



Arsenic removal by a waste metal (hydr)oxide entrapped into calcium alginate beads

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ABSTRACT

In this work, a solid waste material from an electroplating industrial plant has been investigated for As(III) and As(V) sorption. This sorbent, a mixture of mainly Fe(III) and Ni(II) (hydr)oxides, has been used both in its native form and entrapped in calcium alginate. The effect of sorbent concentration in the gel bead, solution pH, contact time and As(III) and As(V) concentration on sorption has been studied. Furthermore the effect of the gel matrix has been investigated. A 10% (w/v) of (hydr)oxide in the gel beads was found to provide both spherical beads shape and good sorption performance. Solution pH was found to exert a stronger influence in As(V) than in As(III) sorption. The optimum pH range resulted to be within 5–10 for As(III) and within 6–9 for As(V). Taking into account these results, pH 8 was chosen for further sorption experiments. Equilibrium was reached after 48 h contact time for the studied systems. Kinetics data of both As(III) and As(V) onto native (hydr)oxide (O) and entrapped in calcium alginate beads (10% O–CA) were successfully modelled according to pseudo-first and pseudo-second order equations. Sorption equilibrium data were evaluated by the Langmuir isotherm model and the maximum capacity q_{\max} were 77.4 and 126.5 mg g⁻¹ for As(III) on O and 10% O–CA, and 26.8 and 41.6 mg g⁻¹ for As(V) on O and 10% O–CA, respectively. The entrapment of the (hydr)oxide in a calcium alginate gel matrix improved the As(III) and As(V) sorption by 60%.

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1. Introduction

Arsenic is a ubiquitous metalloid and its presence in hazardous concentrations in waters is considered as a worldwide problem, often referred to as a 20th–21st century calamity [1–4]. Arsenic occurrence in the environment can be due to human activities such as mining, pesticides use, smelting of non-ferrous metals, burning of fossil fuels and timber treatment. Recent studies carried out northeastern England revealed As enrichment within the urban and industrially affected rivers [5]. Arsenic concentration in the rural areas averaged between 0.6 and 0.9 mg L⁻¹, and between 3.2 and 5.6 mg L⁻¹ for rivers influenced by industrial discharges. In India, health hazards linked with high levels of arsenic in tube well waters (0.2–2.0 mg L⁻¹) have also been reported [6].

Arsenic in groundwater is often associated also to geogenic sources: the Earth's crust is an abundant natural source of arsenic, being present in more than 200 different minerals. Long-term drinking water exposure can cause different dysfunctions and diseases as, loss of appetite and nausea, muscular weakness, neuro-

logical disorders, and cancers [7]. Consequently, the standard level in drinking water has been fixed in 10 µg L⁻¹ in many parts of the world, including Europe [8] and the U.S.A. [9].

The chemistry of this element includes the existence of different oxidation states, the most common in natural waters being As(III) in form of H₃AsO₃⁰ and H₂AsO₃⁻ and As(V), as H₂AsO₄⁻ and HAsO₄²⁻, according to the pH of the solution.

Different methods such as oxidation/precipitation, sorption onto different activated carbons, membrane techniques and ion exchange have been used for arsenic removal [10–12]. All these methods are usually expensive. That is why an increasing attention is currently being paid to the development of new sorbents such as natural raw materials [11], agricultural or industrial wastes [1,13] due to both their local abundance and low cost. Among the different available materials presenting arsenic sorption properties, those containing metals, and especially iron are known for being very effective sorbents [14–19].

In this paper, a non-expensive (hydr)oxide waste, the solid by-product from a chromium electroplating industry, is characterized and used as a low cost sorbent for the removal of either As(III) or As(V) from aqueous solutions. In order to facilitate its application, the raw material has been immobilized into a calcium alginate gel matrix. This entrapment procedure was previously success-

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fully applied for grape stalks powder [20]. In that work, the results proved that Cr(VI) sorption was enhanced when the sorbent was entrapped into the calcium alginate gel matrix. The effect of the gel matrix, sorbent concentration in the gel bead, solution pH, contact time and As(III) and As(V) concentration on sorption has been studied.

2. Experimental

2.1. Materials

The metal (hydr)oxide solid was kindly supplied by an electroplating industry from Valencia (Spain). This material is a by-product formed after the precipitation with NaOH, coagulation and flocculation of metals present in the main waste effluent. All solutions were prepared in HPW (high purity deionized water from Milli-Q apparatus; resistivity 18.2 M Ω cm, TOC < 10 μ g L⁻¹). As(III) and As(V) solutions were prepared by dissolving appropriate amounts of reagent grade sodium (meta)arsenite (NaAsO₂; >99%, Fluka) and sodium arsenate heptahydrate (Na₂HAsO₄·7H₂O; >98.5%, Fluka), respectively, in HPW. Concentrated solutions of NaOH (Panreac) and HNO₃ (Panreac) were used for pH adjustment, and arsenic standard solutions of 1000 mg L⁻¹ (Panreac) for Flame Atomic Absorption calibrations. Sodium alginate salt from brown algae (Fluka) was used as the hydrocolloidal gelling material, with a fixing solution of 0.1 M CaCl₂ (Panreac).

2.2. (Hydr)oxide mixture analysis

Dry waste (hydr)oxide samples (ca. 0.3 g) were digested in a microwave oven (ETHOS, Milestone) with 8 mL of HNO₃ (65%, Suprapur, Panreac) and 2 mL of HCl (37%, Suprapur, Panreac). In the 3-step program, a first heating to 90 °C during 2.5 min is followed by heating to 130 °C for 5 min and finally to 190 °C for 13.5 min. After this process, samples were allowed to cool to room temperature and were diluted with HPW to a final volume of 100 mL. Metal composition of the (hydr)oxide was determined by FAAS spectroscopy (Varian Absorption Spectrometer SpectrAA 220FS).

2.3. Sorbent characterization

Specific surface area (SSA) of the sorbents (raw (hydr)oxide, (hydr)oxide entrapped in calcium alginate beads and calcium alginate beads (blank)) was determined according to the Brunauer–Emmet–Teller (BET) protocol on a Micromeritics Flow-Sorb III equipment. Surface charge distribution as a function of pH and pH_{pzc} of the sorbents were determined from potentiometric titrations of 1 g L⁻¹ solid suspension with 0.01 M NaOH or HNO₃ in 0.01 M NaNO₃ medium as supporting electrolyte and using a PHM 250 (Meterlab) pH meter. The point of zero charge (pH_{pzc}) was evaluated by plotting the surface charge as a function of solution pH according to the method proposed by Davranche et al. [21].

2.4. Sorbent preparation and entrapment in calcium alginate

The raw (hydr)oxide was rinsed, dried at 60 °C and sieved to obtain a fine powder (<250 μ m) before its use in sorption experiments. In order to improve both mechanical and hydrodynamic properties of the (hydr)oxide, the material was entrapped in a calcium alginate gel.

Gel beads containing the (hydr)oxide were prepared according to the scheme given by Fiol et al. [20]. The desired amount of (hydr)oxide (within the range 0–12 g) was added to 100 mL HPW under rapid constant magnetic stirring. To the homogeneous (hydr)oxide suspension, 1 g of sodium alginate powder was slowly

added and the mixture was stirred until total biopolymer dissolution was achieved. A peristaltic pump (Ismatec Reglo) was used to dispense the suspension in a stirred reservoir containing 200 mL of a CaCl₂ 0.1 M solution used for gel formation. At the end of the dispensing tube a micropipette tip (yellow type 5–200 μ L, Deltalab) cut out to get a final diameter of 1 mm was attached and positioned approximately 1 cm above the surface of the fixing solution. The peristaltic pump was programmed to provide a constant flow rate of ca. 350 mL h⁻¹. The beads formed (3 mm diameter) were allowed to cure, under continuous stirring, in the same CaCl₂ solution for 24 h; they were rinsed three times with HPW to ensure the removal of excess Ca²⁺. Total removal of Ca²⁺ ions was checked by FAAS analysis of the supernatant. For all the experiments, the beads with a non-spherical shape were discarded. Water content was 97.6 \pm 0.1 for pure alginate beads and 91.1 \pm 0.3 in the beads loaded with 10% (w/v) of (hydr)oxide.

Along the paper, the sorbents will be named as: raw (hydr)oxide (O), the beads containing X% (w/v) of (hydr)oxide (X% O–CA) and the beads of pure calcium alginate (blank) (CA).

2.5. General uptake procedure

Batch experiments were carried out separately on As(III) or As(V) solutions at 20 \pm 1 °C in stoppered plastic flasks. The experiments consisted of shaking in an orbital shaker (Ikalabortechnik KS 501) at 200 rpm either a mass of (hydr)oxide mixture (O) or the number of beads of 10% O–CA containing the same mass of (hydr)oxide, with 20 mL of either As(III) or As(V) solutions until equilibrium was reached. After agitation the solid was removed by filtration through a 0.45 μ m cellulose filter paper (Millipore) and solution pH was measured. Initial and final arsenic concentration in the filtrates before and after sorption, previously acidified, were determined by Flame Atomic Absorption Spectrometry (FAAS) (Varian Absorption Spectrometer SpectrAA 220FS).

Arsenic concentration in the solid phase, q , was calculated from the difference between initial, C_i and final, C_f concentration in solution. Kinetic and equilibrium experiments were carried out in triplicate.

The U.S. EPA toxicity characteristic leaching procedure (TCLP) [22] was carried out to determine the potential mobility of the metals forming the (hydr)oxide and, thus, to obtain information about the potential hazard of the sorbents before and after arsenic sorption. Samples of sorbents were treated with the standardized extraction fluid (5.7 mL glacial CH₃COOH added to 500 mL of HPW, plus 64.3 mL of 1 M NaOH and diluted to 1 L, pH 4.9), and agitated on an orbital shaker for 18 h. The solid/liquid ratio was 1:20. The concentrations of extracted metals (Fe, Ni, Cu and Cr) and As were determined by FAAS.

2.6. Effect of pH

The pH is an important parameter in sorption-based water treatment processes, because proton concentration can strongly modify the redox potential of sorbates and sorbents, provoke dissolution of the sorbent material and modify chemical speciation of sorbates as well as surface charge of sorbents [23].

The effect of initial pH on As(III) and As(V) sorption onto raw and entrapped (hydr)oxide was studied. For these experiments, the initial pH was varied within the range 2–12.5, temperature was maintained at 20 \pm 1 °C and the agitation time was fixed to 48 h.

2.7. Kinetic study

Sorption kinetic experiments were conducted to obtain information on the equilibrium time and on the effect of entrapment

into the gel matrix on the sorption rate of As(III) or As(V). Initial pH of each solution was adjusted to 8.0 and was allowed to freely evolve during the sorption process. At suitable time intervals within the range 0–72 h, 10 mL samples were withdrawn by using a syringe, filtered and then, pH was measured and arsenic concentration was determined. For a blank the same experiment was performed by using 535 CA beads.

2.8. Isotherm study

A broad concentration range (initial concentration in As(III) or As(V) within 5–500 mg L⁻¹) was selected to evaluate As sorption behaviour, considering that some extreme values have been reported: e.g. up to 850 mg L⁻¹ from a former mining site [24]. The initial pH was adjusted to 8.0, temperature was maintained at 20 ± 1 °C and the agitation time was fixed to 24 h. For a blank, isotherms were also obtained by using 20 CA beads.

2.9. Solid state analysis

Various instrumental techniques were used to characterise the raw (hydr)oxide mixture and to obtain information about changes in properties of the solid due to arsenic sorption.

X-ray diffraction (XRD) analysis on a Siemens D5000 diffractometer using filtered copper K α 1 radiation were performed in order to ascertain crystalline state on the solid. 2 θ angle was varied in the range 10–50° with 2000 steps.

Surface topology and local chemical composition of the sorbent were analysed by Scanning Electron Microscopy (Zeiss DSM 960 A) and Energy Dispersive X-Ray analysis (SEM-EDX, Link Isis Pentafet, Oxford) after carbon coating of the samples.

Infrared spectra with Attenuated Total Reflectance (FTIR-ATR) were obtained by direct measurement on the solid with a Mattson Satellite with MKII golden gate reflection ATR system at 2 cm⁻¹ resolution.

For all these analysis, arsenic-loaded samples were prepared by contacting 1 g of O or the equivalent number of 10% O-CA beads with 200 mL of either As(III) or As(V) 500 mg L⁻¹ solution at pH 8.0 for 48 h. Before the corresponding instrumental analysis, samples were washed with HPW in order to eliminate the non-sorbed arsenic and then dried at 105 °C until constant weight. Arsenic concentration in solution was analysed and its concentration in the solid phase was calculated.

2.10. Quality assurance/quality control

To assure the accuracy, reliability and reproducibility of the collected data, all batch isotherm and kinetic tests were performed in triplicate and average values are reported. The variance in arsenic concentration and sorption capacity were found to be 8% and 7%, respectively.

All the chemicals used in this work are AR grade. All the labware has been previously soaked in 1 M HNO₃, triply rinsed with distilled water and dried. Blank tests have been run in parallel on arsenic solutions without addition of sorbent, showing that the experimental procedure does not lead to any reduction of arsenic concentration and pH variation. Furthermore, blank tests performed with HPW adjusted at pH 8 without arsenic addition have shown that O and 10% O-CA do not release any metal cation to the solution (results not shown).

The accuracy of analytical techniques has been checked by the evaluation of the relative standard deviation (RSD) of each sample analysis. Typical values of the RSD for arsenic are below 7%, while for the standard solution they are lower than 5%.

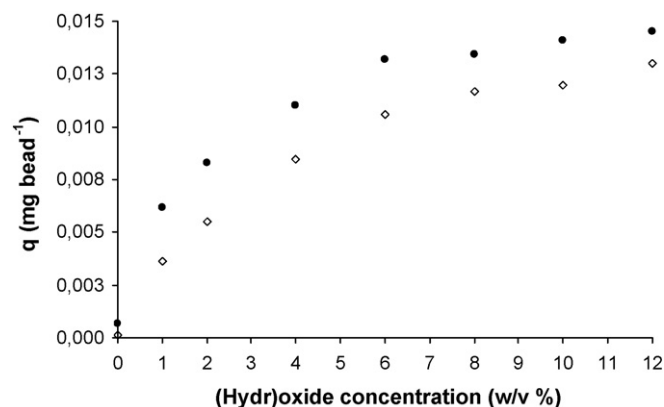


Fig. 1. Effect of (hydr)oxide concentration in gel beads on As(III) (◇) and As(V) (●) removal. Sorbent dose: 1 bead mL⁻¹; initial As concentration: 15 mg L⁻¹; initial pH: 8.0; contact time: 48 h.

Regression analysis of experimental data has been carried out with the statistic software SigmaPlot 9.0[®] for Windows (SPSS Inc.). The correlation coefficient (R^2) and the standard error in parameter evaluation have been reported as indexes of the accuracy of optimal data fitting analysis.

3. Results and discussion

3.1. (Hydr)oxide mixture analysis and sorbents characterization

The content of the major metals of the raw (hydr)oxide was found to be (mg g⁻¹) Fe(III): 142.3 ± 1.4, Ni(II): 174.4 ± 4.1, Cu(II): 15.4 ± 0.4, Cr(III): 15.1 ± 0.6 and Ca: 12.6 ± 0.4. The oxidation states for Fe and Cr were checked with colorimetric methods.

The specific surface area values were 168 ± 6 and 23.5 ± 0.1 and 0.24 ± 0.1 m² g⁻¹ for O, 10% O-CA and CA, respectively.

The point of zero charge pH_{pzc} was 8.2 ± 0.2 and 8.1 ± 0.2 for O and 10% O-CA, respectively. These values are similar to the pH_{pzc} value (8.3) found for a Fe(III)/Cr(III) waste hydroxide mixture [25]. pH_{pzc} of the blank (CA) was 6.5 ± 0.1.

3.2. Effect of (hydr)oxide concentration in beads

An increase of (hydr)oxide concentration in the gel bead provoked an increase of arsenic sorption (Fig. 1). A sorbent concentration of 10% (w/v) in the beads was considered appropriate for sorption experiments. A higher percentage was found to provoke pumping troubles and low sphericity of the beads. Pure CA beads showed a sorption lower than 0.1 × 10⁻³ mg bead⁻¹ (Fig. 1). Therefore, CA was found inefficient for As(III) and As(V) sorption in the experimental conditions used in this work.

3.3. Effect of pH

Fig. 2 shows the percentage of As(III) and As(V) removed by either raw (hydr)oxide or 10% O-CA beads as a function of initial solution pH. As seen in the figure, As(III) sorption removal percentage achieves a plateau around 81% and 87% for O and 10% O-CA, respectively, within a pH range of 5–10. In the case of As(V) both sorbents achieve 95% removal within a narrower pH range (6–9). It is noticeable that the solid entrapment into the gel matrix seems not to have any influence on As(V) uptake, while a slight favourable effect of the gel entrapment is observed in the case of As(III). We also observed that outside the above-mentioned pH ranges As(III) and As(V) sorption removal decreases. The decrease on sorption at pH ≤ 3 could be due to sorbent mass loss by solubilization and/or

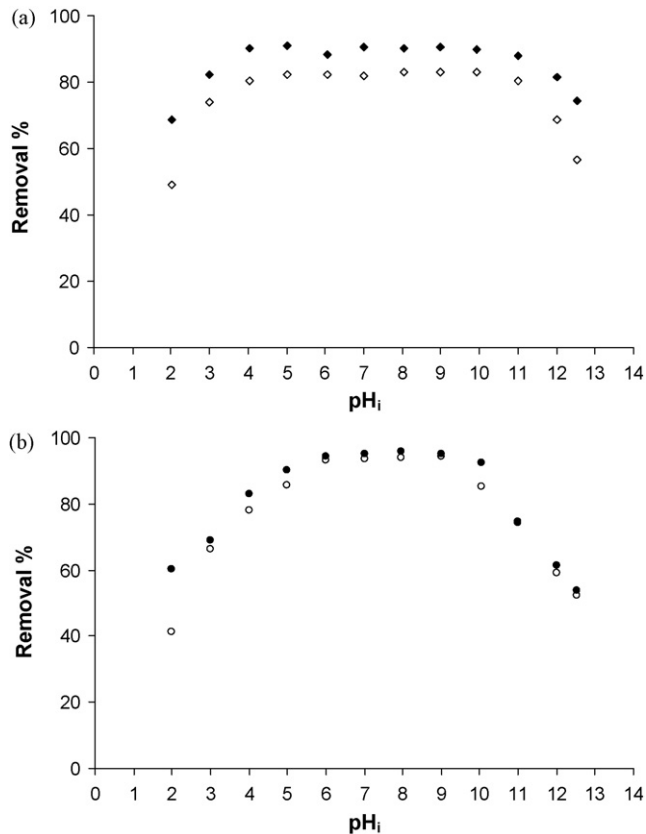


Fig. 2. Effect of initial pH on (a) As(III) (\diamond , \blacklozenge) and (b) As(V) (\circ , \bullet) sorption. Open symbols represent O and closed symbols 10% O-CA. Initial As concentration: 15 mg L^{-1} ; (hydr)oxide dose: 1.83 g L^{-1} .

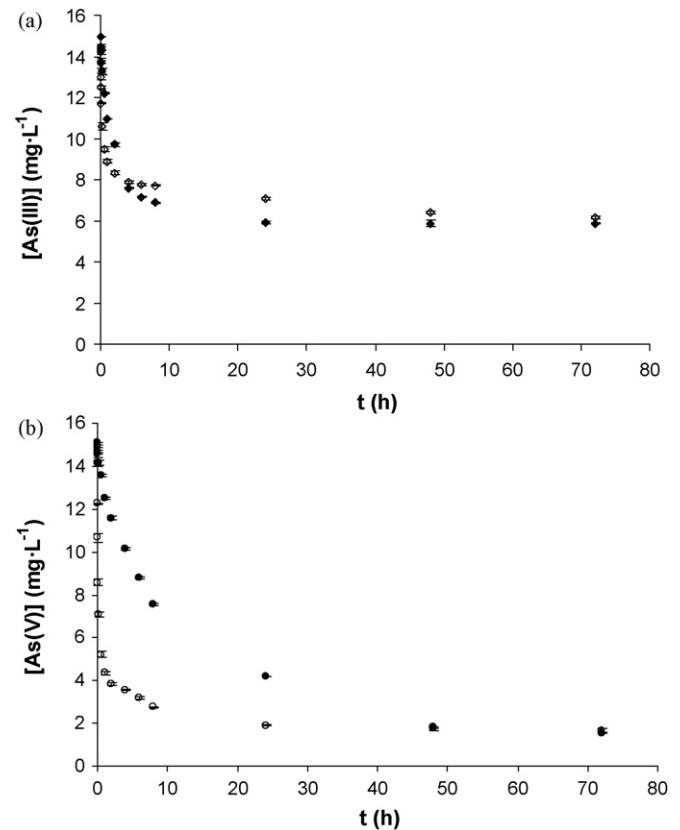


Fig. 3. Arsenic concentration in solution as a function of time for (a) As(III) (\diamond , \blacklozenge) and (b) As(V) (\circ , \bullet) sorption. Open symbols represent O and closed symbols, 10% O-CA. Initial As concentration: 15 mg L^{-1} ; (hydr)oxide dose: 1 g L^{-1} ; initial pH: 8.0.

degradation, while Fe, Ni and Cu were simultaneously released in solution (data not shown).

On the other hand, the decrease of sorption at $\text{pH} > 10$, could be explained by the repulsion of the negative charge of the predominant anionic species in solution of As(III) (H_2AsO_3^-) and As(V) (H_2AsO_4^- and HASO_4^{2-}) [26] and the negative surface charge of the sorbents at $\text{pH} > \text{pH}_{\text{pzc}}$.

From the results in Fig. 2, an initial pH 8.0 was chosen for further experiments. It must be remarked that after arsenic sorption, pH moved to 7.5. This fact seems to indicate that the material acts as a buffer. Indeed, initial pHs within the range 4–9 were found to evolve to final pHs, $6.7 < \text{pH} < 7.9$. Some considerations about the chosen initial pH must be taken into account when discussing sorption results. At the corresponding equilibrium pH 7.5, the surface of the (hydr)oxide is partially positively charged because the pH is lower than pH_{pzc} ; As(III) and As(V) are present in solution as H_3AsO_3^0 and H_2AsO_4^- or HASO_4^{2-} , respectively.

Finally, it must be pointed out that at this pH, no leaching of Fe, Ni, Cu or Cr from the sorbent to the liquid phase due to arsenic sorption was observed (data not shown).

3.4. Sorption kinetics

Fig. 3(a) and (b) shows the effect of contact time on As(III) and As(V) sorption onto O and 10% O-CA gel beads, respectively, for an initial As concentration of 15 mg L^{-1} .

As can be seen, As(III) sorption reaches a plateau at 24 and 48 h for raw and entrapped (hydr)oxide, respectively. In the case of As(V), a contact time of 48 h was needed for both sorbents to reach equilibrium. Therefore, a contact time of 48 h was used in all

subsequent sorption experiments. Other authors reported shorter equilibrium times when studying As(V) and As(III) sorption onto different iron(III)-based sorbents. When using ferrihydrite the time needed to reach equilibrium was 1 h [27] while 4 h were needed when goethite and amorphous iron oxide were used [28]. Longer contact times of ca. 6 and 10 h in the case of As(III) and As(V), respectively, were needed for sorption onto Fe(III)oxyhydroxide-loaded cellulose beads [29] and 24 h were needed to reach equilibrium when the sorbent was a Fe(III)-loaded lignocellulosic substrate [30].

In order to investigate As sorption rate, experimental data were submitted to pseudo-first and pseudo-second order kinetics models [31]. The models characteristic parameters were determined by non-linear regression analysis and are presented in Table 1. Good regression coefficients were obtained when submitting the experimental As(III) and As(V) sorption results to both pseudo-first and pseudo-second order model despite, in general, a slightly better fit was achieved when pseudo-second order model was applied.

As shown in Table 1 the values of the rate constants obtained for native (hydr)oxide were always much higher than those obtained for the entrapped material. These results indicate that the presence of the alginate gel is related to a decrease in sorption rate. It is known that natural hydrocolloid materials, when gelled, form a stable matrix with high porosity and water content. Since the gel forms a quasi-solid structure, however, it would be expected to retard the transport of a solute due to the solute movement through the aqueous regions between the polymer chains [32,33]. Moreover, calcium alginate (pH_{pzc} 6.5), is expected to be partially ionized at $7.5 \leq \text{pH} \leq 8.0$. Therefore, the negative charge on calcium alginate surface could render difficult the diffusion of As(III) (mainly present

Table 1
Pseudo-first and pseudo-second order kinetic parameters for As(III) and As(V) sorption onto O and 10% O–CA

System	k_1 (h^{-1})	q (mg g^{-1})	R^2	k_2 ($\text{g mg}^{-1} \text{h}^{-1}$)	q_e (mg g^{-1})	R^2
As(III) O	7.2 ± 1.8	6.9 ± 0.3	0.897	1.4 ± 0.3	7.2 ± 0.2	0.990
As(III) 10% O–CA	0.58 ± 0.08	8.1 ± 0.3	0.976	0.10 ± 0.01	8.7 ± 0.2	0.958
As(V) O	9.9 ± 1.7	11.3 ± 0.4	0.951	1.1 ± 0.2	11.9 ± 0.2	0.981
As(V) 10% O–CA	0.12 ± 0.01	11.7 ± 0.4	0.980	0.018 ± 0.001	13.4 ± 0.4	0.991

as H_3AsO_3^0) and in a greater extent the diffusion of As(V) (H_2AsO_4^-) species through the gel to reach the sorbent surface.

3.5. Sorption isotherms

Fig. 4(a) and (b) shows the isotherm at $20 \pm 1^\circ\text{C}$ for As(III) and As(V) sorption onto raw and entrapped (hydr)oxide. Sorbents showed a higher capacity for As(III) than for As(V). Moreover, sorption of both arsenic oxidation states is higher with 10% O–CA beads.

The equilibrium experimental data were fitted by the non-competitive Langmuir model, which describes the sorbent surface as homogeneous assuming that all the sorption sites have equal affinity and that sorption at one site does not affect sorption at an adjacent site:

$$q_e = \frac{K_L q_{\max} C_e}{(1 + K_L C_e)} \quad (1)$$

where q_e is the amount of sorbate sorbed per mass unit (mg g^{-1}), C_e is the sorbate concentration remaining in solution at equilibrium (mg L^{-1}), q_{\max} (mg g^{-1}) is the maximum amount of sorbate sorbed per mass unit of sorbent and K_L (L mg^{-1}) is a constant

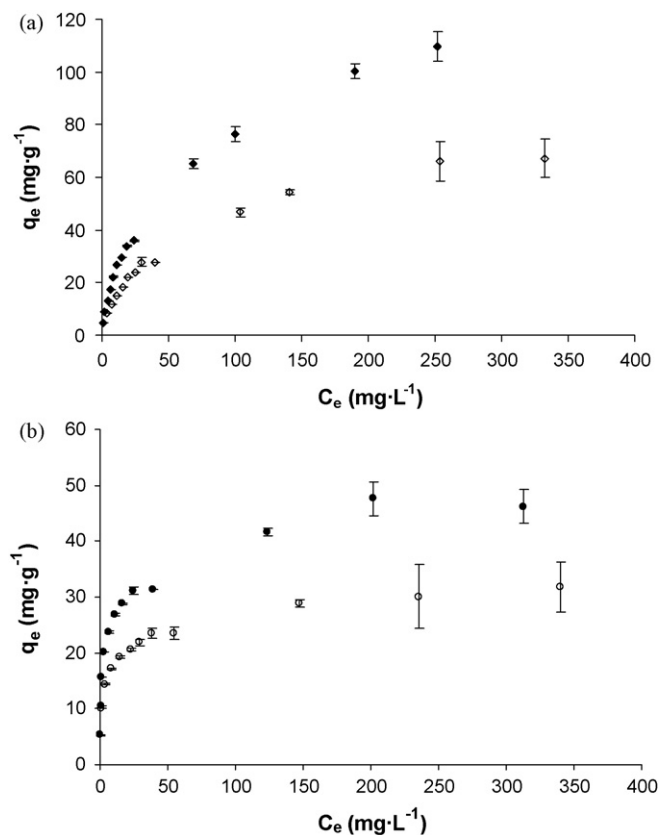


Fig. 4. Sorption isotherms of (a) As(III) (\diamond , \blacklozenge) and (b) As(V) (\circ , \bullet) sorption. Open symbols represent O and closed symbols 10% O–CA. Sorbent dose: 1 bead mL^{-1} ; initial pH: 8.0; contact time: 24 h.

related to the energy of sorption which quantitatively reflects the sorbent–sorbate affinity. Langmuir (q_{\max} and K_L) parameters were obtained by non-linear analysis of the equilibrium experimental data (Table 2): quite good correlation coefficients were obtained with this sorption equilibrium model, for all the studied systems.

For all the equilibrium data points, the pH evolved from the initial pH 8 to pH 7.5. The same pH variation was observed when contacting blank solutions with the sorbent materials.

The value of the parameter K_L is related to the sorbent–sorbate affinity, a higher K_L value being indicative of a more favourable sorption. Our results revealed a similar affinity of both raw and calcium alginate-entrapped (hydr)oxide for a given oxidation state, and a higher affinity of the material for As(V) than for As(III).

From the values of q_{\max} presented in Table 2, an increase of 60% in capacity is evidenced when the solid (hydr)oxide is entrapped. This might be attributed to the presence of calcium alginate but, as said before As(III) and As(V) sorption by pure calcium alginate beads was found to be negligible in the experimental conditions used in this work. However, it has been previously reported that calcium alginate can be efficiently activated for As(V) sorption by partial substitution of calcium by ferric ions [34].

Results obtained in this work are compared to those obtained by several authors who studied As(III) and As(V) sorption by different Fe(III)-rich mineral or oxide-based materials (Table 3). As seen, the maximum sorption values obtained for As(III) when using 10% O–CA are comparable to iron-loaded sorbents as synthetic mixed Fe–Mn oxide [39] and Fe(III)-loaded sponge [42]. In the case of As(V), the results obtained in this work are similar to those obtained with Fe(III)-loaded chelating resin [38] and Fe(III)oxide-loading slag [40].

3.6. Solid state analysis and the sorption mechanism

According to the XRD pattern of native (hydr)oxide (Fig. 5), the (hydr)oxide solid can be identified as a poorly crystalline iron oxyhydroxide, similar to 2-lines ferrihydrite [46]. The almost absence of crystallinity after loading the sample with As(III) and As(V) indicates that there was no crystalline phase transformation after arsenic sorption. Furthermore, despite SEM micrographs revealed an important arsenic surface concentration after treatment with As(III) and As(V) solutions (Fig. 6(b) and (c), respectively), no significant surface topology changes were evidenced when comparing with the micrographs of untreated material (Fig. 6(a)).

The FTIR spectra of native dry (hydr)oxide and after treatment with both As(III) and As(V) solutions (Fig. 7) exhibited a wide band

Table 2
Langmuir isotherm parameters for As(III) and As(V) sorption onto O and 10% O–CA

System	Langmuir model		
	q_{\max} (mg g^{-1})	K_L (L mg^{-1})	R^2
As(III) O	77.4 ± 3.1	0.018 ± 0.002	0.984
As(III) 10% O–CA	126.5 ± 5.8	0.019 ± 0.002	0.985
As(V) O	26.8 ± 1.0	0.26 ± 0.07	0.905
As(V) 10% O–CA	41.6 ± 2.2	0.25 ± 0.07	0.886

Table 3
Maximum arsenic sorption capacity of O and 10% O–CA compared with other sorbents (in mg As per g of solid material)

Sorbent	Capacity (mg g ⁻¹)		Reference
	As(III)/(pH)	As(V)/(pH)	
Raw mixed (hydr)oxide	77.4/(8.0)	26.8/(8.0)	This work
10% O–CA	126.5/(8.0)	41.6/(8.0)	This work
Red mud	0.66/(7.25)	0.52/(3.50)	[35]
FePO ₄ (amorphous)	21/(7–9)	10/(6–6.7)	[36]
FePO ₄ (crystalline)	16/(7–9)	9/(6–6.7)	[36]
Goethite	7.5/(5.5)	12.5/(5.5)	[37]
Ferrihydrite	266.5/(8–9)	111.0/(8–9)	[27]
Fe(III)-loaded chelating resin	62.9/(9.0)	55.4/(3.5)	[38]
Fe(III)oxide pillared clay	13/(<9)	4/(<9)	[28]
Goethite	22/(9)	4/(9)	[28]
Hydrous Fe(III)oxide	28/(<9)	7/(<9)	[28]
Synthetic mixed Fe–Mn oxide	132.6/(4.8)	71.9/(4.8)	[39]
Fe(III)oxyhydroxide-loaded cellulose beads	99.6/(7)	33.2/(7)	[29]
Fe(III)oxide-loaded slag	≈10/(2.5)	≈35/(2.5)	[40]
Fe(III)-doped lignocellulose	11/(6)	22.5/(4)	[30]
Fe(III)-loaded resin	11.2/(1.7)	60.0/(1.7)	[41]
Fe(III)-loaded amberlite resin	15/–	108.6/–	[16]
Fe(III)-loaded sponge	137/(4.5)	18/(9)	[42]
Alginate beads doped with Fe(III)oxide	–	4.75 μg g ⁻¹ /(7)	[43]
Fe(III)oxide-coated alginate beads	–	2.6 μg g ⁻¹ /(7)	[43]
Fe(III)oxide-loaded alginate beads	–	7.2 μg g ⁻¹ /(7)	[43]
NiO	–	≈4/(8.4)	[44]
Fe(III)oxide/activated carbon composite	–	74.4/(5.0)	[45]

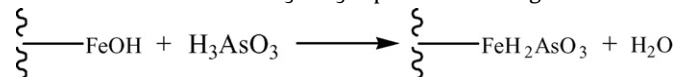
centred at 3360 cm⁻¹, corresponding to bulk OH stretch and free surface OH groups and another band at 1640 cm⁻¹ corresponding to water bending [47]. The large band at 3360 cm⁻¹ confirmed the XRD data for a disordered crystal structure [48]. The band at 1105 cm⁻¹, corresponding to M–OH bending (M = metal), almost disappeared when loading the sorbent with both As(III) and As(V). This result indicated that interactions of M–OH groups with either As(III) and As(V) species would play an important role in the sorption mechanism [47].

In the literature, different arsenic sorption mechanisms on various iron(III)-based sorbents have been reported. Lenoble et al. [36] proposed As(III) removal mechanisms by Fe(III) derivatives based on the oxidation to As(V) and the precipitation of an Fe(II) arsenate salt, like Fe₃(AsO₄)₂·8H₂O. In our case, the absence of iron in solution at pHs within the range 4–11, where As(III) sorption is maximum, indicates that this mechanism is not involved in the removal of As(III).

Taking into account (i) the characteristics of our (hydr)oxide solid, (ii) the absence of crystallinity and (iii) the presence of functional groups on the sorbent surface (mainly free hydroxyls) and

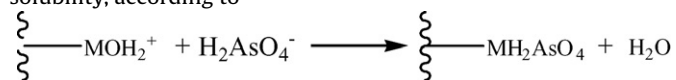
considering (iv) the nature of arsenic species present in solution at the working pH, we proposed in Fig. 8 the mechanisms for As(III) and As(V) sorption onto (hydr)oxide.

For As(III) removal we supposed that the free hydroxyls of the sorbent interact with the H₃AsO₃⁰ species according to



Such a sorption mechanism has been reported in the literature, as responsible for As(III) and As(V) sorption onto an aquifer material of complex mixture mineralogical nature [49].

In the case of As(V), two different mechanisms can contribute to sorption: (i) non-specific coulombic interactions between As(V) species and the positively charged functional groups on the sorbent surface and (ii) coordination of As(V) species onto metal (hydr)oxides with the formation of coordination compounds of low solubility, according to



A question remains: what can be the effect of co-precipitated metal hydroxides (mainly Ni(II))? Although information from literature is scarce, one can refer to Jia and Demopoulos [50] who claimed an enhanced co-precipitation of As(V) with Fe(III) in the presence of Ni(II); this is probably due to sorption on a co-precipitated nickel–ferric hydroxide. Moreover, the As(V) loading capacity of metal-doped goethite decreased in the order: Cu(II)-doped ≥ Ni(II)-doped > Co(II)-doped > pure goethite, whatever the pH [51]. Such a doping led to an increase in pH_{ZPC} and also in surface area, both phenomena allowing to increase the sorption behaviour. Similar explanation can be applied to our mixed (hydr)oxide material.

3.7. Hazard classification of the spent sorbent

The EPA TCLP Test was applied to the As-loaded sorbent used in the sorption experiments to classify this material as inert or hazardous before any disposal [22]. In an attempt to quantify the hazard, the U.S. EPA established the general guidance that if metal

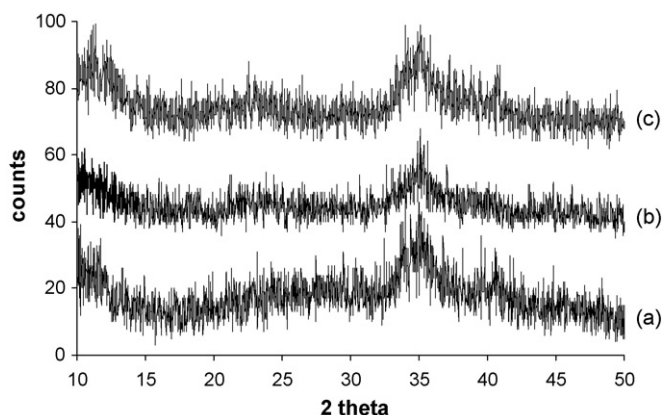


Fig. 5. XRD of (hydr)oxide before (a) and after As(III) (b) or As(V) (c) sorption.

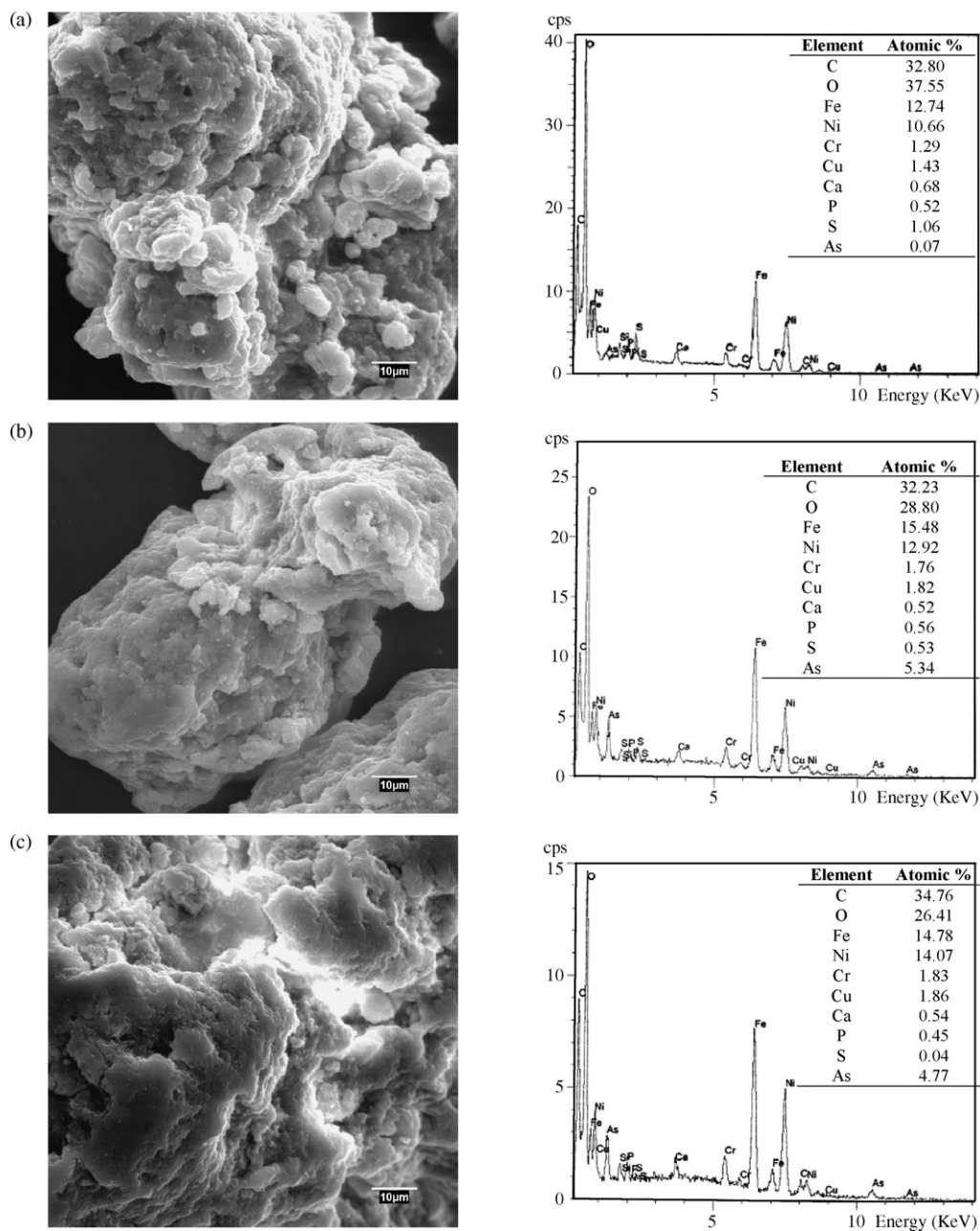


Fig. 6. SEM-EDX analysis of (hydr)oxide before (a) and after As(III) (b) or As(V) (c) sorption.

concentrations in the extract do not exceed 100 times the Maximum Contaminant Level (MCL) in drinking water for that metal, the waste would not be considered hazardous. Among the elements in our (hydr)oxide material, only As, Cu and Cr are included in the EPA listing; iron can be found within the national secondary drinking water standards, with a MCL of 0.3 mg L^{-1} . A recent provisional MCL value of 0.1 mg L^{-1} was given by EPA for nickel in drinking water.

According to the results obtained in the leaching test (Table 4) neither Fe, Cu, Cr nor As extracted amounts exceeded the criteria of 100 times the MCL set by the U.S. EPA. Only according to the data for nickel, the corresponding waste would have to be managed as a hazardous material. However, we have to point out that this TCLP test is a worst-case scenario, not realistic compared to common environmental conditions, and that other standardized tests might give different waste classification.

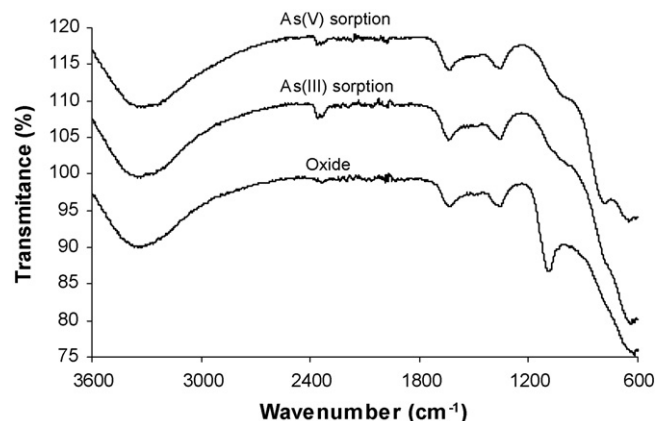


Fig. 7. FTIR-ATR spectra of (hydr)oxide before and after As(III) or As(V) sorption.

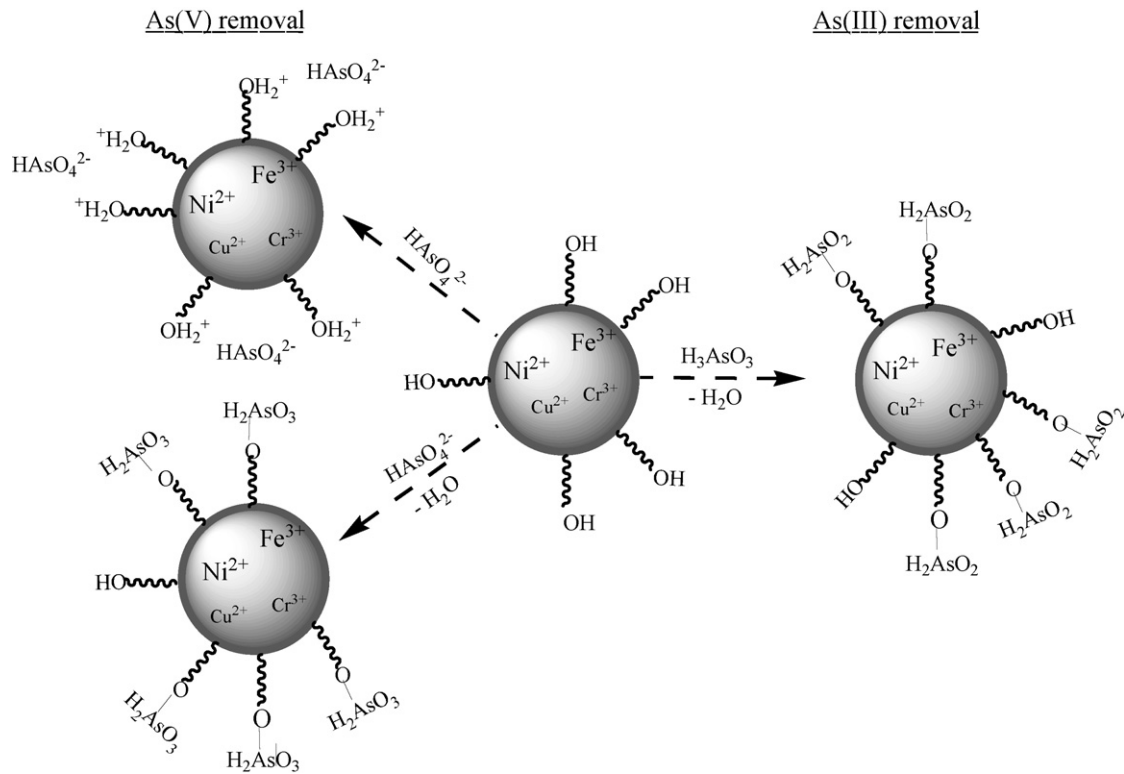


Fig. 8. As(III) and As(V) sorption mechanisms onto (hydr)oxide gel beads.

Table 4

Concentrations in TCLP extracts from different sorbents, before and after As sorption; comparison with the MCL (Maximum Contaminant Level) in drinking water and the TCLP limiting values for hazardous waste

	Concentration (mg L ⁻¹)				
	Fe	Ni	Cu	Cr	As
O	0.08	99.8	1.76	0.88	0.12
O-As(III)	0.08	72.6	1.36	0.86	0.09
O-As(V)	0.12	75.2	1.30	0.86	0.15
10% O-CA	0.059	22.3	2.02	1.01	0.13
10% O-CA-As(III)	0.056	23.8	1.88	1.14	0.07
10% O-CA-As(V)	0.052	21.9	1.25	1.03	0.08
MCL	0.3	0.1	1.3	0.1	0.01
TCLP = 100 × MCL	30	10	130	10	1

4. Conclusion

This (hydr)oxide mixture, a by-product of an electroplating industry, can be used either in its raw form and entrapped in a calcium alginate gel matrix as an efficient sorbent for As(III) and As(V) removal in a quite wide range of pH. Entrapment of the sorbent in a calcium alginate matrix was found to enhance the maximum sorption capacity of (hydr)oxide by ca. 60%, and to decrease sorption rate, especially in the case of As(V). Further investigation must be carried out in order to clarify the role of the gel matrix on the additional arsenic sorption.

Free hydroxyls of the sorbent material seems to play a key role in both As(III) and As(V) removal.

In this work, it has been demonstrated that by using the (hydr)oxide waste as sorbent for arsenic a double goal can be achieved: the valorisation of an industrial solid by-product whose management involves an important economical cost and the removal of arsenic from aqueous solutions, in either As(III) or As(V) form, through low-cost environmentally friendly technologies.

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