Chemical Engineering Journal 165 (2010) 517–523

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

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

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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 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.

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

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doi:10.1016/j.cej.2010.09.058

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, $NaNO_3$, HNO_3 and H_2SO_4 from Merck (Merck, Darmstadt, Germany, pro analysis, p.a.). $K_2Cr_2O_7$ 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^{-1}), prepared by dissolving $K_2Cr_2O_7$ 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_2SO_4 (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^{-1} 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_2SO_4 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^*_{OC}, 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^{-1} were made by dilution of a stock solution, obtained by dissolving $K_2Cr_2O_7$ 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_2SO_4 solutions were used to adjust pH to 2 and 4. The amount of metal sorbed at equilibrium, Q, was calculated from the equation:

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

where V is the volume of the metal solution, C_i is the initial concentration of total Cr in solution (equal to Cr (VI) initial concentration), C_e is the equilibrium concentration of total Cr in solution, measured after Cr (III) oxidation and m_s 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^{-1} 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^{-1} flow rate, the residence time was 23 min.

A column at pH 4 was studied in only one step. A 50 mg L^{-1} 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_3 0.1 M was passed through the column until a constant pH in the effluent was reached. A 50 mg L^{-1} 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^{-1} Cr (III) solution was fed through the column and samples were analysed to determine Cr (III) concentration.

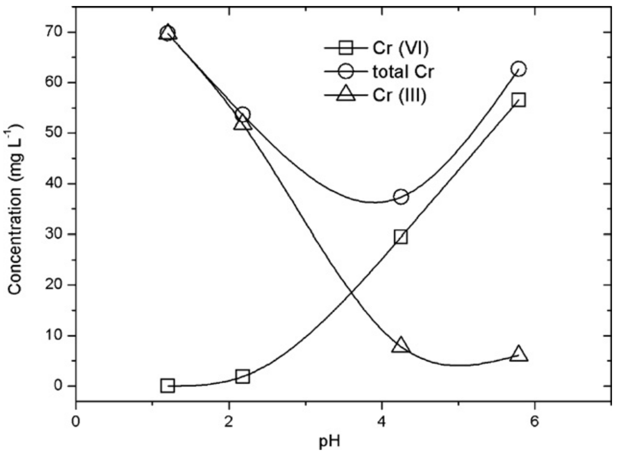

Fig. 1. Influence of pH on chromium concentration on solution for aqueous suspension of bracken fern in deionised water at 25 °C and C_i 100 mg L^{-1} and fern dosage 2.5 g L^{-1}. Contact time: 24 h.

3. Results and discussion

3.1. Effect of pH on metal adsorption

pH dependence experiments were carried out in order to determine the optimum pH for maximum removal of Cr (VI) by bracken fern. The influence of pH on metal removal by biomaterials is closed related to the ionic state of the active functional groups and to the solution chemistry of the metal. The main composition of bracken fern corresponds to a carbonaceous material with aromatic, hydroxyl, methoxyl and carbonyl functionalities. The major component in the dried biomass used as sorbent is most likely lignocellulosic material, the foremost constituent in the cell wall [30,31].

To study the solution chemistry of the metal, it is necessary to take into account that the initial Cr (VI) is reduced to Cr (III) in contact with the biomass, therefore two Cr oxidation states are present in solution simultaneously. It is important to consider this fact when chromium speciation is studied.

Hexavalent chromium exists primarily as chromic acid (H_2CrO_4), hydrogen chromate ion ($HCrO_4^-$) and chromate ion (CrO_4^-) depending on the pH. H_2CrO_4 predominates at pH less than 1.0, $HCrO_4^-$ at pH between 1.0 and 6.0, and CrO_4^- at pH above 6.0. Speciation diagram of Cr (III) shows that Cr^{3+} and $CrOH^{2+}$ are the predominant species up to pH 5.5. At higher pH values, different insoluble compounds could be formed. Cr (III) and Cr (VI) are involved in two different processes, adsorption and reduction, which take place due to the organic compounds present on the biomass surface.

Fig. 1 shows the influence of pH on chromium concentration on solution after 24 h of contact time with biomass. Both Cr (VI) and Cr (III) were affected by solution pH, Cr (III) concentration decreases when pH increases and Cr (VI) removal improves with decreasing pH.

To explain this behaviour, it can be considered that the electron-donor groups of the biomass reduce Cr (VI) to Cr (III). After that, Cr (III) forms complexes with biomaterials or stays in the aqueous phase. In the aqueous phase, Cr (III) will be present as a mixture of the inorganic cations previously mentioned but most likely also forming organic complexes with molecules released into the solution from the biomass in dynamic equilibria. At low pH, a large amount of protons can be easily coordinate with the acidic and amino groups making the biomass surface more positive. These conditions do not only allow the interactions with the anionic species of Cr (VI) but also make Cr (VI) reduction more favourable due to the high proton concentration. Low pH values enhance the redox reaction since the protons take part on it, as the following reactions demonstrate, all of them presenting positive standard potentials:

$$CrO_4{}^{2-} + 8H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O \qquad E^0 = 1.48\,V$$

$$HCrO_4{}^- + 7H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O \qquad E^0 = 1.35\,V$$

$$H_2CrO_4 + 6H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O \qquad E^0 = 1.33\,V$$

When solution pH increases, the biomass surface becomes less positive. Less positive biomass surface charge of the biomaterial implies lower Cr (VI) removal from the aqueous phase.

As it is shown on Fig. 1, Cr (III) behaviour is opposite to Cr (VI). Removal of Cr (III) is due to an adsorption process. Hence the increase in chromium adsorption from pH 1 to pH 6 can be explained by the change in the anionic state of the acid functional groups involved in binding the cationic species of this metal.

Electrostatic interactions can be explained studying the sorbent point of zero charge, pH_{pzc}. Potentiometric mass titration technique has been adapted to determine the pH_{pzc} for bracken fern [32,33]. Point of zero charge is defined as the pH at which the sorbent surface charge takes a zero value. In order to determine pH_{pzc}, different titration curves were obtained for several amounts of sorbent. Equilibrium pH values were plotted as a function of volume of acid added to obtain the potentiometric curves. pH_{pzc} was identified as the intersection point of the potentiometric curves with a blank titration. pH_{pzc} for bracken fern is 4.1.

The point of zero charge determines the surface charge of the sorbent at a given pH and its knowledge provides information about the possible electrostatic interactions between sorbent and chemical species of a metal. At pH_{pzc} the charge of the positive surface sites equal to that of the negative ones. Determination of pH_{pzc} allows to know the ionisation of functional groups and their interaction with metal species in solution [33].

Cr (VI) species interact with the biomass at pHs lower than the pH_{pzc} due to the high proton concentration and hence positive charge of the biomass. On the other hand, at a pH higher than the pH_{pzc}, more groups carry a negative charge and the positively charged Cr (III) ions can be bound, reducing the electrostatic repulsion and increasing the metal uptake. Therefore, adsorption of Cr (III) is favoured at high pH values but a previous step of reduction is required, so it is necessary to choose a pH where both reduction and adsorption can carry on.

As can be seen in Fig. 1, pH near 4 exhibits the best values for total Cr removal. For that reason pH 4 was selected as a compromise pH and isotherms were carried out adjusting solution pH to this value. Experiments were also studied at pH 2, where time needed to reach the equilibrium is shorter than at pH 4.

The elimination percentage can also be calculated using the following equation:

$$E\ (\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad (2)$$

where C_f is the final concentration (at t = 24 h).

At low pH, the percentage of Cr (VI) eliminated is near to 100%, this value become lower when pH increases and reaches the minimum value at pH 6. For Cr (III) the best removal percentages are observed at high pH reaching 94% at pH 6. When total Cr is evaluated, the best elimination percentage is 63% for a pH value close to 4.

3.2. Kinetic studies

Kinetic experiments are necessary to determine the time required for equilibrium to be reached. As mentioned above, two processes take place on solution. Kinetics of the reduction of Cr (VI) in contact with bracken fern biomass were studied at different Cr (VI) concentration and at two different pH values.

Kinetic model proposed by Park et al. [25] was used to study Cr (VI) reduction. It was observed that Cr (VI) was completely reduced to Cr (III) by the biomass and it was considered that Cr (VI) reduction is an irreversible reaction.

Reduction of Cr (VI) is due to single organic compounds present in the biomass, so the mechanism proposed is:

$$OC + \mathrm{Cr\,(VI)} \rightarrow OC(\mathrm{oxidized}) + \mathrm{Cr\,(III)} \qquad (3)$$

The rate coefficient for this reaction is k' and OC represents any organic compound.

At constant pH, the reduction rate of Cr (VI) by a single organic compound is:

$$\frac{d[\mathrm{Cr\,(VI)}]}{dt} = -k'[OC][\mathrm{Cr\,(VI)}] \qquad (4)$$

It was expected that the reduction of Cr (VI) by any single organic compound in the biomass would follow a similar rate equation. If these reactions take place in parallel, then the overall reduction rate of Cr (VI) by the biomass, R, is simply the sum of these individual reactions.

$$R = \frac{d[\mathrm{Cr\,(VI)}]}{dt} = \left(-\sum_{i=1}^{n} k_i[OC_i]\right)[\mathrm{Cr\,(VI)}] \qquad (5)$$

where k_i and $[OC_i]$ are the rate coefficient and the concentration of organic compound i in the biomass, respectively.

A new overall rate coefficient k can be defined by:

$$k = \sum_{i=1}^{n} k_i f_i \qquad (6)$$

where f_i represents the equivalent fraction of organic component, i, on the total concentration of organic compounds $[OCs]$.

$$f_i = \frac{[OC_i]}{[OCs]} \qquad (7)$$

A new rate equation related to total organic compound it is obtained, similar to Eq. (4):

$$\frac{d[\mathrm{Cr\,(VI)}]}{dt} = -k[OCs][\mathrm{Cr\,(VI)}] \qquad (8)$$

where k depends on the fraction or composition of the single organic compounds in the biomass.

It was suggested that the reduction rate equation of Cr (VI) by the biomass was first-order dependent with respect to both Cr (VI) and organic compounds. Therefore, the reduction rate of Cr (VI) will decrease with time due to the depletion of Cr (VI) and the reduced reactivity of the organic compounds as they become oxidized. Thus, the oxidation of the organic compounds that reduce Cr (VI) must be considered.

For a certain time, the concentration of organic compounds that reduce Cr (VI) is:

$$[OCs] = [OCs]_0(1 - X_{oxi}) \qquad (9)$$

X_{oxi} presents the fraction of the organic compounds oxidized, and can be calculated as follows, when considering equivalent reactions between the OCs and the Cr (VI):

$$X_{oxi} = \frac{\Delta[\mathrm{Cr\,(VI)}]}{[OCs]_0} = \frac{[\mathrm{Cr\,(VI)}]_0 - [\mathrm{Cr\,(VI)}]}{[OCs]_0} \qquad (10)$$

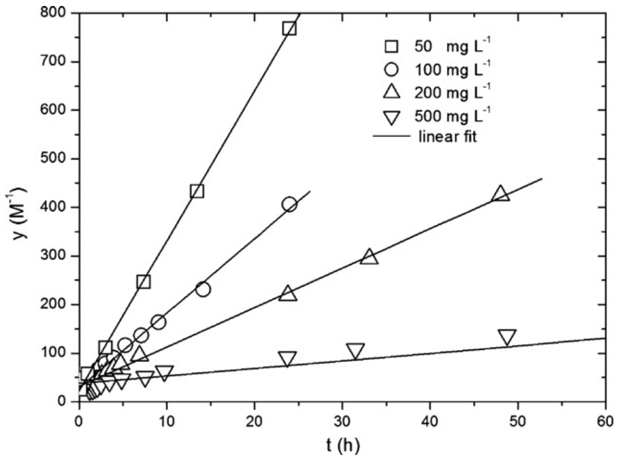

Fig. 2. Plot of y versus time t, according to Eq. (13), for Cr (VI) reduction experiments at pH 2 and 25 °C, fern dosage 2.5 g L^{-1}.

$[OCs]_0$ is the initial equivalent organic compounds capable of reducing Cr (VI) which is calculated as follows:

$$[OCs]_0 = C^*_{OC}[B] \qquad (11)$$

where $[B]$ is the biomass concentration and C^*_{OC} indicates the content of equivalent organic compounds per unit gram of biomass. C^*_{OC} was determined experimentally and its value was 4.86 mmol g^{-1} for bracken fern.

Combining Eqs. (8)–(10) and integrating the resulting equation yields an equation in the general form, as follows:

$$y = kt \qquad (12)$$

where

$$y = \frac{\ln(([\mathrm{CrVI}]_0([OCs]_0 - [\mathrm{CrVI}]_0 + [\mathrm{CrVI}]))/((OCs)[\mathrm{CrVI}]))}{[OCs]_0 - [\mathrm{CrVI}]_0} \qquad (13)$$

At constant pH and temperature, a plot of y versus time, t, should yield a straight line with slope, k, i.e. the rate coefficient of the redox reaction.

It has been found that increasing the pH from 2 to 4, the time required for total Cr (VI) reduction varies from 1 to 7 days. For a Cr (VI) initial concentration of 100 mg L^{-1} and a biomass dosage of 2.5 g L^{-1} it is also observed that Cr (VI) is completely reduced if contact time is long enough.

Data fittings to the kinetic model allow calculating y values for batch experiments at pH 2 and plot them against time (Fig. 2). These curves are nearly linear, indicating a good fitting to the proposed model; the regression coefficients obtained were high, as can be seen in Table 1.

It was observed that the rate coefficient is not constant at pH 2. This fact can be explained taking into account that the model proposed considers that the rate coefficient depends on the fraction or composition of the organic compounds. The biomaterial used in this study presents a high number of functional groups involved on Cr (VI) reduction. These functional groups have different reduction rates, so when k is interpreted by Eq. (6) the different individual terms depend strongly on the initial Cr (VI) concentrations. At

Table 1
Fitting parameters for Cr (VI) reduction according to Eq. (13) for bracken fern at pH 2.

Concentration	pH	k (M^{-1})	r^2
500 mg L^{-1}	2	1.5 ± 0.1	0.96
200 mg L^{-1}	2	8.1 ± 0.1	0.9990
100 mg L^{-1}	2	15.0 ± 0.3	0.998
50 mg L^{-1}	2	30.9 ± 0.2	0.9990

Table 2
Adsorption isotherm models.

Isotherm	Equation	Number of fitting parameters
Langmuir	$Q=\frac{Q_{max}\cdot b\cdot C_e}{1+b\cdot C_e}$	2
Freundlich	$Q=K_f\cdot C_e^{1/n}$	2
Langmuir–Freundlich	$Q=\frac{Q_{max}\cdot(b\cdot C_e)^{1/n}}{1+(b\cdot C_e)^{1/n}}$	3

low Cr (VI) concentration the fraction corresponding to the fastest reducing rate groups will be the predominant, and it will decrease as Cr (VI) concentration increases. Hence, considering the sum of individual rate coefficients, the overall rate it is not necessarily a constant.

Therefore, large variations in the kinetic rate constant can be related to the heterogeneity of functional groups that constitutes the biomass surface. If the biomaterial presented a little amount of oxidizable groups or close similar oxidation rate constants, the slopes obtained would be more similar than those obtained with a heterogeneous biomass.

3.3. Adsorption isotherms

Adsorption isotherms were studied in order to determine the affinity between sorbent (biomass) and sorbate (metal), and its distribution in the liquid and solid phases. Equilibrium data analysis and its modeling allows predicting metal biosorption. The metal uptake (Q) values were calculated by use of Eq. (1). Table 2 shows the different adsorption isotherm models used in this work to fit the experimental data obtained for bracken fern. Q_{max} represents the maximum metal adsorption capacity and b is an affinity constant: a high value indicates a steep desirable beginning of the isotherm reflecting the high affinity of the biosorbent for the sorbate [34]. n is an empirical parameter that varies with the degree of heterogeneity and K_f relates to biosorption capacity.

Before describing equilibrium for Cr (VI) biosorption, it is necessary to take into account that the equilibrium solution contains both Cr (VI) and Cr (III). For this reason, isotherms are drawn based on total Cr concentration eliminated from solution. Isotherms are shown in Fig. 3 where only Langmuir–Freundlich fits are included.

Table 3 shows the fitting parameters obtained for the Langmuir, Freundlich and Langmuir–Freundlich models for Cr (VI) elimination by bracken fern at pH 2 and 4. Langmuir–Freundlich model provides the best fitting. It can also be observed that experimental data follow Langmuir model adequately. Q_{max} allows comparing fern adsorption capacity with the optimum adsorption capacity of other materials. Some examples of maximum adsorption capacities for different kind of biomass and metals are summarised in Table 4.

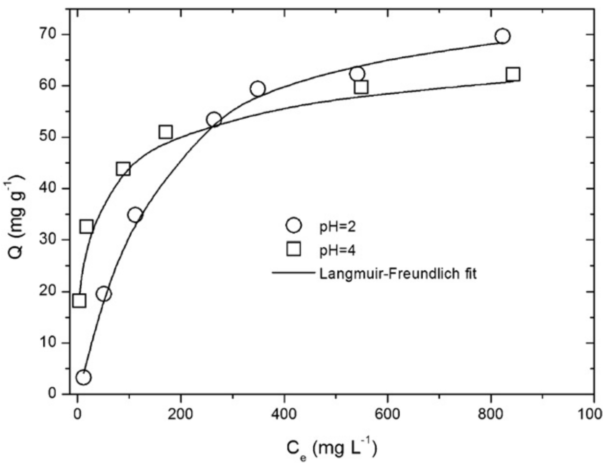

Fig. 3. Total Cr uptake as a function of metal concentration for suspensions of bracken fern (2.5 g L^{-1}) in deionised water at pH 2 (equilibrium time 24 h, circles) and 4 (equilibrium time 7 days, squares).

Table 3
Fitting parameters for the isotherm models shown in Table 2 for total Cr (Cr (VI) and Cr (III)) uptake by bracken fern at pH 2 and 4 at 25 °C.

Model	pH	Q_{max} (mg g^{-1})	K_f	b (L mg^{-1})	n	r^2
Langmuir	2	83 ± 3		0.0064 ± 0.0007		0.995
	4	58 ± 3		0.07 ± 0.02		0.92
Langmuir–Freundlich	2	76 ± 3		0.008 ± 0.001	0.8 ± 0.2	0.998
	4	79 ± 7		0.02 ± 0.01	2.2 ± 0.3	0.996
Freundlich	2		4 ± 2		2.4 ± 0.4	0.94
	4		18 ± 2		5.2 ± 0.6	0.97

As it can be seen in Table 4 maximum uptake values achieved with bracken fern, 1.60 mmol g^{-1} using Langmuir–Freundlich fit, are higher than that reported for other materials such us coffee or tea dust. Bracken fern also was tested as biosorbent with Cd, Pb or Hg; for these metals Q_{max} values are lower than that obtained for Cr (VI). Hence, bracken fern can be considered as a good alternative to eliminate Cr (VI) from solution.

3.4. Column experiments

Column studies were performed by two different ways in order to select the best alternative to a possible application in decontamination of Cr (VI) polluted waters. Batch experiments indicate that pH 4 is the optimal pH for the removal of total chromium, so the first study was carried out at this pH. It also has been proved that pH 2 shows the best conditions for fastest Cr (VI) reduction, for this reason another experiment was designed in order to eliminate Cr (VI) by reduction at pH 2. Subsequently, Cr (III) formed during reduction was eliminated by adsorption at pH 5.

Therefore two alternatives for Cr (VI) removal are proposed using a fixed-bed column: (a) a column in only one step, at pH 4, where both Cr (VI) and Cr (III) were removed from solution by bracken fern. (b) A column used in two steps, a first stage, at pH 2, where Cr (VI) is reduced to Cr (III) and then a second step, at pH 5, where the solution containing Cr (III) obtained in the first stage is feed through the same bed.

These two alternatives were tested. It must be noted that breakthrough point was established as the time necessary to reach the 1% of initial chromium concentration in the inlet effluent.

Results obtained in the experiment at pH 4 are represented in Fig. 4. It can be noted that Cr (VI) concentration shows a sharp rise reaching a plateau close to 40 mg L^{-1} in about 1.5 h. Breakthrough point cannot be determined in this case because 1% of the initial concentration was already achieved at time close to zero. Cr (III) concentration in the effluent was not significant.

For column experiments at pH 2 experimental results are showed in Fig. 5. This plot shows the evolution of Cr (VI) and Cr (III) concentration with time. Given the behaviour for Cr (VI),

Table 4
Maximum metal uptake for different biomaterials.

Biomass	Metal	Q_{max} (mmol g^{-1})	Reference
Tea dust	Cr	0.86	[35]
Coffee dust	Cr	0.75	
Bracken fern	Cr	1.60	This study
Bracken fern	Cd	0.41	[12]
Bracken fern	Pb	0.41	
Bracken fern	Hg	0.32	[11]
Sargassum muticum	Hg	1.03	
Exhausted coffee grounds	Hg	0.20	

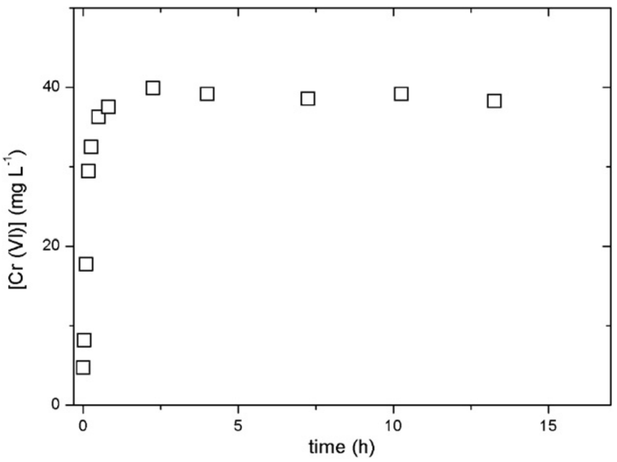

Fig. 4. Breakthrough curve for Cr (VI) biosorption (initial concentration 50 mg L^{-1}) by bracken fern (30 g) and constant flow rate (10 mL min^{-1}). pH at the inlet solution: 4 and pH at the outlet solution: 5.4–5.6.

breakthrough point was attained in 36 h so about 30 L of water contaminated with Cr (VI) can be treated under this conditions. It must be noted that the process responsible of Cr (VI) removal at this pH is the reduction. Therefore, as it can be seen in Fig. 5, Cr (III) from reduction appears in the effluent right in the beginning. Cr (III) concentration increases up to about 30 mg L^{-1}. At this moment the maximum reduction capacity is reached, the groups capable to reduce Cr (VI) to Cr (III) are exhausted, so Cr (VI) concentration starts to increase and Cr (III) concentration decreases. The outlet solution obtained before breakthrough point contains about 30 mg L^{-1} of Cr (III). A fresh solution of the same concentration was used as feed solution for the next step of the treatment in order to obtain the full breakthrough curve.

The oxidized bed column from the first step of reduction was reused to eliminate the Cr (III) from the effluent obtained. To carry out this process the solution containing 30 mg L^{-1} of Cr (III) was feed through the bed column. Based on previous batch experiments the pH of the effluent was maintained at 5.00. The breakthrough curve can be seen in Fig. 6. The breakthrough point is achieved at 1.18 h so 0.70 L of metal free effluent is obtained. From 1.18 h to 75 h Cr (III) concentration in solution steadily rises until the curve reaches a plateau where Cr (III) concentration in the effluent remains constant at 80% of initial metal concentration.

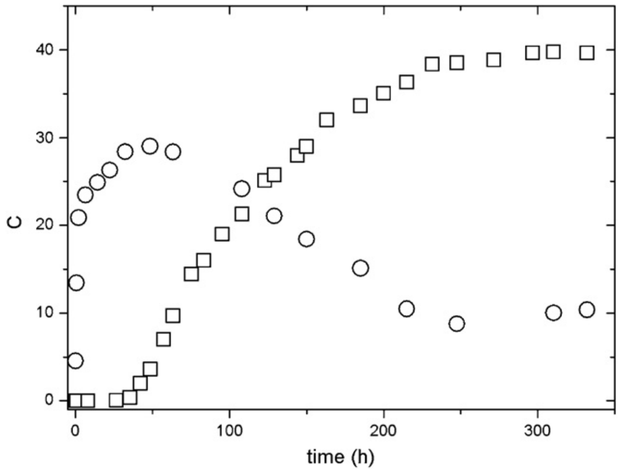

Fig. 5. Breakthrough curve for Cr (VI) reduction (initial concentration 50 mg L^{-1}) by bracken fern (30 g) and constant flow rate (10 mL min^{-1}). *C* (mg L^{-1}) represents the Cr (VI) concentration (squares) and Cr (III) concentration (circles) in the effluent. pH at the inlet and outlet: 1.8–2.0.

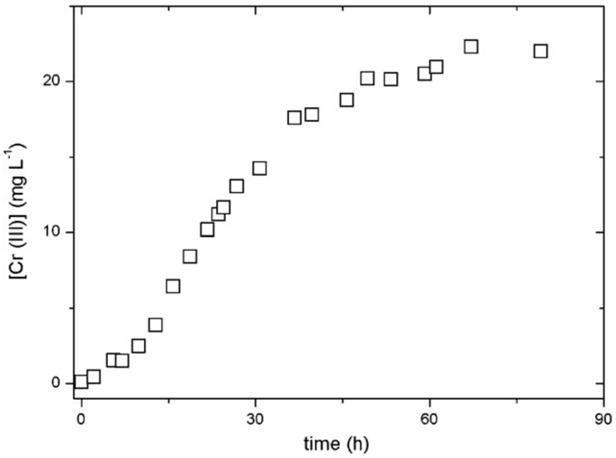

Fig. 6. Breakthrough curve for Cr (III) adsorption (initial concentration 30 mg L^{-1}) at by bracken fern (30 g) and constant flow rate (10 mL min^{-1}). pH at the inlet solution: 5.2 and pH at the outlet solution is: 4.0–4.2.

Column experiments maintained a constant final concentration around 80% of initial chromium concentration. This fact can be explained taking into consideration that biosorption includes a large number of processes and not only adsorption, so Cr (III) in contact with the biomass can suffer other forms of elimination such as precipitation. For this reason 100% of initial metal concentration was not observed in the effluent when the maximum in the breakthrough curve was attained.

After data analysis, the two alternatives proposed can be compared to choose the best choice for Cr (VI) removal.

As it can be seen in batch experiments, pH 4 seemed to be the best conditions for chromium remediation, but in continuous flow conditions it was observed that at this pH fixed bed-columns do not have practical interest. Initially a small amount of oxidizable groups were capable of reducing Cr (VI) but in only 1.5 h they were all exhausted. Hence, in a short period of time, Cr (VI) concentration in the effluent was considerable.

At pH 2, bed-column is capable of reducing Cr (VI) during 36 h. The second step, readjusting the bed-column pH, also was effective to remove Cr (III). Hence this method results efficient for total Cr removal using the same biomass in two steps. Moreover this procedure gave very good results regarding the Cr (VI) elimination, which is the most important problem associated to Cr contamination due its high toxicity. Therefore, the alternative consisting in two steps is selected as the one that provides better results in total Cr elimination.

4. Conclusions

Results obtained in this study allow evaluating the potential use of bracken fern as chromium sorbent. The analysis of the behaviour of bracken fern indicates that it can be used as a sequestering agent for chromium. It has been demonstrated that Cr removal is due to a reduction coupled with adsorption process, strongly dependent on pH. pH 4 was selected as a compromise pH for maximum total Cr removal in batch processes.

Kinetic studies demonstrate that Cr (VI) can be removed totally from solution if contact time is long enough. We can conclude that Q_{max} for bracken fern is similar or even higher than maximum adsorption capacity of materials such as coffee or tea dust.

Column experiments shows that a combined process of reduction of Cr (VI) at pH 2, followed by Cr (III) adsorption at pH 5 gave good results for total Cr elimination.

Acknowledgements

The authors wish to thank Ministerio de Educación y Ciencia for financial support through the research project CTM2006-03142/TECNO and Xunta de Galicia through the project PGDIT06TAM00401CT. P. Lodeiro gratefully acknowledges financial support through Angeles Alvariño project AA 10.02.56B.44.0 (from Xunta de Galicia) co-funded by 80% with European Social Funds.

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