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Removal of inorganic arsenic oxyanions using Ca–Fe(III) alginate beads

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ABSTRACT

Arsenic is a highly soluble oxyanion that is toxic to humans and the environment. Ca–Fe(III) alginate beads were used as a green adsorbent for the removal of inorganic arsenic oxyanions from aqueous solutions. The carboxyl groups present in the Ca-alginate structure are responsible for the binding of divalent cations. The insertion of iron as a dispersed colloidal ferric hydroxide enhances the adsorption efficiency toward arsenic. The adsorption was fitted by the Langmuir and the Freundlich models, the first being more suitable. The Langmuir parameter q, which indicates the maximum uptake capacity of the sorbent, was 0.364 (mg/g) for As(V) and 0.117 (mg/g) for As(III). Our results suggest that the removal mechanism for arsenic species is the adsorption onto the iron in the alginate bead surface. The results demonstrate that the Ca–Fe(III) alginate beads could be used as a green alternative to remove trace levels of arsenic oxyanions.

Keywords: Arsenic; Oxyanions; Ca-Fe(III) alginate beads; Adsorption

1. Introduction

Oxyanions are highly water-soluble species and their speciation is strongly dependent on the pH and redox potential of their surrounding environment. The oxyanion toxicity to humans and wildlife is dependent on their bioavailability and chemical speciation [1,2]. In natural waters, arsenic can exist as As(III) (in the compounds H_3AsO_3 and $H_2AsO_3^-$) and As(V) (in the compounds $H_2AsO_4^-$ and $HAsO_4^{2-}$). As(III) has been shown to be less stable and more toxic than As(V) in oxygenated waters [3]. Arsenic, the 20th element in natural abundance in the earth crust, is present in the environment due to anthropogenic or natural sources. [4,5]. Arsenic may be found in more than 300 different minerals, including scorodite ($FeAsO_4{\cdot}2H_2O$) and arsenopyrite (FeAsS) [6,7], which represent a potential source of natural arsenic contamination due to leaching or erosion of soils. Human activities which represent the major sources of arsenic in the environment are pesticides [8], mining activities [9], ceramic production, burning fossil fuels, petroleum refining industries, among others [10]. In drinking water, the maximum concentration level (MCL) allowed by the Environmental Protection Agency (EPA) and the World Health Organization is 0.010 mg/L. In some countries, the arsenic concentration in drinking water has been reported to exceed the MCL and these include: Argentina, Australia, Bangladesh, Chile, China, Hungary, India, Mexico, Peru, Thailand, and the USA [11,12]. The low permissible level for arsenic is due to

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its toxicological effects on human beings. Studies have shown that a chronic exposure to arsenic could lead to a variety of illness such as hyperkeratosis, melanosis, dyspepsia (gastrointestinal disorder), neuropathy, and various types of cancer [13]. Among the methodologies reported to remediate arsenic from aqueous solutions are nanofiltration [14,15], reverse osmosis [16], electro-ultrafiltration [17], precipitation and coagulation [18], bioremediation [6], and adsorption [10,19]. Most of these approaches are expensive, consume large amounts of energy, or do not remove arsenic to trace concentrations as required for safe human water consumption. In contrast, adsorption is a widely available technology that is inexpensive, easy applicable, and has a higher removal efficiency for a variety of pollutants [20,21]. Ca-alginate beads are efficient adsorbents for divalent cations. Although, the alginate polysaccharide has the capacity to form hydrogels in divalent cations solutions, the addition of ferric hydroxide enhances the removal efficiency toward oxyanions. Previously, Min and Hering had studied the removal of As(V) using Fe (III)-doped alginate beads. In their work, the equilibrium was achieved after 120 h and the As(III) adsorption was less than 3% of the As(V) adsorption under the same conditions [22]. Banerjee et al., Zouboulis and Katsoyiannis, and Lim et al. also published using alginate beads as adsorbents for arsenic oxyanions and none of them report about the adsorption isotherms which allow a statistical comparison with other available sorbents. These authors did not report the adsorption of As(III) either, which is more toxic than As(V) and of more environmental relevance [23–25]. In the present investigation, we include the Langmuir and Freundlich adsorption isotherms, the achievement of As(III) adsorption, and the improvement of the Ca–Fe (III) alginate bead synthesis using a single-step process.

2. Material and methods

2.1. Reagents

As(V) solutions were prepared from sodium hydrogen arsenate (Alfa Aesar Co., ACS Grade) and the As(III) solutions from sodium arsenite (Ricca Chemical Co., Reagent Grade). Nitric acid (Fisher Co., Optima grade) and sodium hydroxide (Fisher Co., ACS grade) were used to regulate the pH. Ca-alginate and Ca–Fe(III) alginate beads were prepared using alginic acid sodium salt (MP Biomedicals LLC, low viscosity), calcium chloride dihydrate (Fisher Co., certified ACS grade), and ferric chloride hexahydrate (Ricca Chemical Co., ACS reagent grade). The acids for desorption tests were hydrochloric acid (Fisher Co., trace metal grade) and sulfuric acid (Midland Scientific Inc., Baker grade). The competitive oxyanions were sodium carbonate monohydrate (Alfa Aesar Co., ACS grade, 99.5%) and sodium sulfate (Fisher Co., 99.5% purity). All solutions were prepared in distilled deionized water at 17.8 MΩ.

2.2. Ca–Fe(III) alginate beads synthesis

Sodium alginate is a polysaccharide hydrogel that exhibits ionic exchange capability by attaching divalent cations, such as Cu^{2+}, Pb^{2+}, and Mn^{2+}, by two of the carboxylic acid functional groups [26]. The Ca–Fe(III) alginate beads were synthesized using a 2% w/v alginic acid solution by its drop wise addition at 0.70 mL/min in a 1,000 mL beaker, which contained 500 mL of 0.1 M $CaCl_2$ and 0.02 M of $FeCl_3$ at slow (60 rpm) magnetic agitation. The pH was adjusted to 8.0 ± 0.1 with 5 M NaOH. After a contact time of 24 h, this allowed the cross linking reaction and immobilization of ferric hydroxide colloids in the polymeric matrix. The resulting beads were recovered and dried at room temperature for three days. In order to compare the corresponding uptake capacities of the Ca-alginate beads in the presence and absence of the dispersed iron ions within the alginate matrix, the same procedure was used without the addition of ferric chloride.

2.3. Ca–Fe(III) alginate beads characterization

2.3.1. Elemental analysis

The iron and calcium concentration in the Ca–Fe (III) alginate beads were determined by mass balance after elemental analyses of the aqueous solutions before and after the bead synthesis. Aliquots were withdrawn before and after the synthesis and diluted up to 10 mL and preserved for analysis with 1% v/v nitric acid. The metal concentrations were measured in an Agilent ICP-MS 7500ce, according to the modified EPA method 200.8. The modification consisted in the use of the reaction cell in the helium mode for arsenic determinations and the hydrogen mode for iron and calcium measurements. The use of the reaction cell removed isobaric interference and improved the method performance. Matrix spikes and method blanks were run in all analyses for quality control.

2.3.2. Beads size and morphology

The Ca–Fe(III) alginate beads were observed through an optical microscope (Nikon SMZ1500) and scanning electron microscope (SEM) (JEOL JSM 5410LV) in order to determine its morphology and the corresponding average diameter.

2.4. Adsorption tests

As(III) and As(V) solutions (0.100–2 mg/L) were independently contacted with 5 g/L of Ca–Fe(III) alginate beads at various pH (2, 4, 6, 8, and 10). All solutions were prepared in duplicate and placed in plastic sealed bottles at room temperature (298 K) in a water shaker bath and agitated at 200 rpm/min for a period up to 24 h. Aliquots were withdrawn at intervals until equilibrium was obtained. Method blanks were treated as samples in order to determine possible contamination or adsorption due the materials used. All samples were quantitatively analyzed in triplicate by an Agilent ICP-MS 7500ce using the reaction cell in helium or hydrogen modes in order to reduce isobaric interference. Yttrium was used as internal standard for arsenic measures and scandium was used for calcium and iron analyses.

2.4.1. Competitive adsorption studies

As(III) and As(V) solutions, each having concentration of 0.100 mg/L, were independently contacted with sulfate and carbonate oxyanions at diverse levels of competition (0.100, 0.300, and 0.500 mg/L) with 5 g/L of Ca–Fe(III) alginate beads at pH 6, as in all other experiments. In order to determine if the difference between the two methods (with and without competitive oxyanions) is significant, the pair test at a confidence level of 95% was calculated.

2.4.2. Desorption analysis

Once the Ca–Fe(III) alginate beads were used for the sorption of As(III) or As(V) experiments, the beads were vacuum filtered and dried for three days at room temperature. Then, 10 g/L of the Ca–Fe(III) beads was placed in 10% v/v sulfuric or hydrochloric acid for up to 24 h at 30 rpm. Then, aliquots of the resulting acid wash were diluted in deionized water and analyzed by means of ICP-MS. The percentage of the arsenic species released by the acid wash was calculated using the mass balance between the initial sorption and the amounts released into the solutions. Blank methods were run for each acid in order to determine any contamination from solutions or containers. Matrix spikes were also used in order to determine possible matrix interferences.

2.5. FT-IR analysis

The FT-IR spectra were taken using an IRaffinity-1 Fourier Transform Infrared Spectrophotometer (Shimadzu). The samples were scanned 200 times per spectrum in the wavenumber range of 900–3,600 cm^{-1} in the attenuated total reflectance (ATR) mode at a resolution of 8 cm^{-1}. The ATR allowed analysis of the alginate beads without any further sample preparation other than compressing the alginate beads using a mortar and pestle.

2.6. Langmuir isotherm

The suitability of the Langmuir isotherm is based on the assumption that the highest adsorption corresponds to the formation of a saturated monolayer of the adsorbate on the homogeneous sorbent surface and that no interaction exists between the boundary adsorbed solute.

The Langmuir model is expressed in the equation shown below:

$$q_e = q_{\max}\, b\, q_e/(1 + b\, C_e)$$

and can be linearized as follows:

$$C_e/q_e = (1/q_{\max})\, C_e + 1/q_{\max}\, b$$

The $q_{\max}$ and b are the Langmuir constants that represent the adsorption capacity of the adsorbent (mg/g) and the affinity of the metal for the sorbent surface (L/mg), respectively. The C_e and q_e represent the concentration of the metal (mg/L) and the adsorption capacity of the sorbent (mg/g) at equilibrium, respectively [27,28].

The R_L parameter, which is a separation factor that describes the favorability of the sorption process, was also calculated:

$$R_L = 1/(1 + C_i\, b)$$

where b is the Langmuir constant and C_i (mg/L) is the initial concentration of the adsorbate. Values of $R_L = 0$ represent an irreversible adsorption, $R_L = 1$ a linear process, $1 < R_L > 0$ a favorable adsorption process, and values greater than one represent nonfavorable processes.

3. Results and discussion

3.1. Characterization

3.1.1. Elemental analysis of Ca–Fe(III) alginate beads

The elemental analysis of the Ca–Fe(III) alginate beads showed 7.3 ± 0.3% w/w Ca and 0.5 ± 0.1% w/w Fe. These results suggest that the alginate matrix is formed with preference toward calcium ions. Although, the initial loading of Ca was already five times higher than ferric ions, the final loading obtained after the synthesis was approximately 15 times higher, thus showing a preferential selectivity toward divalent Ca ions.

3.1.2. Alginate beads size and morphology

The size of the Ca–Fe(III) alginate beads was determined using an optical microscope and with an average diameter of 2.2 ± 0.3 mm.

As shown in the SEM image (Fig. 1(B)), the Ca–Fe (III) alginate beads exhibit a macroporous surface, which permits the adsorption of oxyanions. The Ca–Fe(III) alginate beads show a cracked surface when compared with its Ca-alginate bead counterpart (shown in Fig. 1(B)), which translates into less mechanical resistance.

3.2. Adsorption tests

3.2.1. As(III) and As(V) sorption behavior as a function of solution pH

Ca-alginate beads showed no affinity toward As (III) or As(V) as evidenced by the poor removal efficiency (up to 3%) of these species. In contrast, Fig. 2 shows an improved removal percentage of As(III) and As(V) as a function of pH when using Ca–Fe(III) alginate beads. The initial As concentration was 0.100 mg/L for all solutions. As can be observed from Fig. 2, there is no significant pH dependence for either species. As(III) could be removed up to 54% with optimum performance in the range between pH 4.0 and 8.0. Other studies such as Min and Hering, Lim et al., and Zouboulis and Katsoyiannis did not achieve nor reported the removal of As(III), which is more relevant due to its toxicity [22,24,25]. In comparison, As(V) shows maximum removal efficiency up to 80% at pH 2.0 and the sorption gradually decreases as pH increases. The main mechanism of removal is believed to be the adsorption of arsenic species through the formation of coordination compounds within the iron dispersed in the Ca-alginate matrix [24]. It is also worth mentioning that As(V) is negatively charged ($H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}) over a broad pH range (2.3–14); and, therefore, is attracted toward the partially positive ferric surface by coulombic attractions. In contrast, As(III) has a pKa_1 of 9.1, above which $H_2AsO_3^-$ will be the predominant species. Unlike As(V), the removal of As(III) did not increase with increasing pH, which may be due to the negative net surface charge of iron hydroxide repelling the negative arsenic species at that pH [29]. Taking into consideration the applicability of this remediation process in real effluents, and in order to minimize the liberation of calcium and iron and avoid the use of reagents to sustain the pH, the next experiments were done at 5 g/L of Ca−Fe(III) alginate beads at pH 6.0. This pH is near to that of natural waters, so future applications of this process may be feasible.

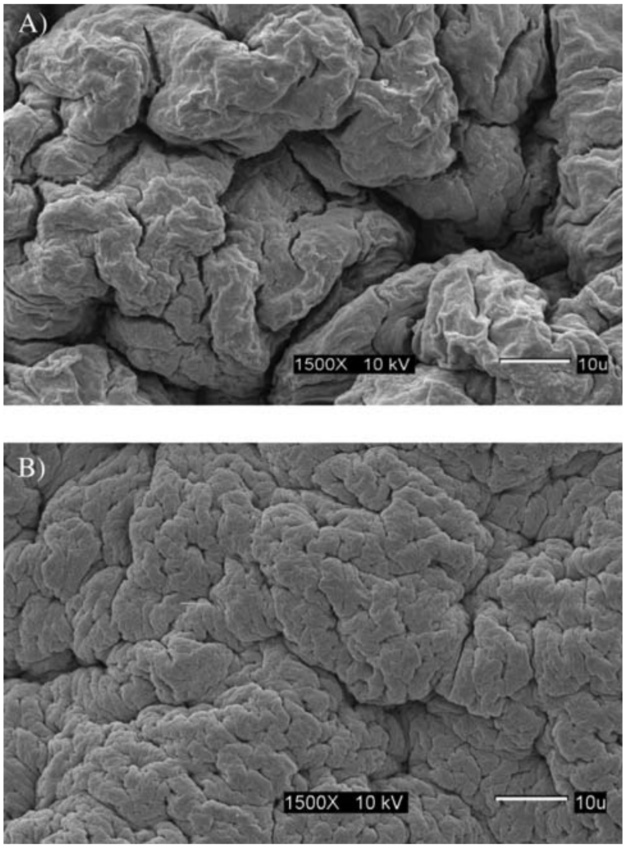

Fig. 1. SEM images of (A) Ca–Fe(III) alginate beads (B) Ca-alginate beads.

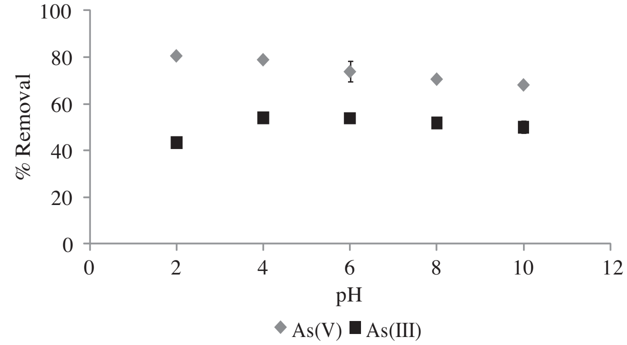

Fig. 2. Removal efficiency of 5 g/L Ca–Fe(III) alginate beads when placed in contact with As(III) and As(V) at 0.100 mg/L initial concentration and pH range from 2 to 10.

3.2.2. Competitive adsorption studies

As seen in Table 1, the removal efficiency for As (V) goes from 93.0 ± 0.1 to 96.3 ± 1.4% removal in the presence of sulfate oxyanions at 0.500 mg/L. The removal efficiency for As(III) goes from 65.0 ± 4.0 to 73.0 ± 0.4% at 0.100 mg/L of carbonate oxyanions used as competitive oxyanions. The results showed that for all the studied concentrations, the difference is not significant with a 95% level of confidence, meaning that an increase in ionic strength did not affect the removal efficiency of either of the arsenic oxyanions. If a strong dependence of the sorption behavior upon the ionic strength existed, then the formation of an outersphere complex characterized by electrostatic coulombic attraction would be expected. In our case, the increasing of ionic strength did not significantly affect the adsorption of arsenic, indicating the formation of innersphere complexes which occur close to the adsorbate surface, and thus form stronger interactions than outersphere complexes. It is worth mentioning that in both the processes, outersphere and innersphere complexes could be formed simultaneously [30,31].

3.2.3. Desorption analysis

The desorption analysis of arsenic oxyanions were conducted using 10% v/v hydrochloric and sulfuric acid. The data in Table 2 showed that As(V) could be removed up to 100% using sulfuric acid and up to 65.07% using hydrochloric acid. In contrast, As(III) was desorbed up to 84.60% using sulfuric acid and 53.72% using hydrochloric acid. This could be explained by the fact that As(V) is easily removed because its interactions include weak coulombic attractions, whereas As(III) is only adsorbed by forming stronger bonds such as innersphere complexes. The difference of recovered arsenic at 2 h and at 24 h was less than 6% in both arsenic species, indicating rapid desorption at a low pH. Our results suggest that at a very low pH, almost all arsenic species exist as neutral species—becoming mobile and easily desorbing from the adsorbent surface [32].

Table 2
Desorption of As(V) and As(III) using 10% v/v nitric, sulfuric, and hydrochloric acids

Time (h)	% Desorbed	As (V)	% Desorbed	As(III)
	H_2SO_4 10% v/v	HCl 10% v/v	H_2SO_4 10% v/v	HCl 10% v/v
2	98.30	63.50	82.01	47.94
5	98.61	63.92	83.02	52.50
20	100.00	64.68	84.97	53.07
24	100.00	65.07	84.60	53.72

3.3. FT-IR spectrum

The FT-IR spectra shown in Fig. 3 for Ca–Fe(III) alginate beads have four bands present: a band at 3,336 cm^{-1} from the OH stretching, a strong band at 1,587 cm^{-1} as a result of CO asymmetric stretching, and two bands at 1,375 and 1,022 cm^{-1}, respectively, related to CO symmetric stretching. The presence of the symmetric CO bands indicates that the carboxylic group of the alginate is associated to a metal as a bidendate ligand [33,34]. Fig. 3(A) shows the As(V) interaction with OH and CO bands, which results in a decrease in the intensity of both the functional groups. In contrast, the spectrum for As(III) shown in Fig. 3(B) resembles that of bare Ca–Fe(III) alginate beads (Fig. 3(C)). These results suggest that As(V) may experience coulombic interactions within the alginate bead surface, whereas the As(III) has no net

Table 1
Competitive adsorption studies for As(III) and As(V) onto 5 g/L Ca–Fe(III) alginate beads at pH 6.0 and diverse ratio of competitive oxyanions (CO)

		As(V)		As(III)	
	Ratio As:CO	% Removal ± SD	*t* student (95%)	% Removal ± SD	*t* student (95%)
	1:0	93 ± 1	–	65 ± 4	–
CO_3^{2-}	1:1	94.5 ± 1.6	3.00	53.1 ± 0.4	0.90
	1:3	94.8 ± 0.8	3.10	52.2 ± 0.7	1.70
	1:5	93.6 ± 1.7	1.10	48.8 ± 2.9	0.40
SO_4^{2-}	1:1	95.3 ± 0.4	2.80	73.0 ± 0.2	2.20
	1:3	96.1 ± 0.1	1.40	70.0 ± 4.4	4.40
	1:5	96.3 ± 1.4	2.30	72.6 ± 2.6	3.90

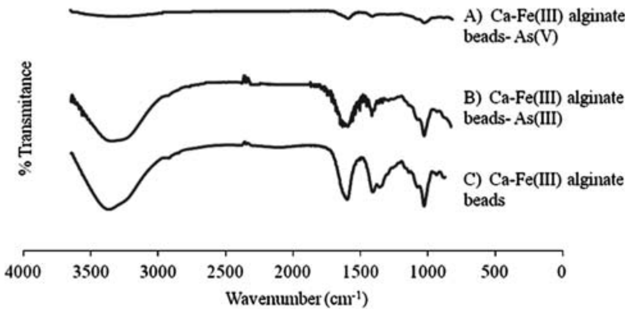

Fig. 3. FT-IR spectra of (A) Ca–Fe(III) alginate beads with As(V), (B) Ca–Fe(III) alginate beads with As(III), and (C) Ca–Fe(III) alginate beads.

charge at that pH, therefore, obstructing these type of interactions.

3.4. Langmuir isotherm

The Langmuir isotherm fits the data better than other models; the results are summarized in Table 3. As shown in Table 3, the $q_{\max}$, Langmuir constant for As(V), is larger than that of As(III), indicating that the adsorption capacity of Ca–Fe(III) alginate beads is greater for As(V). These results also suggest that more than one mechanism may be involved in the removal of As(V). At pH 6.0, As(V) species are predominantly present as anionic oxyanions; in contrast, As(III) exists as a noncharge species at this pH and is unable to interact with the positive charges, which is consistent with the observed results. The isoelectric point of the amorphous ferric hydroxide ranges between 7.1 and 8.5 at acidic pH, thus the Ca–Fe(III) alginate bead surface is positively charged below pH 7.1 [35]. This phenomenon favors coulombic attraction among the arsenate oxyanions within the positively charged bead surface. Our results suggest that for both the species, the main mechanism of removal is adsorption onto the ferric hydroxide surface.

From the Langmuir isotherms, the R_L parameter was between 0.53 and 0.23 for As(V) and 0.21 and 0.12 for As(III) indicating that the adsorption processes for both the species are favorable at a temperature of 298 K.

As seen in Table 4, our results are comparable with some other published adsorbents used to remove arsenic oxyanions from aqueous environments. However, the Ca–Fe(III) alginate beads represent a novel, easily synthesized, and cheap alternative for

Table 3
Langmuir and Freundlich isotherm results for As(III) and As(V) onto 5 g/L Ca–Fe(III) alginate beads at pH 6.0

	Langmuir			Freundlich		
	$q_{\max}$ (mg/g)	b (L/mg)	R^2	K (mg/g) (L/mg)^n	n	R^2
As(III)	0.117	5.21	0.9487	0.122	3.93	0.9056
As(V)	0.364	1.79	0.9849	0.449	2.60	0.8646

$q_{\max}$ Langmuir constant—uptake capacity (mg/g).
b Langmuir constant—affinity of the metal for the sorbent surface (L/mg).
K Freundlich constant—relative uptake capacity (mg/g) (L/mg)^n.
n Freundlich constant—its reciprocal relates to the intensity of the adsorption.

Table 4
Comparison of our results in $q_{\max}$ Langmuir parameters with those of other sorbents reported in literature

Sorbent	$q_{\max}$ (mg/g) As(III)	$q_{\max}$ (mg/g) As(V)	Study
Ca–Fe(III) alginate beads	0.117	0.364	This study, 2012
Activated carbon	0.21	–	[10]
Magnetite alginate beads	–	6.75	[27]
Granulated activated carbon	0.0811	0.2626	[36]
Laterite soil	–	0.18*	[37]
Activated bauxsol	0.541	7.642	[38]
Iron coated sand	0.41	0.043	[39]
Nanostructured akaganeite	–	1.80	[40]

*Total arsenic $q_{\max}$ Langmuir constant—uptake capacity (mg/g).

Table 5
Removal of As(III) and As(V) with diverse Ca-alginate bead experiments

Sorbent	Experimental conditions	As(III) amount adsorbed (mg/g)	As(V) amount adsorbed (mg/g)	Study
Ca–Fe(III) alginate beads	5 g/L at pH 6.0 for 24 h	0.1170*	0.3640*	This study, 2012
Fe(III)-doped alginate gels	Five beads/0.05 L at pH 4.0 for 24 h	–	0.0065	[22]
Iron oxide loaded alginate beads	Column (40 × 2.86 cm) at pH 5.0	_	0.0048	[24]
Alginate-encapsulated magnetic sorbent	0.5 g/L at pH 3.0 for 48 h	_	0.0004	[25]

*$q_{\max}$ Langmuir constant—uptake capacity (mg/g).

the remediation of arsenic oxyanions in comparison with other adsorbents such as activated carbon. Table 5 reports As(III) and As(V) adsorption experiments with diverse Ca-alginate beads and pH. Contrary to the other experiments listed, our study could remove As (III). Our results suggest the use of Ca–Fe(III) alginate beads to remove arsenic species from dilute aqueous solutions such as those found in real contaminated effluents.

4. Conclusions

Our results suggest that the Ca–Fe(III) alginate beads are efficient in the removal of arsenic oxyanions present at trace levels over a broad pH range (4–8) including those found in natural waters. The arsenic adsorption seems to be unaffected by changes in anionic competence suggesting the formation of an inner-sphere complex within the adsorbent. Ca–Fe(III) alginate beads are proposed as a green sorbent for use in the real contaminated effluents including arsenic contaminated natural waters found in many countries around the world. The general mechanism of arsenic removal is suggested to be the formation of inner-sphere surface complexes (Fe–AsO_4) within the Ca–Fe (III) alginate beads. However, in the case of arsenate, the dominant species at pH 6.0 is $H_2AsO_4^-$, therefore, coulombic attractions between the charged iron and the arsenate anions could be responsible for the enhanced arsenate removal at this pH, when compared with arsenite. In the case of arsenite, the dominant species at this pH is H_3AsO_3, a noncharged species.

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