CHEMICAL ENGINEERING TRANSACTIONS Volume 24, 2011
Editor Sauro Pierucci

 ISBN 978-88-95608-15-0 ISSN 1974-9791
DOI: 10.3303/CET1124224

Removal of Hexavalent and Total Chromium from Aqueous Solution by Avocado Shell

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The main aim of this work was to evaluate the potential of Hass avocado (*Persea americana* Mill var. 'Hass') shell to remove hexavalent chromium [Cr(VI)] and total chromium from aqueous solutions. Results showed that avocado shell removed Cr(VI) by two different mechanisms: chromium biosorption and bioreduction of Cr(VI) to Cr(III). The capacity for removing Cr(VI) and total chromium gradually increased as the contact time proceeded, reaching values of 101.81 and 61.67 mg g^{-1} respectively, after 120 h. The opposite behavior was observed concerning the volumetric rates of Cr(VI) and total chromium removal. The pseudo-second order model adequately described the kinetic process of chromium biosorption by avocado shell, which suggests that this process chiefly occurs as a result of chemisorption.

1. Introduction

Chromium compounds are environmental pollutants occurring in soil, water and industrial effluents because they are widely used in many industrial activities. Although chromium has several oxidation states, chromium compounds mainly occur in the environment as trivalent [Cr(III)] and hexavalent [Cr(VI)] chromium. Cr(VI) is highly toxic, mutagenic, carcinogenic and teratogenic. Cr(III) is much less toxic and mutagenic than Cr(VI), but long-term exposure to high Cr(III) concentrations may cause allergic skin reactions, cancer and DNA damage. The World Health Organization has established drinking water guidelines for total chromium of 0.05 mg l^{-1}. Therefore, the removal or reduction of Cr(VI) to Cr(III) is nowadays recognized as a key process for the detoxification of Cr(VI)-contaminated water and wastewater.

In comparison with the conventional methods for the removal of heavy metals from wastewater, the biosorption process offers potential advantages such as low operating cost, minimization of the volume of chemical and/or biological sludge to be disposed of, high efficiency in detoxifying very diluted effluents, and so on (Hajar, 2009). Biosorption utilizes the properties of certain kinds of inactive or dead biomass to bind

Please cite this article as: Cristiani-Urbina E., Netzahuatl-Munoz A.R. and Cristiani-Urbina M.D.C., 2011, Removal of hexavalent and total chromium from aqueous solution by avocado shell, Chemical Engineering Transactions, 24, 1339-1344
DOI: 10.3303/CET1124224

and accumulate heavy metals by different mechanisms. A number of biomaterials have been tested in order to remove Cr(VI) from aqueous solutions.

The main aim of this work was to evaluate the potential of Hass avocado shell, a biowaste from the avocado processing industry, to remove hexavalent and total chromium from aqueous solution. Furthermore, the kinetics of chromium biosorption by Hass avocado shell is described.

2. Material and Methods

2.1 Preparation of the biomaterial

Shells of Hass avocado (*Persea americana* Mill var. 'Hass') were used as biosorbent for the biosorption of chromium ions from aqueous solution. Avocado shells were washed thoroughly with distilled deionized water and then dried in an oven at 60 ºC for 24 hours. Subsequently, they were milled and the resulting particles were screened using ASTM standard sieves. The fraction with particle size 0.3-0.5 mm was used in the Cr(VI) and total chromium removal experiments carried out in this study. An average rejection rate of 35% was obtained during the sieving process.

2.2 Batch experiments

Batch experiments were conducted in 500 ml Erlenmeyer flasks with a working volume of 100 ml. 0.1 g of the biomaterial was brought into contact with Cr(VI) aqueous solution with a concentration of 102 mg Cr(VI) l^{-1} at pH 2.0 ± 0.1. The flasks were agitated in a shaker at 140 rpm constant shaking speed at 28 °C. No efforts were made to maintain constant the solution pH during Cr(VI) removal experiments.

The amount of Cr(VI) or total chromium removed at time t by the unit mass (dry weight) of avocado shell (q_t, mg g^{-1}) was calculated according to the following mass balance relationship:

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

where C_o is initial Cr(VI) or total chromium concentration (mg l^{-1}) at time t_o = 0 h, C_t is residual Cr(VI) or total chromium concentration at time $t = t$ (h), V is the solution volume (l) and W is the dry weight of the biomaterial (g).

Volumetric rate of Cr(VI) or total chromium removal r (mg l^{-1} h^{-1}) was calculated as follows:

$$r = \frac{(C_0 - C_t)}{t - t_0} \qquad (2)$$

2.3 Biosorption kinetics modeling

In order to evaluate the kinetic mechanism that controls the chromium biosorption process, pseudo-first order and pseudo-second order kinetic models were tested to interpret the experimental data.

2.4 Analytical methods

Hexavalent chromium concentration was determined by the 1,5-diphenylcarbohydrazide method. Total chromium concentration was measured by atomic absorption spectrophotometry (SpectrAA 100, Varian, Inc.) with an acetylene-air flame. The evolution of pH during the Cr(VI) and total chromium removal experiments was monitored using a pH meter (Thermo Orion).

3. Results and Discussion

3.1 Hexavalent and total chromium removal kinetics

The concentrations of residual hexavalent chromium and residual total chromium diminished progressively as the experimental contact time proceeded (Fig. 1). Although Hass avocado shell was not able to remove all the chromium initially added to the aqueous solution, at the end of the experiment (120 h) the concentrations of hexavalent chromium and total chromium were only of 0.19 and 40.33 mg l^{-1}, respectively. It was noticed that at all contact times monitored, the concentration of residual total chromium was higher than that of residual hexavalent chromium.

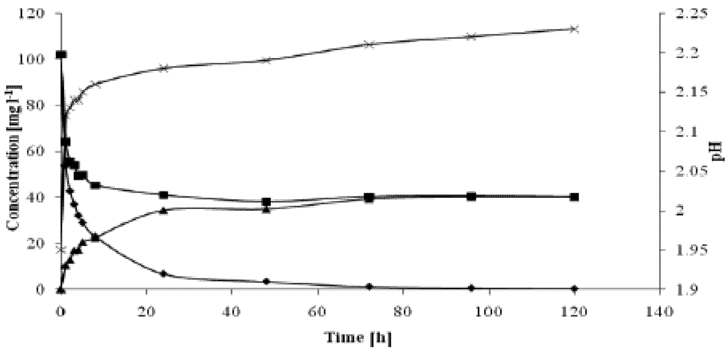

Figure 1: Variations of hexavalent chromium (♦), total chromium (■), and trivalent chromium (▲) concentrations as well as solution pH (×) as a function of contact time.

On the other hand, the Cr(III), which had not been initially present in the aqueous solution, appeared in the aqueous phase and its concentration increased in proportion to the Cr(VI) depletion (Fig. 1). These results show clearly that some of the highly toxic and water-soluble Cr(VI) was reduced to the less toxic Cr(III) when brought into contact with Hass avocado shell under acidic conditions.

Furthermore, Hass avocado shell was capable of removing most of the total chromium initially added to the aqueous solution, indicating that it also has the capacity to biosorb it.

The pH of the aqueous solution increased from 1.95 to 2.23 as contact time increased from 0 to 120 h, which suggests that protons were consumed during the Cr(VI) removal process (Fig. 1). The consumption of protons during the reduction and biosorption of hydrogen chromate [$HCrO_4^-$], which is the major Cr(VI) species at solution pHs 2 and 3, occurs according to the following chemical semi-reactions (Park et al., 2008):

Reduction of Cr(VI):

$$HCrO_4^- + 7H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O \tag{3}$$

Biosorption of Cr(VI):

$$B-NH_2(s)+HCrO_4^-(aq)+H^+(aq)\leftrightarrow B-NH_3^+\cdots HCrO_4^-(s) \quad (4)$$

$$B-COOH(s)+HCrO_4^-(aq)+H^+(aq)\leftrightarrow B-COOH_2^+\cdots HCrO_4^-(s) \quad (5)$$

$$B-SO_3H(s)+HCrO_4^-(aq)+H^+(aq)\leftrightarrow B-SO_3H_2^+\cdots HCrO_4^-(s) \quad (6)$$

On the other hand, the Cr(III) generated during the Cr(VI) reduction process can be released into the aqueous solution and/or form complexes with chromium-binding groups of the biomaterial as follows (Park et al., 2008):

$$B-3(COOH)(s)+Cr^{3+}(aq)\leftrightarrow B-3(COO^-)\cdots Cr^{3+}(s)+3H^+(aq) \quad (7)$$

$$B-3(SO_3H)(s)+Cr^{3+}(aq)\leftrightarrow B-3(SO_3^-)\cdots Cr^{3+}(s)+3H^+(aq) \quad (8)$$

Taking together, the above results show clearly that Hass avocado shell is capable of removing Cr(VI) present in aqueous solution by means of two mechanisms: 1) biotransformation (bioreduction) of Cr(VI) to Cr(III) and 2) biosorption of chromium.

Both Cr(VI) removal capacity and total chromium removal capacity increased as contact time between Cr(VI) aqueous solution and avocado shell increased (Fig. 2). Over the entire range of experimental contact times, the capacity to remove hexavalent chromium was greater than that for total chromium removal, and this was ascribed to the reduction of Cr(VI) to Cr(III). Under the tested conditions, avocado shell exhibited a maximum capacity of hexavalent chromium and total chromium removal of 101.81 and 61.67 mg g^{-1}, respectively, after 120 h of contact.

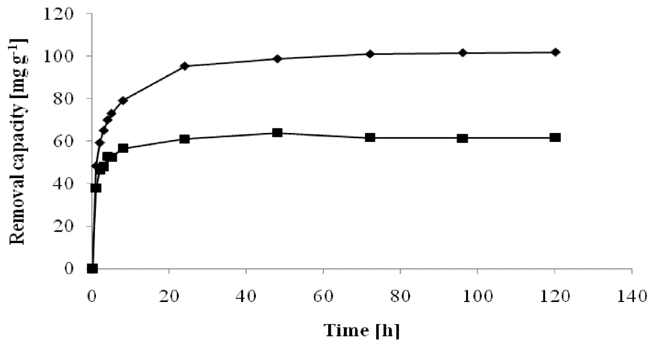

Figure 2: Hexavalent (♦) and total chromium (■) removal capacity variation profiles.

Volumetric rates of Cr(VI) and total chromium removal diminished rapidly during the first hours of contact, the decrease was then slower and subsequently changes in volumetric rates were negligible (Fig. 3). These results indicate that Cr(VI) reduction and chromium biosorption processes were very fast during the first hours of contact after which they gradually became slower due to the exhaustion of functional groups responsible for Cr(VI) reduction and chromium sorption.

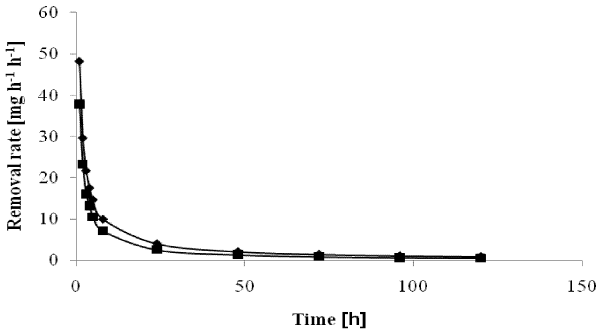

Figure 3: Variation of volumetric rate of hexavalent (♦) and total chromium (■) removal with respect to contact time.

3.2 Chromium biosorption kinetics modeling

In order to determine the mechanism of chromium biosorption onto avocado shell, pseudo-first order and pseudo-second order kinetic models were used to assay experimental data.

The pseudo-first order kinetic model is expressed as follows (Febrianto et al., 2009):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (9)$$

where q_e and q_t are the adsorption capacities (mg g^{-1}) at equilibrium and at time t (h), respectively, and k_1 is the rate constant of the pseudo-first order adsorption (h^{-1}). The integrated and linear form of equation (9) is the following:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (10)$$

The pseudo-second order kinetic model is expressed as follows (Febrianto et al., 2009):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (11)$$

where k_2 is the rate constant of second-order biosorption (g mg^{-1} h^{-1}).

The integrated and linear form of equation (11) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (12)$$

where $k_2 q_e^2$ is the initial sorption rate (h, mg g^{-1} h^{-1}).

The pseudo-first-order model rendered the lowest correlation coefficient (R^2 = 0.856) and predicted a chromium biosorption capacity at equilibrium (q_e = 39.88 mg g^{-1}) that was not in good agreement with the experimental value (exp q_e = 61.67 mg g^{-1}). These results indicate that the pseudo-first order model is inadequate for modeling chromium biosorption kinetics onto Hass avocado shell. In contrast, the pseudo-second order model satisfactorily described the experimental kinetic data (Fig. 4). This tendency comes as an indication that the rate-limiting step in biosorption of chromium ions onto Hass avocado shell is a chemical sorption (chemisorption) involving valence forces through the sharing or exchange of electrons between sorbent and sorbate, complexation, coordination and/or chelation (Febrianto et al., 2009). This model has

been successfully applied to describe the adsorption of metal ions (Nikazar et al., 2008b), among which is included chromium (Nikazar et al., 2008a).
The chromium biosorption capacity at equilibrium predicted by the pseudo-second-order model (q_e = 60.98 mg g^{-1}) was not significantly different (P < 0.05) to that obtained experimentally (exp q_e = 61.67 mg g^{-1}). The initial biosorption rate (*h*) and rate constant (k_2) of the pseudo-second-order model were 243.90 mg g^{-1} h^{-1} and 0.066 g mg^{-1} h^{-1}, respectively.

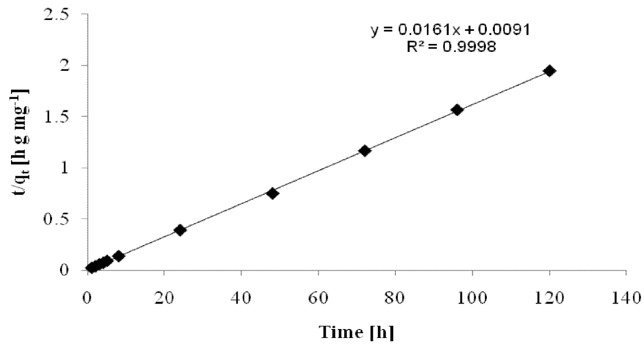

Figure 4: The fitting of pseudo-second order kinetic model for the biosorption of chromium ions onto Hass avocado shell.

4. Conclusions

The present study indicates that the shell of Hass avocado could be used as an effective and environmentally friendly biomaterial for the removal of Cr(VI) and total chromium from aqueous solutions.

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