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REMOVAL OF HEXAVALENT AND TOTAL CHROMIUM FROM AQUEOUS SOLUTIONS BY PLUM (*P. domestica* L.) TREE BARK

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Abstract

The main purpose of the present work was to evaluate the potential of plum (*P. domestica* L.) tree bark (PDB) to remove Cr(VI) and total chromium from aqueous solutions in batch systems. Experimental data showed that the Cr(VI) and total chromium removal capacity was dependent on operating variables such as PDB particle size, PDB pretreatment, solution pH, initial Cr(VI) concentration, and contact time. The mechanism of Cr(VI) removal by PDB implies two simultaneous processes: 1) the reduction of Cr(VI) to Cr(III), and 2) the biosorption of chromium ions. Cr(VI) and total chromium removal rates were affected to a significant extent by PDB particle size. Hydrochloric acid pretreatment proved to be optimum to increase the total chromium biosorption capacity of PDB, whilst also reducing the time needed to reach equilibrium.

The optimum pH value for removal of Cr(VI) and total chromium was 1.0-2.0 and 2.0, respectively. Significant enhancement of Cr(VI) and total chromium removal was observed by increasing initial Cr(VI) concentration. The biosorption kinetic data of total chromium were best described by the pseudo-second-order model. Freundlich's model exhibited the best fit to experimental equilibrium biosorption data. FTIR studies indicated that the main functional groups responsible for total chromium biosorption consist of the amide and carboxyl groups, which may interact with Cr(VI) anionic species and Cr(III) cationic species, respectively. The removal characteristics of Cr(VI) and total chromium exhibited by PDB make it potentially useful for the detoxification of Cr(VI)-polluted water and wastewater.

Key words: bioreduction, biosorption, hexavalent chromium, *Prunus domestica* bark

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1. Introduction

Heavy metal pollution is at present of great concern because of the high toxicity, non-biodegradable nature, increasing discharge and ubiquitous occurrence of these elements in the environment.

Chromium [Cr] is among the heavy metal pollutants causing most concern, largely due to its widespread use in industrial processes and

exceedingly toxic nature (Puentes-Cárdenas et al., 2012).

Although chromium pollution of water sources can occur by natural processes, it is mostly a result of anthropogenic activities, especially the chromium-contaminated discharge from industrial processes such as electroplating, leather tanning, nuclear power plant, metallic alloys production, chromate preparation and corrosion protection painting (Gong et al., 2013; Saha et al., 2011).

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In aqueous systems, chromium usually exists in both trivalent [Cr(III)] and hexavalent [Cr(VI)] oxidation states, which differ widely in physicochemical properties and biological reactivity. While Cr(VI) species (predominantly as chromates (CrO_4^{2-}) and dichromates ($\text{Cr}_2\text{O}_7^{2-}$)) are highly soluble in water and mobile in the environment, Cr(III) species (in the form of oxides, hydroxides or sulfates) are much less soluble and relatively immobile. Moreover, Cr(VI) is a highly toxic agent that has been recognized as a mutagen, carcinogen and teratogen in biological systems, while Cr(III) is an essential trace element necessary for glucose, lipid and amino-acid metabolism, as well as a popular dietary supplement (Morales-Barrera et al., 2008). Cr(III) is also poisonous only at high concentration (Puentes-Cárdenas et al., 2012). Therefore, the removal of Cr(VI) from Cr(VI)-contaminated water and wastewater is nowadays recognized as a key process for the protection of aquatic and terrestrial environments, public health and well-being (Netzahuatl-Muñoz et al., 2012a).

A number of conventional technologies, such as chemical reduction to Cr(III) followed by precipitation under alkaline conditions, ion-exchange, adsorption on activated carbon, membrane separation, electrocoagulation, and electrochemical treatment, have been used to remove Cr(VI) from aqueous solutions (Mohan and Pittman Jr., 2006). However, these methods have certain drawbacks, namely high cost, low efficiency, and/or generation of toxic sludge or other wastes that require treatment and disposal, and imply operational complexity (Mohan and Pittman Jr., 2006). It is therefore imperative to develop financially viable, efficient, secure and environmentally friendly technologies to remove Cr(VI) from contaminated water and industrial wastewaters.

Over the years, increasing interest has developed in exploring the heavy metal sorption potential of various industrial, agricultural, forestry and fishery biowastes due to their advantages like low cost, excellent performance in removing very low levels of heavy metals from dilute solutions, easy handling, lower operating costs and easy generation of biosorbents (Ozdes et al., 2014).

The use of bark as a biosorbent appears as a viable and eco-friendly option for the detoxification of heavy metal polluted wastewaters because bark is one of the most abundant, effective and low cost materials (Netzahuatl-Muñoz et al., 2010; Netzahuatl-Muñoz et al., 2012a, b; Ozdes et al., 2014).

In this context, the plum (*Prunus domestica* L.) tree bark is a potential candidate to remove heavy metals from aqueous solutions because of its high availability in large quantities in nature, low cost, and renewable nature.

The main objective of this work was to evaluate the potential of *Prunus domestica* bark (PDB) to remove Cr(VI) and total chromium from aqueous solutions. The effect of different relevant environmental parameters such as PDB particle size,

PDB pretreatment, solution pH, shaking contact time and initial Cr(VI) concentration on Cr(VI) and total chromium removal was studied. Furthermore, the kinetics and isotherm of chromium biosorption are described. In addition, the functional groups on the surface of PDB involved in chromium biosorption were identified by Fourier transform infrared (FTIR) spectroscopy and the possible mechanisms of biosorption are discussed.

2. Material and methods

2.1. Biomaterial preparation

Samples of PDB used in this work were collected in the municipality of Ixtlahuaca, state of Mexico, Mexico. Bark samples were washed thoroughly with distilled deionized water and then oven dried at 60°C until dry weight was constant. The dried samples were then ground in a hammer mill, and the resulting particles were screened using standard sieves to obtain different particle size fractions. The sieved fractions were stored in airtight plastic containers until used.

2.2. Cr(VI) solutions for chromium removal experiments

Cr(VI) test solutions were obtained by diluting 5 g/L Cr(VI) stock solution, which was prepared by dissolving a weighed quantity of analytical grade K_2CrO_4 in distilled deionized water. In this work, the initial Cr(VI) concentration varied from about 20 to 1000 mg/L and the initial pH of each Cr(VI) solution was adjusted to the desired value in the range of 1.0 to 4.0 with 0.1 N HCl or NaOH solutions.

2.3. Batch experiments for chromium removal

Batch experiments were performed to evaluate the influence of PDB particle size, PDB pretreatment, solution pH, shaking contact time and initial Cr(VI) concentration on Cr(VI) and total chromium removal from aqueous solutions by PDB. All experiments were conducted in 500 mL Erlenmeyer flasks containing 100 mL Cr(VI) solution of known concentration and 1 g (dry weight)/L of PDB. Care was taken to maintain constant pH in each test solution (± 0.1 pH unit) throughout the experiments by periodic checking and adjustment where necessary with 0.1 N HCl or NaOH solutions. Flasks were agitated in a shaker at 120 rpm constant shaking speed and 25°C.

The influence of PDB particle size on Cr(VI) and total chromium removal was assessed in Cr(VI) solution at 100 ± 5 mg/L initial metal concentration, pH 2.0, with different particle size values ranging from 0.15-0.18 mm to 1.44-1.70 mm.

In order to explore the effect of PDB pretreatment on Cr(VI) and total chromium removal, PDB biomass (5 g/L) was physicochemically pretreated in different ways, as follows: a) soaking in

distilled deionized water at 25 and 65°C for 24 h, and at 92°C for 30 min; b) soaking in HCl solution (0.1, 1.0 and 2 N) for 24 h at 25°C; c) soaking in NH₄Cl solution (0.05, 0.1 and 0.5 N) for 24 h at 25°C; d) soaking in NaOH solution (0.01, 0.05 and 0.1 N) for 30 min at 25°C; e) soaking in NH₄OH solution (0.1, 0.5 and 1 N) for 30 min at 25°C; and f) soaking in acetone for 3 min at 25°C (Abbas et al., 2008; Argun and Dursun, 2006). After each pretreatment with chemicals, the PDB biomass was thoroughly washed with distilled deionized water to obtain constant pH of the washing water and then dried at 60°C for 24 h. Cr(VI) and total chromium removal experiments using physicochemically-pretreated and unpretreated PDB were conducted with synthetic Cr(VI) solution at initial metal concentration of 100 ± 5 mg/L and pH of 2.0.

The effect of pH level on Cr(VI) and total chromium removal by PDB was studied by varying the solution pH in the range from 1.0 to 4.0, and an initial Cr(VI) concentration of 100 ± 5 mg/L was used.

To investigate the influence of initial Cr(VI) concentration on kinetic performance, experiments were conducted with Cr(VI) solutions at initial metal concentrations ranging from about 20 to 1000±5 mg/L, at 25°C.

For the isotherm studies, PDB (1g/L) was brought into contact with solutions of different initial Cr(VI) concentrations (≈ 20-1000 mg/L) at 25°C, with constant agitation (120 rpm) for 96 h, to ensure biosorption equilibrium was reached.

PDB-free controls were run concurrently and under exactly the same conditions as used for the Cr(VI) and total chromium removal experiments in order to check for glassware adsorption and other potential side effects (metal precipitation, etc.).

Throughout the experiments conducted in this work, no measurable change in Cr(VI) and total chromium concentration was detected in the PDB-free controls, which indicates that the observed Cr(VI) and total chromium removal in the experiments with PDB was exclusively due to the biosorbent.

Samples were collected at different contact times between PDB and Cr(VI) solutions and filtered through filter paper (0.45 μm). The obtained filtrates were then analyzed for residual Cr(VI) and total chromium concentration.

The amount of Cr(VI) or total chromium removed at time t by the unit mass (dry weight) of PDB (q_t , mg/g), which represents the Cr(VI) or total chromium removal capacity respectively, was calculated according to the mass balance relationship (Eq. 1):

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

where: C_0 and C_t (mg/L) are the initial and the residual Cr(VI) or total chromium concentration at

time $t_0=0$ h and $t=t$ (h), respectively, V is the solution volume (L) and W is the dry weight of PDB (g).

Batch experiments were performed in triplicate and mean values are reported. The maximum coefficient of variation in the three replicates was 5.0%. Chromium removal data were statistically analyzed by analysis of variance (Tukey's method; overall confidence level = 0.05) using SigmaStat 3.5 software.

2.4. Biosorption kinetics modeling

In this work, the kinetics of total chromium removal (total chromium biosorption) data were analyzed using the pseudo-first-order and pseudo-second-order models.

The pseudo-first-order model can be expressed by Eq. (2) (Febrianto et al., 2009):

$$q_t = q_{e1}(1 - e^{-k_1 t}) \quad (2)$$

where: q_t and q_{e1} are the biosorption capacities (mg/g) at time t (h) and at equilibrium, respectively, and k_1 is the rate constant of the pseudo-first-order kinetic model (1/h).

The pseudo-second-order kinetic model is given by Eq. (3) (Ho and McKay, 1999):

$$q_t = \frac{t}{\frac{1}{k_2 q_{e2}^2} + \frac{t}{q_{e2}}} \quad (3)$$

where: q_{e2} and q_t are the adsorption capacities (mg/g) at equilibrium and at any time t (h), respectively, and k_2 is the rate constant of second-order adsorption (g/mg·h).

2.5. Equilibrium modeling

The equilibrium distribution of chromium ions between the liquid phase and the PDB biomass was expressed in terms of a chromium biosorption isotherm. The Langmuir and Freundlich isotherm models were used in the present work to analyze the experimental equilibrium data of chromium biosorption by PDB.

The Langmuir isotherm model is given by Eq. (4) (Mohan and Pittman Jr., 2006):

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \quad (4)$$

where: q_e is the adsorption capacity at equilibrium (mg/g), q_{max} is the maximum adsorption capacity (mg/g), C_e is the liquid phase concentration of adsorbate at equilibrium (mg/L), and b is the sorption equilibrium constant (L/mg) (Mohan and Pittman Jr., 2006).

The Freundlich isotherm model is expressed by Eq. (5) (Mohan and Pittman Jr., 2006):

$$q_e = k_F C_e^{1/n_F} \quad (5)$$

where: k_F [(mg/g)(mg/L)^{1/n_F}] is the Freundlich constant and n_F is the heterogeneity factor (Mohan and Pittman Jr., 2006).

2.6. Analysis of data

All the models parameters were evaluated by non-linear regression analysis of the experimental data using MATLAB® 2010b software. To evaluate the goodness-of-fit of the kinetic and isotherm models to the experimental biosorption data, the determination coefficient (R^2), the root mean squared error (RMSE) of the estimate and the 95% confidence intervals of the models' parameters were calculated.

2.7. FTIR analysis

Chemical composition of the PDB surface was characterized by FTIR. Chemically-pretreated-PDB samples at a concentration of 1 g/L were exposed to a 1000 mg/L Cr(VI) solution, pH 2.0, with constant agitation at 120 rpm for 96 h and 25°C, to saturate the binding sites. All suspensions were subsequently centrifuged for 5 min at 3000 rpm, and the bark pellets were washed with distilled deionized water to remove any unbound metal. Next, metal-loaded bark particles were oven-dried at 105°C. Native (chemically unpretreated biomass unloaded with chromium) PDB, chemically-pretreated PDB, and chemically-pretreated-PDB loaded with chromium were finely ground, mixed with dried KBr at a ratio of 1:5, and immediately analyzed with a FTIR spectrophotometer equipped with a diffuse reflectance FTIR accessory. The FTIR spectra were run in the range of 4000-400 cm⁻¹ with a resolution of 1 cm⁻¹ with 16 scans.

2.8. Analytical techniques

Cr(VI) concentration was measured spectrophotometrically at 540 nm by the 1,5-diphenylcarbohydrazide method (Hach Company, 2008). Total chromium concentration was measured at 357.9 nm by atomic absorption spectrophotometry with an acetylene-air flame (Clesceri et al., 1998).

Cr(III) concentration in solution was calculated by subtracting residual Cr(VI) concentration from residual total chromium concentration (Park et al., 2004).

3. Results and discussion

3.1. Effect of particle size on Cr(VI) and total chromium removal

The effect of PDB particle size on Cr(VI) and total chromium removal capacity at pH 2.0 is shown in Fig. 1.

It is evident that along the first 24 h of contact time, as PDB particle size increased from 0.15-0.18 mm to 1.44-1.70 mm, the capacity and rate of Cr(VI) and total chromium removal decreased. The high experimentally determined Cr(VI) and total chromium removal capacity and rate shown by the smallest particle size compared with the larger particle sizes may be attributed to a larger external surface area for removal.

However, at longer experimental times, the Cr(VI) and total chromium removal capacities shown by all PDB particle sizes tended to approach the same value (Fig. 1A and Fig. 1B). Furthermore, the total chromium removal (biosorption) capacity at equilibrium revealed no significant differences between the assayed particle sizes (Fig. 1B), which indicates that, in porous materials such as PDB, the contribution of the external surface area to the total surface area is limited; thus, particle size reduction has a negligible effect on total surface area and little effect on the equilibrium biosorption capacity (Pérez-Marín et al., 2009).

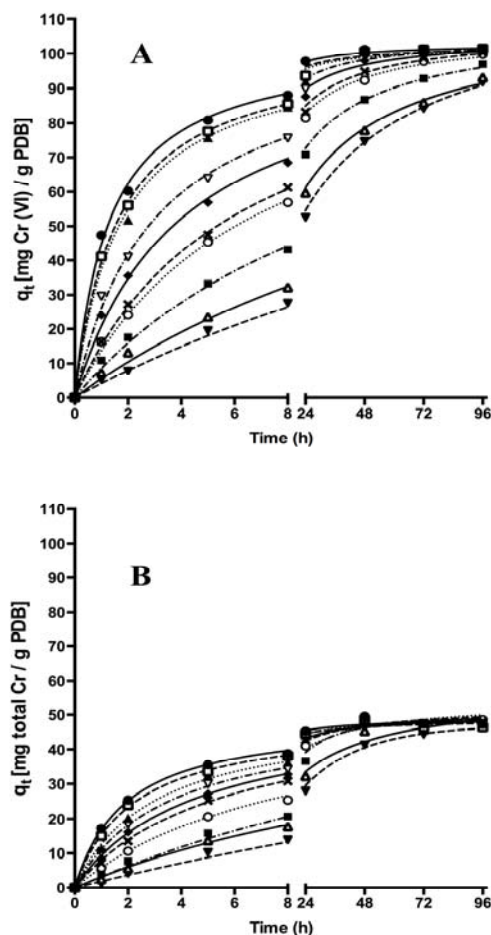


Fig. 1. Effect of PDB particle size on Cr(VI) and total chromium removal capacity [particle size (mm): —●—, 0.15-0.18; ---□---, 0.18-0.212; ...▲..., 0.212-0.25; --▽--, 0.25-0.297; —◆—, 0.297-0.42; ---×---, 0.42-0.5; ...○..., 0.5-0.59; ---■---, 0.59-0.8; —△—, 0.8-1.44; ---▼---, 1.44-1.7]

These results clearly demonstrate that biosorption is not limited to the external particle surface, and emphasize the importance of diffusion into the particle (Schiewer and Patil, 2008), which agrees with Schiewer and Patil (2008) and Pérez-Marín et al. (2009), who reported a negligible influence of protonated lemon peels and orange waste particle size on equilibrium biosorption capacity of Cd(II) and Cr(III) ions, respectively. Based on the above results, it may be concluded that PDB particle size affected the Cr(VI) and total chromium removal rate but not the equilibrium biosorption capacity of total chromium.

At all experimental contact times assayed, the Cr(VI) removal capacity was greater than for total chromium (Fig. 1A and Fig. 1B). This difference was ascribed to the appearance of Cr(III) in the liquid phase, which was not present in the aqueous solution at the start of the experiment (data not shown). These results suggest that reducing organic compounds that form part of PDB, chemically reduced some of the Cr(VI) to Cr(III) when PDB came into contact with the Cr(VI) solution under acidic conditions (pH = 2.0). Thus, PDB has the advantage of transforming Cr(VI) into Cr(III), a form of chromium which is less soluble in water, less mobile in the environment, less bioavailable, 100 times less toxic, and 1000 times less mutagenic and cytotoxic than Cr(VI) (Morales-Barrera et al., 2008).

The ability to reduce Cr(VI) to Cr(III) at acid pH values has been previously reported for diverse biomaterials such as peat moss (Balan et al., 2012), *Ecklonia* sp. (Park et al., 2004), *Schinus molle* bark (Netzahuatl-Muñoz et al., 2010), *Cupressus lusitanica* bark (Netzahuatl-Muñoz et al., 2012a), *Prunus serotina* bark (Netzahuatl-Muñoz et al., 2012b), and olive stone (Martín-Lara et al., 2010), among others. Present results add PDB to this list.

However, from the above results, it is evident that PDB exhibits both reductive and sorptive properties. Therefore, the mechanism for Cr(VI) removal by PDB implies two simultaneous processes: 1) the reduction of Cr(VI) to Cr(III) in the presence of PDB in an acid aqueous solution, and 2) the biosorption of chromium ions. By this mechanism, redox active sites present in the biosorbent reduce the highly toxic Cr(VI) while sorption active sites biosorb Cr(VI) and/or the generated Cr(III) moieties (Zaitseva et al., 2013), as has been suggested for other biomaterials (Park et al., 2004; Netzahuatl-Muñoz et al., 2012a; Nakano et al., 2001). Since the rate of Cr(VI) and total chromium removal increased as particle size decreased, and therefore the maximum removal capacities were reached in a shorter time with the smallest particle size, a PDB particle size of 0.15-0.18 mm was selected for further studies.

3.2. Effect of PDB pretreatment on Cr(VI) and total chromium removal

Fig. 2 shows the Cr(VI) and total chromium removal capacity of the untreated and of the

physicochemically-pretreated PDB biomass samples as a function of contact time. Depending on the physicochemical pretreatment, the PDB samples either increased, decreased or maintained the same removal capacity and rate as that obtained with untreated PDB.

Among the tested physicochemical pretreatments, hydrochloric acid was best to increase the total chromium biosorption capacity compared with the control (untreated PDB) while also reducing the time needed to reach equilibrium; however, it did not have much influence on Cr(VI) removal capacity. The increase in total chromium biosorption capacity after HCl pretreatment could be due to the removal of some minerals and organic matter, and exposure of available binding sites for metal biosorption (Zubair et al., 2008).

Regardless of the concentration of HCl used for PDB pretreatment, the biosorption capacity of total chromium at equilibrium shown by HCl-pretreated PDB was about 53.6% higher than that of untreated PDB. On the basis of these results, further studies were conducted using PDB biomass pretreated with 0.1 N HCl.

3.3. Effect of solution pH on Cr(VI) and total chromium removal

Solution pH is among the most important environmental parameters that influence heavy metal removal from aqueous solutions. pH levels may affect the chemical state of functional groups responsible for biosorption and bioreduction, the chemical speciation of heavy metals in solution (Volesky, 2003), and the competition with coexisting ions in solution (Park et al., 2010). Fig. 3 shows variations in Cr(VI) and total chromium removal capacity of HCl-pretreated PDB as a function of contact time for the different solution pH values assayed. As shown, pH level significantly affected both the capacity to remove Cr(VI) and total chromium.

Cr(VI) removal capacity increased with decreasing solution pH levels and reached its highest level (100-105 mg/g) at pH values from 1.0 to 2.0. Furthermore, the highest total chromium biosorption capacity exhibited by HCl-pretreated PDB was about 74 mg/g, and it was obtained at a pH value of 2.0. These findings can be explained by the fact that the most prevalent forms of Cr(VI) ions in aqueous solution are acid chromates (HCrO_4^-), chromates (CrO_4^{2-}), dichromates ($\text{Cr}_2\text{O}_7^{2-}$) and other oxyanions. At lower pH values, acid chromate ions are the dominant species (Ozdes et al., 2014).

As the pH of the solution was decreased, the surface of the HCl-pretreated PDB biomass became positively charged as a result of protonation by H^+ and H_3O^+ ions, and consequently the increasing electrostatic attraction between the negative Cr(VI) oxyanion species and the positively charged bark surface rendered Cr(VI) removal more favorable at lower pH values. In contrast, as the solution pH value increased, the PDB surface became more negatively

charged and the competition between OH⁻ and Cr(VI) oxyanion species increased as did the electrostatic repulsion between the Cr(VI) oxyanions and the PDB bark surface, which consequently resulted in decreased Cr(VI) removal capacity (Ozdes et al., 2014).

Optimum pH values within the range from 1.0 to 2.0 have been reported for the efficient removal of Cr(VI) and total chromium from Cr(VI) aqueous solutions by different biomaterials such as peat moss (Balan et al., 2012), *Salvinia cucullata* (Baral et al., 2013), *Rosa gruss an teplitz* waste biomass (Shafqat et al., 2008), *Cassia fistula* (Abbas et al., 2008), olive stone (Blázquez et al., 2009), *Pinus brutia* TEN (Ozdes et al., 2014), and raw and chemically modified *Sargassum* sp. (Yang and Chen, 2008), among others.

It was noted that at all experimental times and solution pH levels assayed, the capacity to remove Cr(VI) was higher than for total chromium. This was ascribed to the amount of Cr(VI) which was reduced to Cr(III) by HCl-pretreated PDB and released into the aqueous solution.

Based on the above results, further experiments were carried out at solution pH of 2.0.

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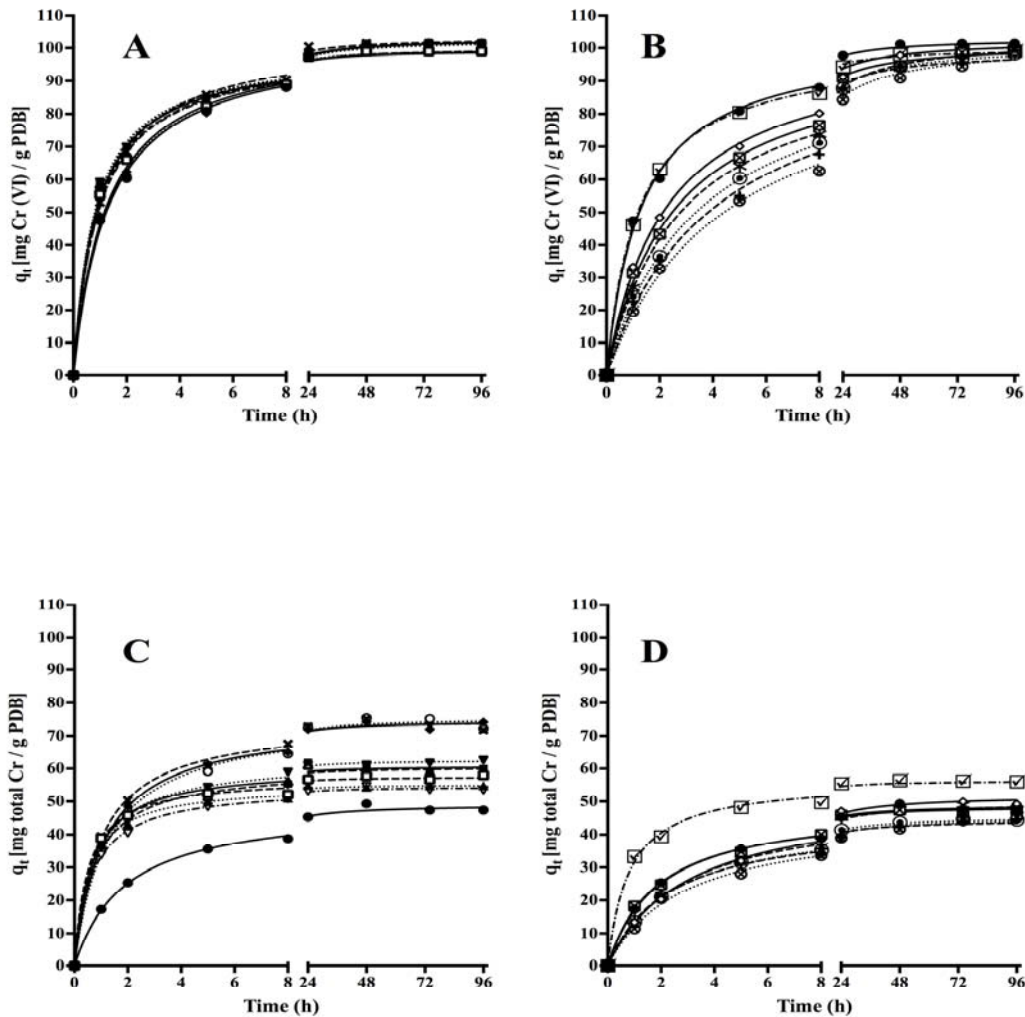


Fig. 2. Influence of PDB pretreatment on Cr(VI) (A, B) and total chromium removal capacity (C, D)

[Pretreatments: —●—, unpretreated; ---□---, H₂O 25°C; ---▲---, H₂O 65°C; ---▽---, H₂O 92°C; —◆—, HCl 0.1 N; ---×---, HCl 1.0 N; ---○---, HCl 2.0 N; —■—, NH₄Cl 0.05 N; ---△---, NH₄Cl 0.1 N; ---▼---, NH₄Cl 0.05 N; —◇—, NaOH 0.01 N; ---+---, NaOH 0.05 N; ---⊗---, NaOH 0.1 N; —⊠—, NH₄OH 0.1 N; ---*---, NH₄OH 0.5 N; ---⊙---, NH₄OH 1.0 N; ---⊡---, Acetone]

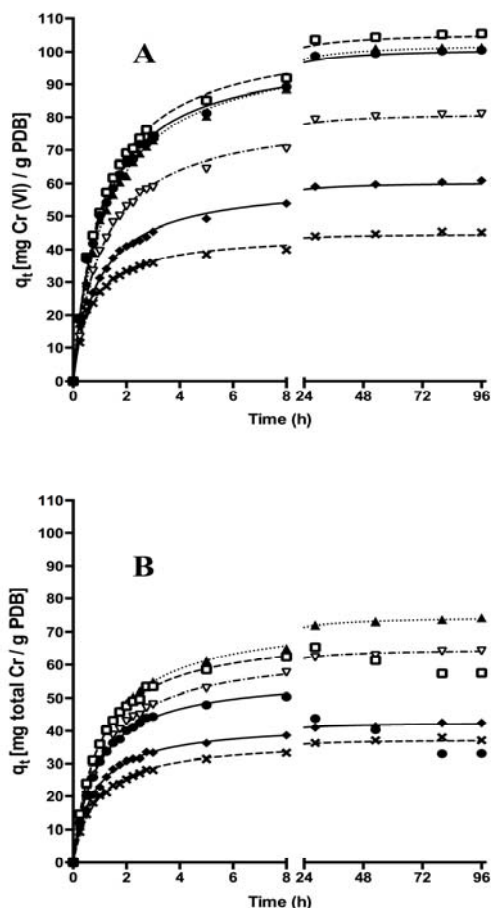


Fig. 3. Effect of solution pH on Cr(VI) and total chromium removal capacity of HCl-pretreated PDB [pH: —●—, 1.0; - -□- - , 1.5; ···▲···, 2.0; - -▽- - , 2.5; —◆—, 3.0; - -×- - , 4.0]

3.4. Effect of initial Cr(VI) concentration on Cr(VI) and total chromium removal

Fig. 4 shows the variations in Cr(VI) and total chromium removal capacity as a function of experimental time for the different initial Cr(VI) concentrations assayed. Data revealed that Cr(VI) and total chromium removal capacity gradually rose as contact time increased, until maximum constant values were attained. Moreover, both Cr(VI) and total chromium removal capacity rose with an increase in initial Cr(VI) concentration, which may be due to higher availability of chromium ions in the solution for removal. Higher initial chromium concentration also caused an increased concentration gradient, which provides a stronger driving force to overcome mass transfer resistance of chromium ions between the aqueous and solid phases, resulting in higher probability of collision between chromium ions and active sites of HCl-pretreated PDB, thus leading to a higher Cr(VI) and total chromium removal levels (Puentes-Cárdenas et al., 2012).

From the results it was also evident that saturation of the HCl-pretreated PDB surface is dependent on initial metal concentration.

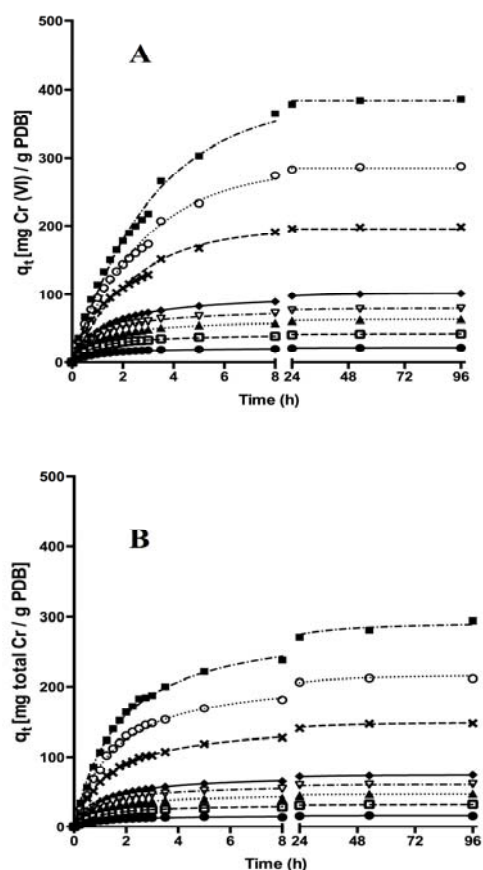


Fig. 4. Influence of initial Cr(VI) concentration on Cr(VI) and total chromium removal capacity of HCl-pretreated PDB [Initial Cr(VI) concentration (mg/L): —●—, 21.77; - -□- - , 42.56; ···▲···, 63.71; - -▽- - , 79.24; —◆—, 101.86; - -×- - , 383.4; ···○···, 659.68; - -■- - , 1002.19]

Under the conditions tested in this work, the highest Cr(VI) and total chromium removal capacities were 384.4 and 288.1 mg/g, respectively, and this difference was due to the reduction of Cr(VI) to Cr(III).

3.5. Kinetic modeling of total chromium biosorption

The kinetic process of total chromium biosorption onto HCl-pretreated PDB at different solution pH values and initial Cr(VI) concentrations was analyzed using the pseudo-first-order and pseudo-second-order models.

Tables 1 and 2 list the kinetic parameter values of the pseudo-first-order and pseudo-second-order models for total chromium biosorption, at solution pH values from 1.0 to 4.0 and initial Cr(VI) concentrations from approximately 20 to 1000 mg/L, together with the corresponding determination coefficients (R^2) and RMSE values.

The pseudo-second-order model yielded higher values of R^2 and lower values of RMSE than the pseudo-first-order model at all pH values and initial Cr(VI) concentrations, indicating that the experimental data showed very good agreement with

the pseudo-second-order model. Moreover, the equilibrium biosorption capacity values predicted by the pseudo-second-order model (q_{e2}) are very close to the experimentally obtained values ($q_{e\text{ exp}}$). Besides, the pseudo-second-order model suitably described the variations in total chromium biosorption capacity at different contact times, pH levels and initial Cr(VI) concentrations assayed (continuous lines in Fig. 3B and Fig. 4B). Thus, the pseudo-second-order model describes the biosorption kinetics of total chromium onto HCl-pretreated PDB more suitably.

The fitness of total chromium biosorption kinetics to the pseudo-second-order model suggests that the rate-limiting step in biosorption of total chromium onto HCl-pretreated PDB is probably a chemical sorption (chemisorption) reaction, implicating valence forces that involve the sharing or exchange of electrons between the PDB surface and chromium ions (Febrianto et al., 2009). This model assumes that two reactions are occurring, the first one is fast and reaches equilibrium quickly, and the second is slower and can continue for long periods of time. These two reactions can occur either in series or in parallel (Khambhaty et al., 2009). The pseudo-second-order model has also been successfully applied to total chromium biosorption by different biosorbents, among them several types of bark such

as from *Cupressus lusitanica* (Netzahuatl-Muñoz et al., 2012a), *Prunus serotina* (Netzahuatl-Muñoz et al., 2012b), *Pinus brutia* (Ozdes et al., 2014), *Schinus molle* (Netzahuatl-Muñoz et al., 2010), and pine bark (Nehrenheim and Gustafsson, 2008).

3.6. Equilibrium modeling

Fig. 5 shows the experimental biosorption isotherm of total chromium at pH 2.0 and 25°C. Evidently, the equilibrium biosorption capacity of HCl-pretreated PDB steadily rises with increasing equilibrium total chromium concentration. The concave shape of the total chromium biosorption isotherm resembles the type L isotherm of the Giles classification (Giles et al., 1974), which is indicative of a gradual decrease in sorption sites as the solute concentration in the solution increases, i.e. it suggests a progressive saturation of the biosorbent. This also implies that the biosorbent has greater affinity for the solute in solution (Limousin et al., 2007).

The Langmuir and Freundlich isotherm models, which are the most widely used for modeling adsorption isotherms due to their simplicity, were used in this work to describe the experimental equilibrium data of total chromium biosorption onto HCl-pretreated PDB.

Table 1. Parameters of the pseudo-first-order and pseudo-second-order kinetic models for total chromium biosorption onto HCl-pretreated PDB at different solution pH values

pH	$q_{e\text{ exp}}$ (mg/g)	Pseudo-first-order				Pseudo-second-order			
		q_{e1} (mg/g)	k_1 (1/h)	R^2	RMSE	q_{e2} (mg/g)	k_2 (g/mg·h)	R^2	RMSE
1.0	50.36 ± 1.23	47.63 ± 0.75	0.978 ± 0.05	0.992	1.313	56.81 ± 0.49	0.020 ± 0.001	0.999	0.523
1.5	62.48 ± 1.93	58.34 ± 1.18	0.920 ± 0.05	0.988	1.981	69.89 ± 0.52	0.015 ± 0.001	0.999	0.531
2.0	73.39 ± 0.72	70.69 ± 1.69	0.599 ± 0.07	0.978	3.893	74.56 ± 0.43	0.012 ± 0.001	0.999	0.834
2.5	63.37 ± 0.48	60.65 ± 1.27	0.628 ± 0.04	0.973	3.013	64.78 ± 0.28	0.014 ± 0.001	0.999	0.587
3.0	41.81 ± 0.37	39.64 ± 0.86	0.807 ± 0.06	0.965	2.177	42.44 ± 0.22	0.030 ± 0.001	0.998	0.472
4.0	37.1 ± 0.36	34.95 ± 0.98	0.719 ± 0.06	0.945	2.403	37.31 ± 0.32	0.030 ± 0.001	0.996	0.680

Table 2. Parameters of the pseudo-first-order and pseudo-second-order kinetic models for total chromium biosorption onto HCl-pretreated PDB at different initial Cr(VI) concentrations

Initial Cr(VI) concentration (mg/L)	$q_{e\text{ exp}}$ (mg/g)	Pseudo-first-order				Pseudo-second-order			
		q_{e1} (mg/g)	k_1 (1/h)	R^2	RMSE	q_{e2} (mg/g)	k_2 (g/mg·h)	R^2	RMSE
21.77	16.31 ± 0.41	15.3 ± 0.260	0.803 ± 0.044	0.982	0.6183	16.74 ± 0.27	0.070 ± 0.006	0.987	0.529
42.56	32.73 ± 0.03	29.84 ± 0.765	0.761 ± 0.061	0.959	1.782	32.68 ± 0.20	0.034 ± 0.001	0.998	0.378
63.71	47.12 ± 0.27	42.93 ± 1.013	0.843 ± 0.066	0.962	2.447	46.98 ± 0.30	0.027 ± 0.001	0.998	0.588
79.24	60.34 ± 0.27	55.9 ± 1.392	0.718 ± 0.054	0.963	3.184	61.00 ± 0.24	0.017 ± 0.001	0.999	0.465
101.86	73.59 ± 0.51	68.48 ± 1.647	0.641 ± 0.044	0.968	3.634	74.66 ± 0.13	0.012 ± 0.001	0.999	0.248
383.40	146.9 ± 0.325	137.3 ± 3.072	0.533 ± 0.032	0.977	6.433	149.7 ± 1.03	0.005 ± 0.001	0.998	1.826
659.68	211.8 ± 0.31	200 ± 4.082	0.495 ± 0.026	0.982	8.384	218.6 ± 2.43	0.003 ± 0.001	0.995	4.206
1002.19	288.1 ± 6.61	269.6 ± 6.045	0.443 ± 0.025	0.979	12.09	294.7 ± 2.63	0.002 ± 0.001	0.997	4.440

The parameter values of the isotherm models, as well as the determination coefficients (R^2) and $RMSE$ values are shown in Table 3. In addition, data predicted by the isotherm models are shown in Fig. 5. Obtained results clearly favored the Freundlich isotherm model compared with the Langmuir model. The higher value of R^2 (0.988) and the lower value of $RMSE$ (11.49) became the indicators of Freundlich model suitability for total chromium biosorption onto HCl-pretreated PDB biomass over the Langmuir model, which showed lower R^2 (0.937) and higher $RMSE$ (26.2) values. The fact that the Freundlich model fits the experimental data very well may be due to a heterogeneous distribution of active sites on the PDB surface and the chromium ions bind as a multi-layer on the PDB surface (Mohan and Pittman Jr., 2006). This model also assumes a logarithmic reduction of the affinity between solute and biosorbent during surface coverage (Pagnanelli, 2011).

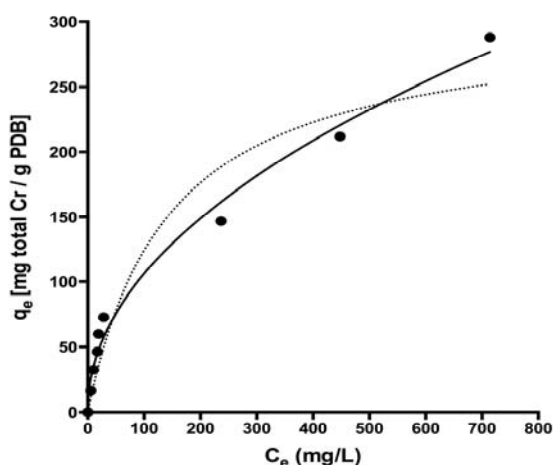


Fig. 5. Comparison between the experimental (●) isotherm data and the calculated isotherm data derived from Langmuir (····) and Freundlich (—) models for total chromium biosorption onto HCl-pretreated PDB

The Freundlich constants, k_F and n_F , which are related to the adsorption capacity and adsorption intensity, respectively, were found to be 11.28 (mg/g)(mg/L) $^{1/n_F}$ and 2.05. As values of $n_F > 1$ represent a favorable condition of adsorption (Ozdes et al., 2014), it can be concluded that the biosorption of total chromium onto HCl-pretreated PDB was favorable under the studied conditions.

The Freundlich isotherm model has also successfully described the equilibrium biosorption of chromium onto different biosorbents (Ozdes et al., 2014; Gong et al., 2013; Zubair et al., 2008; Balan et al., 2012).

In addition, the maximum total chromium biosorption capacity was compared with published results to assess the potential application of HCl-pretreated PDB as a biosorbent for chromium removal from aqueous solutions. Table 4 compares total chromium biosorption capacity of different biosorbents.

The current results of total chromium biosorption capacity were significantly higher than most results reported in the literature. These results indicate that HCl-pretreated PDB is one of the best biosorbents currently available for the removal of chromium from aqueous solutions, and is therefore a promising material to be tested for detoxification of Cr(VI)-polluted water and wastewater.

Table 3. Parameters of the Langmuir and Freundlich isotherm models for total chromium biosorption onto HCl-pretreated PDB

Langmuir							
q_{max} (mg/g)			b (L/mg)			R^2	$RMSE$
302.9	±	43.0	0.007	±	0.003	0.937	26.2
Freundlich							
k_F [(mg/g)(mg/L) $^{1/n_F}$]			n_F			R^2	$RMSE$
11.28	±	2.224	2.053	±	0.1363	0.988	11.49

3.7. FTIR analysis

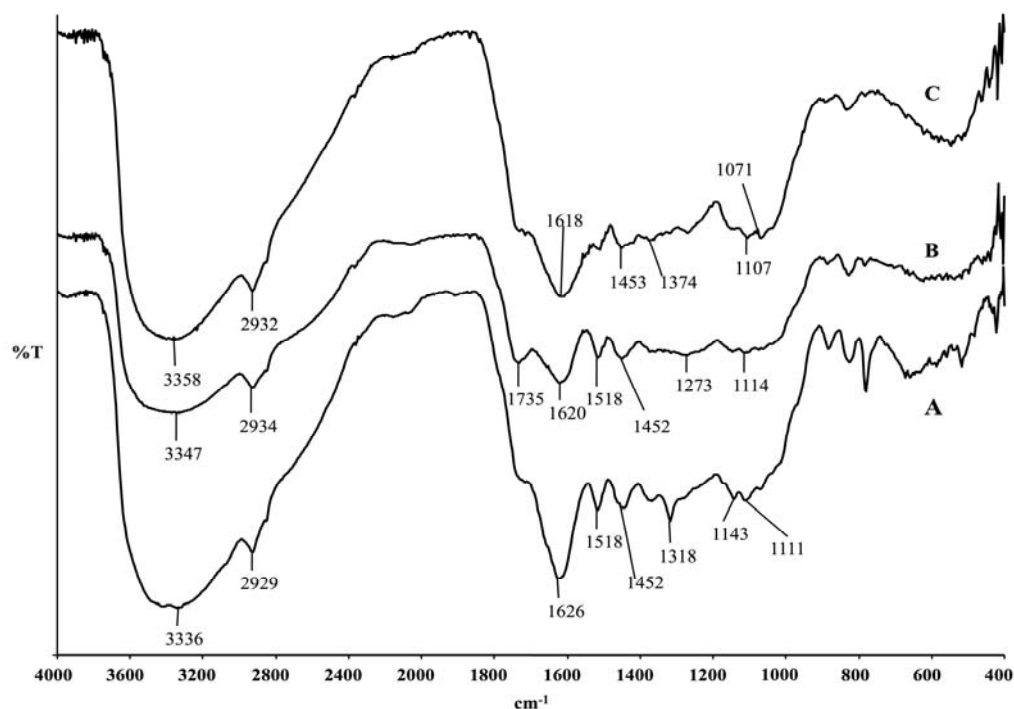
The FTIR spectrum of native PDB displays a number of absorption peaks, indicating the complex nature of the biomass under examination (Fig. 6A). The broad absorption band around 3600-2900 cm^{-1} is indicative of the presence of -OH and -NH groups. Peaks at 1100-1000 cm^{-1} are assigned to C-O and C-N stretching (Mungasavalli et al., 2007; Çelekli and Bozkurt, 2013). The absorption peaks around 2930 cm^{-1} may be due to the stretching of C-H and CH_2 groups present in the lignin structure (Saeed et al., 2009).

The absorption peak at 1620 cm^{-1} is attributable to C=O stretching of amide carboxyl group (Unnithan et al., 2004). The peaks at 1518 and 1452 cm^{-1} are assigned to N-H bending (Çelekli and Bozkurt, 2013). The spectrum of the HCl-pretreated PDB presented a wider band at 3000-2900 cm^{-1} (Fig. 6B), compared with the spectrum of the native PDB, suggesting that acid pretreatment removed dirt which was blocking -NH and -OH groups, and caused the degradation of polysaccharides and protein-like components (Arica et al., 2005). An extra absorption peak was observed in the spectrum of acid-pretreated PDB at 1735 cm^{-1} , which has been attributed to C=O stretching of hemicellulose (Elangovan et al., 2008; Unnithan et al., 2004).

Moreover, the peak at 1318 cm^{-1} in the spectrum of the native PDB shifted to 1273 cm^{-1} in the acid-pretreated PDB spectrum; this peak is due to C=O stretching of carboxyl groups (Mungasavalli et al., 2007). These findings are in agreement with that reported by Elangovan et al. (2008), who suggested that acid pretreatment converts amide and ester groups into corresponding carboxylic acids. A smaller peak was also observed at 1620 cm^{-1} , corresponding to the amide groups. These results indicate that acid pretreatment resulted in additional available binding sites at the surface of the biomass.

Table 4. Comparison of total chromium biosorption capacity of some biosorbents

Biosorbent	Total Cr biosorption capacity (mg/g)	Reference
Raw <i>Sargassum</i> sp.	31.25	Yang and Chen, 2008
Chemically modified <i>Sargassum</i> sp.	58.38	Yang and Chen, 2008
<i>Pinus brutia</i> TEN bark	140.8	Ozdes et al., 2014
<i>Rosa gruss an teplitz</i>	110.24	Shafqat et al., 2008
<i>Citrus reticulata</i>	195.04	Zubair et al., 2008
<i>Cupressus lusitanica</i> bark	87.5	Netzahuatl-Muñoz et al., 2012a
<i>Prunus serotina</i> bark	69.93	Netzahuatl-Muñoz et al., 2012b
<i>Schinus molle</i> bark	73.18	Netzahuatl-Muñoz et al., 2010
<i>Cassia fistula</i> bark	107.1	Abbas et al., 2008
<i>Agave lechugilla</i>	3.3	Mohan and Pittman Jr., 2006
Larch bark	31.3	Mohan and Pittman Jr., 2006
Almond shell	98.0	Mohan and Pittman Jr., 2006
HCl-pretreated <i>Prunus domestica</i> bark	288.1	This work

**Fig. 6.** FTIR spectra of native PDB (A), HCl-pretreated PDB (B) and HCl-pretreated PDB loaded with chromium (C)

The absorption spectrum of acid-pretreated PDB loaded with chromium (Fig. 6C) showed evident changes with respect to that of acid-pretreated PDB. Among these changes was the disappearance of the absorption peaks at 1735, 1518 and 1273 cm^{-1} , and this may be because the biosorption of chromium ions onto acid-pretreated PDB left C=O of the carboxyl group and -NH of amide groups undetectable. These findings indicate that the main functional groups responsible for total chromium biosorption are the amide and carboxyl groups, which may interact with Cr(VI) anionic species and Cr(III) cationic species, respectively.

These results are in agreement with that found for chitinous crab-shell material, where amide groups were involved in the binding of anionic chromate and carboxyl groups were responsible for Cr(III) binding (Volesky, 2003).

4. Conclusions

The removal characteristics of Cr(VI) and total chromium from aqueous solutions by PDB were found to be influenced by several environmental parameters, such as PDB particle size, PDB pretreatment, solution pH level, contact time, and initial Cr(VI) concentration. Kinetic data of total chromium biosorption onto HCl-pretreated PDB agreed well with the pseudo-second-order model.

The equilibrium isotherm data for total chromium biosorption onto HCl-pretreated PDB are best described by the Freundlich model. Present results indicate that HCl-pretreated PDB may be used as an effective and low-cost biomaterial for the removal of Cr(VI) and total chromium from aqueous solutions.

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