



## Reduction of Cr (VI) levels in solution using bracken fern biomass: Batch and column studies

Marta López-García, Pablo Lodeiro, José L. Barriada\*, Roberto Herrero, Manuel E. Sastre de Vicente

Departamento de Química Física e Ingeniería Química I, Facultad de Ciencias, Universidad de A Coruña, Rúa da Fraga nº 10, 15008, A Coruña, Spain

### ARTICLE INFO

#### Article history:

Received 14 July 2010

Received in revised form 9 September 2010

Accepted 12 September 2010

#### Keywords:

Bracken fern

Cr (VI)

Cr (III)

Reduction

Adsorption

Kinetic

Fixed bed-column

### ABSTRACT

This paper proposes an alternative method to the treatment of effluents contaminated with Cr (VI) based on the interaction of Cr solution with bracken fern biomass. Cr removal from solution is due to a combined process of reduction and adsorption by natural biomass of bracken fern. The mechanism consists of a first step of Cr (VI) reduction to Cr (III) and the subsequent complexation of Cr (III) cations by the polymers present in the cell wall of the vegetable biomass. Kinetic studies reveal that Cr (VI) is completely reduced, and the kinetic model used allows calculating rate coefficients for different initial Cr (VI) concentrations. Adsorption experiments showed that bracken fern has a maximum adsorption capacity of  $1.60 \text{ mmol g}^{-1}$ . Column experiments allow proposing a practical application and also select optimal working conditions. Column experiments yielded good results in the removal of Cr (VI) at pH 2 and Cr (III) at pH 5.

© 2010 Elsevier B.V. All rights reserved.

### 1. Introduction

Chemical contamination of water from wide range of toxic derivatives, in particular heavy metals, is a serious environmental problem owing to their potential toxicity for humans. Increasing quantities of chromium compounds have been used in anthropogenic activities and introduced into the environment as a consequence of its wide use in modern industries, mainly in electroplating and tanning factories. The effluents from these industries contain chromium on its most common oxidation states on aqueous phase, Cr (VI) and Cr (III). These two Cr forms exhibit very different toxicity; Cr (III) is an essential nutrient required for sugar and fat metabolism, it has a very large safety concentration range, though large amounts of it can cause allergic skin reactions and cancer [1]. On the other hand, Cr (VI) is highly active and very dangerous due to its carcinogenic and mutagenic properties. Consequently, the removal of Cr (VI) from industrial wastewater has attracted much interest.

Chemical treatment of chromium waste water is usually conducted in two steps [2]. In the first step Cr (VI) is reduced to Cr (III) by use of a chemical reducing agent. Sulphur dioxide, sodium bisulphite and sodium metabisulphite are commonly used as reducing agents. Following reduction of Cr (VI), sodium hydroxide or lime is added to the wastewater to precipitate Cr (III). This procedure produces large quantities of solid sludge containing toxic chromium

compounds with high cost of disposal and even a possibility of ground water contamination [3].

A method consisting of reduction coupled with adsorption constitutes an eco-friendly and cost effective alternative to the existing treatments [4]. Sorption by natural materials is due to metabolism independent mechanisms. It is based on the physicochemical reaction that occurs between metal ions and polymeric components of dead biomass. This process includes several chemical mechanisms, among others adsorption, ion exchange and covalent bonding with functional groups of the polymers present in the cell wall [5,6]. A sorbent can be assumed as low cost if it requires little processing, it is abundant in nature or it is a by-product or waste material from another industry. Potential adsorbent materials can be found among easily available biomass types such as algae, fungi, agricultural waste products, etc. The common feature of all the mentioned materials is the presence of natural biopolymers in their structure, such as alginate, chitin/chitosan, pectin or lignin. These biopolymers represent an interesting and attractive alternative as adsorbents because of their particular structure, physicochemical characteristics, chemical stability and selectivity towards metals, which is a result of the presence of carboxyl, hydroxyl, sulphate, acetamide or amino groups in the polymer chains [7–10].

Little is known about bracken fern (*Pteridium aquilinum*) properties as adsorbent, only a few papers dedicated to the adsorption of different metals like mercury [11], cadmium and lead [12], or Cr (III) [13].

Regarding to chromium, there is a great amount of papers devoted to chromate anions biosorption by different kinds of organic materials. Recently, several authors [14–23] and specially

\* Corresponding author. Tel.: +34 981167000x2199; fax: +34 981167065.  
E-mail address: [jbarriada@udc.es](mailto:jbarriada@udc.es) (J.L. Barriada).

the extensive work by Park et al. [24–27] have demonstrated that the interaction of Cr (VI) anions with organic matter is mainly a redox process. That is, the elimination of Cr (VI) pollution by biomass is due to the reduction of Cr (VI) anions to Cr (III) cations. Moreover, X-ray photoelectron spectroscopy studies demonstrate that the oxidation state of chromium bound to the biomaterials is mostly or totally in its trivalent form [26]. Hence, the elimination of Cr (VI) pollution by biomass is due to the adsorption coupled with reduction of Cr (VI) and not a simple adsorption process on the biomass surface.

This study presents equilibrium and kinetic data on Cr (VI) remediation by use of bracken fern. Parameters affecting Cr (VI) removal like pH, initial metal concentration and contact time were studied. Kinetic studies were fitted to the advanced kinetic model proposed by Park et al. [28]. Column experiments were also carried out in order to determine the best operational conditions for a practical application.

## 2. Experimental methods

### 2.1. Materials

Reagents used were NaOH, KOH, NaNO<sub>3</sub>, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> from Merck (Merck, Darmstadt, Germany, pro analysis, p.a.). K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> p.a. from Panreac (Panreac Química S.A., Barcelona, Spain). All solutions were prepared with deionised water.

Sun dried bracken fern (*P. aquilinum*) was collected in Galicia (NW Spain) ground with an analytical mill (IKA A 10, Werke GmbH & Co. KG, Staufen, Germany) and sieved to obtain particles of 0.5–1 mm diameter.

### 2.2. Chromium analysis

Cr (VI), Cr (III) and total Cr in solution were measured. A standard colorimetric method was employed to determine Cr (VI) concentration that remains in solution. This procedure measures only hexavalent chromium by reaction with 1,5-diphenylcarbazide in acid solution [29]. A red-violet complex is formed and measured spectrophotometrically at 540 nm (Cary 100 Bio UV-visible, Varian, Palo Alto, CA, USA). Total Cr concentration in solution was determined by oxidation of the sample containing Cr (III) in a 705 UV digester (Metrohm, Herisau, Switzerland) during 120 min in order to ensure that all chromium species were present as Cr (VI). Afterwards, Cr (VI) concentration was determined as mentioned above.

### 2.3. Effect of pH on metal removal

The dependence of chromium removal with the pH of the solution was studied through batch experiments in the pH range 1–6. For this purpose, 0.1 g of bracken fern were placed in conical flasks with 40 mL of chromium solution (100 mg L<sup>-1</sup>), prepared by dissolving K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in deionised water. The mixtures were stirred on a rotary shaker at 175 rpm for 24 h at room temperature. The pH was adjusted by addition of NaOH and H<sub>2</sub>SO<sub>4</sub> (Merck p.a.) solutions. Chromium concentration in solution was determined as mentioned in Section 2.2.

### 2.4. Kinetic studies

The experiments were done in a thermostatically controlled vessel (25.0 ± 0.1 °C) where 0.25 g of bracken fern and 100 mL of Cr (VI) solution (50, 100, 200 and 500 mg L<sup>-1</sup> concentration) were mixed with agitation. Biomaterial was placed in contact with water during approximately 12 h before starting experiments because bracken fern does not get wet fast.

Kinetic studies were carried out at pH 2 and pH 4. pH of the solutions was fixed by addition of NaOH or H<sub>2</sub>SO<sub>4</sub> solutions as required. In this case, only Cr (VI) was determined by taking aliquots periodically and analysing them.

The content of equivalent organic compounds per unit gram of biomass represented by C<sub>OC</sub><sup>\*</sup>, was calculated as indicated by Park et al. [28]. For that purpose, 200 mL of Cr (VI) solutions were placed in contact with 0.01 mg of biomass in conical flasks and stirred on a rotary shaker at 175 rpm until Cr (VI) concentration did not change (42 days).

### 2.5. Adsorption isotherms

For equilibrium studies, several chromium solutions with concentrations ranging from 20 to 1000 mg L<sup>-1</sup> were made by dilution of a stock solution, obtained by dissolving K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in deionised water. The experiments were performed in 100 mL conical flasks containing 0.1 g of bracken fern and 40 mL of the metal solution. The mixtures were agitated on a rotary shaker at 175 rpm at constant room temperature during a period of time long enough to achieve equilibrium (24 h at pH 2 and 7 days at pH 4). NaOH and H<sub>2</sub>SO<sub>4</sub> solutions were used to adjust pH to 2 and 4. The amount of metal sorbed at equilibrium, Q, was calculated from the equation:

$$Q = \frac{V \times (C_i - C_e)}{m_s} \quad (1)$$

where V is the volume of the metal solution, C<sub>i</sub> is the initial concentration of total Cr in solution (equal to Cr (VI) initial concentration), C<sub>e</sub> is the equilibrium concentration of total Cr in solution, measured after Cr (III) oxidation and m<sub>s</sub> is the mass of sorbent (dry weight).

### 2.6. Column experiments

The experiments were carried out in a glass column of 40 cm length and 3 cm of internal diameter filled with 30.00 g of dried bracken fern. A filter was attached at the bottom of the column to ensure a uniform inlet flow and to support the biomass, followed by a layer of glass beads (1 mm diameter) of 3 cm height. Bracken fern was mixed with glass beads in order to obtain a good liquid distribution into the column. Another glass beads layer was placed on the top of the column to avoid the loss of biomass and also ensure a closely packed arrangement.

Solutions were fed through the bed in up-flow mode at 10 mL min<sup>-1</sup> flow rate with a peristaltic pump (from Watson Marlow) connected at the bottom of the column. With this experimental conditions, 33 cm of bed depth and 10 mL min<sup>-1</sup> flow rate, the residence time was 23 min.

A column at pH 4 was studied in only one step. A 50 mg L<sup>-1</sup> Cr (VI) solution was fed through the column and samples were collected and analysed. This column was stopped when Cr (VI) concentration in the effluent remained constant.

A new column at pH 2 was previously conditioned in order to achieve this pH. Therefore, HNO<sub>3</sub> 0.1 M was passed through the column until a constant pH in the effluent was reached. A 50 mg L<sup>-1</sup> Cr (VI) solution was fed in up-flow mode. Samples were periodically collected and analysed to determine Cr (VI) and Cr (III) concentration. The operation of the column was stopped when Cr (VI) in the effluent remained constant and then the pH of the bed was readjusted to pH 5. This regenerated column was employed in the next step. A 30 mg L<sup>-1</sup> Cr (III) solution was fed through the column and samples were analysed to determine Cr (III) concentration.

Download English Version:

<https://daneshyari.com/en/article/151730>

Download Persian Version:

<https://daneshyari.com/article/151730>

[Daneshyari.com](https://daneshyari.com)