

Preparation and Evaluation of Chitosan Beads Immobilized with Iron(III) for the Removal of As(III) and As(V) from Water

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O adsorvente quitosana-Fe(III)-reticulado (Ch-FeCL) foi desenvolvido usando Fe(III) imobilizado em esferas de quitosana. Após o processo de secagem, as esferas apresentam um diâmetro de cerca de 1 mm e são estáveis ao ar. O comportamento de adsorção do As(III) e As(V) na Ch-FeCL foi avaliado em pH 7 por estudos realizados em batelada e em coluna. As máximas capacidades de adsorção estimadas pelo modelo de adsorção de Langmuir foram 21,24 e 27,59 mg g⁻¹ para As(III) e As(V), respectivamente. A cinética de adsorção é descrita pela equação cinética de pseudo-segunda ordem. Os resultados de adsorção em coluna indicaram que o arsênio não foi encontrado na solução efluente até cerca de 60 e 759 volumes de leito para As(III) e As(V), respectivamente. Os resultados foram satisfatórios quando se empregou o adsorvente na remoção de As(III) e As(V) de amostras de águas subterrâneas, torneira e rio.

The crosslinked chitosan-Fe(III) (Ch-FeCL) adsorbent was developed using Fe(III) immobilized on chitosan beads. After drying, the beads presented a diameter of approximately 1 mm and are stable in air. The adsorption behavior of As(III) and As(V) on the Ch-FeCL was evaluated at pH 7 by studies conducted in batch and in columns. Maximum adsorption capacities estimated by the Langmuir adsorption model were 21.24 and 27.59 mg g⁻¹ for As(III) and As(V), respectively. Adsorption kinetics is described by the pseudo second order kinetic equation. The results of column adsorption indicated that arsenic was not found in the effluent solution from roughly 60 and 759 bed volumes for As(III) and As(V), respectively. Results were satisfactory when employing the adsorbent for removal of As(III) and As(V) from groundwater, tap water and river water samples.

Keywords: iron-chitosan, arsenic, removal, adsorption isotherm, groundwater

Introduction

Arsenic is a highly toxic element mainly present in drinking water and seafood, and its contamination may cause dermatitis, skin cancer, neurological disorders, hepatomegaly, heart problems, internal cancers and poisoning.¹ Arsenic can be encountered in high concentrations in surface and ground waters as a consequence of natural wear of arsenic-bearing minerals (especially arsenopyrite), as well as by human activities that promote its availability in the soil.² Arsenic is found in water in several different forms depending on pH and redox potential (E_h) of the medium, where the inorganic species, arsenite and arsenate are more toxic than the organic species. Arsenate (As(V)) and arsenite (As(III)) are the primary forms of arsenic found in natural waters, being that As(V) is more thermodynamically

stable in oxygenated surface waters and As(III) in groundwater.³ These species exist as oxyanions, in which the dominant arsenite species is the neutral species H_3AsO_3 ($pK_1 = 9.22$) and the dominant arsenates are the negative species $HAsO_4^{2-}$ ($pK_1 = 2.20$) and $H_2AsO_4^-$ ($pK_2 = 6.97$) when the pH is within an intermediate range between 3 and 9. Arsenic(V) is indicated as the predominant species in conditions of extreme acidity and alkalinity, H_3AsO_4 and AsO_4^{3-} , respectively.^{3,4} Arsenic compounds present different toxicities depending on the chemical form. The toxicity scale of arsenic decreases in the following order: arsine > inorganic As(III) > organic As(III) > inorganic As(V) > organic As(V) > arsonium compounds and elemental As.⁵ Compounds of As(III) are more toxic due to higher cellular uptake and a greater ability to bind to sulfhydryl groups of proteins, as well as forming free radicals causing oxidative stress.⁶

Concern regarding to the contamination of water by arsenic has gained importance after discovering the

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incident in Bangladesh, where thousands of people suffer from arsenicosis due to the consumption of water enriched with arsenic. Several other incidents around the world in many countries (Chile, China, India, Hungary, Mexico, Romania, Taiwan, Vietnam and others) have resulted in the inclusion of arsenic on the list of elements to be routinely measured in laboratory water analysis. Given the obvious risks of accumulation and chronic toxicological effects of arsenic in drinking water, in 1993, the World Health Organization (WHO) temporarily changed the maximum permissible limit from 50 to 10 $\mu\text{g L}^{-1}$ of total arsenic in drinking water.⁷ In Brazil, the ordinance of the Ministry of Health, which normalizes quality of drinking water, also indicates a value of 10 $\mu\text{g L}^{-1}$ of total As as the maximum allowed.⁸ Considering the risk to life and health caused by arsenic, there is growing interest in the use of low cost materials and methods for its removal from drinking water before it can cause significant contamination.⁹ In this context, several techniques are being developed to remove arsenic from water, including ion exchange, activated alumina, reverse osmosis, coagulation/filtration, reverse electrolysis and oxidation/filtration, in which solid phase adsorption appears to be a promising method.^{10,11} Methods available for arsenic removal have been thoroughly reviewed.⁹ Among the materials used for adsorption of arsenic in the solid phase are, for example, mud, zeolites, activated alumina and hydrotalcite.^{2,11-13} Materials used in the adsorption of arsenic from water include chitin and chitosan impregnated with molybdate, aluminum and iron ions.¹⁴⁻²² Several iron-containing materials are being more effectively used as adsorbents for arsenic compounds because of the advantages that they present mainly due to the formation of the very stable Fe:As complex.¹⁸⁻²⁴

Based on the fact that the Fe(III) presents high affinity for arsenic, this study initially focused on the synthesis of chitosan-iron in the form of beads which have high efficiency for removal of As(III) and As(V) from water. Thus, chitosan beads crosslinked with glutaraldehyde (Ch-CL) were initially synthesized. Next, the spheres formed were maintained in contact with a FeCl_3 solution, resulting in immobilization of Fe(III). The dry Ch-FeCL beads formed presented an average diameter of 0.1 mm and were stable in air during development of the experimental part. Preparation of chitosan-iron from the initial mixture of Fe(III) salts with chitosan, in which a viscous gel is formed to later be dripped in a strong basic medium to form a precipitate in the form of spheres, showed less capacity to remove As(III) and As(V).²⁰⁻²²

Thus air dried Ch-FeCL beads were assessed as an adsorbent for As(III) and As(V) in aqueous solutions. The optimum conditions, equilibrium data, isotherms and the

effect of temperature, adsorption kinetics, and competing ions including chloride, nitrate, sulfate and phosphate ions were obtained for As(III) and As(V). The Langmuir and Freundlich isotherms were fitted to the equilibrium adsorption data. Pseudo-first-order, pseudo-second-order and intra-particle diffusion equations were adopted to test the experimental kinetic data. The reusability of the adsorbent was demonstrated. It was found in this study that the Ch-FeCL was effective for As(III) and As(V) removal from experiments in batch and column settings. Finally, the dry Ch-FeCL beads were used for decontamination of both As(III) and As(V) from surface and groundwater collected in the region of the Quadrilátero Ferrífero, Minas Gerais State, Brazil. In this region, arsenic concentrations exceeding 2200 $\mu\text{g L}^{-1}$ have been observed in surface water and groundwater.²⁵ The high levels of arsenic in water are related to both local lithology as well as past and present mining and smelting activities.²⁵

Experimental

Reagents and solutions

All solutions were prepared with analytical grade reagents and high purity deionized water produced with a Milli-Q® system (Millipore, Bedford, MA, USA). The glassware and recipients for storage of the solutions were washed with neutral detergent, immersed in nitric acid 10% (v/v) and rinsed with deionized water before use. A standard stock solution of 1000 mg L^{-1} As(III) was prepared by dissolving 1.3203 g of As_2O_3 (Vetec, Rio de Janeiro) in 25 mL of potassium hydroxide 20% (m/v) followed by neutralization with sulfuric acid 20% (v/v) and further dilution to 1000 mL with H_2SO_4 1% (v/v). A standard stock solution of 1000 mg L^{-1} As(V) was prepared by dissolving 4.1645 g of $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Vetec) and further diluted to 1.00 L with deionized water.

Preparation of the Ch-FeCL beads

Beads were prepared by dissolving 2 g of chitosan (low molecular weight, 75-85% deacetylated, Sigma Aldrich) in 50 mL of acetic acid 5% (m/v). The gel formed was agitated for 24 h until complete dissolution, after which the mixture was dripped into a NaOH 0.5 mol L^{-1} solution using a Masterflex® peristaltic pump, forming beads upon contact of the gel drops with the alkaline solution.

The beads remained in contact with the NaOH solution for 30 min. After this time, they were washed with deionized water until the rinse water presented a pH 7.0. The polymer in the form of beads remained in contact

with a glutaraldehyde 2.5% (v/v) solution maintaining a ratio of 1.0 g of moist beads to 1.5 mL of solution for 24 h. Next, its complexation with Fe³⁺ ions was promoted via adaptation of the method proposed by Ngah *et al.*²⁶ Crosslinked beads were placed in contact with a solution of Fe³⁺ under agitation; and this solution was prepared by dissolving a mass of FeCl₃ obtaining a Fe³⁺ concentration in the proportion determined by

$$[\text{Fe(III)}] = \frac{\text{mass of moist crosslinked beads (g)} \times 6 \text{ mg L}^{-1} \text{ Fe}^{3+}}{0.010 \text{ g of chitosan}}$$

The system remained under agitation for 40 min. After this period, the Ch-FeCL complex was agitated for the same period with deionized water in order to remove excess Fe(III) not complexed to the polymer surface. The final step of synthesis included drying the beads in an oven for 18 h at 45 °C. Dry Ch-FeCL beads presented an average diameter of 1 mm and were stable in air. These were stored in plastic bottles and used in the experiments.

Characterization of Ch-FeCL

The prepared materials were characterized by complementary techniques: X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR) and determination of iron concentration in the Ch-FeCL beads. X-ray diffraction analyses were performed with an XRD System model X' Pert PRO (PANalytical, Almelo, The Netherlands) using a Ni filter, Co K_α radiation (λ = 1.78890 Å) and angular variation of 10-80° (2θ). The infrared spectroscopy analysis was performed using a Perkin Elmer infrared spectrophotometer (FTIR 1000, Waltham, Massachusetts) in the region of 400 to 4000 cm⁻¹. To obtain pellets of the samples, approximately 1.50 mg were mixed with 100 mg KBr previously dried in an oven. After homogenization, the mixture was pressed in a hydraulic press to obtain 0.200 mm thick pellets. For analysis of iron, 0.2000 g of the Ch-FeCL sample was weighted and subjected to acid digestion with 7.00 mL HNO₃ 65% (m/m), 3.00 mL HCl 37% (m/m), 5.00 mL HF 40% (m/m), 5.00 mL H₂O and 1.00 mL H₂O₂ 30% (m/m) in a microwave oven, increasing the temperature to 180 °C over 5 min (1000 W) and maintaining this temperature for 10 min. The samples were then filtered through quantitative filter paper and iron concentration was determined using an atomic absorption spectrometer (AAS).

Determination of arsenic

Quantification of arsenic was performed by hydride generation atomic absorption spectrometry (HG-AAS)

using a Varian VGA77 hydride generator. The formation of hydrides was obtained using NaBH₄ 0.6% (m/v) in NaOH 0.5% (m/v) and 6 mol L⁻¹ HCl. Total arsenic was determined by the reduction of As(V) to As(III) via addition of KI 50% (m/v) and 6 mol L⁻¹ HCl, obtaining concentrations of 10% (m/v) and 1 mol L⁻¹ for the two reagents, respectively. For determination of As(III), 250 mL of the sample and 2 mL of citrate buffer at pH 4.5 were added. The concentration of As(V) was determined as the difference between total arsenic and As(III).²⁷ All analyses were carried out in duplicate.

Adsorption experiment

Effect of pH

The effect of pH on the adsorption process was studied in batch processing, using 10 mL solutions of As(III) or As(V) at concentrations of 75 mg L⁻¹ and 50 mg of adsorbent (mass obtained as optimum in studies on the effect of adsorbent doses). The pH value of the sample was adjusted in the range of 2 to 12 with diluted solutions of HCl and NaOH. A portable digital pH meter (WTW brand, model 340i, Manchester, UK) equipped with combination electrodes of glass and silver/silver chloride, and automatic temperature correction accurate to three decimal places was used for determining pH. The system was maintained under constant stirring in a thermostatically controlled system at 25 ± 0.5 °C for 24 h. After this contact time, the adsorbent was separated from the solution by filtration, and the pH and arsenic concentrations were determined in the filtrate.

Adsorption kinetics

Evaluation of adsorption kinetics was carried out in batch processing under agitation in a thermostatically controlled system at 25 ± 0.5 °C. For the tests, 50 mg of adsorbent and 10 mL of As(III) or As(V) at the concentration of 75 mg L⁻¹ were used; and the pH of the solutions was adjusted to 7.0. The adsorbent was in contact for a time period ranging from 0-12 h. After the different contact times, the solutions were filtered and arsenic concentration was determined in the filtrate.

Isotherms and the effect of temperature

To obtain the adsorption isotherms, tests were done in batch using 10 mL solutions of As(III) or As(V) with concentrations ranging from 1 to 160 mg L⁻¹ and 50 mg of the adsorbent, adjusting the pH to 7.0. The solutions were kept under constant agitation in a system maintained at 25 ± 0.5 °C for a period of 2 and 3 h for As(V) and As(III), respectively (time of adsorption equilibrium). Enthalpy of adsorption was determined for the adsorption of As(V) by

varying temperature among the values of 25, 30, 35, 40 and 45 °C. After the contact time, the solutions were filtered and the arsenic concentration was determined in the filtrate.

Effect of the interference of chloride, nitrate, sulfate and phosphate ions

The chloride, nitrate, sulfate and phosphate ions in this study were selected because they are commonly found in natural waters, where the presence of other ions in solution may cause competition for the Fe^{3+} adsorption site. In this study, it will be possible to obtain information on the specific adsorbent for arsenic species in the presence of these ions. Therefore, the interfering effect of common ions including chloride, nitrate, sulfate and phosphate ions on the adsorption capacity of As(III) or As(V) was evaluated using solutions with concentrations of 1, 10, 30 and 50 mmol L^{-1} for each ion and a concentration of As(III) or As(V) of 1 mmol L^{-1} (75 mg L^{-1}). The pH value of the solution was adjusted to 7.0, and the salts NaCl, NaNO_3 , Na_2SO_4 and KH_2PO_4 were used in its preparation. Samples were maintained under agitation in a thermostatic bath at 25 ± 0.5 °C for 2 and 3 h for As(V) and As(III), respectively. After the contact time, the solutions were filtered and the arsenic concentration was determined in the filtrate.

Desorption

For desorption experiments, 50 mg of the adsorbent were saturated with As(III) or As(V) in 75 mg L^{-1} solutions whose pH had been adjusted to 7.0. After 2 and 3 h of contact for As(V) and As(III), respectively, washing cycles of the adsorbent were performed to remove the excess As(III) or As(V) not adsorbed. Next, 5 mL of the desorbent solutions were added and agitated for 12 h. Desorbent solutions used were citric, hydrochloric and tartaric acids at concentrations of 10^{-2} , 10^{-1} and 1.00 mol L^{-1} . After this contact time, the solutions were filtered and the arsenic concentrations were determined in the filtrates.

Column study

The column study was conducted to evaluate the use of Ch-FeCL as a low cost technology for removal of As(III) and As(V) from contaminated waters. Experiments were performed in a column measuring 0.5 cm in inner diameter, filled with 0.25 and 1.0 g to give a bed height of 5 and 20 cm of Ch-FeCL beads for As(V) and As(III), respectively. The influent solution presented a As(V) concentration of 0.5 mg L^{-1} at pH 7.0 and was percolated through the column at a flow rate of 2 ml min^{-1} . Samples of the effluent solution were collected to determine the concentrations of As(III) and As(V).

Results and Discussion

Characteristics of Ch-FeCL

The XRD analyses were performed for crosslinked chitosan (Ch-CL) and Ch-FeCL bead samples. In the diffractogram of Figure 1, four characteristic peaks of 2θ between 9 and 25° were observed for the crosslinked chitosan. The peaks between 9 and 13° are related to the amorphous portion of the chitosan structure due to the presence of random amino groups (NH_2^-), and the peak in the 2θ region between 15 and 25° is related to the crystalline portion of the biopolymer structure, resulting from packing of the polymer chain and their inter-chain interactions.²⁸ The diffractogram of Ch-FeCL presented a crystallinity index much lower than that of Ch-CL. According to Webster *et al.*,²⁹ the interactions between biopolymers with chitosan and metal ions such as Cr(VI), Ni(II), Fe(II) and Fe(III) affect the crystallinity, resulting in the formation of new crystalline phases via new covalent bonds between the biopolymer and the ions or organic molecules.

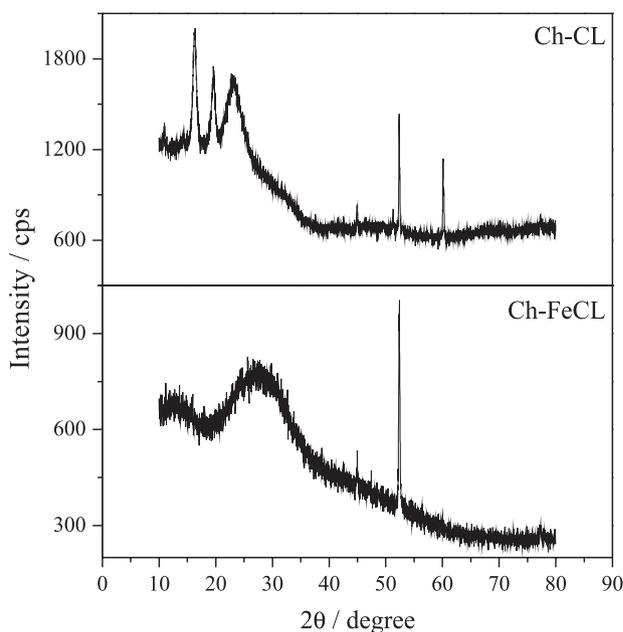


Figure 1. XRD patterns of crosslinked chitosan (Ch-CL) and crosslinked chitosan-Fe(III) (Ch-FeCL).

Figure 2 shows the FTIR spectra of Ch-FeCL before and after As(III) and As(V) adsorption. The broad and strong band at the wavenumber region 3300-3500 cm^{-1} is characteristic of the $-\text{NH}$ stretching vibration.³⁰ Due to the crosslinking of chitosan, a peak at 1650 cm^{-1} is observed corresponding to stretching vibrations of C=N bond. This peak indicated the formation of Schiff's base as a result of the reaction between

carbonyl group of glutaraldehyde and the amine group of chitosan.¹⁹ The deformation band of the primary amine ($-\text{NH}$) appears in 1560 cm^{-1} , the band corresponding to axial deformation of the $\text{C}-\text{N}$ amide appears with low intensity at 1430 cm^{-1} . At 1020 cm^{-1} , it is the band indicating a stretching of the $\text{C}-\text{OH}$ group of the primary alcohol and an asymmetric $\text{C}-\text{O}-\text{C}$ stretching band in the 1145 cm^{-1} region, defined by the β -1-4 glycosidic bond in the polymer chain. At 1100 cm^{-1} , it is a band of aliphatic amines. The axial deformation band $-\text{CN}$ of the amino group appears at approximately 1320 cm^{-1} .³⁰ In the Ch-FeCL spectrum, two characteristic bands of iron complexation appear at 580 cm^{-1} due to stretching of the $\text{Fe}-\text{N}$ bond and another at 460 cm^{-1} related to stretching of the $\text{Fe}-\text{O}$ bond. The bands at 892 cm^{-1} of Ch-FeCL after the adsorption of arsenite and arsenate match well with the stretching frequencies of $\text{As}-\text{O}$ in the H_2AsO_4^- group.¹⁹

The amount of iron determined by FAAS in the dry Ch-FeCL beads was 6.45 mg g^{-1} .

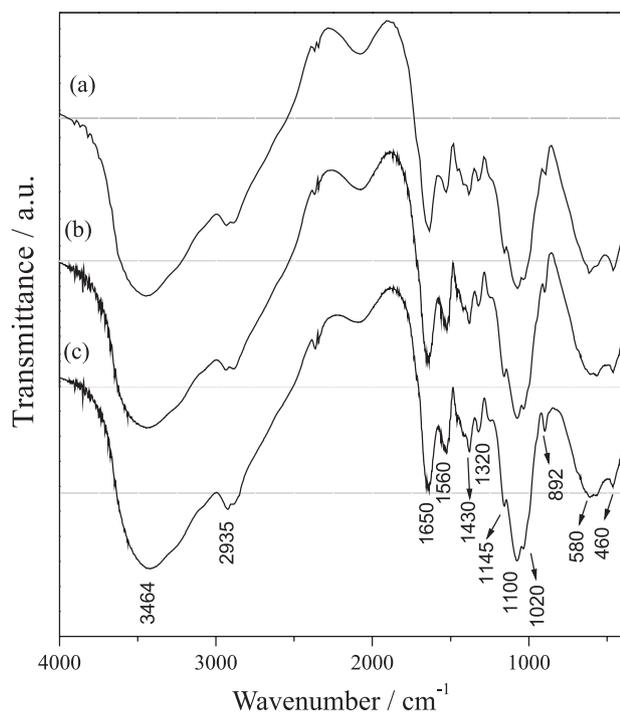


Figure 2. FTIR spectra of Ch-FeCL (a) before, and after loading with (b) As(III) and (c) As(V) .

Effect of initial pH

The adsorption percentage of As(III) and As(V) by Ch-FeCL depending on the initial pH is presented in Figure 3. It can be observed in Figure 3 that the adsorption of As(V) by the adsorbent presents low efficiencies at pH values both very low ($\text{pH} < 2$) and very high ($\text{pH} > 10$), in which the best results are between 6-8.

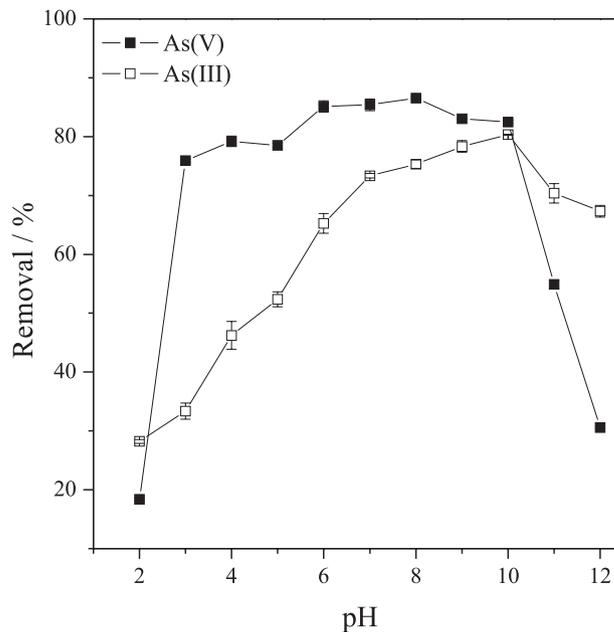


Figure 3. Effect of pH on adsorption of As(III) and As(V) by Ch-FeCL . Conditions: initial concentration of As(III) and As(V) 75 mg L^{-1} ; time = 24 h.

The explanation for this behavior is related to the distribution of As(V) species in the aqueous medium, in which a decrease in pH increases the amount of H_3AsO_4 , at pH 3-4, the predominant arsenic species are H_2AsO_4^- , and at pH 4 to 10, the arsenic species are controlled by the equilibrium $\text{H}_2\text{AsO}_4^- \rightleftharpoons \text{HAsO}_4^{2-} + \text{H}^+$ (pK_a 6.7).³¹

Chitosan has a point of zero charge (pH_{pzc}) at pH 6.3, and 99% of total amino groups protonated at pH 4.3. With the increase in pH, the charge of the adsorbent becomes less positive. At $\text{pH} > \text{pH}_{\text{pzc}}$, its surface becomes negatively charged, so that it repels the anionic species.³² Thus, it can be concluded that as pH increases, there occurs formation of deprotonated As(V) species in the form of oxyanions (H_2AsO_4^- , HAsO_4^{2-}) which are adsorbed by the positive adsorption site generated by iron complexed with chitosan.⁴ At $\text{pH} > 10$, adsorption is hindered by competition between hydroxyls in the medium for adsorption sites. Maximum adsorption at pH 7 has been reported for As(V) in studies involving the removal of arsenic with iron-coated materials.^{18,19} In Figure 3, it can be observed that there is a marked increase in the removal of As(III) up to pH 7 and maximum adsorption is reached at pH 10 (removal percentage similar to As(V)). The As(III) species in aqueous medium and in the pH interval of 3-11 are controlled by $\text{H}_3\text{AsO}_3 \rightleftharpoons \text{H}_2\text{AsO}_3^- + \text{H}^+$ (pK_a 9.22).³¹ At pH greater than 9, As(III) is present exclusively as an anion, while at pH 6-9 only a small percentage of H_3AsO_3 is dissociated.³³ The uncharged As(III) species (H_3AsO_3) cannot undergo electrostatic interaction with

the adsorbent. As(III) species can undergo only Lewis acid-base interaction and adsorption occurs by inner-sphere complexation mechanism with Fe(III).³³ Therefore, at pH greater than 9, As(III) can be adsorbed by Ch-FeCL owing to electrostatic interactions with the positive site generated by Fe(III) complexed with chitosan. Final pH measured after reaching adsorption equilibrium for the entire pH range studied did not change, showing that the adsorbent presented stability at extreme pH values.

Considering that one of the objectives of this study is the use of dry adsorbent (Ch-FeCL) in the removal of both As(III) and As(V) from surface and groundwater, which have a pH near neutral, all studies were performed at pH 7.0.

Adsorption kinetics

The kinetic adsorption process was carried out to verify the rate at which the Ch-FeCL polymer adsorbed As(III) and As(V). Adsorption of arsenic by Ch-FeCL is dependent on contact time. A rapid decay in initial concentration during the beginning was observed for both As(V) and As(III) (90% reduction), in which the equilibrium was achieved after 2 h of contact for As(V) and 3 h for As(III) (Figure 4). This fact demonstrates that the As(III) adsorption process is slower than that of As(V).

Mathematical models of adsorption kinetics

Pseudo-first order Lagergren, pseudo-second order kinetic and intraparticle diffusion models were studied to examine the mechanism that controls the adsorption process.³⁴⁻³⁶ Validity of these models can be assessed by the linear graphs of each equation: $\log(q_e - q_t)$ vs. t for the pseudo-first order model (equation 1), t/q_t vs. t for the pseudo-second order model (equation 2) and q_t vs. $t^{0.5}$ for the intraparticle diffusion model (equation 3). Kinetic parameters of the adsorption process of As(III) and As(V) by Ch-FeCL were obtained by linear regression of the graphs for each model (R^2) and by the calculated q_e vs. experimental q_e

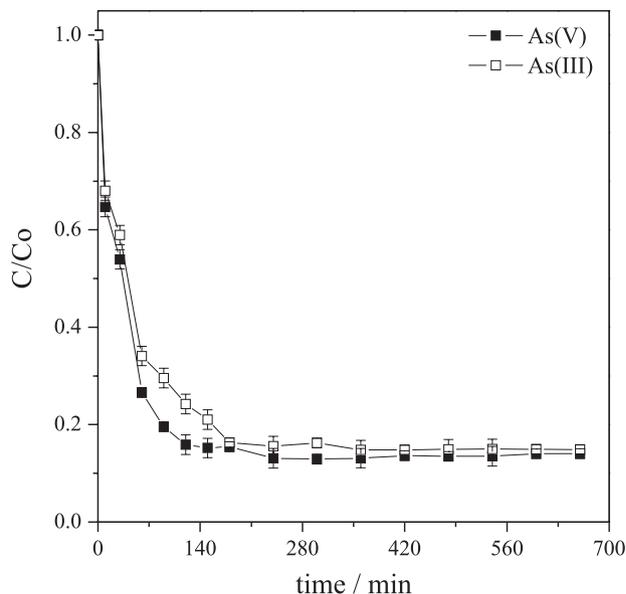


Figure 4. Kinetics of adsorption of As(III) and As(V) by Ch-FeCL. Conditions: initial concentration (C_0) of As(III) and As(V) 75 mg L⁻¹.

(Table 1). Quantitative evaluation of the models was done by comparing the correlation coefficients. The pseudo-first order equation based on the adsorption of solute from solution can be expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (1)$$

where k_1 is the rate constant of pseudo-first-order adsorption (min⁻¹), q_e (mg g⁻¹) and q_t (mg g⁻¹) are the amounts of As(III) and As(V) adsorbed at equilibrium and the instant t (min). The results showed that the adsorption process that best fits the experimental data ($R^2 > 0.999$) was the pseudo-second order model (Figure 5a). The pseudo-second order model is described by equation 2, in which k_2 is the rate constant of pseudo-second-order adsorption (g mg⁻¹ min⁻¹). This model shows chemisorption or activated mechanical adsorption as a determining step in the adsorption mechanism and not a mass transfer in solution.³⁷

Table 1. Kinetic parameters for adsorption of As(III) and As(V) on Ch-FeCL

	$q_e, \text{exp} /$ (mg g ⁻¹)	$q_e /$ (mg g ⁻¹)	Pseudo-first-order		Pseudo-second-order			Intra-particle diffusion		
			$k_1 \times 10^{-3} /$ min ⁻¹	R^2	$k_2 \times 10^{-3} /$ (g mg ⁻¹ min ⁻¹)	$q_e /$ (mg g ⁻¹)	R^2	$k_{id} /$ (mg g ⁻¹ min ^{0.5})	$C /$ (mg g ⁻¹)	R^2
As(III)	12.10	3.84	6.47	0.801	3.86	13.45	0.999	0.815	2.37	0.990
As(V)	12.89	0.094	5.76	0.375	7.09	13.24	0.999	0.987 ^a	2.23	0.994
								0.016 ^b	13.32	0.910

^aFirst and; ^bsecond linear region. q_e, exp : experimental values for the quantities of adsorbed at equilibrium; q_e : quantity of ions adsorbed at equilibrium; k_{id} : intraparticle diffusion coefficient; C: constant related to diffusion resistance.

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

The quantities of As(III) and As(V) adsorbed at equilibrium (q_e) calculated from the pseudo-second order equation and the experimental values (q_e , exp) (Table 1) present results with similar values, confirming fit of the pseudo-second order model to this experiment and, consequently, in the control of rate a chemisorption or activated adsorption mechanism must be involved.^{35,37}

The intraparticle diffusion coefficient (k_{id}) is determined by equation 3:

$$q_t = k_{id} t^{0.5} + C \quad (3)$$

where q_t is the amount of As(III) and As(V) adsorbed (mg g^{-1}), t (min) is the agitation time and C (mg g^{-1}) is

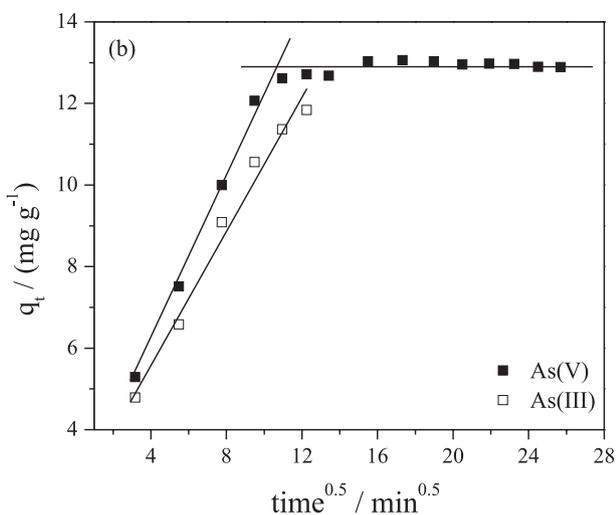
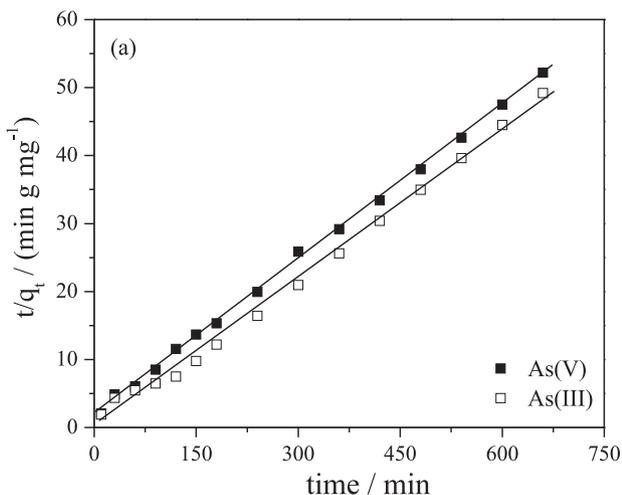


Figure 5. (a) Pseudo-second-order kinetic model and (b) intra-particle kinetic diffusion model for adsorption of As(III) and As(V) onto Ch-FeCL. Conditions: initial concentration of As(V) 75 mg L^{-1} ; time = 3 h for As(III) and 2 h for As(V).

a constant related to diffusion resistance. According to equation 3, the values of k_{id} ($\text{mg g}^{-1} \text{ min}^{-0.5}$) and C can be obtained from the slope of the q_t vs. $t^{0.5}$ graph, respectively (Figure 5b). The values of C (Table 1) provide an estimate of the boundary layer thickness, i.e., the greater the value of C , greater is the effect of the boundary layer.³⁸ There are studies indicating that the graph can present multi-linearity, which characterizes different stages of adsorption: external mass transfer followed by intraparticle diffusion in the macro, meso and micropore.³⁹ Figure 5b shows that the lines of the q_t vs. $t^{0.5}$ graph for As(III) and As(V) do not pass through the origin, indicating that the mechanism of intraparticle diffusion is not the only limiting step of the adsorption process and that other interaction mechanisms must be acting simultaneously. It was also noted that there are two linearities for As(V), in which the first represents instantaneous adsorption or external adsorption and second, the stage of gradual adsorption by intraparticle diffusion.³⁶

Isotherms and the effect of temperature

The amount of arsenic adsorbed *per* unit mass of Ch-FeCL (q_e in mg g^{-1}) was correlated with the concentration in the liquid phase at equilibrium at a constant temperature (C_e in mg L^{-1}), using the Langmuir and Freundlich adsorption isotherms.

The Langmuir linear expression is given by equation 4:

$$\frac{C_e}{q_t} = \frac{1}{Q_{\max} b} + \frac{C_e}{Q_{\max}} \quad (4)$$

where C_e is the concentration of As(III) or As(V) ions at equilibrium (mg L^{-1}), q_e the amount adsorbed at equilibrium (mg g^{-1}), Q_{\max} the constant related to maximum adsorption capacity (mg g^{-1}) and b the constant related to adsorption energy (L mg^{-1}). The parameter R_L (equation 5) is a dimensionless constant denominated the equilibrium parameter, which is defined as:

$$R_L = \frac{1}{1 + b C_0} \quad (5)$$

where C_0 is the initial greater concentration (mg L^{-1}) and b is the Langmuir constant. The value of R_L between 0 and 1 indicates favorable adsorption.

The linear Freundlich expression is given by equation 6:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (6)$$

where q_e is the quantity of ions adsorbed at equilibrium (mg g^{-1}), C_e is the concentration of As(III) or As(V) ions in

Table 2. Parameters of the Langmuir and Freundlich isotherms for adsorption of As(III) and As(V) by Ch-FeCL

Temperature / K	Langmuir model				Freundlich model		
	R_L	$b / (\text{L mg}^{-1})$	$Q_{\text{max}} / (\text{mg g}^{-1})$	R^2	$K_f / (\text{L mg}^{-1})$	n	R^2
298 ^a	0.038	0.1570	21.24	0.975	4.872	2.743	0.987
298 ^b	0.048	0.1252	27.59	0.954	5.9706	2.6099	0.986
303 ^b	0.078	0.0859	25.98	0.995	3.5123	2.1731	0.990
308 ^b	0.086	0.0667	19.90	0.982	2.1117	2.0013	0.988
313 ^b	0.119	0.0462	20.98	0.997	1.9792	1.9970	0.976
318 ^b	0.146	0.0365	17.64	0.980	1.3929	1.8754	0.995

^aAs(III); ^bAs(V); q_e : quantity of ions adsorbed at equilibrium; R_L : equilibrium parameter; b : Langmuir constant; Q_{max} : constant related to maximum adsorption capacity; K_f : constant related to the adsorption capacity; $1/n$: the Freundlich constant.

the liquid phase at equilibrium (mg L^{-1}), k_f is the constant related to the adsorption capacity (L mg^{-1}) and $1/n$ is the Freundlich constant. Values of n between 1 and 10 represent favorable adsorption. The Langmuir and Freundlich constants were determined by linear regression of the linearized equations and presented for Ch-FeCL in Table 2.

Estimates of the Langmuir parameters showed good applicability of this model for adsorption of As(III) and As(V) by Ch-FeCL, in which from the constant value of b , a good affinity of the adsorbate to the adsorbent can be observed, also being confirmed by the dimensionless separation factor (R_L) calculated for As(III) at 25 °C (298 K) and As(V) in the temperature range from 25 °C (298 K) to 45 °C (318 K) (Table 2).

The adsorption of As(III) and As(V) by Ch-FeCL can also be explained by the Freundlich model. Values of n are between 1 and 10, indicating a favorable adsorption, as shown in Table 2. Thus, both models can be used to explain the adsorption of As(III) and As(V) by Ch-FeCL beads. The adsorption capacities of Ch-FeCL estimated by the Langmuir adsorption model at 25 °C (298 K) were 21.24 and 27.59 mg g^{-1} for As(III) and As(V), respectively. Adsorption by Ch-FeCL showed a good efficiency in pH 7.0 when compared with other adsorbents employing modified chitosan for the removal of As(III) and As(V).

Boddu *et al.*,¹⁷ using alumina coated with chitosan showed adsorption capacities at pH 4.0 of 56.40 and 96.46 mg g^{-1} for As(III) and As(V), respectively. Although this adsorbent shows a high adsorption capacity, its efficiency must be evaluated in the presence of various interfering ions and with groundwater and surface water contaminated with arsenic. Chitosan impregnated with molybdate has also been used to remove As(III) and As(V) in water samples.¹⁶ Although this adsorbent is efficient and presents adsorption capacities of 1.98 and 2.00 mg g^{-1} for As(III) and As(V), respectively, the phosphate ion causes serious interference, in which the removal of arsenic does not occur in the

presence of phosphate. Gupta *et al.*¹⁹ studied the chitosan-iron composite in the form of flakes and granules for removal of arsenic from groundwater. The capacities of the flakes (16.15 mg g^{-1} for As(III) and 22.47 mg g^{-1} for As(V)) were significantly higher when compared to the granules (2.32 mg g^{-1} for As(III) and 2.24 mg g^{-1} for As(V)), both of which were obtained at pH 7.0.

The Ch-FeCL beads developed in the present study showed greater adsorption at pH 7.0 when compared with those made of the chitosan-iron composite.²⁰⁻²² The synthesis process used in this study, in which the chitosan beads are first prepared and subsequently maintained in contact with a FeCl_3 solution for immobilization of Fe(III), resulted in increased adsorption capacity. This is possibly due to increased porosity of the adsorbent material which facilitates the migration of ions through the pores, collaborating with intraparticle adsorption.

Thus, the main advantage of the adsorbent in the form of beads as developed in this study is that it is stable in air after the drying process, can be easily removed from the solution by filtration (diameter of 1 mm) and permits the removal of As(III) and As(V) at neutral pH.

Changes in the adsorption process caused by temperature were evaluated using the thermodynamic parameters determined by the Langmuir isotherm. Thermodynamic parameters such as changes in Gibbs energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) are calculated using equations 7 and 8:

$$\Delta G^\circ = -RT \ln b \quad (7)$$

$$\ln b = \frac{\Delta G^\circ}{R} + \frac{\Delta H^\circ}{RT} \quad (8)$$

where R is the ideal gas constant (8.314 $\text{J mol}^{-1} \text{K}^{-1}$), T is temperature in Kelvin (K) and b is the Langmuir constant (L mol^{-1}). ΔH° and ΔS° are calculated from the

slope and intercept of the van't Hoff plot for $\log b$ versus $1/T$. The calculated values for ΔG° (temperature) are -22.66 (298 K), -22.09 (303 K), -21.81 (308 K), -21.21 (313 K) and -20.71 kJ mol^{-1} (318 K); ΔS° is -95.75 $\text{J mol}^{-1} \text{K}^{-1}$ and ΔH° is -51.20 kJ mol^{-1} . Negative values of ΔG° indicate spontaneous adsorption of As(V) by the adsorbent and the negative value of ΔS° suggests a decrease in disorder at the solid-solution interface during the adsorption of As(V) in aqueous solution by Ch-FeCL. The negative value of ΔH confirms the exothermic nature of the adsorption process.

Desorption of As(III) and As(V)

Desorption studies were performed using citric acid, hydrochloric acid and tartaric acid solutions for extraction. Saturation of the adsorbent with As(III) or As(V) was initially promoted and after this procedure, the Ch-FeCL beads were placed in contact with the desorbent.

Citric acid showed the best ability for desorption compared to the other acids, presenting a removal of 36% for As(III) and 56% of As(V) at the concentration of 0.01 mol L^{-1} . Desorption performed in cycles was carried out with the objective of obtaining greater recovery of the adsorbent. After five cycles, removals of 74 and 100% of As(III) and As(V) were obtained, respectively, for the Ch-FeCL beads. The best performance obtained with respect to desorption with citric acid is due to its ability to form complexes with Fe^{3+} , which facilitates the removal of arsenic species (HAsO_4^{2-} , H_2AsO_4^- , H_2AsO_3^-) adsorbed on the Fe^{3+} adsorption site.⁴⁰ Furthermore, the use of citric acid as an arsenic extracting solution is promising because it is a natural organic acid, non-toxic, easily degraded in the environment and low cost.⁴⁰

Ch-FeCL was submitted to four adsorption/desorption cycles in order to evaluate the reuse of the adsorbent material. In this procedure, the beads saturated with arsenate ions were submitted to five desorption cycles of 12 h each and reused in adsorption. The procedure was repeated until completing four successive adsorption/desorption cycles and at the end of this process there was a decrease in the adsorption capacity of Ch-FeCL by about 42 and 20% for As(III) and As(V), respectively. Thus, the adsorbent presents the ability to be reused several times without the need to exchange it for new beads.

Effect of interference of chloride, nitrate, sulfate and phosphate ions on the adsorption capacity of As(III) and As(V)

Figure 6 shows the values of As(III) and As(V) adsorption capacity in solutions containing chloride, nitrate, sulfate and

phosphate ions. It is observed that the percentage of As(III) and As(V) removal decreases with increase in charge and concentration of the interfering ion. Therefore, PO_4^{3-} was the anion that caused the greatest reduction in adsorption, followed by sulfate, nitrate and chloride ions which had the smallest influence on adsorption of As(III) and As(V) when compared with adsorption in the absence of the studied anions (blank). Reductions of 17 and 25% can be observed in Figure 6 for the adsorption of As(III) and As(V), respectively, when phosphate concentration is 1 mmol L^{-1} (95 mg L^{-1}), close to that of arsenate (75 mg L^{-1}); and reductions were 80 and 77% for As(III) and As(V), respectively, when phosphate concentration increased to 50 mmol L^{-1} (9497 mg L^{-1}). Gupta *et al.*,¹⁹ studying the effect of sulfate, phosphate and silicate anions on the adsorption of As(III) and As(V) by an chitosan-iron composite in the form of granules, also observed a greater percentage of adsorption reduction for phosphate followed by sulfate for As(III) and As(V). This interference effect is probably explained by the chemical similarity of arsenate and phosphate in aqueous solution: both ions can form very stable complexes with iron.^{18,23}

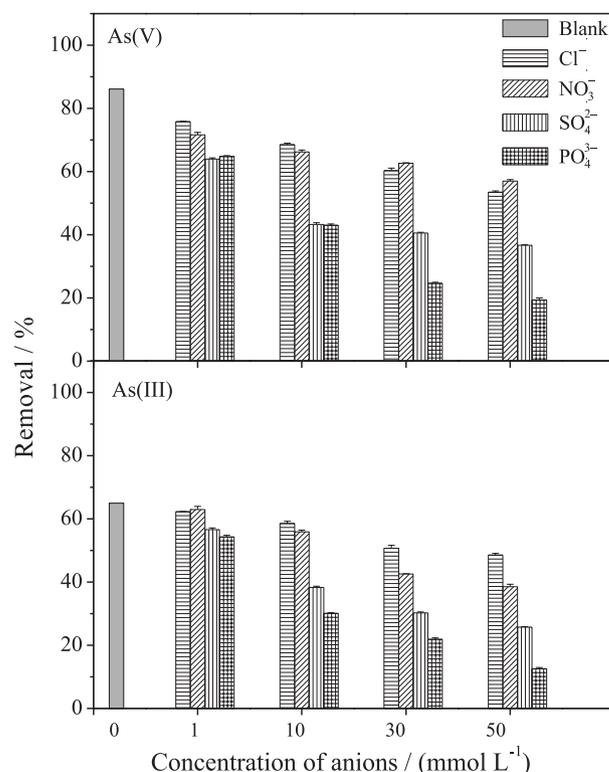


Figure 6. Effect of chloride, nitrate, sulfate and phosphate ions on adsorption of As(III) and As(V) by Ch-FeCL.

Column study

Column adsorption studies were performed to demonstrate the applicability of the Ch-FeCL adsorbent

for removal of As(V) and As(III) from water. Figure 7 shows the breakthrough curve for a feed concentration of 0.5 mg L^{-1} at pH 7. It is observed that the concentrations of As(V) and As(III) could be reduced from 0.5 to 0.01 mg L^{-1} with 759 and 60 bed volumes (BV), respectively. Gupta *et al.*¹⁹ conducted column tests using iron-chitosan composites from real-life arsenic contaminated groundwater. Their results showed that iron-chitosan flakes (ICF) could treat 147 BV of As(III) and 112 BV of As(V)-spiked groundwater with an As(III) or As(V) in concentration of 0.5 mg L^{-1} and pH adjusted to 7. Gupta and Sankararamkrishnan²⁰ also performed column studies using iron chitosan spacer granules (ICS), which after their preparation were maintained in a saturated sucrose solution to improve porosity. Their results showed that iron chitosan spacer granules (ICS) could treat 132 BV of As(III) and 210 BV of As(V)-spiked groundwater with an As(III) or As(V) concentration of 0.5 mg L^{-1} and pH adjusted to 7. Boddu *et al.*,¹⁷ using a chitosan-coated biosorbent (CCB) reported that the breakthrough point was about 40 and 120 BV for As(III) and As(V) removal in concentration of 91 and 101 mg L^{-1} , respectively, in aqueous solutions adjusted to pH 4. Gang *et al.*²¹ studied the behavior of the rupture curve for iron-impregnated chitosan granules in the adsorption of As(III) in aqueous solutions adjusted to pH 8 with an influent concentration of 0.308 mg L^{-1} . Results showed that the iron-impregnated chitosan granules can treat 768 BV for removal of As(III). The studies presented above involving adsorption of arsenic in the column differ by the initial concentration used, pH and flow rate of the feed solution to the column, which results in different values for the BV. The results of BV previously encountered for As(V) were lower than those found in the present study. Gang *et al.*²¹ found a much higher BV (768) for As(III) when compared to other studies, which used a flow rate of 0.41 mL min^{-1} and

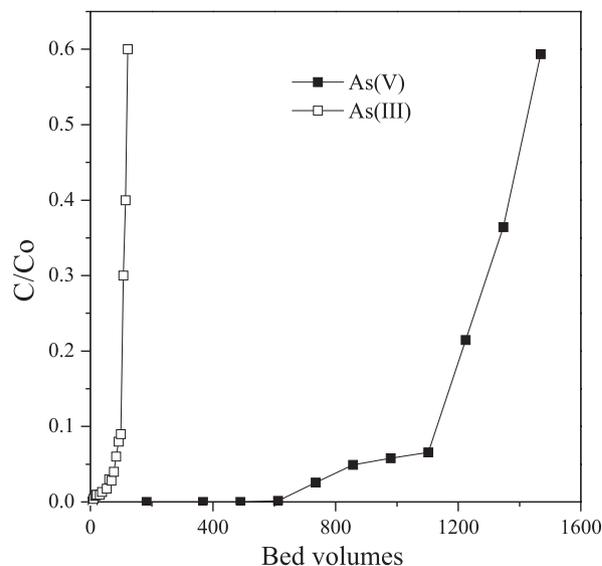


Figure 7. Breakthrough adsorption curves of As(III) and As(V) using Ch-FeCL. Conditions: initial concentration = 0.5 mg L^{-1} ; pH 7; flow rate = 2 mL min^{-1} ; amount of the adsorbent: 0.25 g As(V) and 1.0 g As(III).

pH 8. In other studies, the conditions used were flow rate of 2.5 mL min^{-1} , pH 7 and flow rate of 2.0 mL min^{-1} , as in the present study and two others.^{17,19,20} The higher BV found (768 BV) for As(III) can be justified by the use of lower flow rates through the column which result in greater contact time of As(III) with the column bed, and pH 8 increases the number of anionic species of As(III) which is controlled by $\text{H}_3\text{AsO}_3 \rightleftharpoons \text{H}_2\text{AsO}_3^- + \text{H}^+$ (pKa 9.22), increased the quantity adsorbed by the adsorbent.

Accuracy of the analytical method

The accuracy of the developed analytical method for determination of As(III) and As(V) was checked by addition and recovery experiment performed on mine (mine D) and river samples (Ribeirão Carmo) shown in

Table 3. Physicochemical characterization and As(III) and As(V) concentrations in water samples collected in the region of the Quadrilátero Ferrífero

Sample	pH	Eh / mV	Temperature / °C	Electrical conductivity / ($\mu\text{S cm}^{-1}$)	Salinity / (mg L^{-1})	Dissolved oxygen / ($\text{mg O}_2 \text{ L}^{-1}$)	As(III) ^a / ($\mu\text{g L}^{-1}$)	As(V) ^a / ($\mu\text{g L}^{-1}$)
Mine A	6.4	153.9	20.1	22.6	19.0	14.10	< 0.20	2.58 ± 0.71
Mine B	6.6	21.8	19.9	90.0	78.0	21.48	31.28 ± 0.87	164.61 ± 2.75
Mine C	5.6	88.0	25.6	133.7	116.0	13.80	18.54 ± 0.20	120.67 ± 1.48
Mine D	6.9	90.3	22.3	180.7	156.0	14.16	< 0.20	7.90 ± 0.12
Mine E	6.6	81.2	19.2	22.7	20.0	13.26	1.18 ± 0.26	5.56 ± 0.51
Mine F	6.1	163.2	20.4	29.3	25.0	12.24	1.50 ± 0.05	12.27 ± 0.41
Tap water	5.8	131.6	20.3	84.5	73.0	14.46	11.04 ± 0.34	79.94 ± 1.06
Ribeirão do Carmo	7.2	16.6	23.5	135.0	203.0	15.24	4.40 ± 0.03	22.86 ± 0.14

Eh: reduction potential.

Table 3. The two water samples were spiked with 1, 3 and 10 $\mu\text{g L}^{-1}$ of the 1 mg L^{-1} stock solutions of As(III) and As(V). For each spiked level, three quantification tests were performed. Recoveries obtained from the sample of mine water fortified at 1, 3 and 10 $\mu\text{g L}^{-1}$ were 97.2, 96.3 and 102.1% for As(III), and 96.4, 103.4 and 99.7% for As(V). Recoveries obtained from the sample of river water spiked with 1, 3 and 10 $\mu\text{g L}^{-1}$ were 98.5, 102.8 and 97.8 for As(III), and 98.4, 102.1 and 103.4 for As(V). Therefore, the determination of As(III) and As(V) in natural waters showed good agreement with addition-recovery experiments.

Analyses of As(III) and As(V) in natural water samples were performed using two calibration curves in the range 1 to 10 $\mu\text{g L}^{-1}$, one for As(III) and the other for As(V). The calibration curves presented straight line equations of

$$A = 0.0299[\text{As(III)}] + 0.0092 \quad (R^2 = 0.9991) \text{ and} \\ A = 0.0434[\text{As(V)}] + 0.0107 \quad (R^2 = 0.9997).$$

The limits of detection (3σ) and of quantification (10σ) were calculated as 0.20 and 0.43 $\mu\text{g L}^{-1}$ for As(III), and 0.54 and 0.89 $\mu\text{g L}^{-1}$ for As(V), respectively. Precision was expressed in terms of repeatability, based on calculation of the estimate of the relative standard deviation (RSD). Samples of river (Carmo River) and mine water (mine D) were spiked with 1, 3 and 10 $\mu\text{g L}^{-1}$ of As(III) and As(V) ($n = 3$), in which the obtained RSD was less than 8% for the different arsenic concentrations.

Applicability of the adsorbent to water naturally contaminated with arsenic

To verify the influence of the natural water matrix, dry Ch-FeCL beads were applied to water samples naturally contaminated with As and collected from various groundwater and surface water sources located in the region of the Quadrilátero Ferrífero. Eight sampling points were used, consisting of six from mines, one tap water sample and one sample from the Carmo River (Table 3). The water samples were collected and physico-chemically characterized by *in situ* analyses for pH, E_h , temperature, electrical conductivity, salinity and dissolved oxygen, according to the procedure described by Mendes *et al.*²⁷ To the water samples, 1 mg L^{-1} of As(III) and As(V) was added. This addition was necessary to evaluate the efficiency of the adsorption process for removal of As(III) and As(V) in natural matrices, and in regions of the Quadrilátero Ferrífero, groundwater concentrations exceeding 1 mg L^{-1} were already observed.²⁵ Natural waters after treatment presented arsenic concentrations below the maximum

allowed by Brazilian legislation (10 $\mu\text{g L}^{-1}$), making them appropriate for human consumption.

Conclusions

The crosslinked chitosan-Fe(III) adsorbent (Ch-FeCL) was prepared in the form of beads, which after drying presented an average diameter of 1 mm and were stable in air. The dry Ch-FeCL beads was initially evaluated in the adsorption/desorption of As(III) and As(V) from aqueous solutions at pH 7.0. Equilibrium adsorption values fit well to the Langmuir and Freundlich models. The maximum adsorption capacities of Ch-FeCL estimated by the Langmuir adsorption model at 25 °C were 21.24 and 27.59 mg g^{-1} for As(III) and As(V), respectively.

Column studies presented promising results, mainly because of their applicability at neutral pH for removal of As(III) and As(V) which makes the Ch-FeCL beads attractive for development of filters for use in water treatment in areas with arsenic contamination.

The results were also satisfactory when employing dry Ch-FeCL beads for the removal of As(III) and As(V) from samples of mine water, tap water and river water collected in the region of the Quadrilátero Ferrífero, Minas Gerais State, Brazil. Based on these results, it is suggested that dry Ch-FeCL beads have the potential to be an efficient adsorbent for removal of As(III) and As(V) from water samples in contaminated regions.

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References

1. Shevade, S.; Ford, R. G.; *Water Res.* **2004**, *38*, 3197.
2. Genç-Fuhrman, H.; Bregnhøj, H. D.; McConchie, D.; *Water Res.* **2005**, *39*, 2944.
3. Ko, I.; Kim, J.-Y.; Kim, K.-W.; *Colloids and Surfaces, A* **2004**, *234*, 43.
4. Ghimire, K. N.; Inoue, K.; Yamaguchi, H.; Makino, K.; Miyajima, T.; *Water Res.* **2003**, *37*, 4945.
5. Mondal, P.; Majunder, C. B.; Mohant, B.; *J. Hazard. Mater.* **2006**, *137*, 464.
6. Tapio, S.; Groshe, B.; *Mutation Research.* **2006**, *612*, 215.
7. World Health Organization (WHO); *Guidelines for Drinking-Water Quality*, vol. 1, 2nd ed.; Genève, Swiss, 1993.

8. Brazilian Ministry of Health; *Establishes Procedures and Responsibilities Relating to Control and Surveillance of Water Quality for Human Consumption and Pattern of Drinking and other Matters*, Decree No. 518 of March 25, 2004, Repealing Ordinance No. 1469 of December 29, 2000.
9. Mohan, D.; Pittman Jr., C. U.; *J. Hazard. Mater.* **2007**, *142*, 1.
10. United States Environmental Protection Agency (US EPA); *Technologies and Costs for Removal of Arsenic from Drinking Water*, US EPA, Office of Water: Washington, DC, USA, 2000.
11. Machado, N. R. C. F.; Bigatão, D. M. M. M.; *Quím. Nova* **2007**, *30*, 1108.
12. Lin, T.-F.; Wu, J.-K.; *Water Res.* **2001**, *35*, 2049.
13. Yang, L.; Shahrivari, Z.; Liu, P. K. T.; Sahimi, M.; Tsotsis, T. T.; *Ind. Eng. Chem. Res.* **2005**, *44*, 6804.
14. Kartal, S. N.; Imamura, Y.; *Bioresource Technol.* **2005**, *96*, 389.
15. Dambies, L.; Vicent, T.; Guibal, E.; *Water Res.* **2002**, *36*, 3699.
16. Chen, C.-Y.; Chang, T.-H.; Kuo, J.-T.; Chen, Y. F.; Chung, Y.-C.; *Bioresource Technol.* **2008**, *99*, 7487.
17. Boddu, V. M.; Abburi, K.; Talbott, J. L.; Smith, E. D.; Haasch, R.; *Water Res.* **2008**, *42*, 633.
18. Fagundes, T.; Bachmann, A. W. L.; Tomaz, H. S. O.; Rodrigues, C. A.; *Quím. Nova* **2008**, *31*, 1305.
19. Gupta, A.; Chauhan, V. S.; Sankararamkrishnan, N.; *Water Res.* **2009**, *43*, 3862.
20. Gupta, A.; Sankararamkrishnan, N.; *Bioresource Technol.* **2010**, *101*, 2173.
21. Gang, D. D.; Deng, B.; Lin, L.; *J. Hazard. Mater.* **2010**, *182*, 156.
22. Santos, H. H.; Demarchi, C. A.; Rodrigues, C. A.; Nedelko, J. M. G. N.; Waniewska, A. S.; *Chemosphere* **2011**, *82*, 278.
23. Bradruzzaman, M.; Westerhoff, P.; Knappe, D. R. U.; *Water Res.* **2004**, *38*, 4002.
24. Toledo, T. V.; Bellato, C. R.; Rosário, R. H.; Marques Neto, J. de O.; *Quím. Nova* **2011**, *34*, 561.
25. Deschamps, E.; Cimineli, V. S. T.; Lange, F. T.; Matschullat, J.; Raue, B.; Schimidt, H.; *J. Soil Sediments* **2002**, *2*, 216.
26. Ngah, W. S. W.; Ghani, S. A.; Kamari, A.; *Bioresource Technol.* **2005**, *96*, 443.
27. Mendes, G.; Bellato, C. R.; Marques Neto, J. O.; *Quím. Nova* **2009**, *32*, 1471.
28. Zhang, Y.; Xue, C.; Xue, Y.; Gao, R.; Zhang, X.; *Carbohydr. Res.* **2005**, *340*, 1914.
29. Webster, A.; Halling, M. D.; Grant, D. M.; *Carbohydr. Res.* **2007**, *342*, 1189.
30. Wang, S.-G.; Sun, X.-F.; Liu, X.-W.; Gong, W.-X.; Gao, B.-Y.; Bao, N.; *Chem. Eng. J.* **2008**, *142*, 239.
31. Reed, B. E.; Vaughan, R.; Jiang, L.; *J. Environ. Eng.* **2000**, *126*, 869.
32. Udayabhaskar, P.; Iyengar, L.; Rao, A. V. S. P.; *J. Appl. Polym. Sci.* **1990**, *39*, 739.
33. Katsoyiannis, I. A.; Zouboulis, A. I.; *Water Res.* **2002**, *36*, 5141.
34. Zhang, Y.; Yang, M.; Huang, X.; *Chemosphere* **2003**, *51*, 945.
35. Ho, Y. S.; Mckay, G.; *Process Biochem.* **1999**, *34*, 451.
36. Bhattacharyya, K. G.; Sharma, A.; *Dyes and Pigm.* **2005**, *65*, 51.
37. Vitali, L.; Laranjeira, M. C. M.; Fávère, V. T.; Gonçalves, N. S.; *Quím. Nova* **2008**, *31*, 1400.
38. Dizge, N.; Aydiner, C.; Demirbas, E.; Kobya, M.; Kara, S.; *J. Hazard. Mater.* **2008**, *150*, 737.
39. Allen, S. J.; Mckay, G.; Khader, K. Y. H.; *Environ. Pollut.* **1989**, *56*, 39.
40. Silva, A. M. N.; Kong, X.; Parkin, M. C.; Cammack, R.; Hider, R. C.; *Dalton Trans.* **2009**, *40*, 8616.

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