^{-1}).

After definite integration by applying the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ the Equation (1) becomes the following,

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

A straight line of $\ln(q_e - q_t)$ versus t suggests the applicability of this model, and q_e and k_1 can be determined from the intercept and slope of the plot, respectively.

The pseudo-second order kinetic model is expressed as[38];

$$\frac{d_q}{d_t} = k_2(q_e - q_t)^2 \tag{3}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of the second order equation; q_t (mg g^{-1}) is the amount of biosorption at time t (min), and q_e (mg g^{-1}) is the amount of biosorption at equilibrium.

After definite integration by applying the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ the Equation (3) becomes the following,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

The plot of t/q_t versus t should give a straight line if second order kinetics is applicable, and q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

In order to investigate the biosorption kinetics of Cr(VI) onto *P. brutia* bark, the pseudo-first order and the pseudo-second order kinetic models were used to fit the experimental data. By testing the plots of $\ln(q_e - q_t)$ versus t (for pseudo-first order) and t/q_t versus t (for pseudo-second order), the rate constants k_1 and k_2 and the corresponding correlation coefficients were calculated. The value of correlation coefficient obtained from the pseudo-first order kinetic model (Table 2) is not satisfactory, and also $q_{e\,cal}$ determined from the model is not in a good agreement with the experimental value of $q_{e\,exp}$. These results indicated that the biosorption of Cr(VI) onto bark biomass does not fit the pseudo-first order kinetic model. However the value of the correlation coefficient for the pseudo-second order model is relatively high, and the biosorption capacity ($q_{e\,cal}$) calculated by the model is close to the experimental value ($q_{e\,exp}$). Therefore, it has been concluded that the pseudo-second order model is more suitable to describe the biosorption of Cr(VI) onto *P. brutia* bark. The results indicated that the biosorption rate of Cr(VI) depends on the concentration of ions on the bark surface, and the behaviour of

Table 2. Parameters of pseudo-first order, pseudo-second order and intraparticle diffusion models

	Pseudo-first order			Pseudo-second order			Intraparticle diffusion				
$q_{e\,exp}$ (mg g^{-1})	k_1 (min^{-1})	$q_{e\,cal}$ (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2	$k_{id,1}$ (mg g^{-1} min$^{-1/2}$)	R^2	$k_{id,2}$	R^2	C
13.01	-1.51×10^{-2}	3.87	0.788	1.25×10^{-2}	13.23	0.999	1.619	0.954	0.012	0.982	5.86

biosorption is in agreement with the chemical biosorption being the rate controlling step.[39]The intraparticle diffusion model is expressed as[40];

$$q_t = k_{id} t^{1/2} + C \tag{5}$$

where q_t (mg g^{-1}) is the amount of biosorption at time t (min), and k_{id} (mg g^{-1} min$^{-1/2}$) is the rate constant of intraparticle diffusion. The magnitude of C gives an idea about the thickness of the boundary layer. The multilinearity of the plot of q_t versus $t^{1/2}$ indicates that any biosorption process takes place in three main steps. The first stage is film diffusion which is attributed to the transport of biosorbate molecules from the bulk solution to the biosorbent external surface by diffusion. The second stage is pore or intraparticle diffusion in which the biosorbate molecules diffuse from the external surface into the pores of the biosorbent. The last step, which is related to the biosorption of the biosorbate on the active sites on the internal surface of the pores, occurs rapidly and hence it can be said that a biosorption process should be controlled by either film or pore diffusion, or a combination of both. If C value obtained from the intercept of the plot of q_t versus $t^{1/2}$ is zero, the pore diffusion is the only rate limiting step; if not, it is considered that the biosorption process is controlled by a combination of both film and pore diffusion.[41,42]

The intraparticle mass transfer curve of Cr(VI) biosorption followed two distinct phases, which were film diffusion (first stage) and intraparticle diffusion (second step). The intraparticle rate constants for the first phase ($k_{id,1}$) and second phase ($k_{id,2}$) and C parameters were obtained from the plot of q_t versus $t^{1/2}$ (Table 2). The lower value of $k_{id,2}$ than $k_{id,1}$ indicated that the rate limiting step is intraparticle diffusion, and the C value is not zero. Hence it can be concluded that the biosorption of Cr(VI) onto bark biomass is a complex process, and both intraparticle and film diffusion contribute to the rate-limiting step.

Biosorption Isotherms and the Effect of Bark and Initial Cr(VI) Concentrations

The equilibrium biosorption isotherms are one of the most important means in order to describe the interaction between the metal ions and biosorbents. Although different isotherm models can be used for that purpose, the Langmuir and Freundlich isotherm models are the most widely used models due to their simplicity.

The Langmuir isotherm is feasible for the biosorption on homogeneous surfaces and based on the assumption that the biosorption occurs at specific homogeneous sites on the biosorbent and the biosorption energy is always constant. The model is presented by[43];

$$q_e = \frac{b q_{max} C_e}{1 + b q_{max}} \tag{6}$$

where q_e is the equilibrium metal ion concentration on the biosorbent (mg g^{-1}), C_e is the equilibrium metal ion concentration in the solution (mg L^{-1}), q_{max} is the Langmuir constant related to the maximum monolayer biosorption capacity (mg g^{-1}), and b is related to the free energy or net enthalpy of the biosorption (L mg^{-1}). The Langmuir model in linear form is;

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{b q_{max}} \tag{7}$$

The essential characteristics of the Langmuir isotherm can be expressed by means of 'R_L', a dimensionless constant called the separation factor or equilibrium parameter. R_L can be calculated using the following equation [44];

$$R_L = \frac{1}{1 + b C_0} \tag{8}$$

where C_0 (mg L^{-1}) is the initial amount of biosorbate, and b (L mg^{-1}) is the Langmuir constant described above.

The R_L parameter is considered as more reliable indicator of the sorption process. There are four probabilities for the R_L value: (i) for favourable sorption $0 < R_L < 1$, (ii) for unfavourable sorption $R_L > 1$, (iii) for linear sorption $R_L = 1$ and (iv) for irreversible sorption $R_L = 0$.

The Freundlich isotherm model assumes that the biosorption takes place on heterogeneous surfaces which have different sorption energies and provides no information about the monolayer biosorption capacity.[45] The Freundlich model has the form;

$$q_e = K_f C_e^{1/n} \tag{9}$$

where K_f is a constant related to the biosorption capacity (mg g^{-1}), and $1/n$ is an empirical parameter related to the biosorption intensity. The Freundlich model in linear form is;

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{10}$$

In order to analyse the effects of bark and Cr(VI) concentrations on the uptake of this metal, the biosorption process was carried out with initial Cr(VI) concentrations between 50 and 1000 mg L^{-1} and various bark concentrations in the range of 1.0–20.0 g L^{-1}. At equilibrium (120 min of contact time) the Cr(VI) concentration in each system was measured, and the Langmuir and Freundlich isotherms were plotted as a function of bark concentration, as displayed in Figure 3a and b, respectively. At a constant bark concentration, as the initial Cr(VI) concentration increased, the amount of Cr(VI) biosorbed (mg) per gram mass of the bark (g) increased, whereas at a constant Cr(VI) concentration, as the bark concentration increased, the amount of Cr(VI) biosorbed (mg) per gram mass of the bark (g) decreased.

The isotherm constants and correlation coefficients were calculated from the linear Langmuir and Freundlich plots by plotting C_e/q_e versus C_e (Figure 3a) and $\ln q_e$ versus $\ln C_e$ (Figure 3b). The Langmuir constants q_{max} and b were obtained from the slope and intercept of the linear plots of C_e/q_e versus C_e, respectively, and Freundlich constants K_f and $1/n$ were determined from the

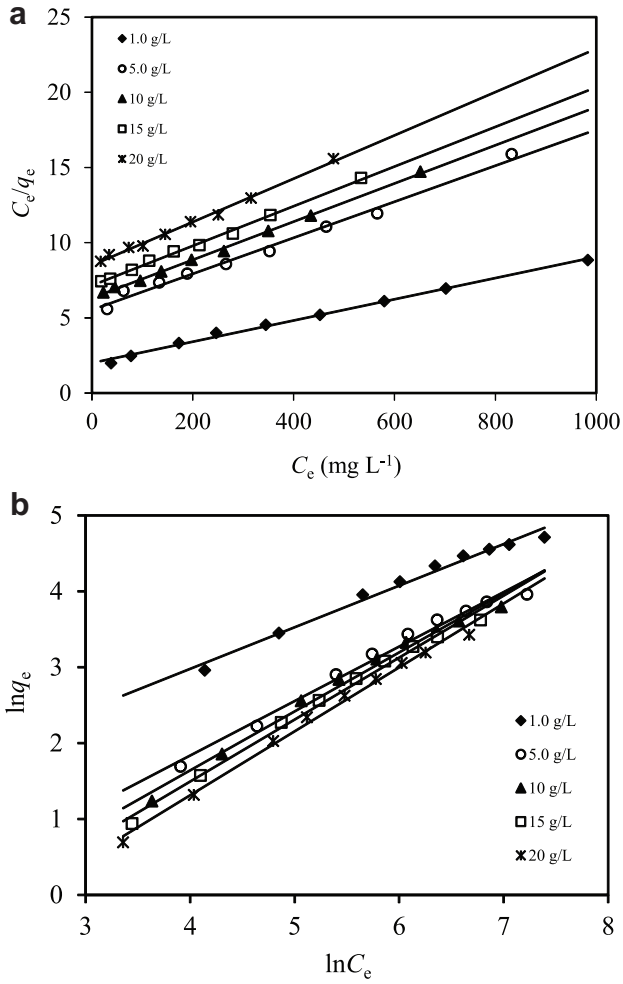

Figure 3. Relationship between equilibrium Cr(VI) concentration and its uptake at various bark concentrations using (a) Langmuir isotherm model (b) Freundlich isotherm model (bark particle size: 150–355 μm; initial pH: 2.0).

intercept and slope of the linear plots of $\ln q_e$ versus $\ln C_e$, respectively (Table 3). In all cases correlation coefficients were higher than 0.97, which strongly supports the fact that the biosorption of Cr(VI) onto *P. brutia* bark perfectly fits both Langmuir and Freundlich isotherm models. Furthermore, the values of $1/n$ were smaller than 1 indicating that the present biosorption process was favorable under studied conditions. Also the R_L values calculated for initial Cr(VI) concentration range of 50–1000 mg L^{-1} were in the range of 0.315 and 0.902, at constant bark concentration

Table 3. Langmuir and Freundlich isotherm constants for the biosorption of Cr(VI) ions onto bark biomass at various bark concentrations at pH 2.0

	Langmuir constants			Freundlich constants		
Bark conc. (g L^{-1})	q_{max} (mg g^{-1})	b (L mg^{-1})	R^2	K_f (mg g^{-1})	n	R^2
1.0	140.8	0.00356	0.9952	2.88	1.82	0.9854
5.0	83.3	0.00217	0.9895	1.97	1.39	0.9839
10.0	78.7	0.00201	0.9930	0.34	1.29	0.9878
15.0	75.8	0.00185	0.9729	0.26	1.23	0.9925
20.0	69.4	0.00169	0.9879	0.19	1.19	0.9936

Table 4. Comparison of the maximum adsorption capacity of *P. brutia* bark with other reported adsorbents

Adsorbent	Adsorption capacity (mg g^{-1})	Refs.
Hydrolyzed keratin/polyamide 6 blend nanofibres	59.9	Aluigi et al.[48]
Acacia mangium wood carbon	37.16	Danish et al.[49]
Phoenix dactylifera L. stone carbon	32.76	Danish et al.[49]
Anion exchanger based nano-sized ferric oxyhydroxide hybrid adsorbent	123	Ren et al.[50]
Prunus serotina bark	93.61	Netzahuatl-Muñoz et al.[51]
carnation flowers waste	6.25	Vargas et al.[52]
Polyaniline/polystyrene nanocomposite	19.0	Lashkenari et al.[53]
P. brutia bark	140.8	This work

(5.0 g L^{-1}). This result also supports the fact that the biosorption of Cr(VI) onto *P. brutia* bark was favourable. In the view of these results it can be said that the surface of *P. brutia* bark is made up of both homogeneous and heterogeneous biosorption parts.

The maximum adsorption capacity (q_{max}) of *P. brutia* bark was obtained as 140.8 mg g^{-1} at 1.0 g L^{-1} bark suspension. Table 4 lists the maximum adsorption capacity of different adsorbents reported in the literature for the adsorption of Cr(VI) ions. In general *P. brutia* bark exhibited comparable adsorption capacity in comparison with other adsorbents.

The Effect of Bark Particle Size

In order to evaluate the effect of the bark particle size on the biosorption of Cr(VI), the bark biomass with sizes in the range of <150, 150–355 and 355–710 μm were treated with a series of Cr(VI) solutions in the initial concentration range of 50–1000 mg L^{-1}. At equilibrium Langmuir and Freundlich isotherms were obtained as a function of particle size, and the results are depicted in Figure 4a and b, respectively. The results indicated that the particle size affected the biosorption process, and uptake of Cr(VI) by bark biomass increased with decreasing the particle size of bark. This is an expected result because as the particle size of bark biomass decreases, the number of active biosorption sites on the surface of bark increases, and these particles attach more Cr(VI) ions to their surfaces. The linear Langmuir and Freundlich isotherm models were fitted to the experimental data, and the isotherm constants and correlation coefficients for each particle size are shown in Table 5.

The Effect of Temperature and Thermodynamic Parameters of Biosorption Process

In order to determine the effect of temperature on the biosorption of Cr(VI) onto bark, the biosorption experiments were conducted at different temperatures in the range of 0–40°C with initial Cr(VI) concentrations of 100 mg L^{-1} at pH 2.0. The degree of biosorption increased from 10.23 mg g^{-1} (51.2% removal) to 14.45 mg g^{-1} (72.2% removal) when the temperature was increased from 0 to 40°C, which may be due to the increase of the mobility of Cr(VI) ions and availability of more active biosorption sites on the surface of the bark at higher temperatures.

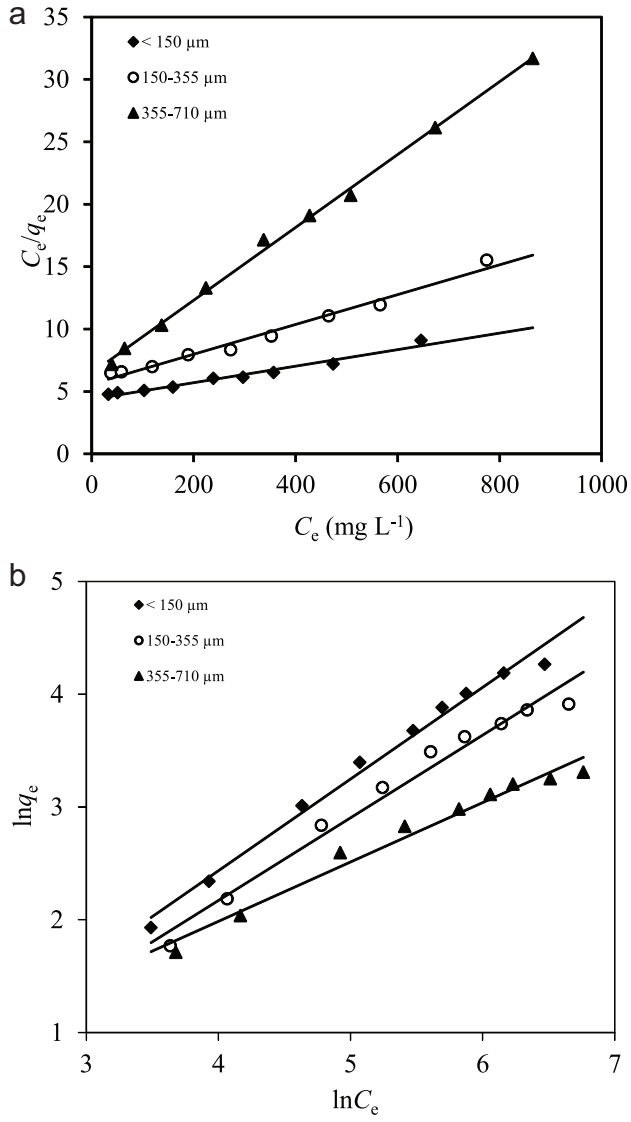

Figure 4. Relationship between equilibrium Cr(VI) concentration and its uptake by bark at various bark particle sizes using (a) Langmuir isotherm model (b) Freundlich isotherm model (bark concentration: 5.0 g L^{-1}; initial pH: 2.0).

Thermodynamic parameters including the changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were calculated from the following equations;

$$\Delta G = -RT \ln K_d \tag{11}$$

Table 5. Langmuir and Freundlich constants at different bark particle sizes at pH 2.0 and 5.0 g L^{-1} of bark concentration

	Langmuir constants			Freundlich constants		
Particle size (μm)	q_{max} (mg g^{-1})	b (L mg^{-1})	R^2	K_f (mg g^{-1})	n	R^2
<150	151.5	0.00151	0.970	0.44	1.23	0.989
150–355	84.0	0.00213	0.982	0.47	1.36	0.978
355–710	34.2	0.00452	0.997	0.88	1.90	0.976

Table 6. Thermodynamic parameters for the Cr(VI) biosorption onto bark at different temperatures

T (°C)	Thermodynamic equilibrium constant (K_d)	ΔG (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})[a]	ΔH (kJ mol^{-1})
0	0.92	0.18		
10	1.18	−0.40		
20	1.47	−0.93	51.15	14.11
30	1.74	−1.40		
40	2.04	−1.86		

[a] Measured between 273 and 313 K.

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K), and K_d is the distribution coefficient. The K_d value was calculated using the following equation [46];

$$K_d = \frac{q_e}{C_e} \tag{12}$$

where q_e and C_e are the equilibrium concentration of metal ions on the biosorbent (mg L^{-1}) and in the solution (mg L^{-1}), respectively. The enthalpy (ΔH) and entropy (ΔS) changes of the biosorption were estimated from the following equation;

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

This equation can be written as;

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{14}$$

The thermodynamic parameters of ΔH and ΔS were obtained from the slope and intercept of the plot of $\ln K_d$ versus $1/T$, respectively. The Gibbs free energy changes (ΔG) were calculated from Equation (11), and the values of ΔG, ΔH and ΔS for the biosorption of Cr(VI) onto bark were given in Table 6. The negative values of ΔG in the temperature range of 10–40°C indicated that the biosorption process is spontaneous. And also the increase in ΔG values with increase in temperature shows the feasibility of the biosorption process at higher temperatures. The positive value of ΔH suggests the endothermic nature of the biosorption process. The magnitude of ΔH gives an idea about the type of the sorption. Two main types of biosorption may occur, physical and chemical. In physical biosorption the equilibrium is usually rapidly attained and easily reversible, because the energy requirements are small. The enthalpy for physical biosorption is usually no more than 1 kcal mol^{-1} (4.2 kJ mol^{-1}) since the interactions are weak. The chemical biosorption involves interactions much stronger than in physical biosorption, and the enthalpy for chemical biosorption is more than 5 kcal mol^{-1} (21 kJ mol^{-1}),[47] so it seems that the biosorption of Cr(VI) ions onto bark is almost a chemical process. Finally, the positive value of ΔS suggested an increase in randomness at the solid/solution interface during the biosorption of Cr(VI) ions onto bark.

Reusability of the Bark Without Regeneration

The bark was tested for its ability without regeneration. The tests were performed using an initial Cr(VI) concentration of 100 mg L^{-1} at pH 2.0 with 5.0 g L^{-1} of bark suspension. The biosorption experiment was carried out for 120 min, and the bark was separated, dried in air for 1 day, then transferred to another 100 mg L^{-1} of Cr(VI) solution. The process was repeated for five

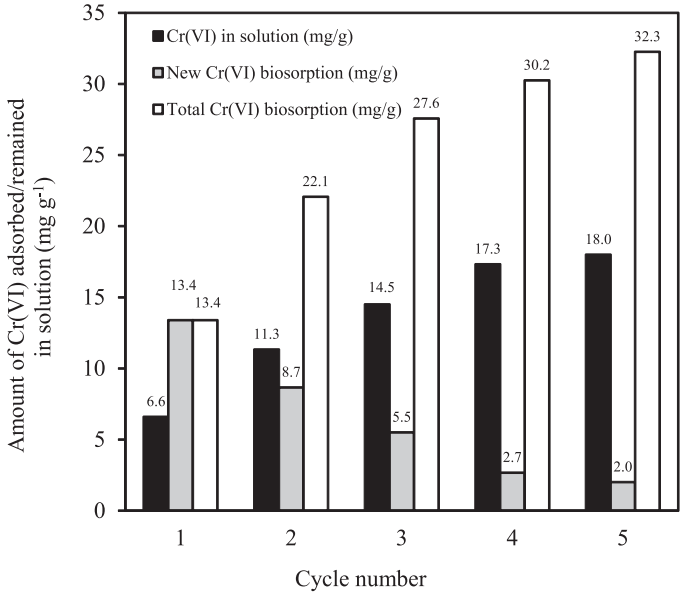

Figure 5. Reuse of the bark without regeneration (initial Cr(VI) concentration: 100 mg L^{-1}; bark concentration: 5.0 g L^{-1}; initial pH: 2.0).

times and each time the bark was able to biosorb some Cr(VI) ions. The largest amount of Cr(VI) biosorbed was onto fresh bark, and in each subsequent loading the biosorption capacity of the bark decreased (Figure 5). Consequently, the bark biomass can be used at least five times effectively without regeneration.

Desorption of Cr(VI) ions

Desorption tests were also carried out by batch technique. The recovery of Cr(VI) ions from the bark was tested with HCI and NaOH solutions as desorbing agent. For that purpose 50 mg of bark was added to 100 mg L^{-1} of Cr(VI) solution at pH 2.0, and the system was agitated on a shaker for 120 min. After reaching equilibrium, the bark was separated by filtration and the filtrate was analysed by FAAS. The bark loaded with Cr(VI) ions was washed with deionized water for three times to remove the surface residual Cr(VI) ions and then dried in air for 1 day. The bark loaded with Cr(VI) ions was treated with 10 mL of HCI solution (in the concentration range of 0.01–0.5 M) and 10 mL of NaOH solution (in the concentration range of 0.01–3.0 M), separately for 120 min. The regeneration efficiency reached from 10% to 43% when the concentration of NaOH solution was increased from 0.01 to 3.0 M, and from 12% to 34% when the concentration of HCI solution was increased from 0.01 to 0.05 M. It is clear that, both eluents could not achieve the complete desorption of the biosorbed Cr(VI) ions from the bark. This may be due to the strong interactions between the Cr(VI) ions and the functional groups on the surface of the bark biomass.

The Effect of Foreign ions over the Biosorption Yield of Cr(VI) Ions

The foreign ions such as Na^+, K^+, Mg^{2+} and Ca^{2+} always exist in natural waters and industrial wastewaters, which may interfere the uptake of heavy metals by a biomass. Thus, the effect of these ions on the biosorption of Cr(VI) ions onto bark should be studied. For that purpose, the biosorption studies were carried out by adding 100 mg L^{-1} of Na^+, K^+, Mg^{2+} and Ca^{2+} individually, and the mixture of these ions in 100 mg L^{-1} of Cr(VI) solution containing 5.0 g L^{-1} of bark suspension. The presented biosorption procedure described above was applied to these solutions. The results are given in Figure 6a. It is clear that all of these ions partially depressed the uptake of Cr(VI) ions by bark, and also all of them exhibited approximately the same inhibition.

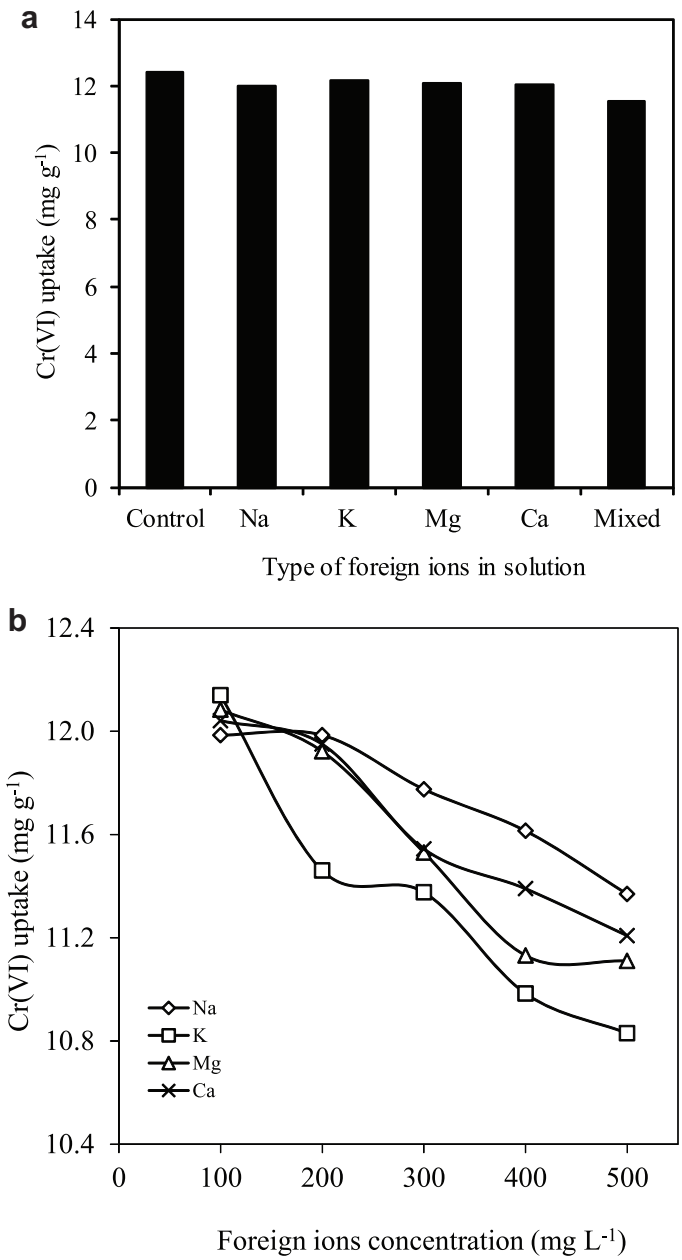

Figure 6. (a) Effect of foreign ions on Cr(VI) uptake by bark (initial Cr(VI) and foreign ions concentrations: 100 mg L^{-1} of each) (b) Effect of foreign ions concentrations on Cr(VI) uptake by bark (initial Cr(VI) concentration: 100 mg L^{-1}).

In order to investigate the effect of concentration of foreign ions on the biosorption of Cr(VI) ions onto bark, the biosorption experiments were carried out by adding foreign ions in the concentration range of 100–500 mg L^{-1}, individually in 100 mg L^{-1} of Cr(VI) solution containing 5.0 g L^{-1} of bark suspension. The results indicated that as the concentration of these foreign ions was increased in the range of 100–500 mg L^{-1}, the uptake of Cr(VI) ions by bark biomass decreased (Figure 6b).

CONCLUSIONS

P. brutia bark can be used as an effective and low cost biosorbent for the removal of Cr(VI) ions from aqueous solutions. The

utilisation of an easily available agricultural material in removal of a highly toxic heavy metal may be the main advantage of the present study. Another feature of this study was to use the bark biomass without any previous activation treatment which decreases the sorption costs.

Biosorption characteristics of Cr(VI) onto bark biomass were found to be influenced by several experimental parameters. The process was pH dependent, and the maximum Cr(VI) uptake was observed at initial pH 2.0. The equilibrium data fitted well to the Langmuir and Freundlich isotherm models. The monolayer biosorption capacity of bark biomass was found to be 140.8 mg g^{-1} when 1.0 g L^{-1} of bark suspension at particle size in the range of 150–355 μm were used. By applying the kinetic models to the experimental data, it was found that the kinetics of Cr(VI) ions biosorption onto bark biomass followed the pseudo second order kinetic. The negative value of ΔG and the positive value ΔS showed that the biosorption of Cr(VI) onto bark biomass is feasible and spontaneous. The positive value of ΔH confirmed the endothermic nature of biosorption. From these results, it may be concluded that the *P. brutia* bark can be used effectively for the removal of Cr(VI) ions from aqueous solutions using present biosorption process.

REFERENCES

[1] B. Volesky, "Removal and recovery of heavy metals by biosorption", in Biosorption of Heavy Metals, B. Volesky, Eds., CRC Press, Boca Raton, Florida 1990, pp. 7–43.

[2] R. Zhang, B. Wang, H. Ma, *Desalination* 2010, *255*, 61.

[3] K. Mohanty, M. Jha, B. C. Meikap, M. N. Biswas, *Chem. Eng. Sci.* 2005, *60*, 3049.

[4] E. Browning, Chromium in Toxicity of Industrial Metals, 2nd edition, Butterworths and Co, London 1969, pp. 76–96.

[5] J. O. Nriagu, E. Nieboer, Chromium in the Natural and Human Environment, Wiley, New York 1988.

[6] World Health Organization. Guidelines for Drinking Water Quality, 2nd edition, Vol. 1 Geneva, Switzerland 1993.

[7] N. Ahalya, T. V. Ramachandra, R. D. Kanamadi, *Res. J. Chem. Environ.* 2003, *7*, 71.

[8] L. Yang, J. P. Chen, *Bioresour. Technol.* 2008, *99*, 297.

[9] M. Ghaedi, B. Sadeghian, A. A. Pebdani, R. Sahraei, A. Daneshfar, C. Duran, *Chem. Eng. J.* 2012, *187*, 133.

[10] M. Ghaedi, H. Tavallali, M. Sharifi, S. N. Kokhdan, A. Asghari, *Spectrochim. Acta A* 2012, *86*, 107.

[11] M. Ghaedi, G. R. Ghezelbash, F. Marahel, S. Ehsanipour, A. Najibi, M. Soylak, *Clean – Soil, Air, Water* 2010, *38*, 877.

[12] J. Ye, H. Yin, B. Mai, H. Peng, H. Qin, B. He, N. Zhang, *Bioresour. Technol.* 2010, *101*, 3893.

[13] M. G. A. Vieira, R. M. Oisiovici, M. L. Gimenes, M. G. C. Silva, *Bioresour. Technol.* 2008, *99*, 3094.

[14] M. Soylak, M. Tuzen, D. Mendil, I. Turkekul, *Talanta* 2006, *70*, 1129.

[15] A. Sari, D. Mendil, M. Tuzen, M. Soylak, *Chem. Eng. J.* 2008, *144*, 1.

[16] B. Nanthakumar, E. Arinaitwe, M. Pawlik, *Adsorption* 2010, *16*, 447.

[17] S. Reddy, V. M. Boddu, A. Krishnaiah, *Can. J. Chem. Eng.* 2011, *89*, 833.

[18] S. Bailliez, A. Nzihou, E. Bèche, G. Flamant, *Process Saf. Environ.* 2004, *82*, 175.

[19] C. H. Weng, S. N. Upadhyay, *Can. J. Chem. Eng.* 2009, *87*, 921.

[20] L. Cui, G. Wu, T.-S. Jeong, *Can. J. Chem. Eng.* 2010, *88*, 109.

[21] D. K. V. Ramana, D. H. K. Reddy, B. N. Kumar, Y. Harinath, K. Seshaiah, *Can. J. Chem. Eng.* 2012, *90*, 111.

[22] A. I. Oke, S. Lukman, J. A. Otun, *Can. J. Chem. Eng.* 2010, *88*, 241.

[23] H. Hasar, *J. Hazard. Mater.* 2003, *B97*, 49.

[24] Y. Icgen, Z. Kaya, B. Cengel, E. Velioglu, H. Oztürk, S. Önde, *Forest Ecol. Manag* 2006, *225*, 328.

[25] S. E. Bailey, T. J. Olin, R. M. Bricka, D. D. Adrian, *Water Res.* 1999, *33*, 2469.

[26] S. Sousa, P. Jiménez-Guerrero, A. Ruiz, N. Ratola, A. Alves, *Environ. Technol.* 2011, *32*, 673.

[27] F. G. Braga, S. Pinto, M. C. G. Antunes, *Microchim. Acta* 2011, *173*, 111.

[28] Y. Li, B. Chen, L. Zhu, *Bioresour. Technol.* 2010, *101*, 7307.

[29] A. P. Khokhotva, *J. Water Chem. Technol.* 2010, *32*, 336.

[30] M. E. Argun, S. Dursun, M. Karatas, *Desalination* 2009, *249*, 519.

[31] D. Park, C. K. Ahn, Y. M. Kim, Y.-S. Yun, J. M. Park, *J. Hazard. Mater.* 2008, *160*, 422.

[32] B. Acemioglu, M. H. Alma, *Fresen. Environ. Bull.* 2004, *13*, 585.

[33] A. Gundogdu, D. Ozdes, C. Duran, V. N. Bulut, M. Soylak, H. B. Senturk, *Chem. Eng. J.* 2009, *153*, 62.

[34] H. P. Boehm, *Carbon* 2002, *40*, 145.

[35] APHA, American Public Health Association. Standard Methods for the Examination of Water and Wastewater, 18th edition, American Public Association, Washington, DC 1985.

[36] E. Malkoc, Y. Nuhoglu, *Sep. Purif. Technol.* 2007, *54*, 291.

[37] S. Lagergren, *Kung Sven. Veten. Hand.* 1898, *24*, 1.

[38] Y. S. Ho, G. McKay, *Process Biochem.* 1999, *34*, 451.

[39] E. Guibal, C. Milot, J. M. Tobin, *Ind. Eng. Chem. Res.* 1998, *37*, 1454.

[40] W.J. Weber, Jr. J. C. Morriss, *J. Sanitary Eng. Div., Am. Soc. Civil Eng.* 1963, *89*, 31.

[41] B. H. Hameed, M. I. El-Khaiary, *J. Hazard. Mater.* 2008, *153*, 701.

[42] W. Cheng, S. G. Wang, L. Lu, W. X. Gong, X. W. Liu, B. Y. Gao, H. Y. Zhang, *Biochem. Eng. J.* 2008, *39*, 538.

[43] I. Langmuir, *J. Am. Chem. Soc.* 1918, *40*, 1361.

[44] Y. S. Ho, C. T. Huang, H. W. Huang, *Process Biochem.* 2002, *37*, 1421.

[45] H. M. F. Freundlich, *Z. Phys. Chem.* 1906, *57*, 385.

[46] R. Niwas, U. Gupta, A. A. Khan, K. G. Varshney, *Colloid Surf. A* 2000, *164*, 115.

[47] M. Khormaei, B. Nasernejad, M. Edrisi, T. Eslamzadeh, *J. Hazard. Mater.* 2007, *149*, 269.

[48] A. Aluigi, C. Tonetti, C. Vineis, A. Varesano, C. Tonin, R. Casasola, *J. Nanosci. Nanotechnol.* 2012, *12*, 7250.

[49] M. Danish, R. Hashim, M. N. M. Ibrahim, M. Rafatullah, O. Sulaiman, *J. Anal. Appl. Pyrol.* 2012, *97*, 19.

[50] J. Ren, N. Li, L. Zhao, *Chem. Biochem. Eng. Q* 2012, *26*, 111.

[51] A. R. Netzahuatl-Muñoz, L. Morales-Barrera, M. D. C. Cristiani-Urbina, E. Cristiani-Urbina, *Fresen. Environ. Bull* **2**012, *21*, 1793.

[52] C. Vargas, P. F. B. Brandão, J. Ágreda, E. Castillo, *Bioresources* **2**012, *7*, 2711.

[53] M. S. Lashkenari, B. Davodi, M. Ghorbani, H. Eisazadeh, *High Perform. Polym.* **2**012, *24*, 345.

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