BIOADSORPTION USING COMPOST: AN ALTERNATIVE FOR REMOVAL OF CHROMIUM (VI) FROM AQUEOUS SOLUTIONS

Claudia Vargas, Pedro F. B. Brandão, Jesús Ágreda, and Elianna Castillo*

The removal of Cr(VI) from aqueous solutions was studied using a compost generated from carnation flowers waste. The highest percentage of removal achieved (*ca.* 99 %) was obtained at pH 2.0, using a 10 mg L^{-1} of Cr(VI) solution, a dose of 10 g L^{-1} of compost, and with an equilibrium time of 3 hours. Under these conditions, the kinetics and adsorption isotherm were examined varying the initial Cr(VI) concentration from 15 to 200 mg L^{-1}. The maximum sorption capacity at equilibrium (Q_m), from the Langmuir model, was found to be 6.25 mg g^{-1}. The evaluation of Cr(VI) removal at pH 2.0 showed a second order kinetics and showed that the process mechanism can be modeled by the "adsorption-coupled reduction" hypothesis. Also, the monitoring of Cr(VI) and total Cr in aqueous solutions showed that Cr(VI) and total Cr were removed from solution, and that part of the Cr(III) was retained on the compost. According to the results, the removal of Cr(VI) with the assayed compost can be explained by the following steps: (i) adsorption of Cr(VI) species onto compost, (ii) Cr(VI) reduction to Cr(III), and (iii) adsorption of part of Cr(III) on the compost. Thus, this study suggests that the carnation flower waste compost can be used as a remediation system for water contaminated with Cr(VI).

Keywords: Compost; Residue; Carnation flower; Removal; Cr(VI); Bioadsorbent

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INTRODUCTION

The increase of industrial activities by humankind has intensified stress and several contamination problems to the environment, which has resulted in deteriorated ecosystems (Gao *et al.* 2008). Nowadays, heavy metals are considered major environmental contaminants and one of the most toxic pollutants due to their persistence in the environment, mainly due to their non-degradability, which results in potential problems for public health. Chromium (VI) is among the most toxic metals and is considered a priority pollutant due to its mutagenic and carcinogenic characteristics (Blázquez *et al.* 2009). The main anthropogenic pollution sources of this metal in natural water bodies are the electroplating, the textile, and the steel manufacturing industries, as well as the processing of hides (Park *et al.* 2008a).

The conventional treatments to remove metals from contaminated environments include physical and chemical processes such as precipitation, ion exchange, reverse osmosis, and oxidation (Gheju and Balcu 2011; Gheju *et al.* 2008). Generally, these methodologies are expensive and generate wastes that have to be further treated, and usually the metal removal is incomplete when it is at low concentrations. To circumvent limitations and to provide an alternative to these methods, in recent years research has focused on various low-cost adsorbents to remove toxic metals from contaminated water (Babel and Kurniawan 2003). The advantages of using unconventional materials for metal adsorption are their low cost, high efficiency, the possibility that the bioadsorbent can be regenerated, and its easy accessibility. Agro-based waste materials can be used as efficient adsorbents for the removal of Cr(VI), and many examples can be found in the literature such as, olive waste (Blázquez *et al.* 2009), rice shells (Bhattacharya *et al.* 2008), Neem bark (Park *et al.* 2008a), eucalyptus bark (Sarin and Pant 2006), green tea waste (Park *et al.* 2008a), grape stalk (Fiol *et al.* 2008), sawdust pine (Uysal and Ar 2007), cactus leaves (Dakiky *et al.* 2002), sawdust (Gode *et al.* 2008), *Tamarindus indica* seeds (Agarwal *et al.* 2006), coconut (Gonzalez *et al.* 2008), almond shell (Pehlivan and Altun 2008), wheat bran (Son *et al.* 2008), and rice bran (Singh *et al.* 2005).

It can be found in the literature that compost is an appropriate material for adsorbing metal ions (Boni and Sbaffoni 2009; Gibert *et al.* 2005; Lister and Line 2001; Paradelo and Barral 2012; Wei *et al.* 2005) due to characteristics such as biomass content, organic functional groups on the surface, and cellulosic materials composition. However, there are few studies concerning the removal of Cr(VI) by compost in acidic conditions. Wei *et al.* (2005) used kitchen waste compost to remove chromium from water containing either Cr(III) or Cr(VI) under acidic conditions. Our research contributes further insights on the removal of Cr(VI) from aqueous solutions under acidic conditions, using a compost generated from vegetal wastes.

Compost is widely available in Colombia, and it can be prepared in large amounts at the site where a treatment is required. In this work, the compost used was derived from residues of carnation flowers, which are produced on a very large scale, since Colombia is the second-largest exporter of flowers in the world. The major production hub is located around Bogotá, the capital of Colombia. Approximately 7266 ha are dedicated to the growing of ornamental species under greenhouse conditions, where the most important are roses (*Rosa spp*.) and carnations (*Dianthus caryophyllus*). The production of compost is an efficient way for the disposal of the generated wastes, and the large amounts obtained generates a cheap material for which the commercial demand in Colombia is relatively low. For this reason, we consider it important to find some additional use for this kind of material. We have previously studied other compost material derived from different sources for the removal of Cr(VI) from aqueous solutions, and the results indicated that compost from a vegetal source is a potential adsorbent of this metal (Vargas *et al.* 2011). This paper presents and discusses the results of experiments evaluating the effects of the contact time, adsorbent doses, pH, stirring type, and initial chromium concentration on the adsorption process of Cr(VI) onto compost from an agriculture waste source. Furthermore, batch adsorption experiments were carried out to find the maximum Cr(VI) loading capacity of the adsorbent, the adsorption kinetics, and the removal mechanism.

EXPERIMENTAL

Adsorbent

The commercial compost used as adsorbent in the experiments was obtained after the stabilization of carnation flowers residues from farm processes at the countryside area of Bogotá, Colombia, South America. This compost, named Ferticompost®, was produced and supplied by the company Compostar Ltda. Before its use in the experimental assays the compost was dried in the laboratory under direct sun light at room temperature for 3 days and then passed through an 80-mesh screen.

Reagents

A stock solution containing 1000 mg L^{-1} of Cr(VI) was prepared by dissolving 1.4143 g of AR grade $K_2Cr_2O_7$ (Merck) in 500 mL of deionized water. The Cr(VI) standard solutions initial concentration used in the experiments were prepared using an appropriate dilution of this stock solution.

Batch Adsorption Studies

All experiments were carried out at room temperature (18 ± 2 °C) using 0.25 g of compost in a 50 mL Falcon tube containing 25 mL of Cr(VI) solution with appropriate dilution for the particular experiment under study. Three types of agitation were evaluated during Cr(VI) removal with compost: 1) orbital shaking at 180 rpm (Joel 228, CEIF-UN), 2) magnetic stirring at 600 rpm (POLY 1515, Variomag), and 3) vertical circular rotation at 36 rpm (RD 5512, Glas-Col). Depending on the particular experiment under study, batch adsorptions were carried out at the desired pH value, contact time, and adsorbent dosage level. A synthetic solution of known Cr(VI) concentration was added to the compost-containing tube, and the samples were agitated to ensure equilibrium was reached. Then, the samples were centrifuged at 5000 rpm for 10 min, and the supernatants were tested for the residual chromium ion concentration. Batch experiments were performed in triplicate, and average values are presented.

Determination of Cr(VI) and Cr(III) Concentration

The concentrations of Cr(VI) ions were analyzed using a spectrophotometer UV-Vis Lambda 2S (Perkin Elmer) following the standard method for examination of water and wastewater with 1,5-diphenylcarbazide (Merck) at pH 2.0 (APHA 2005b). The absorbance of the formed complex was measured at 540 nm after 10 minutes of reaction. Total chromium was analyzed using an atomic absorption spectrophotometer AAnalyst 300 (Perkin Elmer) (APHA 2005a). The concentration of Cr(III) was determined by calculating the difference between the total chromium concentration and the Cr(VI) concentration.

The amount of sorbed Cr(VI), q_e, was calculated in mg g^{-1} according to,

$$q_e = \frac{(C_0 - C_e) * V}{m_s} \tag{1}$$

where, C_0 and C_e are, respectively, the initial and the equilibrium Cr(VI) concentration (mg L^{-1}) in the aqueous solution, m_s is the mass of compost used (g), and V is the volume of the solution (L). The removal percentage of Cr(VI) was calculated according to

$$Removal\ (\%) = \frac{(C_0 - C_e)}{C_0} * 100 \tag{2}$$

Adsorption Isotherms

Two adsorption isotherm models were selected to fit the data, namely the Langmuir and Freundlich models (Bradl 2004). The Langmuir isotherm assuming a monolayer adsorption is,

$$q_e = \frac{Q_m b C_e}{1 + bC_e} \tag{3}$$

where q_e is the amount of Cr(VI) adsorbed per unit mass of adsorbent (mg g^{-1}) at equilibrium, C_e is the Cr(VI) concentration remaining in solution (mg L^{-1}), b is the Langmuir adsorption constant, and Q_m is the amount of adsorbate required to form a monolayer on a unit mass (mg g^{-1}), also called maximum load. Rearranging the equation (3), a linear equation is obtained:

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \tag{4}$$

A linear plot of C_e/q_e vs. C_e is used to determine the values of Q_m (mg g^{-1}) and b (L mg^{-1}). The Langmuir isotherm essential characteristics may be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined as:

$$R_L = \frac{1}{(1 + bC_0)} \tag{5}$$

The R_L parameter can be associated with the favorability of the adsorption, when $0 < R_\mathrm{L} < 1$. If R_L is higher than 1, then the adsorption is unfavorable.

Additionally, the experimental data were fitted to the Freundlich adsorption isotherm, which can be expressed by the following equation:

$$q_e = K_f C_e^{n_f} \tag{6}$$

The Freundlich isotherm is empirical, and it is used for non-ideal adsorption and when the surface is heterogeneous. This isotherm describes a nonlinear adsorption where K_f is the Freundlich constant, indicating the relative adsorption capacity related to the binding energy. The factor n_f, known as the heterogeneity factor or the Freundlich coefficient, represents the deviation from linearity of the adsorption. Linearization yields the following equation:

$$\log q_e = \log K_f + n_f \log C_e \tag{7}$$

Adsorption isotherm studies were carried out with nine different initial concentrations of Cr(VI), from 15 to 200 mg L^{-1}, at pH 2.0, a contact time of 3 hours, and an adsorbent dosage level of 10 g L^{-1}. Each point on the isotherm was carried out five times, and the coefficients of variation were found to be lower than 15%.

SEM and FTIR Analysis

Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray spectroscopy (EDX), and Fourier-Transform Infrared spectroscopy (FTIR) were used to analyze the compost before and after the Cr(VI) adsorption experiments. The samples used in SEM and EDX analyses were metalized by Au-Pd sputtering, and assays were performed using a scanning electron microscope (FEI QUANTA 200). FTIR analysis was performed using a Fourier-Transform Infrared spectrometer Nicolet Is (Thermo). The FTIR, SEM, and EDX analyses were performed before and after 24 hours of contact time of the compost with a solution of 200 mg L^{-1} of Cr(VI), following the batch adsorption procedure described above.

RESULTS AND DISCUSSION

Effect of the Contact Time

The effect of the contact time on the removal of Cr(VI) by compost at initial metal concentrations of 5, 15, and 20 mg L^{-1}, at pH 2.0, is shown in Fig. 1. The percentage of Cr(VI) removal by compost was 99%, 92%, and 82%, respectively for each initial Cr(VI) concentration. In all cases, the metal adsorption rate was high at the start of the contact reaction and then gradually decreased and became almost constant after the equilibrium point, which was reached at 180 min.

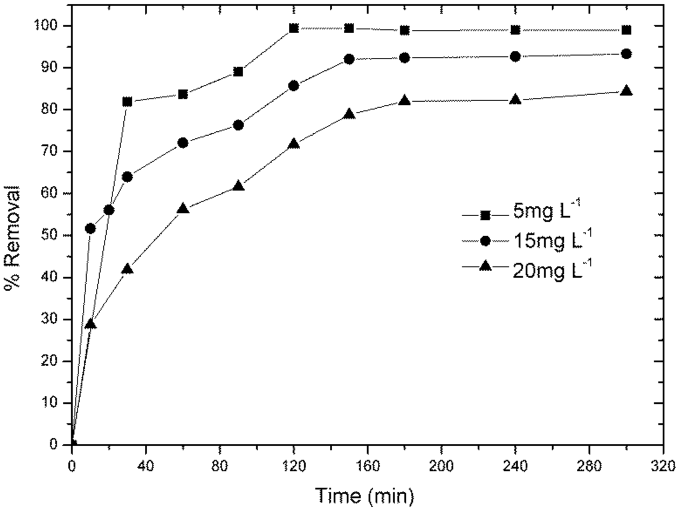

Fig. 1. Effect of the contact time on the removal of Cr(VI) by compost. Experimental conditions: pH 2.0; initial Cr(VI) concentration 5, 15, and 20 mg L^{-1}; adsorbent dose 10 g L^{-1}

Effect of the Adsorbent Doses

Adsorbent dose is a factor for metal removal, as it determines the sorbent-sorbate equilibrium of the system. In order to investigate the effect of compost dose on the Cr(VI) sorption, different amounts of the adsorbent (5 to 40 g L^{-1}) were suspended in 25 mL of 10 mg L^{-1} of hexavalent chromium solution. The results showed that the percentage of Cr(VI) removal is dependent on the dose of adsorbent (Fig. 2). The removal of hexavalent chromium was 88% with 5 g of compost per liter of solution, and it increased to 99% with 10 g of compost per liter. This adsorbent dose is enough for the maximum possible removal of Cr(VI) from a solution with 10 mg L^{-1} of Cr(VI). Therefore, a dose of 10 g L^{-1} of compost was selected for the next experiments. This dose of adsorbent is similar to those reported for the removal of Cr(VI) with sawdust (Gupta and Babu 2009) and rice straw (Gao *et al.* 2008).

The initial increment in the percentage of Cr(VI) removal as the dose of compost increases could be explained because the area available for Cr(VI) adsorption becomes larger; thus, at a high dose the compost will be able to remove most of the Cr(VI) ions from the solution. As expected, the adsorbed Cr(VI) per gram of compost decreases as the dose of compost increases (Fig. 2). At a low adsorbent dose, all active sites of the compost are fully exposed and get occupied by the Cr(VI) that is in excess, saturating the surface and yielding a higher q_e value (Albadarin *et al.* 2011; Garg *et al.* 2007; Gupta *et al.* 2010). On the other hand, at higher adsorbent doses the surface area is in excess and the Cr(VI) adsorbed per gram of compost decreases.

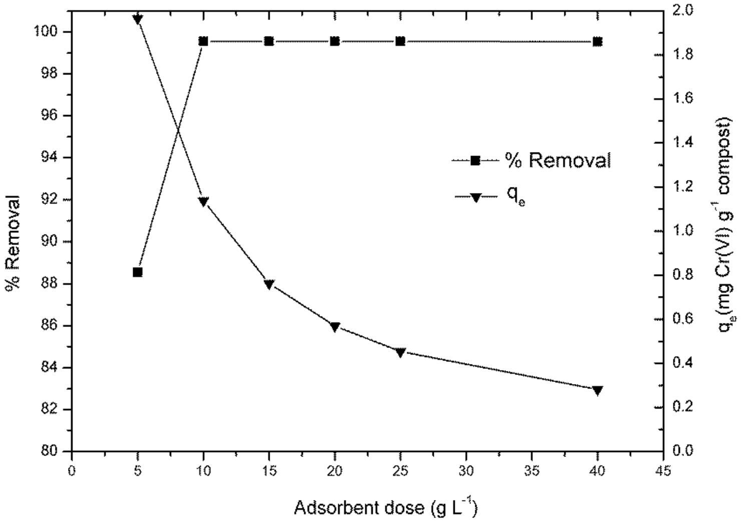

Fig. 2. Effect of the adsorbent dose on the removal of Cr(VI) by compost. Experimental conditions: pH 2.0; initial Cr(VI) concentration 10 mg L^{-1}; contact time 3 h; circular rotation at 36 rpm

Effect of the Initial pH

The pH of the aqueous solution governs the speciation of metals and the properties of the surface. For concentrations lower than 500 mg L^{-1} of Cr(VI), the predominant Cr(VI) species are $HCrO_4^-$ and CrO_4^{2-} anions. At a low pH the species $HCrO_4^-$ is predominant, whereas CrO_4^{2-} is mainly present at higher pH values (Blázquez *et al.* 2009). Hexavalent chromium removal by compost was found to be highly dependent on the pH of the solution, as illustrated in Fig. 3. It was observed that the optimal pH value for removal of 10 mg L^{-1} Cr(VI) by the tested compost was pH 2.0 (99 % of removal). One of the reasons for the observed better adsorption at low pH values may be attributed to the surface of the compost, which becomes positively charged due to the protonation of its functional groups. The positively charged surface causes an increased attraction of the negatively charged chromate ions to the compost (Albadarin *et al.* 2011; Blázquez *et al.* 2009; Gupta *et al.* 2010). Consequently, at higher pH values, as the [H^+] in the solution decreases, the sorbent surface charge becomes negative, thus decreasing the chromium species retention. This behavior has been observed for removal of Cr(VI) using sugarcane bagasse (Garg *et al.* 2007), grape stalk (Albadarin *et al.* 2011; Escudero *et al.* 2009), banana peel (Park *et al.* 2008a), and sludge biomass (Wu *et al.* 2010).

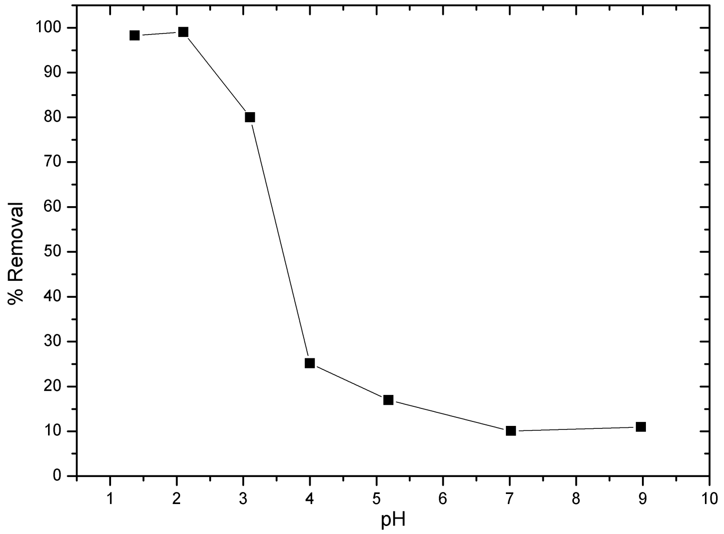

Fig. 3. Effect of initial pH on the removal of Cr(VI) from aqueous solution using compost. Experimental conditions: adsorbent dose 10 g L^{-1}; initial Cr(VI) concentration 10 mg L^{-1}; contact time 3 h; circular rotation at 36 rpm

Effect of the Type of Stirring

The assays with the three agitation systems showed that the removal percentage of Cr(VI) by compost was independent of the type of agitation used: orbital shaking at 180 rpm, magnetic stirring at 600 rpm, or vertical circular rotation at 36 rpm. Hence, vertical circular rotation was chosen for subsequent experiments, since it had operational advantages, such as the formation of less waste volume, and it offered the possibility to perform more experimental sets at the same time.

Adsorption Isotherm

The effect of the initial Cr(VI) concentration on the adsorption process was investigated in a range of different initial concentrations (15 to 200 mg L^{-1}), while other parameters (pH, adsorbent dose, and contact time) were kept constant (Fig. 4). It was observed that as the initial Cr(VI) concentration increased, the removal percentage decreased from 99% to approximately 30%. This behavior can be explained by the fact that the number of active sites remains constant (constant dose of compost), while the concentration of Cr(VI) increases; thus, at high concentrations of Cr(VI) there are not enough active sites to remove the total Cr(VI) present in the solution. On the contrary, as the initial Cr(VI) concentration increased, the adsorption capacity of compost increased from 0.33 to 5.92 mg g^{-1}. This could be explained by the increased rate of mass transfer from the solution to the solid adsorbent, due to the higher availability of Cr(VI) ions in the solution (Gao *et al.* 2008). Similar results have been reported by other researchers (Malkoc *et al.* 2006; Wang *et al.* 2009; Zhang *et al.* 2010).

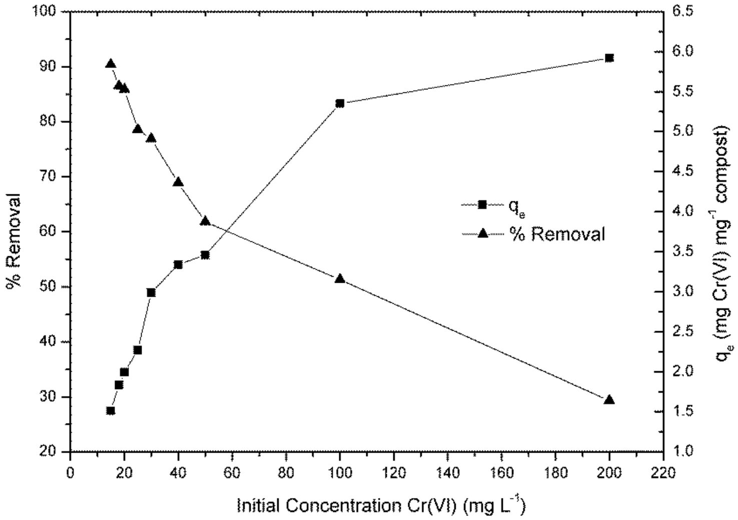

Fig. 4. The effect of initial Cr(VI) concentration on the removal of the metal from aqueous solution using compost. Experimental conditions: pH 2.0; adsorbent dose, 10 g L^{-1}; initial Cr(VI) concentration 10 mg L^{-1}; contact time 3 h; circular rotation at 36 rpm

The experimental results shown in Fig. 4 were fitted to the Langmuir and Freundlich isotherms. The Langmuir and Freundlich model constants determined are presented in Table 1. The results show that the experimental data are best described by the Langmuir isotherm. Also, according to the R_L parameter value of the Langmuir isotherm, which was found to be between 0.46 and 0.76 for the used range of initial Cr(VI) concentration, the adsorption of Cr(VI) by the evaluated compost was judged to be favorable.

Table 1. Langmuir and Freundlich Isotherm Results for the Adsorption of Cr(VI) on Carnation Flower Derived Compost.

Model	Parameter		
Langmuir	Q_m (mg g^{-1}) 6.25	b (L mg^{-1}) 0.103	R^2 0.9946
Freundlich	K_f (mg g^{-1}) 1.12	n_f (g L^{-1}) 0.31	R^2 0.9771

The maximum capacity for sorption (Q_m) of Cr(VI) using the carnation flower waste derived compost was 6.25 mg g^{-1}. This value was compared with those reported in literature for other bioadsorbents (Table 2). It can be observed that the adsorption capacity of the tested compost to remove Cr(VI) from aqueous solutions, although it was not the best, was in the same order of magnitude as other biologically derived adsorbents.

Table 2. Comparison of Maximum Load Values Using Different Bioadsorbents for Removal of Cr(VI)

Adsorbent	**Q_m (mg g^{-1})**	**Reference**
Rice husk	25.64	Krishnani *et a*l. 2008
Rice straw	3.15	Gao *et al*. 2008
Wheat bran	40.80	Son *et al*. 2008
Coconut	6.30	Gonzalez *et al.* 2008
Hazelnut	8.28	Agarwal *et al*. 2006
Shell walnut	8.01	Pehlivan and Altun 2008
Cactus leaves	7.08	Dakiky *et al*. 2002
Eucalyptus bark	45.00	Sarin and Pant 2006
Carnation compost	6.25	This work

SEM and FTIR Analysis Before and After the Removal Process

The SEM and FTIR analyses of the compost before and after the Cr(VI) adsorption experiments were performed respectively to detect the adsorbent morphology and its functional groups. Furthermore, these analyses can provide insights about the adsorption sites (Chen *et al.* 2005). The changes in the morphology and the vibration frequencies of the functional groups after the absorption can be used as an indication of the removal process (Albadarin *et al.* 2011; Cui *et al.* 2011). The results obtained showed evidence of a change in the compost surface morphology (Fig. 5), and the presence of

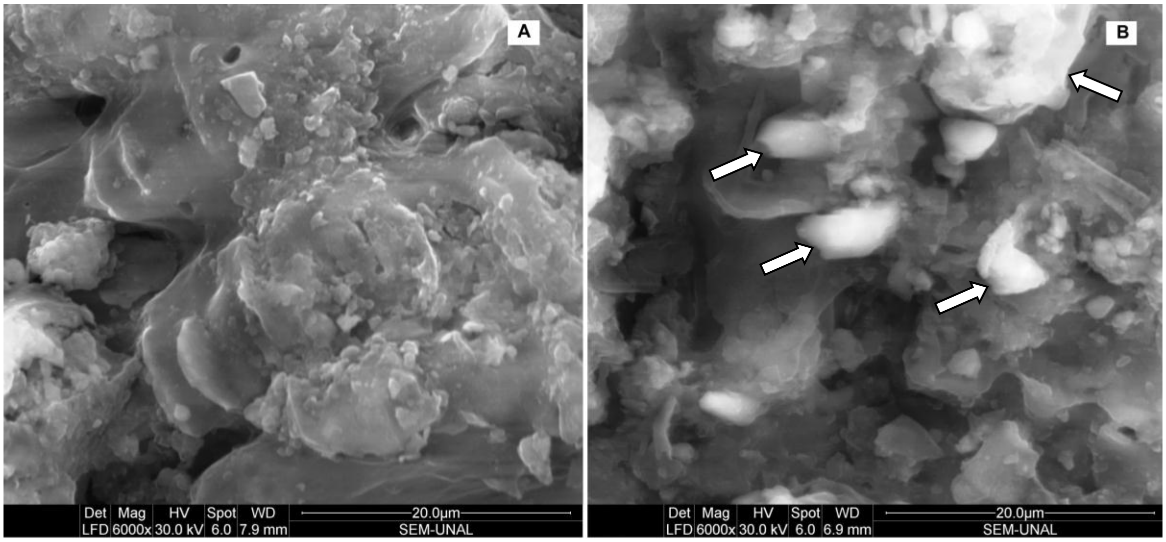

Fig. 5. SEM micrographs of the compost used to remove Cr(VI) from aqueous solution (A) before and (B) after the adsorption process. Arrows indicate possible chromium adsorbed on the compost particles

bright spots in the micrograph after the adsorption process suggests that Cr was adsorbed on the compost particles (arrows in Fig. 5B). This was confirmed by the semi-quantitative EDX chemical analysis of the compost after the Cr(VI) adsorption process, which showed C: 51.3%, O: 37.2%, Al: 1.8%, Si: 6.5%, P: 0.57%, and Cr: 2.4%, indicating that Cr was adsorbed to the material because no Cr was found in the original material.

The FTIR spectra of compost before and after the Cr(VI) adsorption experiment are shown in Fig. 6. The spectrum of the compost shows a broad band at 3389 cm^{-1}, indicating the presence of –OH groups on the compost surface, while the band observed at 2920 cm^{-1} is characteristic of the C–H group. The band located at 1620 cm^{-1} is attributed to the C=O stretching of the carboxyl group, the band near 1396 cm^{-1} indicates the presence of CH_3 stretching or OH stretching, and the broad band at 1032 cm^{-1} is related to the C–O stretching of alcoholic groups or polysaccharides. These results indicate that the functional groups with oxygen are the most probable sites for Cr(VI) adsorption, because it was observed that, after the removal of Cr(VI), the intensities of these bands decreased and particularly the –OH band had a shift to 3307 cm^{-1} (Fig. 6b). The changes between the FTIR spectra of compost thus confirm the binding of chromium with the functional groups present in the tested adsorbent. Similar results have been reported to assess the interactions of Cr (VI) with the functional groups of olive stone (Blázquez *et al.* 2009).

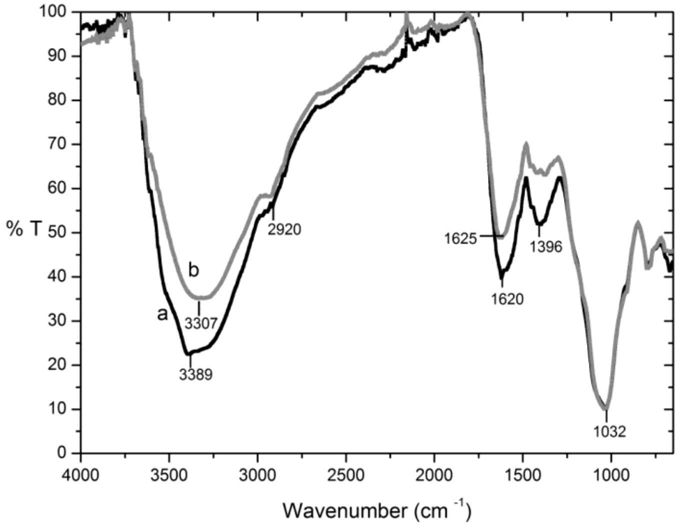

Fig. 6. FTIR spectra of the compost (a) before and (b) after Cr(VI) removal

Removal Mechanism of Cr(VI) onto Compost

There have been recent reports concerning the Cr(VI) removal mechanism that indicate that "adsorption-coupled reduction" is the mechanism of Cr(VI) adsorption by natural biomaterials under acidic conditions (Anandkumar and Mandal 2011; Miretzky and Cirelli 2010; Park *et al.* 2007; Park *et al.* 2008b). That mechanism was tested in this study, applied to the removal of Cr(VI) by compost generated from carnation flowers waste. According to our results, the Cr(VI) removal by the tested compost could be explained by the following three steps:

Step (a): The Cr(VI) anion species are adsorbed on the positively charged compost surface. To evaluate this, solutions with different Cr(VI) concentration were agitated with compost for three hours, and their initial and final pH was measured (Fig. 7). It was observed that the pH increased as the initial Cr(VI) concentration increased, suggesting that the protons in the solution are involved in the course of Cr(VI) adsorption. In order to explain this behavior, we studied the pH as a function of time by performing two experiments consisting of compost mixed with water at pH 2.0 (adjusted with HNO_3, 1M) and with or without the addition of 50 mg L^{-1} Cr(VI) (Fig. 8). It was observed that the $[H_3O^+]$ concentration decreased (pH increased) with time for both cases, following a second order kinetics, although the kinetic constant changed. This result might be attributed to the compost protonation, particularly of the oxo groups (C_xO and C_xO_2) which are in the surface of the bioadsorbent (Cimino *et al.* 2000), as shown by the following reaction:

$$C_xO + H_3O^+ \leftrightarrow C_xOH^+ + H_2O \qquad (i)$$

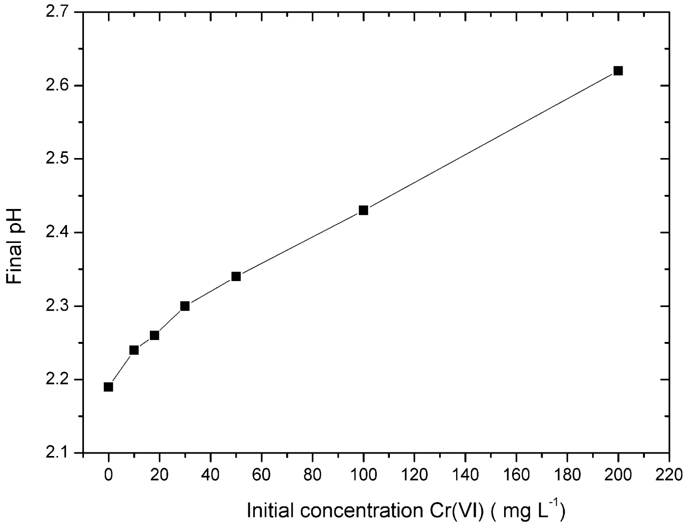

Fig. 7. Final pH of the solutions used to test the adsorption of Cr(VI) onto compost. All solutions started at pH 2.0 ± 0.1

The results in Fig. 8 show that the protonation process of the compost without the presence of Cr(VI) ions followed a second order kinetics, as suggested by reaction (*i*) with a rate constant of 30.90 ± 0.06 M^{-1} s^{-1}. A similar behavior was observed with the presence of 50 mg L^{-1} Cr(VI), although with a lower value for the kinetic constant, 24.63 ± 0.08 M^{-1} s^{-1}. This second order behavior can be interpreted as a sum of reactions (*i*) and (*ii*) that result in the global reaction (*iii*), which together indicate that the hydronium ion is necessary for the adsorption process of Cr(VI) (Cimino *et al.* 2000).

$$C_xOH^+ + HCrO_4^- \leftrightarrow C_x(OH)(HCrO_4) \qquad (ii)$$

$$C_xO + H_3O^+ + HCrO_4^- \leftrightarrow C_x(OH)(HCrO_4) + H_2O \qquad (iii)$$

The Cr(VI) adsorption on compost is represented by reaction (*iii*), which shows that the adsorption of one mol of $HCrO_4^-$ decreases the hydronium ion concentration, which increases the pH of the solution.

These results are comparable with those from other authors who used, instead of compost, grape stalks (Fiol *et al.* 2008), eucalyptus bark (Sarin and Pant 2006), and sawdust (Gupta and Babu 2009). These authors explain the increase of the solution pH obtained after Cr(VI) removal, by a similar mechanism.

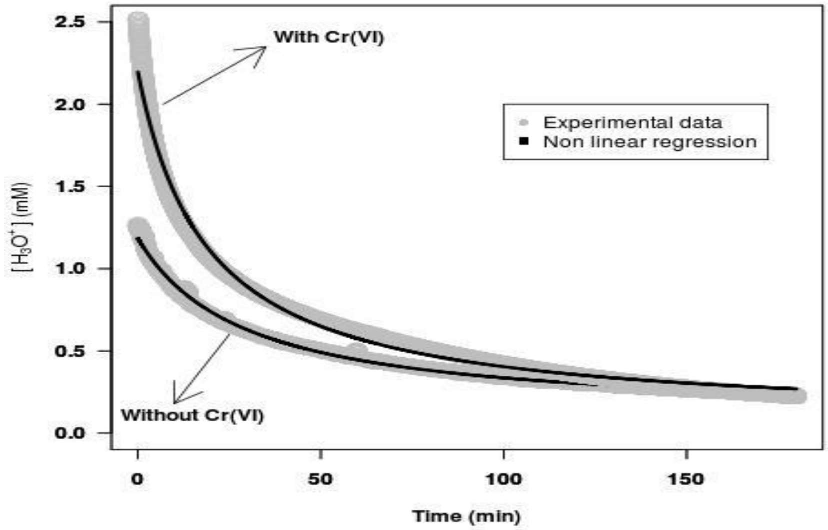

Fig. 8. Second order behavior of Cr(VI) adsorption onto compost. Experimental conditions: initial pH 2.0; adsorbent dose, 10 g L^{-1}; initial Cr(VI) concentration 50 mg L^{-1}; contact time, 3 h; circular rotation at 36 rpm

Step (b): The reduction of Cr(VI) to Cr(III) by compost electron-donor groups. This reaction also increases the pH because the hydronium ions are consumed (Krishnani *et al.* 2008), as shown by the following simplified reaction:

$$Compost_{(Red)} + HCrO_4^- + H_3O^+ \rightleftharpoons Compost_{(Ox)} + Cr^{3+} + H_2O \quad (iv)$$

In order to confirm the Cr(VI) reduction, the redox potential as a function of time, and at initial pH 2.0 was measured for three solutions (Fig. 9): Cr(VI) alone, compost alone, and Cr(VI) with compost.

Tsuchida and Muir (1986) performed comparable measurements demonstrating that a similar redox process occurs during the adsorption of $Au(CN)_2^-$ and $Ag(CN)_2^-$ onto activated carbon (Tsuchida and Muir 1986). Thus, the results shown in Fig. 9 are a reasonable proof that Cr(VI) is reduced to Cr(III) by the compost surface. Other authors have confirmed the reduction of Cr(VI) to Cr(III) by biomaterials under acidic conditions (Park *et al.* 2007; Park *et al.* 2008b; Wei *et al.* 2005).

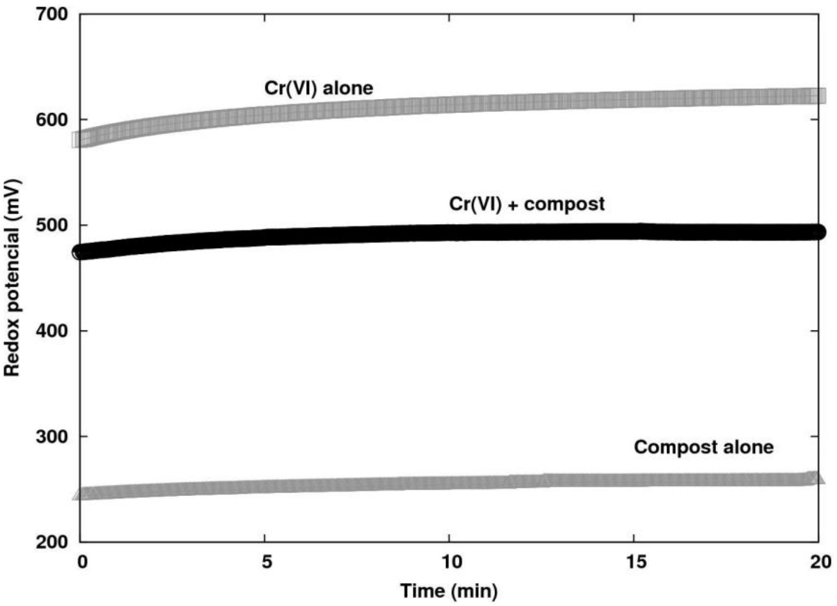

Fig. 9. The redox potential of a Pt electrode as a function of time for a Cr(VI) solution with compost. Experimental conditions: initial pH 2.0; adsorbent dose 10 g L^{-1}; initial Cr(VI) concentration 50 mg L^{-1}; circular rotation at 36 rpm

Step (c): The retention of Cr(III) species on the compost surface (Wei *et al.* 2005). To confirm this, the total hexavalent and trivalent chromium concentrations were monitored in the aqueous solution during the removal process (Fig. 10). As observed, the total chromium and Cr(VI) concentrations decreased with time, while the Cr(III) concentration increased initially up to approximately 4 mg L^{-1} in the aqueous solution and then remained practically constant as the experiment proceeded.

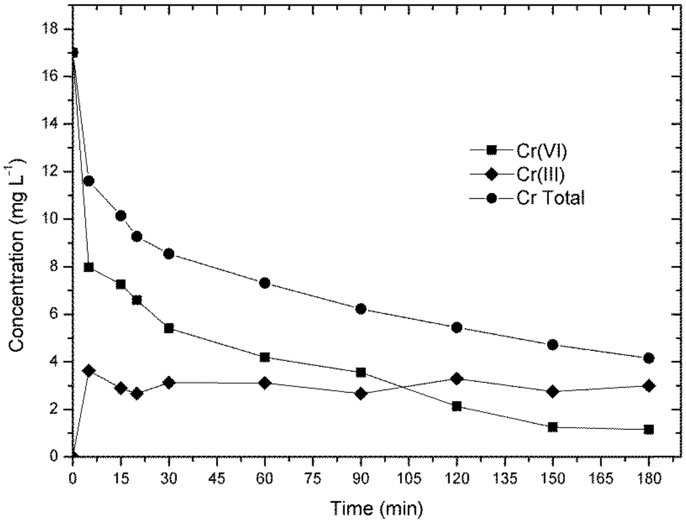

Fig. 10. Kinetics for Cr(VI) removal using compost. Experimental conditions: initial pH 2.0; adsorbent dose, 10 g L^{-1}; initial Cr(VI) concentration 17 mg L^{-1}; contact time, 3 h; and circular rotation at 36 rpm

This Cr(III) concentration was less than 20% of the initial Cr(VI) concentration used, and then the major part of the Cr(III) must have been adsorbed on the compost. These observations are similar with the work reported by (Escudero *et al.* 2009), who argue that a partial sorption of the formed trivalent chromium occurs onto the tested bioadsorbent (grape stalk). On the other hand, our results are contrary to those observed in other studies using different bioadsorbents, which showed that while the Cr(VI) concentration decreased in solution, the Cr(III) concentration increased (Park *et al.* 2008b; Wu *et al.* 2010).

CONCLUSIONS

1. It was successfully demonstrated that a local compost, generated from carnation flower waste, can be used as a low cost adsorbent for the removal of Cr(VI) from aqueous solutions in acid conditions and that its maximum load capacity is comparable to that of other bioadsorbents reported in literature.
2. The Cr(VI) removal percentage of the tested compost was found to be dependent on the contact time, adsorbent doses, and initial concentration of Cr(VI). Moreover, it was found that the Cr(VI) adsorption has a remarkable dependence with respect to the initial pH of the solution. Thus, the removal of Cr(VI) is only possible at low pH, because a protonation of the compost is required in order to have a significant Cr(VI) adsorption.
3. The pH kinetics studies showed that the compost protonation and the removal of Cr(VI) follow a second order process, indicating the strong activity of the hydronium ion in the Cr(VI) adsorption process.
4. The monolayer adsorption capacity (Q_m) of the carnation flower waste derived compost was 6.25 mg g^{-1}, according to the Langmuir model.
5. The mechanism for the removal of Cr(VI) with compost in acidic media could be described by the adsorption of Cr(VI) and the subsequent reduction to Cr(III). Part of the Cr(III) formed during the reduction process is retained by the compost. This fact is in agreement with the general previously proposed “adsorption-coupled reduction” mechanism.

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