Application of Anodic Stripping Voltammetry to assess sorption performance of an industrial waste entrapped in alginate beads to remove As(V)

Francesca Garlaschelli, Giancarla Alberti, Núria Fiol, Isabel Villaescusa

Abstract
A solid waste material containing Fe(III) and other metal (hydr)oxides produced in a metal surface treatment industry has been investigated for As(V) removal. In order to facilitate sorbent application, 2% of raw material has been entrapped in calcium alginate gel matrix (2% O-CA).

An accurate characterization of the sorption on gel beads was undertaken, considering thermodynamic and kinetic aspects. All experiments were carried out at pH 8, since the maximum As(V) sorption was reached between pH 6 and 9. About isotherms, the best fit was obtained considering the Langmuir model and a capacity of 1.9 mg/g was achieved. The kinetic profiles evidenced that a quantitative sorption was obtained within 10 h. The 2% O-CA beads were also tested for continuous As(V) removal in a fixed bed column. Experiments were performed at constant flow rate, and varying the inlet As(V) concentration. With a view to design an automatic system for As(V) analysis in the outlet flow, the suitability of applying Anodic Stripping Voltammetry was evaluated: the method resulted appropriated to follow the As(V) content in the outlet solutions of columns with metal inlet concentration < 1 mg/L.

These results suggested that 2% O-CA beads could be a promising sorbent candidate for As(V) removal.

1. Introduction

Arsenic is one of the oldest poisons known to men. Its applications throughout history are wide and varied: murder, make-up, paint and even as a pesticide. Arsenic exists in both organic and inorganic species and either form can also be present in a trivalent or pentavalent oxidation state. Long-term health effects of exposure to these As species are severe and highly variable: skin and lung cancer, neurological effects, hypertension and cardiovascular diseases (Vahidnia et al., 2007). Sources, occurrence and health effects of arsenic in drinking
water have been reviewed, recently (Villaescusa and Bollinger, 2008).

The environmental fate of As is contamination of surface and groundwater with a pollutant level higher than 10 μg L\(^{-1}\) as set by World Health Organization (WHO). A plethora of detection methods for arsenic determination has been developed, reported and reviewed elsewhere (Komorowicz and Baralkiewicz, 2011; Radke et al., 2012). Most of them obtain limits of detection below the WHO arsenic guideline. However, some of the existing methods are not suitable for on-line routine monitoring of large numbers of samples or the analysis is time consuming. The use of electrochemical methodologies has recently come to the forefront of research as a possible means of fulfilling these requirements (Hung et al., 2004). Anodic Stripping Voltammetry with a gold microelectrode has been used for inorganic arsenic speciation in water and seawater (Salaun et al., 2007). Also cathodic stripping voltammetry has been applied for As(III) and total inorganic arsenic determination in natural waters (Profumo et al., 2005).

Several methods such as oxidation/precipitation, sorption onto different activated carbons, membranes and ion exchange resins have been applied for arsenic removal (Garelick et al., 2005; Mondal et al., 2006; Wang and Mulligan, 2006), however they are usually expensive. Sorption has been proved to be one of the most efficient strategies therefore, from the beginning of the 90s, an increasing attention is being paid to the development of new low cost and abundant sorbents, such as natural raw materials, industrial and agricultural wastes (Garelick et al., 2005). The wide variety of potential low-cost sorbent materials and metals that can be sorbed makes this process a promising technique for the detoxification of different metal-polluted effluents (Nurchi and Villaescusa, 2012; Nurchi et al., 2010). A brief survey on the literatures evidences that most of the studies in this field are devoted to the removal of metals such as copper, cadmium, lead, and chromium; conversely studies on arsenic removal are scarce (Nurchi and Villaescusa, 2008).

It has been reported that iron-rich materials are effective sorbents for the removal of arsenic, either as As(III) or As(V); so the important iron content in several industrial by-products leads us to think of a possible use of these wastes as sorbents for arsenic from aqueous solutions. The main attraction of the use of these by products is based on two aspects. The first one is their intrinsic low cost and the second is the added value confered to them when used as sorbents; otherwise, they would be considered as hazardous wastes, raising the operational costs for the industry.

In this study a solid waste material containing Fe(III) and other metal (hydr)oxides produced in a metal surface treatment industry has been investigated for As(V) removal. In order to facilitate sorbent application, 2% of raw material has been entrapped in calcium alginate gel matrix. This kind of procedure was successfully applied for the entrapment of grape stalk waste from wine production and a solid by-product from a chromium electroplating industry (Fiol et al., 2005; Fiol et al., 2004; Escudero et al., 2009).

An accurate characterization of As(V) sorption on the gel beads containing the solid waste has been undertaken in the batch mode considering the effect of pH and ionic strength and both kinetic and thermodynamic aspects. Experimental data were submitted to kinetic and equilibrium models.

The design of industrial processes requires lots of preliminary series of column laboratory and pilot-plant experiments in order to predict what might happen in a full-scale column. Therefore, a preliminary study of As(V) adsorption onto the gel beads under continuous operation fixed bed mode at different inlet arsenic concentrations was carried out. In view to design an automatic system for As(V) analysis in the outlet flow, the suitability of applying Anodic Stripping Voltammetry (ASV) was evaluated. In particular, an ASV method for As(V) has been validated and applied to assess the performance of the synthetized beads to remove As(V) from an aqueous solution.

2. Experimental

2.1. Materials and reagents

The metal (hydr)oxide solid was kindly supplied by a metal surface treatment industry from Barcelona (Spain). This material is a by-product formed after chromium electrochemical reduction and metal (hydr)oxide precipitation after coagulation/flocculation with FeCl₃. Before its use, it was washed with distilled water and dried in an oven at 60 °C until constant weight. Afterwards, it was ground, powdered and sieved to obtain a fine powder (< 250 μm particle size).

All solutions were prepared in HPW (High Purity Deionized water from Milli-Q apparatus; resistivity 18.2 M Ωcm, TOC < 10 μg L\(^{-1}\)).

As(V) solutions were prepared by dissolving an appropriate amount of reagent grade sodium arsenate heptahydrate (Na₂H₂AsO₄·7H₂O; > 98.5%, Fluka) in HPW and As(V) standard of 1 g L\(^{-1}\) (Fluka) was used to prepare diluted solutions for ICP-OES calibrations. Concentrated solutions of NaOH (Panreac) and HNO₃ (Panreac) were used for pH adjustment. Sodium alginate salt from brown algae (Fluka) was used as the hydrocolloidal gelling material, with a fixing solution of 0.1 M CaCl₂ (Panreac).

All solutions used for the voltammetric analysis were prepared from reagents of the purest grade available to minimize contamination.

2.2. (Hyd)oxide mixture characterization

The metal hydr(oxide) used as sorbent was previously characterized. In order to determine the humidity and ash content, a fixed amount of the hydr(oxide) was placed in an oven at 105 °C or 550 °C, respectively, until the mass was kept constant. The density was determined by a pycnometer. For metal content determination, the hydr(oxide) was dissolved in HNO₃ (Merck Suprapur quality) and digested in a microwave oven (Milestone Ethos Sel). After digestion the filtrate was analysed by Inductively Coupled Plasma (ICP-MS, ICP-OES) (Agilen 7500c). Point zero charge (pHpzc) was determined using the mass titration technique described elsewhere (Fiol and Villaescusa, 2009). The pH was measured using a pH meter (Basic 20, Crison) equipped with a combined glass electrode.

2.3. Preparation of the beads

The procedure and the experimental setup for the preparation of the beads have been previously reported.
(Nurchi and Villaescusa, 2008) and here summarized. A 1% (w/v) Na-alginate solution was prepared by dissolving 1 g of sodium alginate into 100 mL HPW water at about 65 °C. Then, the gel was allowed to cool down at room temperature and 2.0 g of (hydr)oxide was added to the gel with continuous stirring. Once the mixture was homogeneous, it was forced through a micropipette tip by a peristaltic pump. The resulting gel droplets were collected in a stirred reservoir containing 200 mL of a fixing solution of 0.1 M CaCl₂. The beads were allowed to harden in this solution for 24 h. After this time, hard spherical beads containing 2% (hydr)oxide waste were obtained.

The beads were filtered and rinsed several times with HPW water to remove calcium chloride from the bead surface. They were then stored in HPW water until their use. Calcium alginate beads used as “blank”, were prepared following the same procedure but without the addition of (hydr)oxide.

The diameter average of the obtained beads determined by optical microscopy was 3.14 ± 0.14 mm. The beads will be named as CA (calcium alginate beads) and 2% O-CA (beads containing 2% of (hydr)oxide entrapped in calcium alginate).

2.4. Characterization of As(V) sorption features of 2% O-CA beads. Batch studies

2.4.1. General As (V) sorption procedure
All the experiments were performed in plugged plastic tubes. Forty beads of 2% O-CA were added to 15 mL of As(V) solution. Stirring was carried out in an oscillating stirrer (Asal 711). After equilibration, the beads were separated from the solution by filtration on cellulose filter Whatman No. 40 and in the liquid phase the arsenic concentration was determined by ICP-OES (Perkin Elmer Optima 3300 DV (dual view)). The pH of the solutions before and after the sorption process was measured by a pH meter (Basic 20, Crison) equipped with a combined glass electrode.

2.4.2. Effect of pH
Before kinetic and equilibrium studies, the effect of the solution pH on the sorption of As(V) on 2% O-CA beads was examined. For this purpose, solutions of 11 mg L⁻¹ As(V) in 0.1 M KCl adjusted at different pH within the range (2–12) were equilibrated with 40 2% O-CA beads for 72 h under agitation.

2.4.3. Sorption kinetic study
Sorption kinetics was studied considering As(V) solutions with initial concentration of 13.5 mg L⁻¹. Solutions were prepared in 0.1 M NH₄Cl/NH₃ buffer at pH 8. Several tubes were prepared and left to stir for different time intervals within the range of 0–1400 min. Then the solution was separated from the beads by filtration, the pH measured and the arsenic concentration determined.

2.4.4. Isotherm study
To obtain sorption isotherms, solutions at different As(V) content (ranging between 1 and 250 mg L⁻¹), in NH₄Cl/NH₃ buffer at pH 8 were prepared and, after addition of the 2% O-CA beads, the tubes were left to stir overnight to ensure the equilibrium achievement. Sorption isotherms at different ionic strengths (I = 1.0, 0.1 and 0.01 M) were constructed.

2.5. Fixed bed column experiments
Experiments were carried out using four glass chromatography columns (Omnifit, UK) of 100 mm length and 10 mm internal diameter. Columns were filled with 95 crystal beads and 230 2% O-CA beads or 145 CA beads. As(V) solutions in constant stirring were pumped up-flow at a constant flow rate of 16 ml h⁻¹ by a peristaltic pump (Gilson, Minipuls 3, USA). Fixed volumes (8.5 mL) of the solution once passed through the column were collected in a fraction collector (Gilson, FC203B, USA). For these experiments solutions of different arsenic initial concentrations adjusted at pH 8 were used without adding any other salts to buffer the ionic strength. Determination of the outlet As concentrations was performed by Anodic Stripping Voltammetry (ASV) or ICP-OES.

2.6. Arsenic analysis by Anodic Stripping Voltammetry (ASV)
Anodic Stripping Voltammetry was chosen as a possible and suitable method of analysis to determine As(V) concentration in the continuous sorption experiments. ASV can be coupled to an automatic sampler and injection system that would facilitate As(V) analysis.

2.6.1. Equipment
A 797 VA Computrace Metrohm Voltammetric equipment equipped with a Dosino 807 Unit burette was used for ASV measurement. The voltammetric cell incorporates three electrodes: a silver–silver chloride electrode (1 M KCl) as reference, a glassy carbon as auxiliary electrode and a gold working electrode. In particular, the working electrode is a rotating one whose active surface is located on the side (6.1204.150 Lateral Gold Electrode Tip – Metrohm).

2.6.2. ASV method
For the determination of the total arsenic content, As(III) and As(V) are reduced at the surface of the gold electrode at −1.200 mV by nascent hydrogen to As(0), which is preconcentrated on the electrode surface. During the subsequent voltammetric determination the preconcentrated As(0) is again oxidized to As(III). The voltammogram is recorded with the parameters recommended by the operating instruction manual of the instrument (Metrohm) and here summarized (Metrohm, 2010).

The first stage is the deposition step at −1.2 V: in this stage the preconcentration of As on the electrode is obtained, so the deposition time is selected on the basis of the As concentration in the sample. The potential is then increased to +0.04 V for 10 s and, after 2 s of equilibration, the stripping using a differential pulse procedure is considered. For this last step the starting potential is selected at −0.2 V and the end potential at +0.3 V by applying a scan rate of 20 mV/s and a pulse amplitude of 50 mV. The determinations are carried out in 10 mL of sample + 10 mL of HCl 30% as supporting electrolyte. Following these operation conditions a peak of As(V) appeared at around 0.1 V.

2.6.3. As(V) analysis
Before starting with the voltammetric determination of arsenic, a cleaning and a conditioning of the gold electrode have to be performed. The procedure applied is that suggested
by the operating instruction manual of the instrument (Metrohm) and here briefly summarized (Metrohm, 2010). The cleaning solution is HCl 0.1 M. As the first stage 50 cycles by applying the cyclic voltammetry scanning the potential from −1 to −1.4 V followed by a 60 s step at 0.4 V are performed to clean the surface of the electrode. After few seconds of equilibration, another 20 cycles by applying the cyclic voltammetry scanning the potential from −0.2 to +0.3 V were performed to restore the electrode surface with the aim of obtaining a bright and clean electrode.

As(V) determination in the samples was performed by the standard addition method. The addition of 30 μL of 1 mg L⁻¹ As(V) standard solution was automatically performed by the Dosino unit, i.e. the burette connected with the instrument. For each addition the measurement was repeated twice (no more repetitions were necessary because the signal is very reproducible).

### 2.6.4. Sample preparation

The ASV method is an example of an ultra-sensitive analysis; all reagents used should have the highest possible degree of purity and be arsenic-free. Moreover, ASV is very sensitive to the presence of organic matter. Therefore, to avoid problems of fouling of the gold electrode surface, the organic matter has to be destroyed by UV digestion of the sample before the voltammetric analysis.

In order to assess the organic matter released from the beads some preliminary experiments were done. In particular 40 2% O-CA beads or CA beads were contacted with 15 mL of HPW water and the suspensions were stirred for 2 h in a rotary shaker at 30 rpm; then the solid was removed by filtration through a filter paper and the absorbance at 275 nm of the solutions collected was measured. The wavelength of 275 nm was selected because it corresponds to a maximum peak in the UV spectra of aromatic compounds: aromatics are the most difficult compounds to be eliminated, so in general they are used as a tool to measure the content of organic matter.

As expected the release of organic matter is bigger for 2% O-CA than for CA beads, whose absorbance is similar to that of the simple HPW. So solutions contacted with 2% O-CA than for CA beads, whose absorbance is similar to that of the simple HPW. Solutions contacted with 2% O-CA beads or CA beads were contacted with 15 mL of HPW and the suspensions were stirred for 2 h in a rotary shaker at 30 rpm; then the solid was removed by filtration through a filter paper and the absorbance at 275 nm of the solutions collected was measured. The wavelength of 275 nm was selected because it corresponds to a maximum peak in the UV spectra of aromatic compounds: aromatics are the most difficult compounds to be eliminated, so in general they are used as a tool to measure the content of organic matter.

As it can be seen in the figure, the maximum sorption is obtained within the pH range of 6–9. According to these results the pH was chosen for further experiments.

### 2.6.5. Validation

Before using an analytical method it is necessary to validate it in order to confirm if it is suitable for its intended use. There exists different method validation techniques employed to ensure that the results obtained are accurate and reliable. In particular we have considered the following method performance parameters: the precision and repeatability of the signals, the range of linear response, the limit of detection (LOD), the limit of quantification (LOQ) and the accuracy (checked by some recovery tests).

In order to check the repeatability of the signal, 10 mL of HPW and 10 mL of 30% HCl were analysed before and after four additions of 30 μL of 1 mg L⁻¹ As(V) standard solution. For each addition six repetitions of the measurement were done.

To examine the linear range of response some calibration curves were performed exploring a wide range of As(V) concentrations between 0.5 to 50 μg L⁻¹.

The LOD and LOQ of the ASV method were determined by multiplying the standard deviation (σ) of the obtained results from thirteen replicates of 10 mL of HPW and 10 mL of 30% HCl (blank) by a suitable factor, 3σ and 10σ for LOD and LOQ, respectively.

The recovery was evaluated by fortification of the supporting electrolyte solution (10 mL HPW + 10 mL 30% HCl) with As(V) concentration of 5 μg L⁻¹. For each sample the analyte concentration was obtained by the standard additions procedure.

### 3. Results and discussion

#### 3.1. Results on the material characterization

The (hydr)oxide waste humidity resulted to be 4.5% and the ash content 89.4%. This high percentage of ash indicates the waste was an essentially inorganic matrix material. Concentration of the major metal ions was found to be (g kg⁻¹): Fe(III): 7.2 ± 0.4, Cr(III): 0.95 ± 0.06, Ca(II): 0.16 ± 0.01, Cu(II): 0.057 ± 0.003, Al(III): 0.0117 ± 0.0003 and Ni(II): 0.0079 ± 0.0004. These results reveal that iron represents more than 85% of the total metal content and the waste suitability for arsenic removal. The density of this waste material was 2.35 ± 0.15 kg dm⁻³ and the point zero charge pHₚzc 7.39 ± 0.03.

#### 3.2. Characterization of As(V) sorption on calcium alginate beads containing 2% (hydr)oxide. Batch studies

Before kinetic and thermodynamic studies, the effect of the solution pH on the sorption of As(V) on 2% O-CA beads was examined. In Figure 1, the plot of the sorbed fraction (f) versus pH (measured in the solutions after 72 h) is reported. As it can be seen in the figure, the maximum sorption is obtained within the pH range of 6–9. According to these results pH 8 was chosen for further experiments.

#### 3.2.2. Kinetics of As(V) sorption on 2% O-CA beads

Kinetic experiments were performed to obtain information about the time required to reach the maximum sorption of As(V) on the beads and to establish the appropriate kinetic model to fit the experimental data.

In Fig. 2, kinetic experimental data of As(V) sorption corresponding to an initial concentration of 13.5 mg L⁻¹ are presented. It can be observed that the time needed to reach the
complete sorption of As(V) \( (f = 1) \) is higher than 10 h; so for the following thermodynamic studies an equilibration time of 24 h was considered.

One model generally used to describe sorption experiments, from the kinetic point of view and here considered, is the homogeneous particle diffusion model (Cortina et al., 2003). In this model, the sorption mechanism involves the counter diffusion of metal ions (ex. As(V)) from the solution and counter ions from the solid phase through a number of possible resistances. The exchange of ions can be rigorously described by the Nernst-Plank equation. This applies to the counter diffusion of two species in a quasi-homogeneous media.

The species originally in the solution phase must diffuse across the liquid film surrounding the solid particle. If this liquid film diffusion controls the rate of the process, the following equation can be applied:

\[
f = 1 - \exp(-kt) \quad \text{where} \quad k = \frac{3Dc_{\text{tot}}}{r_o \delta c}
\]

where \( f \) is the fraction of metal sorbed, i.e. the ratio of sorbed to total metal ion \( f = \frac{c}{c_{\text{tot}}} \), \( k \) the rate constant \( (s^{-1}) \), \( r_o \) the radius of the ion exchanger \( (m) \), \( D \) the diffusion coefficient in the film \( (m^2 \text{s}^{-1}) \), and \( \delta \) the film thickness.

After this stage, there is a transfer of the species across the solution/particle interface and then the species diffuse into the bulk of the solid phase. If this is the limiting step, the following equation is applied:

\[
f = \sqrt{1 - \exp(-2kt)} \quad \text{where} \quad k = \frac{3Dc_{\text{tot}}^2}{r_o^2}
\]

The third, generally fast, not limiting step is the chemical reaction between the metal ion and the active sites of the solid phase.

In Fig. 2 calculated values obtained from Eqs. (1) and (2) have been superimposed on the experimental data. A satisfactory fitting is obtained when considering particle diffusion as the limiting step on the sorption process.

### 3.2.3. Sorption isotherms of As(V) on 2% O-CA beads

Equilibrium data obtained at 0.1 and 0.01 M ionic strength are plotted in Fig. 3. It was impossible to perform the isotherm at 1 M ionic strength because the gel beads collapsed.

To fit the experimental data, the Langmuir model one of the most widely used model to describe the equilibrium behaviour of metal uptake, was considered (Ho, 2004).

**Langmuir sorption isotherm:**

\[
q = \frac{K_l q_{\text{max}} c_{\text{eq}}}{1 + K_l c_{\text{eq}}}
\]

where \( q \) is the solute (metal) concentration in the sorbent, \( q_{\text{max}} \) is the maximum uptake \( (\text{mol g}^{-1}) \), \( c_{\text{eq}} \) is the equilibrium concentration of the metal ion in the solution phase and \( K_l \) \( (\text{L mol}^{-1}) \) is a constant related to energy of adsorption which quantitatively reflects the affinity between the sorbent and the sorbate.

The theoretical assumptions of Langmuir model are here summarized: the sorption reaction can be represented as a coordination reaction with 1:1 stoichiometry (i.e. monolayer sorption); the activities of the surface sites are proportional to their concentration and the number of sorption sites is fixed.

In Fig. 3 the isotherms obtained at both ionic strengths 0.1 and 0.01 M are shown. It can be seen that Langmuir model
gives a good fit of both series of experimental data. The goodness of the fit is also confirmed by the values of the correlation coefficient (R) and of the relative error (R.E.) reported in Table 1, where the values of the Langmuir constant $K_L$ and the capacity of the beads for the As(V) at pH 8 ($q_{\text{max}}$) are also shown. From the values of $K_L$ and $q_{\text{max}}$ it is clear that the sorption is independent of the ionic strength at least in the range from 0.01 to 0.1 M.

### Table 1

<table>
<thead>
<tr>
<th>Ionic media</th>
<th>$K_L$</th>
<th>$q_{\text{max}}$ (mg g$^{-1}$)</th>
<th>R</th>
<th>R.E.</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl 0.1 M</td>
<td>0.14(2)</td>
<td>1.9(3)</td>
<td>0.983</td>
<td>0.379</td>
</tr>
<tr>
<td>KCl 0.01 M</td>
<td>0.13(2)</td>
<td>1.9(3)</td>
<td>0.986</td>
<td>0.377</td>
</tr>
</tbody>
</table>

3.3. Fixed-bed column studies: breakthrough curves for As(V) sorption on 2% O-CA beads

Sorption experiments in packed bed-up flow columns using 2% O-CA beads as sorbent were carried out to evaluate the performance of this material to remove As(V) in a continuous process.

The performance of packed beds is described through the breakthrough curve. The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of a biosorption column. The general position of the breakthrough curve along the volume axis depends on the capacity of the column with respect to the feed concentration and flow rate. The breakthrough curve would be a step function for favourable separations, i.e. there would be an instantaneous jump in the effluent concentration from zero to the feed concentration at the moment the column capacity is exhausted or maximum capacity of the column is reached.

Various simple mathematical models have been developed to predict the dynamic behaviour of the column. Among them, the Bohart–Adams model characterizing fixed bed performance is discussed (Aksu and Gönen, 2004; Deb Nath et al., 2010).

The fundamental equations describing the relationship between $C/C_0$ and $t$ in a flowing system were established by Bohart and Adams (1920) for the adsorption of chlorine on charcoal. Although the original work by Bohart–Adams was done for this particular system, its overall approach can be applied successfully in quantitative description of other column processes (Chu, 2010). This model assumes that the adsorption rate is proportional to both the capacity of the solid phase and the concentration of the sorbing species. The equation to describe the breakthrough curve is the following:

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left(\frac{km}{C_0} - kC_0t\right)}$$

(4)

where $k$ (mL min$^{-1}$ mg$^{-1}$) is the rate constant, $C_0$ and $C$ are the inlet and effluent concentrations (mg L$^{-1}$), respectively, $N_0$ is the saturation concentration (mg L$^{-1}$), $Z$ is the height of the column (cm), and $U_0$ is the superficial velocity (cm min$^{-1}$). From this equation values describing the characteristic operational parameters of the column can be determined from a plot of $\ln C/C_0$ against $t$ at a given bed height and flow rate.

As suggested by other authors (Chu, 2010), this expression is formally equal to the so-called Thomas equation:

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left(\frac{km}{C_0} - kC_0t\right)}$$

(5)

where $k$ (mL min$^{-1}$ mg$^{-1}$) is the rate constant; $q$ is the equilibrium uptake capacity (mg g$^{-1}$); $m$ is the mass of adsorbent packed in the column (g); $v$ is the flow rate (mL min$^{-1}$); and $C_0$ and $C$ are respectively the concentrations (mg L$^{-1}$) of metal ion in the influent and in the effluent at any time $t$ (min).

In the present study, column experiments were performed with solutions containing different concentrations of arsenic(V) from 0.2 to 5.2 mg L$^{-1}$. The fractions collected from the solutions with initial concentrations within the range 0.2–0.75 mg L$^{-1}$ were opportune diluted and the As(V) content was measured by ASV. Fractions collected from the solutions with initial As(V) concentration of 5.2 mg L$^{-1}$ were analysed by ICP-OES to avoid errors due to the great dilution required.

In Fig. 4 the graph $C/C_0$ vs. $t$ is shown. The symbols are the experimental data and the continuous lines are the calculated curves obtained by applying the Eq. (5). The values of the rate constant $k$ corresponding to the different inlet concentrations used are summarized in Table 2.

From the results obtained it is evident that As(V) can be removed from the aqueous solutions by using 2% O-CA beads. Nevertheless, from the obtained breakthrough curves it is evident that the flow rate employed (16 mL h$^{-1}$) was too high, indeed the concentration of As(V) in the first fractions collected was significantly different from zero.

![Figure 4](image-url)

**Figure 4** Comparison of the experimental and predicted breakthrough curves obtained at different As concentrations (from 0.2 to 5.2 mg L$^{-1}$) according to the Thomas model. ▲ As(V) = 0.2 mg L$^{-1}$; ○ As(V) = 0.25 mg L$^{-1}$; ● As(V) = 0.33 mg L$^{-1}$; □ As(V) = 0.75 mg L$^{-1}$; ○ As(V) = 5.2 mg L$^{-1}$. 
As higher the inlet As(V) concentration the lower is the total effluent volume treated: for example, when the initial inlet concentration was 0.2 mg L\(^{-1}\) the column did not raise saturation during the time of the experiment (8 h). On the other hand 8 h (120 mL), was enough to obtain the complete column saturation in the case of 0.75 and 5.2 mg L\(^{-1}\) initial As(V) concentrations.

From the results obtained it is also possible to observe that the \(k\) values are not significantly different, considering the high uncertainty due to the scattering of the experimental data.

It is important to highlight that these are preliminary results and additional work is needed in order to study the operation parameters influencing sorption performance, in particular the flow rate, in order to optimize the overall process and increase the metal sorption efficiency (See Table 3).

3.4. Validation of the voltammetric method for As determination

As shown in the voltammogram reported in Figure 5 the signals corresponding to the same standard addition are overlapped proving a very good repeatability.

The LOD and the LOQ resulted to be: LOD = 1.1 µg L\(^{-1}\) and LOQ = 3.7 µg L\(^{-1}\). The LOD obtained is in a pretty good agreement with that reported on the “Application Bulletin 226/2” by Metrohm (Metrohm, 2010).

Results obtained when determining the linear range of As(V) ASV determination: plot of linearity of 1 mg L\(^{-1}\) As(V) standard solution. Additions of 30 µL of 1 mg L\(^{-1}\) As(V) standard solution and the error related to the use of the Dosino unit.

\[ \text{slope of the straight line is lower. Our results are in accordance with those reported by Metrohm (11 µg L}^{-1}). \]

Results from the recovery experiments performed in different days for As(V) concentration of 5 µg L\(^{-1}\) are reported in Table 1. The mean recovery, \(R_m\), and the uncertainty associated to this value, \(u(R_m)\) are computed for each concentration. \(u(R_m)\) was obtained by using the following equation:

\[ u(R_m) = R_m \cdot \sqrt{\frac{s_{obs}^2}{N} + \left(\frac{u(m_{spk})}{m_{spk}}\right)^2} \]  

where: \(R_m\) is the mean recovery, \(N\) is the number of samples (12), \(s_{obs}\) is the standard deviation of the observed concentrations, \(m_{spk}\) is the spiked concentration, and \(u(m_{spk})\) is the uncertainty associated with the spiked concentration and it is calculated considering the errors associated to the preparation of the standard solution and the error related to the use of the Dosino unit.

### Table 2 Bohart–Adams model applied to the column experimental data for different inlet As(V) concentrations. Numbers in parenthesis are the 95% confidence intervals, and refer to the last significant digit.

<table>
<thead>
<tr>
<th>(C_0) (mg L(^{-1}))</th>
<th>(k_{BA}) (L mg(^{-1}) h(^{-1}))</th>
<th>(R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>0.60(6)</td>
<td>0.956</td>
</tr>
<tr>
<td>0.25</td>
<td>0.95(5)</td>
<td>0.984</td>
</tr>
<tr>
<td>0.33</td>
<td>1.1(1)</td>
<td>0.970</td>
</tr>
<tr>
<td>0.75</td>
<td>0.59(4)</td>
<td>0.983</td>
</tr>
<tr>
<td>5.20</td>
<td>0.13(2)</td>
<td>0.974</td>
</tr>
</tbody>
</table>

### Table 3 Results of the recovery test for 5 µg L\(^{-1}\) As(V) solutions.

<table>
<thead>
<tr>
<th>Sample (5 µg L(^{-1}))</th>
<th>Found concentration (µg L(^{-1}))</th>
<th>% recovery</th>
<th>Summary recovery test</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.46</td>
<td>109.2</td>
<td>(R_m) = 1.1</td>
</tr>
<tr>
<td>2</td>
<td>6.97</td>
<td>139.4</td>
<td>(u(R_m)) = 100</td>
</tr>
<tr>
<td>3</td>
<td>6.12</td>
<td>122.5</td>
<td>(u (% R_m)) = 14</td>
</tr>
<tr>
<td>4</td>
<td>6.21</td>
<td>124.2</td>
<td>(m_{spk}) (ppb) = 5.0</td>
</tr>
<tr>
<td>5</td>
<td>5.31</td>
<td>106.1</td>
<td>(m_{obs}) = 5.5</td>
</tr>
<tr>
<td>6</td>
<td>5.67</td>
<td>113.4</td>
<td>(s_{obs}) = 0.7</td>
</tr>
<tr>
<td>7</td>
<td>5.51</td>
<td>110.1</td>
<td>(u (R_m)) = 0.2</td>
</tr>
<tr>
<td>8</td>
<td>4.64</td>
<td>92.8</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>5.05</td>
<td>101.0</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>4.70</td>
<td>94.0</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>4.64</td>
<td>92.8</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>5.54</td>
<td>110.7</td>
<td></td>
</tr>
</tbody>
</table>

![Figure 5](image.png)  
As(V) voltammogram showing the peaks’ repeatability.  
Standard additions: 30 µL of As(V) 1 mg L\(^{-1}\). 1: first addition, 2: second addition, 3: third addition and 4: fourth addition.

![Figure 6](image.png)  
Arsenic(V) ASV determination: plot of linearity obtained by the standard additions method. Additions of 30 µL of 1 mg L\(^{-1}\) As(V) standard solution.
As seen in the tables, the recovery and the accuracy were quite good and in agreement with the Metrohm note (Metrohm, 2010).

4. Conclusions

A solid waste material containing mainly Fe(III) and Cr(III) (hydr)oxides was entrapped in calcium alginate for arsenic removal. In particular a 2% (w/v) of (hydr)oxide in the gel beads (2% O-CA) was found to provide both spherical bead shape and good performance.

The effect of pH was evaluated, obtaining a maximum As(V) sorption in the range of pH 6–9. Therefore, all the subsequent experiments were carried out using solutions at pH 8. The sorption was not affected by ionic strength.

An accurate characterization of the As(V) sorption on 2% O-CA was undertaken, considering both thermodynamic and kinetic aspects.

From the result of the isotherms, the best fit was obtained considering the Langmuir model and a capacity of 1.9 mg g⁻¹ (0.03 mmol g⁻¹) was achieved.

The kinetic profiles evidenced that a quantitative sorption of As(V) on the 2% O-CA beads was obtained within 10 h. The sorption process was described by the HPDM model the particle diffusion being the limiting step.

After the characterization of the sorbent behaviour, it was applied for continuous arsenic removal in a fixed bed column, at constant flow rate of 16 mL h⁻¹, and varying the inlet As(V) concentration. The Bohart–Adams model successfully described the obtained breakthrough profiles. These preliminary results suggested that 2% O-CA beads could be a promising sorbent candidate for the removal of arsenic.

The suitability of Anodic Stripping Voltammetry (ASV) on gold electrode to determine arsenic(III) at μmol L⁻¹ levels, was evaluated. The validation of the ASV method was done by determining the limit of detection of 1.1 μg L⁻¹, the limit of quantification of 3.7 μg L⁻¹ and a linear range of response up to 12 μg L⁻¹. The repeatability of the signals was excellent and the recovery was 110 ± 14%.

ASV resulted appropriated to follow the As(V) content in the outlet solutions of sorption columns filled with 2% O-CA beads for the As(V) inlet concentrations lower than 1 mg L⁻¹. To test higher outlet As(V) concentrations less sensitive techniques such as ICP-OES can be employed.

References

Williams, J., 2010. Ref Type: Electronic Citation.