Removal of Cd (II) from aqueous solutions by batch and continuous process using chitosan sulfate dispersed in a calcium alginate hydrogel

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Eliminación de Cd (II) de soluciones acuosas por lote y proceso continuo usando sulfato de quitosano dispersado en un hidrogel de alginato de calcio

Eliminació de Cd (II) de solucions aquoses per lot i procés continu, fent servir sulfat de quitosà dispersat en un hidrogel d'alginat de calci

SUMMARY

A novel chitosan sulfate (ChS) which is insoluble at acidic pHs was synthesized and then dispersed in calcium alginate hydrogel beads to be used to remove Cd(II) from aqueous solutions at acidic pHs using a batch process and a continuous process. By batch wise experiments, it was found that the equilibrium adsorption capacity of the Alg-ChS beads increase with the increase in the initial concentration of Cd; however, the percentage of Cd removal decreased. The Freundlich model had the best fit to the experimental adsorption equilibrium data. The adsorption rate of Cd onto Alg-ChS beads followed the kinetic model of pseudo-second order and the time to reach equilibrium increased slightly with increasing initial concentration of Cd(II). The removal of Cd using a fixed bed column (continuous process) packed with the Alg-ChS beads had a much higher efficiency than the Batch process. An adsorption mechanism of Cd(II) onto the Alg-ChS beads was proposed using the FTIR, and XPS spectra of samples of Cd(II) adsorbed onto ChS and the mechanisms of adsorption of metals by alginate and chitosan proposed by other authors.

Keywords: Alginate; chitosan sulfate; permeation column; cadmium adsorption.

RESUMEN

Se sintetizó un novedoso sulfato de quitosano (ChS) que es insoluble a pHs ácidos y luego se dispersó en un hidrogel de alginato de calcio (Alg) para ser utilizado para eliminar Cd(II) de disoluciones acuosas a pHs ácidos usando un proceso discontinuo y un proceso continuo. En experimentos por lotes, se encontró que la capacidad de adsorción en equilibrio de las perlas de Alg-ChS aumentaba con el incremento de la concentración inicial de Cd; sin embargo, el porcentaje de eliminación de Cd disminuyó. El modelo de Freundlich tuvo el mejor ajuste a los datos experimentales de equilibrio de adsorción. La cinética de adsorción de Cd(II) con las perlas de Alg-ChS siguió el modelo cinético de pseudo-segundo orden, y el tiempo para alcanzar el equilibrio aumentó ligeramente con el aumento de la concentración inicial de Cd(II). Se encontró que la eliminación de Cd(II) utilizando una columna de lecho fijo (proceso continuo) empacada con perlas de Alg-ChS es mucho más eficiente que el proceso por cargas (discontinuo). Se propuso un mecanismo de adsorción de Cd(II) con las perlas de Alg-ChS tomando como base los espectros de FTIR

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y XPS de muestras de Cd(II) adsorbido por ChS y los mecanismos de adsorción de metales por alginato y quitosana propuestos por otros autores.

RESUM

Es va sintetitzar un nou sulfat de quitosà (CHS) que és insoluble a pH àcid i després es va dispersar en un hidrogel d'alginat de calci (Alg) per a ser utilitzat per eliminar Cd(II) de dissolucions aquoses a pHs àcids usant un procés discontinu i un procés continu. En experiments per lots, es va trobar que la capacitat d'adsorció en equilibri de les perles de Alg-CHS augmentava amb l'increment de la concentració inicial de Cd; però, el percentatge d'eliminació de Cd es reduïa. El model de Freundlich va tenir el millor ajust a les dades experimentals d'equilibri d'adsorció. La cinètica d'adsorció de Cd(II) amb les perles de Alg-CHS va seguir el model cinètic de pseudo-segon ordre, i el temps per assolir l'equilibri va augmentar lleugerament amb l'augment de la concentració inicial de Cd(II). Es va trobar que l'eliminació de Cd (II) utilitzant una columna de llit fix (procés continu) empacada amb perles de Alg-CHS és molt més eficient que el procés per càrregues (discontinu). Es va proposar un mecanisme d'adsorció de Cd (II) amb les perles de Alg-CHS prenent com a base els espectres de FTIR i XPS de mostres de Cd (II) adsorbit per CHS i els mecanismes d'adsorció de metalls per alginat i quitosà proposats per altres autors.

INTRODUCTION

Water contamination due to heavy metals has become a major problem due to its persistence, bioaccumulation and high toxicity. Water quality criteria when referring to heavy metals have to consider their environmental effects and consequence on living organisms [1] then, selective and efficient removal of heavy metals is necessary [2]. Cadmium is regarded as one of the most toxic metals along with lead and mercury [3,4]. The health organization (WHO) has recommended a maximum permissible limit of 5 μgL^{-1} of cadmium in blood [3]. Industrial effluents from metallurgical plants, manufacture of cadmium-based pigments, textile operations, plastic stabilizers, nickel-cadmium batteries, as well as effluents from treatment plants are considered sources of cadmium contamination [4]. For the removal of these metals from aquatic systems, different processes: ion exchange, chemical precipitation, coagulation, activated sludge, membrane technology or combinations of these methods have been used [2]; however, risks of generating secondary pollutants are associated with the majority of these methods. Removal of metal ions by adsorption using biomaterials reduces these risks [5,6]. Chitosan (Ch) is a biomaterial that has been used for the removal of cadmium ions [7–9] however; it is soluble in acidic pHs, which restricts its use. To be able to use the Ch in acidic media, it has been modified by crosslinking using glutaraldehyde, ethylene glycol, 1,4-butanediol or di-glycidyl ether [10], however, the number of amino groups decrease during the modification leaving fewer active groups for adsorption [11]. Alginate (Alg) is another biomaterial that has been used to remove metals from water, where the -COO⁻ group is the main responsible for the removal of the metal and to a lesser extent the OH group [12-14].

Recently we reported the obtaining of a partially sulfated chitosan without modifying the amine groups. This chitosan sulfate (ChS) was used for the removal of dyes from water solutions at acidic pHs in a batch process [15].

For the efficient and economical adsorption of metal ion from large volumes of wastewater, the process must be carried out continuously by using percolation columns; then it is necessary that the adsorbent be in particles of a given size and shape; small particles can cause a high-pressure drop or even column clogging [16]. The obtaining of the adsorbents in the form of beads represents an option for the packing of the columns.

In this work, a chitosan sulfate (ChS) which is insoluble at acidic pHs was synthesized to be used as an adsorbent to study its efficacy of removal of Cd(II) from aqueous solutions at acidic pHs using a batch process and a continuous process. However, because ChS is in the form of tiny particles, it cannot be used directly in an adsorption column because it would cause a high-pressure drop in the bed. To circumvent this problem, Alg-ChS hydrogel composites in the form of beads were used. Using the Alg-ChS beads as adsorbents, the kinetics and adsorption isotherm of cadmium at 25 ⁰C were investigated in a batch process. In addition, removal of Cd (II) was carried out using a fixed bed column (permeation column) packed with the Alg-ChS beads where the break point and the saturation point were determined.

EXPERIMENTAL

Materials

Chitosan sulfate (ChS) was synthesized in the Environmental Remediation Research Laboratory (CUCEI, UdeG) using a modification to the procedure reported by Rios et al.[17], Sodium alginate (Sigma-Aldrich, UK), Cadmium Chloride (Golden Bell), double distilled water. The beads were obtained using a Büchi Model 390 encapsulator; to feed the column with the cadmium solution a Masterflex 07557 peristaltic pump was used with Masterflex L/S 13 silicone hoses.

Characterization of chitosan sulfate

The ChS and the ChS-Cd were characterized by Fourier Transform Infrared Spectroscopy on a FTIR (Perkin Elmer) spectrometer and by X-ray Photoelectron Spectroscopy using a XPS (SPECS System, Berlin, Germany). The XPS spectra were obtained with

monochromatic Al Kα source (1486.6 eV) working at 400 W and a base pressure of 3E-9 mbar in the analytical chamber. The high-resolution scans were conducted with pass energy of 20 eV and step sizes of 0.2 eV. A flood gun source was used to compensate charge using 40.0 eV of emission and 2 eV of energy. The fitting was carried out with AAnalyzer 1.33 software [18]. The spectra fitting was adjusted with the main C1s peak at 284.8 eV due to the C-C bonding in the structure. The sulfur/nitrogen (S/N) ratio was quantified in an Elemental Analyzer, Leco TruSpec Micro Series (Missouri, USA). Sulfamethazine (Leco, Missouri, USA) was used as the standard reference. The analysis was carried out in triplicate.

The pka's, the protonable amino groups and the fraction of sulfated groups of ChS were determined by potentiometric titration following the method reported by Rios et al. [19], titration curves were obtained by titrating 0.2 g of ChS suspended in 8 mL of 0.1 M HCl with 0.1 M NaOH.

Preparation of the Alg-ChS beads

500 mL of a 1.5% aqueous solution of sodium alginate was prepared in a pressure bottle and were added 5 g of ChS (particle size less than 75 μm) under stirring to keep the ChS particles dispersed. The flask was connected to the Büchi encapsulation equipment and to obtain the beads the dispersion was passed through a nozzle of 1000 μm in diameter; a pressure of 276 bar, a frequency of 600 Hz and a voltage of 500 V were applied. The beads were collected in a 0.1 M solution of CaCl$_2$ and left for one hour in the solution so that the calcium ions diffused towards the inner part of the beads to harden them. They were then washed and stored in distilled water under refrigeration until use.

The morphology of the Alg-ChS beads was determined by microscopy (Digital microscope) and their average diameter by measuring 100 beads using a digital electronic calibrator.

To determine the amount of ChS in the pearls, 1.00 gram of beads was introduced into propylene centrifuge tubes, then 10 mL of 0.100 M sodium citrate solution was added [20]. The tubes were placed in a thermoshaker (MCR, AccesoLab) and shaken at 125 rpm the time required for the complete dissolution of the pearls. The tubes were centrifuged at 3200 RPM for 5 minutes, the liquid was discarded, and the precipitate was washed 3 times with distilled water and dried to constant weight in an oven at 50 °C. The amount of calcium alginate was determined by weighing five grams of beads and drying them in an oven at 60 °C to constant weight. The % of calcium alginate in the beads was obtained by:

$$\% A \lg = \frac{mass_{xerogel} - mass_{ChS}}{mass_{beads}} \, x \, 100 \qquad (1)$$

Batch Adsorption

Aqueous solutions were prepared at different concentrations (mg/L) of Cd(II) at pH= 5.0; the pH of the solution was adjusted using aqueous solutions of 0.1 M HCl and 0.1 M NaOH. To 15 mL propylene cen-trifuge tubes were added 10 mL of the Cd(II) solution and 1.0 g of Alg-ChS hydrogel beads to which the excess moisture was previously removed with blotting paper. Then the tubes were placed in a Thermoshaker (MCR, AccesoLab) maintaining the temperature at 25 °C under continuous agitation (125 RPM). At predetermined time intervals, a centrifuge tube was removed from the water bath and the aqueous phase solution was separated by decantation and analyzed by atomic absorption spectroscopy in a Varian SpectrAA 220 spectrometer at a wavelength of 228.8 nm to determine the residual concentration of Cd(II). The mass of cadmium adsorbed at time t, q_t, was calculated by equation (2). Sampling was continued until equilibrium was attained:

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad (2)$$

where C_0 is the initial concentration of Cd(II) (mg L^{-1}), C_t is the concentration of Cd(II) at time t (mg L^{-1}), V is the volume of the aqueous solution (10 mL), and m is the mass of Alg-ChS beads (g). Each run was carried out in triplicate, and the average result was reported.

Fixed Bed Column

The Alg-ChS beads to which the excess moisture was previously removed with blotting paper were packed in a glass column with an inner diameter of 1.8 cm and 33 cm in height. Approximately 47 g of Alg-ChS beads were used. The concentration of Cd(II) was 125 mg/L, the pH of the solution was 5.0. The Cd(II) solution was fed to the column at a flow rate of 100 mL/h. The concentration of Cd(II) at the exit was determined in a Varian SpectrAA 220 spectrometer at a wavelength of 228.8 nm.

RESULTS AND DISCUSSION

The ChS was obtained as an amber-colored solid, water insoluble in the pH range of 2-12 with molecular weight greater than 12,000 Da, and with a S/N ratio of 0.40.
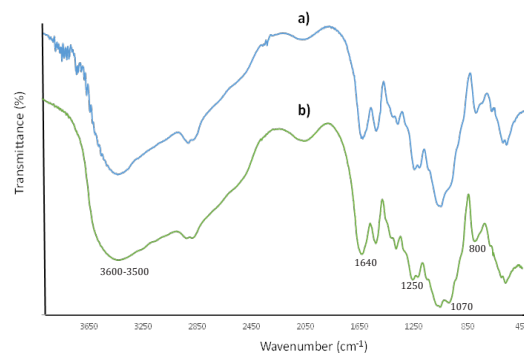

Figure 1. *FTIR spectra: a) ChS, b) ChS-Cd*

Figure 1a shows the ChS spectrum, where it can be observed a broad peak at 3600-3500 cm^{-1} due to the superposition of the stretching of the O-H and N-H groups, a peak at 1640 cm^{-1} due to the carbonyl group

and the pyranose ring signal at 1070 cm⁻¹, [19, 21, 22]. Also, peaks of C-O-S (800 cm⁻¹) and S=O (1250 cm⁻¹) are present confirming that the ChS was obtained

With the titration data, it was determined that the fraction of units with amino groups were about 88%, a value similar to the degree of deacetylation reported by the Ch supplier. The molar fraction of the amino groups of the sulfated units was about 0.324. Insolubility of the ChS was observed throughout the studied pH range (2-11). Applying the Hendersson-Hasselbalch equation, it was determined that pKa1 and pKa2 of ChS had a value of 5.85 and 8.18, respectively.

Characterization of Alg-ChS beads

The beads contained about 1% ChS and 3% of alginate. Figure 2 shows the morphology of the beads, where pearls are observed to be quasi-spherical, with a rough surface and with pores. The average diameter of the beads was of 2.06 mm, with a standard deviation of 0.273 mm.
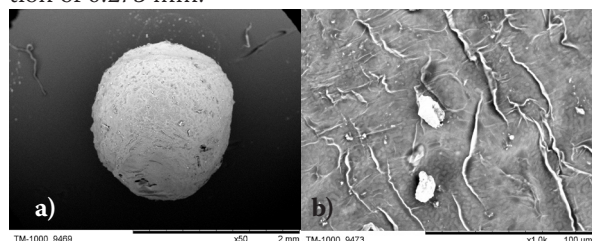

Figure 2. *Morphology of the Alg-ChS beads at an (a) x50 increment, and (b) x1.0k increment, where adsorbent particles can be observed.*

Figure 3 shows the adsorption kinetics of Cd(II) onto the Alg-ChS beads carried out at T= 25 °C, pH=5.0 and initial Cd(II) concentrations of 20, 50 and 114 mg/L. This Figure shows that the equilibrium adsorption capacity (q_e) increased as the initial concentration of the ion was augmented. The higher ion concentration gradient when using higher initial Cd(II) concentration (C_0) explains the q_e increase. Figure 3 also shows that the time to reach equilibrium increases slightly when raising the initial Cd(II) concentration, it was reported similar behavior on the adsorption of Cd(II) by cane bagasse [18].
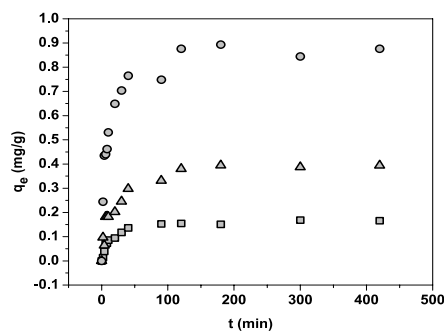

Figure 3. *Adsorption kinetics of Cd(II) onto Alg-ChS at 25 ⁰C. Initial concentrations of Cd(II); □ 20 mgL⁻¹, ○50 mgL⁻¹, △114 mgL⁻¹.*

To determine the adsorption kinetic´s order, the experimental data were adjusted to the Lagergren model (pseudo-first order):

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \qquad (3)$$

and to the Ho model (pseudo-second order):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}\, t \qquad (4)$$

where q_e is the amount of cadmium adsorbed at equilibrium (mg Cd/g of beads), q_t is the amount of cadmium adsorbed at time t (mg Cd/g of beads); k_1 and k_2 are the kinetic constants of the pseudo-first order and pseudo-second order models respectively.

Figure 4 shows that the pseudo-second order model best fits the experimental data for the adsorption kinetics of Cd(II) at C_o = 50 mg/L; similar results were obtained for the other two concentrations (20 and 114 mg/L). Table 1 displays that at all initial Cd(II) concentrations used the correlation coefficients (R^2) are closer to 1.0 and the calculated q_e values, are much nearer to the experimental data for the pseudo-second-order model than those for the pseudo-first-order model. Then, it is concluded that Cd(II) adsorption onto Alg-ChS follows the pseudo-second-order kinetic model indicating that the rate-limiting step might be by chemisorption by sharing or exchange of electrons between sorbent and sorbate [11].
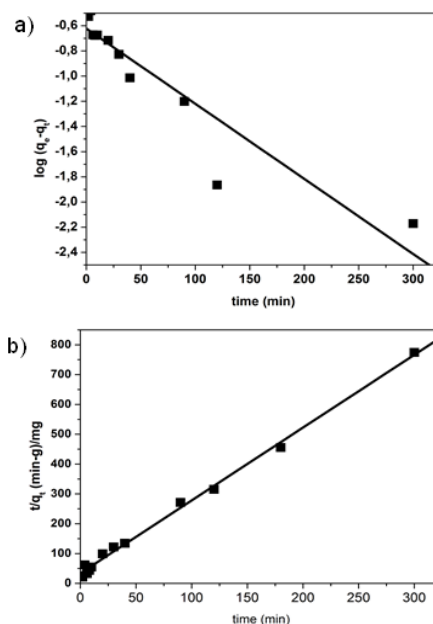

Figure 4. *Kinetics of adsorption of Cd(II) using Alg-ChS, t=25 ⁰C, C_0 0 50 mg/L. a)pseudo-first-order, b)Pseudo-second order*

Table 1. *Parameters of the kinetic models for the adsorption of Cd(II) onto Alg-ChS.*

	Pseudo-first-order				Pseudo-second-order		
C^0	$q^{e,exp}$	$q^{e,cal}$	$k^1 \times 10^2$	R^2	$q^{e,cal}$	$k^2 \times 10^4$	R^2
mg/L	mg/g	mg/g	1/min		mg/g	g/(min-mg)	
20	0.163	0.106	1.52	0.8176	0.171	0.449	0.9975
50	0.374	0.238	1.38	0.8674	0.406	0.202	0.9974
114	0.818	0.539	2.37	0.9542	0.900	0.195	0.9989

To obtain the equilibrium isotherm at 25 ^{0}C, aqueous solutions of Cd (II) with concentrations of 10, 20, 50, 114, 250, 700 and 3700 mg/L were used. The adsorption equilibrium data were fitted using the Langmuir and Freundlich isotherms. In the Langmuir isotherm (Eq. 5) a straight line is obtained by plotting $1/q_e$ versus $1/C_e$, where the y-intercept and the slope of this straight line are $1/q_m$ and $1/(K_L q_m)$, respectively.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \qquad (5)$$

C_e is the concentration of Cd(II) at equilibrium (mg L^{-1}), K_L is the Langmuir constant related to the affinity of binding sites (L g^{-1}), q_e is the amount of Cd(II) adsorbed at equilibrium (mg g^{-1}) and q_m is the maximum adsorption capacity of ChS (mg g^{-1}).

When fitting the data using the Freundlich isotherm (Eq. 6), plotting log qe versus log Ce results in a straight line with a slope of 1/n and the y-intercept is log KF. :

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (6)$$

where K_F is the Freundlich isotherm constant related to the adsorption capacity (mg$^{1-1/n}$ L$^{1/n}$ g^{-1}) and n is the intensity of adsorption.

Figure 5 displays linear graphs for both models where it can be observed that the Freundlich model has a better fit than the Langmuir model, and Table 2 shows that the correlation coefficient (R^2) is higher for the Freundlich model than that of the Langmuir model. Table 2 also indicates that the maximum adsorption capacity of the Alg-ChS hydrogel beads is 7.60 mg/g. However, as the bulk of the hydrogels was water, the combined adsorption capacity of the adsorbents (calcium alginate and ChS) was determined to be 190.0 mg/g of dry adsorbents (xerogel). Similar results have been reported for the adsorption of Cd(II) onto chitosan. Bamgbose et al. [8] reported that Cd(II) adsorption isotherm onto chitosan was better described by the Freundlich isotherm than for the Langmuir model and that the maximum adsorption of Cd(II) was greater than 100 mg/g. Klimiuk et al. [13] reported that the maximum adsorption of Cd onto a mixture of alginate and poly(vinyl chloride) was 176 mg/g. By gelation using aqueous sodium alginate it was found that the maximum adsorption capacity of Cd(II) of the gel was 179.0 mg/g of dry weight [12]. When a simulated wastewater containing was treated with an aqueous solution of a mixture 1:1 of sodium alginate and chitosan 1:1, 39.44 g of Cd(II)/g of dry adsorbents were adsorbed [14].
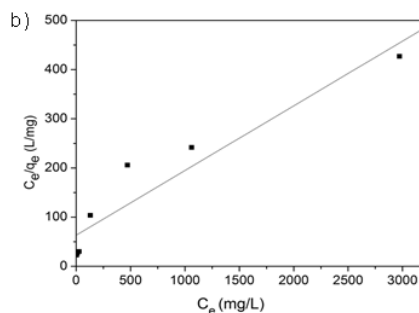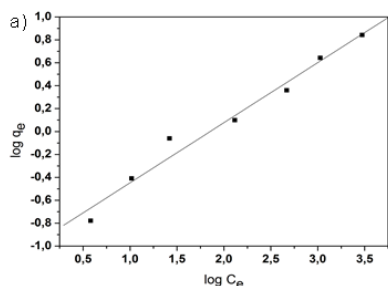

Figure 5. *Data fitting to the (a) Freundlich and (b) Langmuir models.*

Table 2. *Isotherm constants of the Langmuir and Freundlich models for adsorption of Cd(II)*

T (°C)	pH	Freundlich			Langmuir		
		K_F (mg$^{1-1/n}$ L$^{1/n}$/g)	n	R^2	q_m (mg/g)	K_L (L/mg)	R^2
25	5.0	0.106	1.90	0.975	7.6	9.39x10^{-3}	0.899

Adsorption Mechanism

Metal ions can interact with the calcium alginate by an ion exchange reaction by replacing the protons of the COOH group [13] and by the formation of complexes between metal cations and ligands of the alginate [12, 23, 24]. It has been reported that the ion exchange reaction between metal ions and calcium ions of the calcium alginate contribute to metal adsorption onto alginate and that the alcoholic hydroxyl groups of the alginate also participate in the adsorption of the metals [23, 24].

The interactions between ChS and Cd(II) were determined by XPS and FTIR on ChS containing adsorbed Cd. Figure 1 compares the FTIR spectra of ChS and ChS-Cd where it can be observed that in the region between 1000 and 1200 cm^{-1}, the signal at 1060 cm^{-1} due to the stretching of the C-OH bonds of the pyranose ring is separated into two signals (1093 and 1000 cm^{-1}) when Cd(II)is present. A slight modification in the band 800 cm^{-1} of the sulfate groups (C-O-S) attributable to the incorporation of cadmium is also detected. Similar results were reported by Bamgbose et al. [8], the band at 1000 cm^{-1} corresponds to the stretching of the C-O bond of C6 (primary OH) which verifies the complexation of chitosan to Cd(II).

XPS high-resolution spectra of N1s and Cd3d regions are shown in Figure 6. The spectra of core level N1s from the ChS can be deconvoluted into three individual components peaks, as shown in Figure 1a. The two larger peaks at 400.2 eV and 397.9 Ev correlate with the nitrogen of the amino group and with the nitrogen of the acetylamino group. The smallest peak at 402.4 eV corresponds to the nitrogen of the amine which is electrostatically bound to the sulfonate group, and this link is what enables the sulfated chitosan to be acid insoluble.

The cadmium adsorption onto the ChS is shown in Figure 6b, where the core level of Cd3d shows the two characteristic peaks, the 3d$^{5/2}$ (at 404.1 eV) and the 3d$^{3/2}$ with 6.8 eV of splitting, and a displacement of -1.1 eV by the interaction of Cd^{2+} with ChS. Deconvolution of the 3d$^{5/2}$ peak shows two peaks; the large peak at 404.1 eV, combined with the peak shift of the

nitrogen from 400.2 to 401.1 indicates that the Cd is bound to the nitrogen of the amine group.

The smaller Cd peak at 406.3 eV indicates that the Cd is attracted to the OH group although in much lesser amount. Dambies et al.[25] using XPS found that nitrogen is the main sorption site of metals and that their protonation controls sorption efficacy. Hasan et al.[26] using XPS analysis and adsorption data at various pHs, reported that in the adsorption of Cd(II) from aqueous solutions on chitosan-coated perlite beads, the chitosan functional groups (-NH$_2$, -OH) were bound to cadmium and the amine was the main adsorption site of Cd(II) ions. Beside Vazquez et al.[27] found that removal of Cu(II) and Cd(II) ions using a chitosan-coated polyethylene/agave compound, they determined by XPS analysis that ions are attracted primarily by the amine groups of ChS and to a lesser extent by the -OH groups of ChS and cellulose.
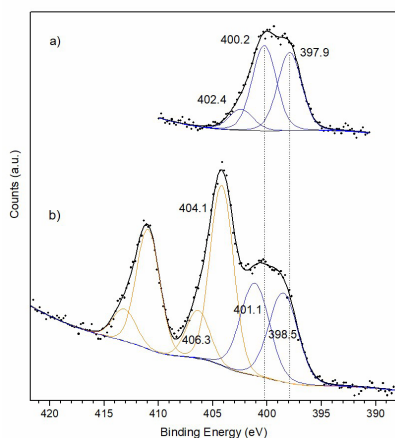

Figure 6. *XPS spectra of Alg-ChS-Cd*

Bamgbose et al.[8] reported that cadmium was preferably adsorbed by the amino group and that the adsorption is carried out mainly by complexation. It has been reported that is more likely the formation of intermolecular complexes between Cd(II) and Ch because the size of the ion favors such interactions [25, 28] and that cadmium can also be attached to Ch by electrostatic interactions [28].

Here, taking into account the FTIR and XPS spectra of Cd adsorbed onto ChS, and the mechanisms of adsorption of metals by alginate and Ch reported by other authors, it is proposed that the adsorption of Cd (II) onto the Alg-ChS is due to the groups –COO$^-$ and -NH$_2$ by electrostatic interactions and in a smaller amount by the OH groups of ChS and alginate; although some complexation of Cd (II) may also occur with alginate and ChS.

The removal of Cd(II) from the aqueous solution using a fixed bed column (percolation column) is shown in Figure 7. This Figure shows that the column was capable of removing virtually all cadmium ions from 0.90 L of the solution before reaching the break point (5%). At the break point, an adsorption capacity of 2.39 mg Cd/g of hydrogel (beads) was obtained. However, considering only the active adsorbents (Alg and ChS), the adsorption capacity was 60 mg Cd/g xerogel. The

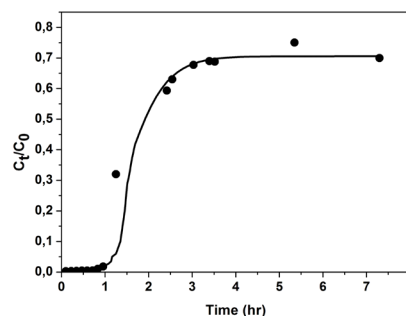study was continued until reaching the saturation of the column, which occurred at a volume of 3.50 L.

Figure 7. *Cadmium ion adsorption curve using a column packed with Alg-ChS beads. Initial Cd(II) concentration 125 mg/L, pH 0 5.0, flow rate 100 mL/h. Experimental data (symbol).*

Table 3 shows that regardless of the initial concentration of Cd(II), the process using the percolation column (up to the point of rupture) removes a higher percentage of metal than the batch process at the equilibrium and obtaining a much greater Cd(II) adsorption per gram of bead. As can be deduced from the data in the table, the continuous adsorption process (percolation column) has a much higher efficiency since a larger amount of contaminated water can be treated and obtaining water with lower concentrations of metal, even when using higher Cd(II) concentrations.

Table 3. *Comparison of the adsorption process of Cd (II) per batch with that using a percolation column.*

Process	C_0 mg/L	% removal	C_e (mg/L)	q_e (mg/g)
Batch At equilibrium	20	81.5	3.70	0.163
	50	74.8	12.60	0.374
	114	71.7	32.20	0.818
Percolation column at break point	125	95.0	6.25	2.390

CONCLUSIONS

Alg-ChS hydrogels in the form of beads with high capacity to adsorb Cd(II) were obtained. The Freundlich model had better fit than the Langmuir model to the experimental adsorption equilibrium data. The maximum Cd(II) adsorption capacity of the Alg-ChS was determined to be 190 mg Cd/g xerogel. The adsorption rate of Cd onto Alg-ChS beads followed the kinetic model of pseudo-second order and the time to reach equilibrium increased slightly with increasing initial concentration of Cd(II). The removal of Cd(II) using a fixed bed column (permeation column) packed with the Alg-ChS beads had a much higher efficiency than the Batch process. The Cd(II) is adsorbed mainly by the -COO$^-$ and -NH$_2$ groups by electrostatic interactions.

ACKNOWLEDGMENTS

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