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Grape Stalks Wastes Encapsulated in Calcium Alginate Beads for Cr(VI) Removal from Aqueous Solutions

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Abstract: In this study, a low-cost effective adsorbent based on grape stalks encapsulated in calcium alginate beads was investigated as a possible sorbent for the removal of Cr(VI) from aqueous solution. The present paper deals with the procedure for the preparation of calcium alginate beads and the encapsulation of grape stalks powder into calcium alginate beads, the characterization of these beads and the study of their behavior on Cr(VI) adsorption from aqueous solutions. The influence of grape stalks powder concentration in the calcium alginate beads, metal solution pH, sodium chloride, and metal concentration on metal removal has been studied. Uptake showed a pH-dependent profile. Maximum Cr(VI) sorption was achieved at pH 3.0. High NaCl concentrations significantly reduce the mechanical resistance of the beads, however, this does not have a significant effect on metal removal. Langmuir and Freundlich isotherms were used to describe sorption equilibrium data. The experimental data were fitted better by the Langmuir adsorption isotherm. The Langmuir adsorption capacity for calcium alginate beads containing 2% (w/v) grape stalks powder was found to be 71.98 10^{-3} mg/bead ($\approx$225 mg Cr(VI)/g grape stalks).

Keywords: Adsorption, Chromium, Calcium alginate, Vegetable waste

INTRODUCTION

The use of dead biosorbents for removal of toxic heavy metals from waste streams has emerged as an alternative to the existing

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methods as a result of the search for low-cost, biodegradable, innovative methods.

Recently, biosorption of hexavalent chromium using grape stalks wastes has been reported (1). Metal sorption was found to be pH-dependent and maximum sorption (59.8 mg Cr(VI)/g dry sorbent) was found at initial pH 3.0. In view to a possible application of grape stalks wastes as chromium adsorbent in environmental technology, it is evident that the use of these wastes in their native form is not practicable for large-scale process utilization, i.e., the fragility of these residues due to their low mechanical strength provokes losses of adsorbent, their relatively low density renders difficult their separation from the liquid stream (2). In addition, their either nonuniform and nonspherical shape makes difficult to model the adsorption process. The entrapment of these wastes in a polymeric matrix would partially or completely solve all the above mentioned problems and would enable grape stalks wastes to be used in continuous flow processes for the Cr(VI) decontamination of waste streams. In other words, encapsulation provides better morphology, processability, and mechanical properties (3). On the other hand, the use of dead biomass to remove metals from aqueous solutions has advantages over the use of alive biomass as dead biomasses do not need nutrients and are resistant to the physical-chemical properties of heavy metal solutions.

The use of calcium alginate as encapsulation gel material has been used extensively because the technique is simple, biocompatible, and low cost. Alginate is a linear block copolymer of α-D-mannuronic acid and α-L-guluronic acid. It forms hydrogels in the presence of divalent ions, except for Mg^{2+} and Hg^{2+} (4). When the carboxylic groups are replaced by metal ions, alginate beads are formed. During the last years, divalent metals removal by using different biomass entrapped in calcium alginate beads, i.e., bacteria (5), algae (6), and humic acid (7), has been widely investigated. Nevertheless, literature on Cr(VI) removal by biomass encapsulated in calcium alginate is scarce. Niyogi et al. (8) and Bai and Abraham (2) studied Cr(VI) removal by fungal biomass encapsulated in calcium alginate and other gel matrices.

The objective of this paper is to obtain the basic information for the design of Cr(VI) sorption process using grape stalks powder encapsulated in calcium alginate beads, i.e., optimal concentration of grape stalks in the beads, sorption kinetic data, capacity, performance in different testing conditions: pH, ionic strength, desorption.

EXPERIMENTAL

Materials and Solutions

Grape stalks wastes were kindly supplied by a wine manufacturer of the Empordà-Costa Brava region, Girona, Spain. The wastes were first cut into small pieces, then rinsed three times with distilled water and finally dried in an oven at 110°C until constant weight. Once dried, the waste particles were sieved and the smallest ones were ground to get a fine powder ($<500\,\mu m$). Alginic acid, sodium salt from brown algae purchased from Fluka (Switzerland) was used as the hydrocollodial gelling material. As fixing solution a calcium chloride ($CaCl_2 \cdot 2H_2O$) solution was used. Chromium solutions were prepared by dissolving appropriate amounts of potassium dichromate ($K_2Cr_2O_7$) in distilled water. 0.1 M HCl and NaOH solutions were used for pH adjustment. NaCl was used as the ionic medium. For desorption experiments, HCl and NaOH solutions within the concentration range (10^{-6}–10^{-1} M) were used. These reagents were analytical grade and were purchased from Panreac (Barcelona, Spain). Chromium standard solution of 1000 mg L^{-1}, purchased from Carlo Erba (Milano, Italy), was used for Atomic Absorption calibrations.

Preparation of the Beads

A 1% (w/v) Na-alginate solution was prepared by solving 1 g of sodium alginate into 100 mL distilled water at a temperature of about 65°C. Then, the gel was allowed to cool down at room temperature and the desired amount of grape stalks powder was added to the gel with continuous stirring. Once the mixture was homogeneous it was forced through a micropipette tip by a peristaltic pump. The resulting gel droplets were collected in a stirred reservoir containing 200 mL of a chemical "fixing" solution of 0.1 M $CaCl_2$. The beads were allowed to harden in this solution for 24 h. After this time hard spherical beads containing different percentage (w/v) of grape stalks were obtained. The beads were filtered and rinsed several times with distilled water to remove calcium chloride ions from the bead surface. They were then stored in distilled water until their use. When calcium alginate beads were used as a blank, the same procedure as before was followed but in this case there was no addition of grape stalks powder. The experimental setup for beads production can be seen in Fig. 1. The different beads will be named as CA (calcium alginate beads) and X%GS-CA [beads containing different percentage (X) of grape stalks encapsulated in calcium alginate].

Characterization of the Beads

Some characteristics of calcium alginate (CA) beads and calcium alginate containing 2% of grape stalks beads (2% GS-CA), i.e., diameter, density, water content, weight swelling ratio (WSR), and mechanical resistance, were determined. The results are presented in Table 1.

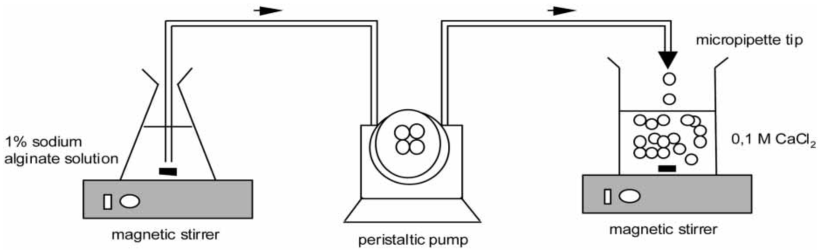

Figure 1. Encapsulation experimental setup.

Bead Diameter

The beads were observed under a stereoscopical microscope (Nikon SMZ1000). Different groups of beads were photographed by attachment of a digital camera (Nikon Coolpix 950). The diameter of the beads in different directions was measured directly on the photographs. Calibration of the image and definition of bead characteristics was achieved by a photograph in the same condition of a size calibration standard for optical microscopy. Ten digital images containing 10–15 beads were examined and the average diameter and standard deviation were determined. In Fig. 2, digital images of CA and 2%GS-CA beads are presented.

Water Content and Weight Swelling Ratio (WSR)

Dry weight of 40 beads was determined after the spheres were dried for 4 days at room temperature until a constant weight was reached. For beads' wet weight determination, 40 filtered beads were placed on a cellulose filter paper for 1 minute and weighted immediately after. The average of five dry and wet weight determinations, as well as the standard deviations, was determined. The weight swelling ratio (WSR) relative to the dry beads was estimated by the weight ratio of wet and dried beads.

Table 1. Characteristics and physical properties of CA and 2% GS-CA beads

Properties	CA beads	2% GS-CA beads
Bead diameter (mm ± SD)	3.139 ± 0.138	3.127 ± 0.228
Bead density (mg/mL ± SD)	0.911 ± 0.012	1.182 ± 0.021
Water content (% ± SD)	98.13 ± 2.20	94.90 ± 1.01
WSR ± SD	53.67 ± 0.23	19.64 ± 0.66
Mechanical resistance (N/bead ± SD)	0,057 ± 0.08	0.045 ± 0.06

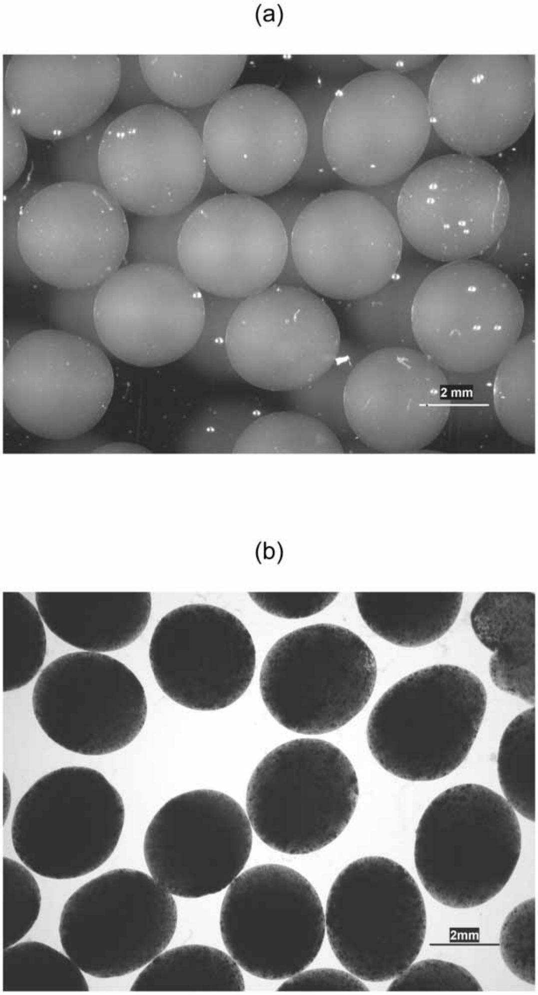

Figure 2. Digital photographs of (a) CA beads and (b) 2% GS-CA beads.

Mechanical Resistance

The mechanical resistance of the beads was determined using a Texture Analyser (TA-XTS2i, Stable Micro Systems, England) as the mean force (newtons) necessary to generate a 20% compression of a bead placed under a cylinder probe P10 (Batch 2370, Stable Micro Systems, England). The mechanical resistance of beads was expressed in newtons (N) per bead instead of the conventional Young modulus since it is very difficult to monitor the evolution, with the compression path, of the contact area between the beads and the piston (3). Compression experiments were carried out on 20 beads and the average values and standard deviation were calculated.

Use and Preservation of the Beads

Preliminary experiments were performed in order to check the convenience or not of using dry alginate beads instead of gel alginate beads. It is evident that the use of dry beads presents some advantages: measurements of the mass to be used in the experiments are more accurate and beads are more rigid and have higher mechanical strength. On the other hand, it has been reported that dry alginate beads showed more favourable uptake of metal ions than the gel type beads (9). Therefore, in some experiments, gel and dried 2% GS-CA beads were used to investigate in which conditions the beads showed the best performance in Cr(VI) sorption (results not shown). Results indicated that metal uptake rate is higher when gel beads are used. Since gel beads contain mostly water ($\geq$95%) mass transport is determined by diffusion in water and the contact of metal ions and grape stalks is more favored than in dry beads. In addition, as expected, dry beads lost their sphere shape, increased their rigidity, and after swelling (in contact with the aqueous solution) they did not recover the sphere shape, and the grape stalks powder was not homogeneously distributed into the bead. Consequently, once the different beads were obtained following the procedure indicated they were stored in Milli-Q water for further use in sorption experiments.

Metal Uptake Procedure

Batch experiments were conducted by putting into contact 40 beads with 10 or 15 mL of different aqueous Cr(VI) solutions in stoppered glass tubes. The tubes were shaken at 25 rpm in a rotary mixer (Cenco Instrument) until equilibrium was reached. Then, the beads were filtered through a 0.45 mm cellulose filter paper (Millipore Corporation). After filtration, the pH of the remaining aqueous solutions was measured using a Crison Model Digilab 517 pH meter. Initial chromium concentration as well as the metal concentration in the filtrates was determined by Flame Atomic Absorption Spectrometry (FAAS) using a Varian Absorption Spectrometer, Model SPECTRAA 220FS. The adsorbed metal concentration was obtained from the difference between initial and final metal concentration in solution. The percent removed was calculated as $\%R = [(C_i - C_{eq})/C_i) \times 100]$, where, C_i and C_{eq} are the initial and final equilibrium metal concentration in solution, respectively. Initial metal concentration was 20 mg L^{-1} when the influence of grape stalks content in the calcium alginate beads, and 10 mg L^{-1} when the pH and the NaCl concentration on chromium uptake were investigated. In order to investigate the influence of grape stalks content on chromium removal, calcium alginate beads containing different percentage of grape stalks powder within the range 0.25–2.5 % (w/v) were produced. For these experiments, two different chromium solutions were tested with the different beads obtained. The initial pH of one of these solutions was adjusted, at pH 3.2 while the pH of the other solution was not adjusted, resulting in an initial pH 5.1.

The effect of pH on Cr(VI) removal was studied by varying the chromium solution's initial pH within the range 1.0–10.0 pH units. Once the initial pH was adjusted to the desired pH no efforts were made to maintain the solution pH while the sorption process was on.

The effect of ionic strength on metal removal was studied by varying initial NaCl concentration within the 0.1–1.0 mol L^{-1} range. In this case, the initial pH of chromium solution was adjusted at pH 3.0.

In order to study the influence of Cr(VI) initial concentration on metal uptake by calcium alginate beads containing 2% grape stalks and to obtain the isotherms, initial metal concentration was varied within the range 10–1000 mg L^{-1}. For these experiments 40 beads were put into contact with 15 mL of Cr(VI) solutions whose pH was adjusted at pH 3.0. Since the alginate matrix was also identified as a good metal adsorbent (9, 10), similar experiments were performed to clarify the capacity of calcium alginate beads for Cr(VI) uptake in the same experimental conditions.

Desorption experiments were carried out by treating 40 of Cr(VI)-loaded beads (after gentle washing with distilled water) with 10 mL of solutions of different concentration of either HCl or NaOH for 24 h. In all sets of experiments each test was carried out in duplicate, and the average results are presented in this work.

RESULTS AND DISCUSSION

Effect of Grape Stalks Content in the Calcium Alginate Beads

In order to investigate the grape stalks percentage of the calcium alginate beads that gave the best sorption yields, calcium alginate beads containing different percentage of the biomaterial were obtained and their efficiency on metal uptake was determined. The experiments consisted of putting into contact for 24 h 40 beads containing different amount of grape stalks encapsulated in calcium alginate with 20 mg L^{-1} chromium solutions adjusted at initial pH 3.2 and chromium solutions at pH 5.1 (no pH adjustment). In Fig. 3, the percentage of metal removal has been plotted vs. the percentage of grape stalks content in the calcium alginate beads for the two initial

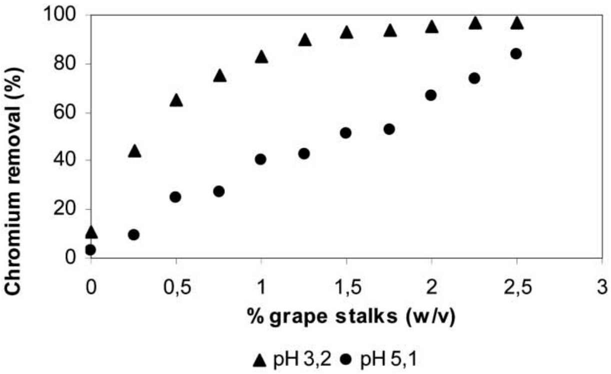

Figure 3. Chromium removal percentage as a function of grape stalks content in calcium alginate beads at two different initial pHs (3.2 and 5.1). Initial Cr (VI) concentration: 20.0 mg/L. Beads concentration: 40 (X% GS-CA) beads/10 mL. Contact time: 24 h.

studied pHs. As can be seen the maximum uptake was obtained when using initial pH 3.2 and concentration of grape stalks in the beads around 2%. It must be pointed out that grape stalks concentrations higher than 2% provoked the loss of the beads spherical shape. This is the reason why a concentration of 2% of grape stalks in the beads was assumed suitable for subsequent sorption experiments. The same percentage of biomass was used by Niyogi et al. (8) and Bai and Abraham (2), when studying Cr(VI) removal by immobilized biomass of *Rhizopus arrhizus* and *Rhizopus nigricans* in calcium alginate, respectively.

Effect of Contact Time

Before undertaking the study of Cr(VI) sorption on 2% GS-CA beads, preliminary experiments were carried out in order to ascertain the contact time that was necessary to achieve the equilibrium state characterized by unchanging sorbate concentration in the solution. Experiments were performed stirring in different tubes 40 (2% GS-CA) beads with 15 mL of 100 mg L^{-1} of metal solution at initial pH 3.0. Samples were drawn at predetermined intervals of time for chromium analysis. In Fig. 4 the percentage of metal removed by the beads vs. contact time is shown together with variation of final pH. It can be seen that the major sorption took place during the first hour, the process was completed after 20 h, and the curve became flattened. It can also be seen that during the first hour of contact pH evolved from pH 3.0 to neutral pH values and after this time no changes in

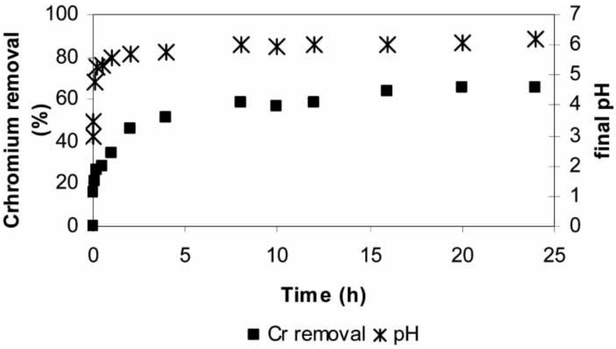

Figure 4. Chromium removal percentage and evolution of pH as a function of contact time. Initial Cr (VI) concentration: 100.0 mg/L. Initial pH: 3.0. Beads concentration: 40 (2% GS-CA) beads/10 mL.

final pH were observed. However, a shaking time of 24 h was used in all further sorption experiments to ensure equilibrium. Other authors using biomass entrapped in calcium alginate for chromium removal found similar sorption kinetics (8).

Effect of pH

It has been reported that pH is a very important parameter controlling hexavalent chromium sorption process. To study the influence of this parameter on chromium sorption by grape stalks encapsulated in calcium alginate beads, initial pH was varied from 1.0 to 10.0 units. In Fig. 5, the percentage of

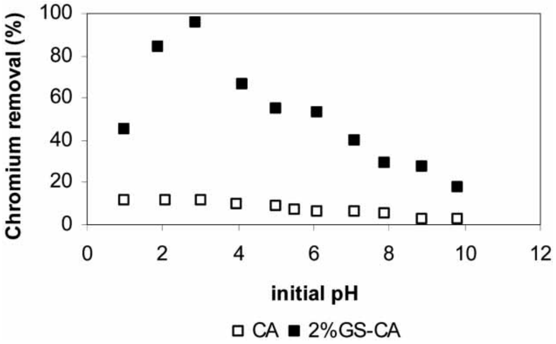

Figure 5. Chromium removal percentage as a function of initial pH. Initial Cr(VI) concentration: 10.0 mg/L. Beads concentration: 40 beads/10 mL. Contact time: 24 h.

Cr(VI) removed by 2% GS-CA beads vs. initial pH has been plotted. As shown, for an initial metal concentration of 10 mg L^{-1}, metal uptake increased with increasing pH solution from 1.0 to 3.0 where the maximum uptake (97%) took place. When pH was increased above pH 3.0 the percent removal decreased. Recently, we have reported the same trend and the same optimal adsorption pH when studying Cr(VI) adsorption on grape stalks wastes (1). Optimal pHs around pH 2.0–3.0 have been reported by other authors when studying hexavalent chromium adsorption on peat moss (11), on activated carbon (12). Also, Niyogi et al. (8) and Bai and Abraham (2) reported pH 2.0 as optimal pH for Cr(VI) removal by immobilized biomass in calcium alginate beads. The solution chemistry of chromate shows that at acidic pH (1.5–3.5) the predominant species of Cr(VI) in solution are $HCrO_4^-$ and $Cr_2O_7^{2-}$ (13). On the other hand, it has been reported that even after the formation of calcium alginate beads the structure of this biopolymer leaves free carboxylic groups which can react with metal ions (9) and that the complete dissociation of the functional groups may be taking place at pH around 4.5. Fourest and Volesky (14) reported the apparent dissociation of alginic acid to be $K = 10^{-4}$. The literature also shows that the pK values of guluronic acid and mannuronic acids are 3.65 and 3.38, respectively (15). Taking into account all these reported data about alginates and alginic acid, it might be supposed that the calcium alginate surface is charged positively at pH below 2.5, neutral at pH around 3.0–3.5, and negatively charged at pH higher than 4.0. Thus, if electrostatic attraction was the main mechanism governing Cr(VI) sorption by 2% GS-CA beads, a decrease in pH should lead to an increase of metal sorption. Conversely, as indicated before, an increase of initial pH from 1.0 to 3.0 favored metal uptake. As Chen et al. (16) suggest that calcium alginate beads can be treated as analogues to complex ligands in solution, in addition to possible electrostatic attractions, complexation of metal by GS-CA beads surface functional groups should be considered as another possible mechanism for Cr(VI) uptake that would explain the increase of metal adsorption observed. Up to pH 3.0 value the decrease of Cr(VI) uptake would be explained by the electrostatic repulsion since beads surface is negatively charged. Similar behavior was found in chromium adsorption by CA beads. Results plotted in Fig. 5 show that metal removal percentage by CA was around 11% within the initial pHs (1–3) and decreased when increasing pH. It is evident that in this study the real mechanism or mechanisms involved in Cr(VI) uptake by either calcium alginate and grape stalks encapsulated in calcium alginate has not been elucidated. In addition to the supposed metal ion uptake mechanisms, i.e., surface complexation and ion exchange, Cr(VI) reduction followed by precipitation has been reported to play a role in the hexavalent chromium removal by several biomaterials (17, 18). The last possible mechanism of Cr(VI) reduction to Cr(III) is now being investigated in our laboratory.

Sorption Isotherms

Equilibrium sorption experiments resulted in adsorption isotherms which were fitted by the noncompetitive Langmuir model:

$$q = \frac{q_{\max} b\, C_e}{1 + b\, C_e} \tag{1}$$

where q is the amount of sorbate adsorbed by the sorbent (mg per bead), $q_{\max}$ is the maximum metal uptake by the sorbent (mg per bead), C_e is the equilibrium concentration of sorbate in solution (mg L^{-1}), and b is the Langmuir constant related to energy of sorption (L mg^{-1}) which reflects quantitatively the affinity between the sorbent and the sorbate. The evaluation of the specific uptake q was performed according to equation:

$$q = V(C_i - C_e)/40 \text{ beads} \tag{2}$$

where V(L) is the volume, C_i and C_e (mg L^{-1}) are the initial and unadsorbed concentrations of the metal ion at equilibrium. Equation (1) can be linearized as:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}} C_e + \frac{1}{q_{\max} b} \tag{3}$$

Equilibrium sorption data were also fitted by Freundlich isotherm model:

$$q = K C_e^{1/n} \tag{4}$$

where q is the amount of sorbate adsorbed per unit mass of sorbent (mg per bead), C_e is the sorbate concentration remaining in solution at equilibrium (mg L^{-1}), and K and n are empirical constants indicative of sorption capacity and sorption intensity, respectively. Equation (4) can be linearised as:

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e \tag{5}$$

The Langmuir model parameters ($q_{\max}$ and b) and the Freundlich model constants (K and n) were obtained by fitting the experimental data, corresponding to chromium sorption by CA and 2% GS-CA beads, to the linearized Eqs. (3) and (5), respectively. These parameters and constants as well as the correlation coefficient are presented in Table 2. If we calculate the ratio between the maximum Cr(VI) adsorbed by 2% GS-CA and CA beads, it results that the maxium uptake by the 2% GS-CA (71.98×10^{-3} mg Cr(VI)/bead) is around 3.5 folds higher than the uptake by CA beads. Nevertheless, it must be taken into account that in our calculations the contribution of calcium alginate on the metal uptake is overestimated, as for approximately

Table 2. Langmuir and Freundlich isotherms parameters for chromium adsorption by CA and 2% GS-CA beads at pH 3.0

	Langmuir isotherm			Freundlich isotherm		
Beads	$q_{\max} \times 10^{-3}$ (mg/bead)	b (L/mg)	R^2	$K \times 10^{-3}$	$1/n$	R^2
CA	19.93	0.011	0.968	1.62	0.370	0.767
2.0% GS-CA	71.98	0.025	0.994	7.36	0.352	0.947

the same volume of bead in the 2% GS-CA beads part of the volume is occupied by grape stalks powder.

In order to check the effect of encapsulation on Cr(VI) removal by comparing the present results to our previously reported ones obtained by using grape stalks wastes in their native form (59.8 mg Cr(VI)/g GS) (1), the Langmuir maximum adsorption value found for 2% GS-CA beads (71.98×10^{-3} mg Cr(VI)/bead) must be referred to grams of grape stalks. Taking into account the number of obtained beads per gram of added GS powder by following the procedure indicated in the experimental section, the resulting maximum uptake is around 225 mg Cr(VI)/g GS, which implies an increase of four folds of native GS wastes capacity. Conversely, other authors who encapsulated fungal biomass in different polymeric matrix for Cr(VI) sorption found that free biomass possessed higher capacity than the immobilized biomass (2,8). In our case, it is obvious that the improvement in metal uptake is in great part due to the low particle size ($<500\,\mu$m) employed in this work compared to the (1.0–1.5 mm) particle size used in our previous work using native grape stalks. As known, adsorption increases when particle size decreases due to the major surface of the sorbent in contact with the sorbate. Nevertheless, it is also evident that encapsulation enables the possibility of working with such a small particle size that otherwise would provoke handling difficulties and loss of sorbent during the sorption process.

From the values obtained for Langmuir and Freundlich parameters, the theoretical curves were calculated. In Fig. 6, the experimental data of chromium sorption and the respective Langmuir and Freundlich isotherms for CA and 2% GS-CA beads are plotted. We can observe that data points have a good compliance with the calculated Langmuir isotherm curves. The applicability of the Langmuir model to the experimental data indicates monolayer coverage on the beads surface by Cr(VI). Niyogi et al. (8) and Bai and Abraham (2) who studied Cr(VI) removal by fungal biomass entrapped in PVA and CA, respectively, found that experimental data were better fitted by Freundlich isotherm model.

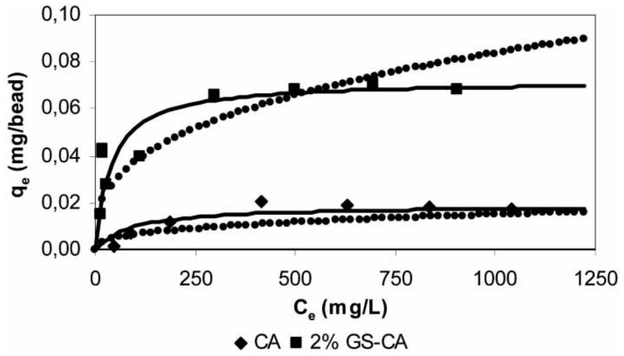

Figure 6. Fitting of the Langmuir (—) and Freundlich (····) isotherms models to the data gathered from the experiments (symbols) for chromium adsorption by CA and 2% GS-CA beads. Initial pH: 3.0. Beads concentration: 40 beads/15 mL. Contact time: 24 h.

Effect of Sodium Chloride Concentration

In order to study the effect of sodium chloride concentration of metal uptake, different NaCl concentrations in the 0–1.0 mol L^{-1} range were investigated. The obtained results are shown in Table 3. As can be seen, the presence of this salt did not provoke any significant decrease in sorption efficiency. This fact might indicate that chromate ions are not bonded on the charged surface by forming outersphere complexes through electrostatic attraction as changes in ionic strength strongly influence on adsorption processes through this mechanism (19). Nevertheless, it must be pointed out that after 24 h, the presence of NaCl concentrations higher than 0.5 mol L^{-1} provoked an important loss on the mechanical resistance of the beads that did not affect metal efficiency removal. These observations are in agreement with the ones reported in literature. Ibáñez and Umetsu (9) found that high ionic

Table 3. Influence of NaCl concentration on metal uptake by 2% GS-CA beads. Initial Cr(VI) concentration: 11.3 mg/L. Beads concentration: 40 beads/10 mL. Contact time: 24 h

[NaCl] (mol L^{-1})	Cr(VI) removal (%)
0.10	99
0.25	98
0.50	100
0.75	99
1.00	96

Table 4. Percentage of desorbed chromium from 2% GS-CA chromium-loaded beads after contact with different stripping solutions. Initial chromium concentration in beads: 4.4×10^{-3} mgCr/bead. Beads concentration: 40 beads/10 mL. Contact time: 24 h

Stripping solution		Desorption (%)
HCl	10^{-1} M	22
	10^{-2} M	3
NaOH	10^{-3} M	19
	10^{-4} M	3
	10^{-5} M	0
	10^{-6} M	0

strengths deteriorate the rigid structure of calcium and barium alginate beads in the course of a long time of contacting without affecting trivalent chromium uptake by the beads.

Desorption Experiments

From the results shown in Fig. 2, it might be expected that a change of pH could desorb the metal from the beads notably in basic pH conditions. Thus, HCl and NaOH solutions of different concentrations were tested to remove metal from Cr(VI)-loaded beads. After 24 h of contact with NaOH solutions within the concentration range 10^{-4}–10^{-2} M the structure of the beads was destroyed and the grape stalks were floating in the solution. The effect of OH^- ion on the hydrogen bound to the β-carbon resulting on the destruction of calcium alginate beads structure and generation of H_2O has already been reported (2, 9). The best desorption results (only 22% metal removal) were obtained with 0.1 M HCl concentrations. Similar results in acidic conditions were obtained by Bai and Abraham (2) when studying hexavalent chromium desorption from calcium alginates containing immobilized fungal biomass. From the obtained results, it is evident that additional experiments to investigate chromium desorption in order to reuse beads in cycles of sorption/desorption are not worthwhile, taking into account that the sorbent is low cost and biodegradable.

CONCLUSIONS

In this work, grape stalks wastes have been successfully encapsulated in calcium alginate beads and the performance in Cr(VI) removal from aqueous solution has been investigated. In the experimental conditions used, a composition of 2% (w/v) of grape stalks encapsulated in calcium alginate beads was found to be the most efficient for Cr(VI) removal. Metal adsorption by 2% GS-CA beads is pH-dependent and the maximum sorption was found to occur at initial pH 3.0. High NaCl concentrations significantly reduce the mechanical resistance of the beads; however, this does not have a significant effect on metal removal. Equilibrium isotherms fit Langmuir equation adequately, and maximum Langmuir adsorption is 71.98×10^{-3} mg Cr(VI)/bead.

The major contribution of this paper lies in the use of grape stalks wastes encapsulated in calcium alginate beads. Encapsulation provides grape stalks wastes with two advantages: they can be used in a powdered form which implies an increase of wastes capacity for metal removal, and they get the appropriated spherical and uniform shape to be used in continuous flow processes. In addition, the uniform shape of the sorbent particles (beads) is suitable for modeling studies. Finally, this work opens new opportunities for the fragile materials that are lately proposed as low-cost sorbents for decontamination of metal-containing effluents.

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