Electro-oxidation of As(III) with dimensionally-stable and conductive-diamond anodes

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ABSTRACT

In this work, arsenic oxidation by an electrochemical process was studied in a batch bench-scale electrolysis plant equipped with mono- and bi-compartment cells, dimensionally-stable anodes (DSAs) and conductive-diamond anodes (CDAs). The results demonstrate that the electrolysis is an adequate technology to transform As(III) into As(V) species, which is an important pre-treatment stage for removing of arsenic from water using technologies such as coagulation or electro-coagulation. The process requires large current densities in non-divided cells to obtain a good As(V)/As(III) ratio, but it can be more efficiently performed at low current densities in cells divided by cationic membranes. The presence of chlorides or sulphates can significantly affect the results due to the formation of powerful oxidants that contribute to the net oxidation process.

1. Introduction

Arsenic can produce severe toxic effects on human health, mainly through its presence in drinking water. The World Health Organization (WHO) recommends a maximum level of $10 \, \mu g \, dm^{-3}$ arsenic in drinking water [1]. Arsenic pollution in ground and surface water arises mainly from natural processes (e.g., dissolution of arsenic minerals) and/or from anthropogenic activities (e.g., effluent discharge from the mining and metallurgical industry, the use of arsenic-based pesticides and the dissolution of wood preservatives).

In natural waters and soils, inorganic arsenic is mainly present as As(III) and As(V) oxo-anions [2], and the distribution of the species depends on the redox conditions and the pH of the water [3–7]. The standard potential of the oxidation of As(III) to As(V) is +0.56 V, which is lower than the oxidation potential of Fe(II) to Fe(III) and other species typically found in groundwater. However, it is known that although Fe(II) oxidation occurs rapidly in the presence of air, the oxidation rate of As(III) is extremely slow. Although As(V) is thermodynamically favoured under oxidising conditions, As(III) is only slowly oxidised by dissolved O_2, and half-lives of around 9 d in low iron-content, air-saturated, pH 7.6–8.5 water have been reported [8]. Due to this slow oxidation, arsenic is found as As(III) in underground water, whereas arsenic in surface water is mainly found as As(V).

As a water pollutant, As(V) is less toxic and more easily removed than As(III) [9]. Unlike the arsenate anions $H_2AsO_4^-$ and $HAsO_4^{2-}$ (the primary species in the typical pH range of natural waters), the primary As(III) species in pHs up to 8 is the non-ionic H_3AsO_3, which is not adsorbed by mineral surfaces as strongly as As(V) [10]. Consequently, As(III) is more mobile in groundwater and is also more difficult to remove using most treatment technologies [11,12].

As it is easier to remove As(V), pre-treatment by oxidising As(III) to As(V) using different types of oxidation technologies is usually recommended [13]. In this context, several techniques have been reported for oxidising As(III) to As(V), including biological oxidation [14] and chemical oxidation with conventional oxidants, such as chlorine dioxide or permanganate [15,16], manganese oxides [17,18], and ozone [19]; novel oxidants, such as ferrates [20]; and photo-oxidation using ultraviolet and visible radiation [21] and photo-catalytic oxidation [22]. The electrochemical oxidation process has not been widely studied thus far, although Zhao et al. [23] have recently demonstrated the viability of this electrochemical process for oxidising As(III) to As(V) using dimensionally-stable anodes (DSAs). Electrochemical oxidation is a technology that combines two important oxidation processes: direct electro-oxidation on the anode surface and indirect electro-oxidation mediated by electrochemically formed oxidants, such as hydroxyl radicals, chlorine and persulphates. Consequently, the technique is expected to produce a good yield. The main advantages of the electrochemical oxidation are their reliability and the possibility to remove arsenic, almost completely, from the water.

Once As(III) has been oxidised to As(V), a variety of technologies can be used to remove arsenates from water, including adsorption into different types of solids, ion exchange, membrane

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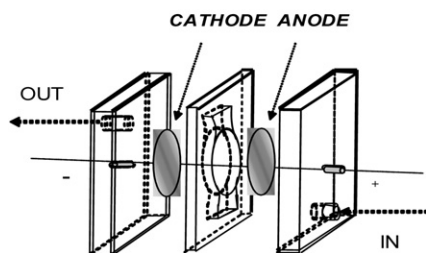*E-mail address:* Manuel.Rodrigo@uclm.es (M.A. Rodrigo).
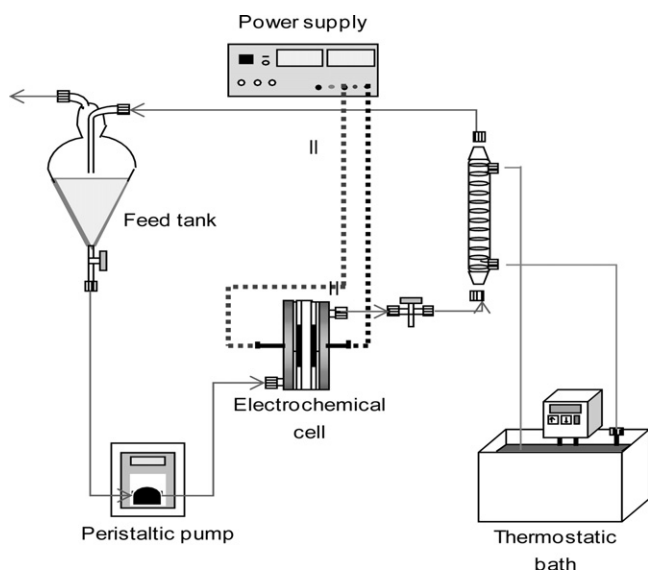
Fig. 1. The layout of the electrochemical coagulation bench-scale plant. The details of the electrochemical cell.

processes and coagulation followed by filtration [24]. The great efficiencies obtained by the other electrochemical technology, electro-coagulation [25], are notable. With this method, the limits set by the WHO can easily be achieved using a single cell [26] in which even some degree of As(III) to As(V) oxidation can be obtained.

The goal of this work was to study the influence of the anode material and supporting electrolyte in the As(III) electrochemical oxidation process, applying a current density in a range typical of different electrolytic processes (from 0.15 to 30 mA cm^{-2}). It examined the transformation of arsenic species into species that are easier to electro-coagulate (As(V)) using two different anodic materials, a conductive diamond anode (CDA) and a DSA, which are frequently used as anode models due to their distinct electrolytic behaviour when treating different pollutants.

2. Experimental

2.1. Experimental procedure

Bench-scale electro-oxidation experiments were conducted to study the feasibility of the As(III) to As(V) oxidation process. The electro-oxidation bench-scale plant used in this work is shown in Fig. 1. It consisted of a 500 mL feed tank that stored the synthetic water, a peristaltic pump that allowed the solution to recirculate to the electrolytic cell and a power supply directly connected to electrodes.

Electro-oxidation experiments were conducted in batch operation mode. Commercial CDAs were provided by Adamant Technologies. The single-compartment cell had a boron content of

1200 ppm, a diamond carbon to graphite carbon ratio (sp^3/sp^2) of 115 and a thickness of 1.53 μm. The double-compartment cell had a boron content of 500 ppm, an sp^3/sp^2 ratio of 165 and a thickness of 3.27 μm. DSA electrodes, made of mixed metal oxide with a ruthenium oxide (MMO (Ru)), were used as the anodic materials, and stainless steel (SS) AISI 304 was used as the cathodic material in all the experiments. The electrodes had a circular shape (100 mm in diameter) and a geometric area of 78 cm^2. In the one-compartment cell, the electrode gap was 9 mm. In the two-compartment cell, the gap was 20 mm, and the membrane was a cationic exchange membrane (STEREOM L-105) provided by Hydrogen Works. In the experiments carried out with the two compartment cells the pH was constantly monitored and controlled by dosing NaOH 0.1 M. A heat exchanger was used to maintain the temperature at the desired set point. The experiments were conducted under galvanostatic conditions, with a current density varying from 0.15 to 30 mA cm^{-2}. The electrical current was applied using a FA-376 PROMAX DC Power Supply.

The synthetic water used in the experiments contained sodium arsenite (20 mg dm^{-3}) and 1000 mg dm^{-3} of supporting electrolyte. Two compounds, NaCl and Na$_2$SO$_4$, were used as the supporting electrolytes. More information related to the experimental set-up and procedures have been previously reported [27].

2.2. Analysis procedure

Arsenate was measured by the molybdenum blue method [28], whereby 1 ml of ascorbic acid solution and 2 ml of reagent A were successively added to a 40-ml sample aliquot in a 50-ml volumetric flask, with the balance of the flask filled with Milli-Q water. The analysis of this mixture was performed in 1-cm quartz cells with a Shimadzu US-1603 UV–vis spectrometer [29]. Reagent A was prepared by mixing two separate solutions containing 13 ± 0.5 g/100 ml of (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O and 0.35 ± 0.05 g/100 ml of K(SbO)C$_4$H$_4$O$_6$·H$_2$O with 9 M H$_2$SO$_4$ in a 500-ml volumetric flask. The 10 ± 0.5 g/100 ml ascorbic acid solution was prepared daily before use. The total arsenic concentration was measured off-line using an inductively coupled plasma spectrometer (Liberty Sequential, Varian) according to a standard plasma emission spectroscopy method [30]. To ensure total arsenic solubility, the samples were previously diluted with 1% HNO$_3$.

The anions present in the solution (Cl$^-$, ClO$^-$, ClO$_3$$^-$, ClO$_4$$^-$, SO$_4$$^{2-}$) were characterised using ion chromatography with Shimadzu LC-20A equipment (column, Shodex IC I-524A; mobile phase, 2.5 mM phthalic acid at pH 4.0; flow rate, 1.0 ml min^{-1}). The hypochlorite peak on the chromatogram interferes with the chloride peak; therefore, hypochlorite was determined by titration with As$_2$O$_3$ in 2-M NaOH. Furthermore, I$_2$/I$^-$ assays were performed to measure electrogenerated oxidants, such as S$_2$O$_8$$^{-2}$.

3. Results and discussion

Fig. 2 shows the changes in the concentration of As(III) and As(V) species when a solution containing 20 mg dm^{-3} of As(III) was electrolysed using a CDA or a DSA in a single-compartment electrochemical cell at current densities ranging from 5 to 30 mA cm^{-2}. The solution also contained 1000 mg dm^{-3} of sodium chloride as a supporting electrolyte. The As(III) was rapidly oxidised to As(V) during the first stage of the electrolyses (with a current below 2 A h dm^{-3}), in which a greater than 90% conversion to As(V) was obtained for the three current densities used. In the second stage, the trend of the first stage reversed, and the reduction of the oxidised form became more significant. It reached a final plateau with As(III) to As(V) conversion rates ranging between 70 and 90% of the total As present in solution.
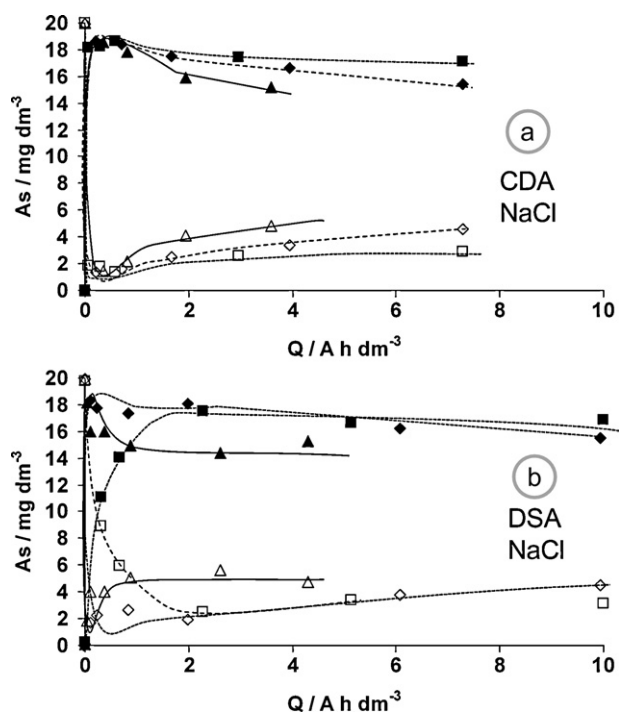
Fig. 2. Production of As(V) during the electrolyses of 20 mg dm^{-3} As(III) solutions in sodium chloride (1000 mg dm^{-3}) with a CDA (part a) and a DSA (part b). Current densities: (■, □) 30 mA cm^{-2}; (♦, ◊) 10 mA cm^{-2}; (▲, △) 5 mA cm^{-2}. Full points = As(V), hollow points = As (III).

The shape of the concentration vs. electrical charge applied (Q) plot is unusual, as it is not what would be expected in a system with a direct and a reverse reaction acting simultaneously (which usually has a simpler monotonous continuous trend). Instead, it is a typical reverse response, with a clear maximum in the As(V) concentration at a given time or current. This type of change in the process dynamics indicates the coexistence of two different sub-processes (one rapid and the other less rapid but more intense at a given time) that contribute to the overall rate of the process.

Initially, this result was interpreted in terms of the mediated electro-reduction processes, assuming that As(V) is not reduced at a constant rate over the process and that the reduction during the beginning of the second stage was more efficient. It was suspected that the formation of a significant amount of a reducing agent, particularly hydrogen (which it is produced on the cathode surface by water reduction), helped to reduce As(V) to As(III). However, the addition of electrochemically-generated hydrogen did not reduce As(V) under the same operating conditions as no other reducing agent was expected to be present in the solution (only sodium chloride was present in the initial aqueous solution with the arsenic species), the reduction of As(V) was likely the result of direct electrolytic processes.

An important explanation of this behaviour was obtained from the plots of the pH changes during the different electrolyses. Those for the previously discussed experiments are shown in Fig. 3. An abrupt decrease in the pH occurred during the first stage of the process, corresponding to the As(V) formation. A continuous increase up to a final value close to the initial pH of the electrolysed solution was observed during the second stage.

The influence of pH on the speciation of arsenic oxo-anions can easily be obtained from Eqs. (1) to (6), in which the acid dissociation constant is also given.
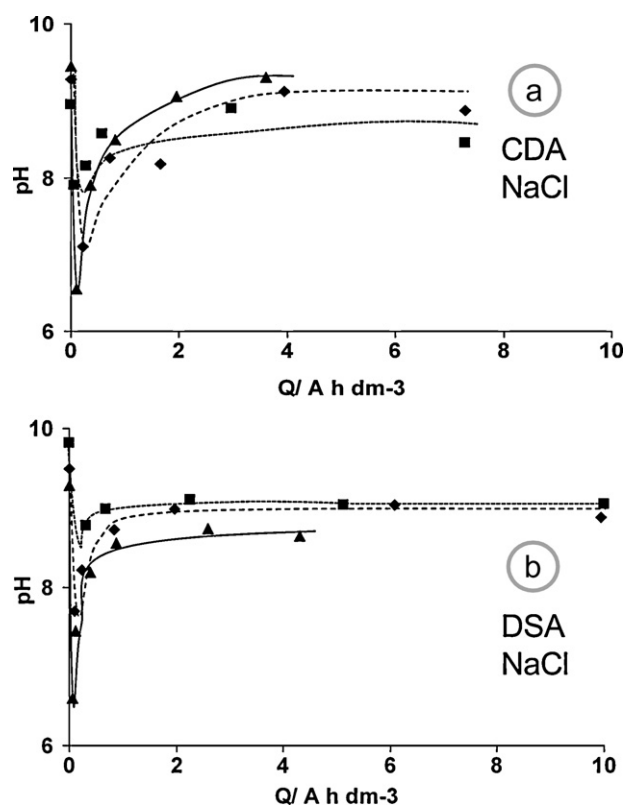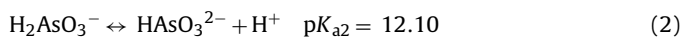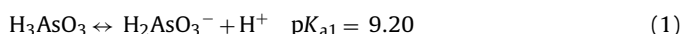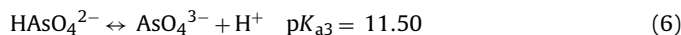
$$H_3AsO_3 \leftrightarrow H_2AsO_3^- + H^+ \quad pK_{a1} = 9.20 \tag{1}$$

$$H_2AsO_3^- \leftrightarrow HAsO_3^{2-} + H^+ \quad pK_{a2} = 12.10 \tag{2}$$

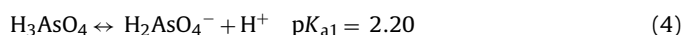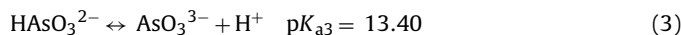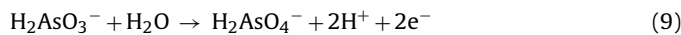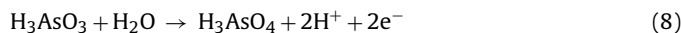**Fig. 3.** Changes in the pH during the electrolyses of 20 mg dm^{-3} As(III) solutions in sodium chloride (1000 mg dm^{-3}) with a CDA (part a) and a DSA (part b). Current densities: (■) 30 mA cm^{-2}; (♦) 10 mA cm^{-2}; (▲) 5 mA cm^{-2}.

$$HAsO_3^{2-} \leftrightarrow AsO_3^{3-} + H^+ \quad pK_{a3} = 13.40 \tag{3}$$

$$H_3AsO_4 \leftrightarrow H_2AsO_4^- + H^+ \quad pK_{a1} = 2.20 \tag{4}$$

$$H_2AsO_4^- \leftrightarrow HAsO_4^{2-} + H^+ \quad pK_{a2} = 6.94 \tag{5}$$

$$HAsO_4^{2-} \leftrightarrow AsO_4^{3-} + H^+ \quad pK_{a3} = 11.50 \tag{6}$$
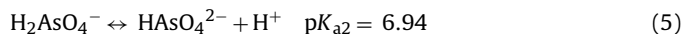
It is important to note the high pK_a for the first As(III) oxo-anion, especially compared to the values of the As(V) oxo-anions. This difference clearly predicts that the primary species present in the electrolytic media within the range of pH values observed in Fig. 3 should be non-ionic H_3AsO_3 and the $H_2AsO_3^-$, $H_2AsO_4^-$ and $HAsO_4^{2-}$ oxo-anions. It also indicates that changes in the oxidation state of the As oxo-anions should be accompanied by significant pH changes due to the different dissociation constants of the acids.

From an electrolytic viewpoint, the main reactions occurring on the anode surface should be the oxidation of water and the As(III) oxo-anions (Eqs. (7)–(9)).

$$H_2O \rightarrow 0.5O_2 + 2H^+ + 2e^- \tag{7}$$

$$H_3AsO_3 + H_2O \rightarrow H_3AsO_4 + 2H^+ + 2e^- \tag{8}$$

$$H_2AsO_3^- + H_2O \rightarrow H_2AsO_4^- + 2H^+ + 2e^- \tag{9}$$

Based on the acid dissociation constants, these electrolytic reactions should be followed by a rapid dissociation to $H_2AsO_4^-$ and $HAsO_4^{2-}$, which helps to explain the rapid pH decrease shown in Fig. 3. Therefore, the rapid dissociation of the electrochemically produced As(V) species may explain the abrupt change in the pH during the first stage of the electrolyses.

Simultaneous to the oxidation processes, the main reactions that are expected to occur on the cathode surface are the reduction of water (Eq. (10)) and the As(V) oxo-anions (Eqs. (11) and (12)). These reactions would neutralise the system and cause the increase in
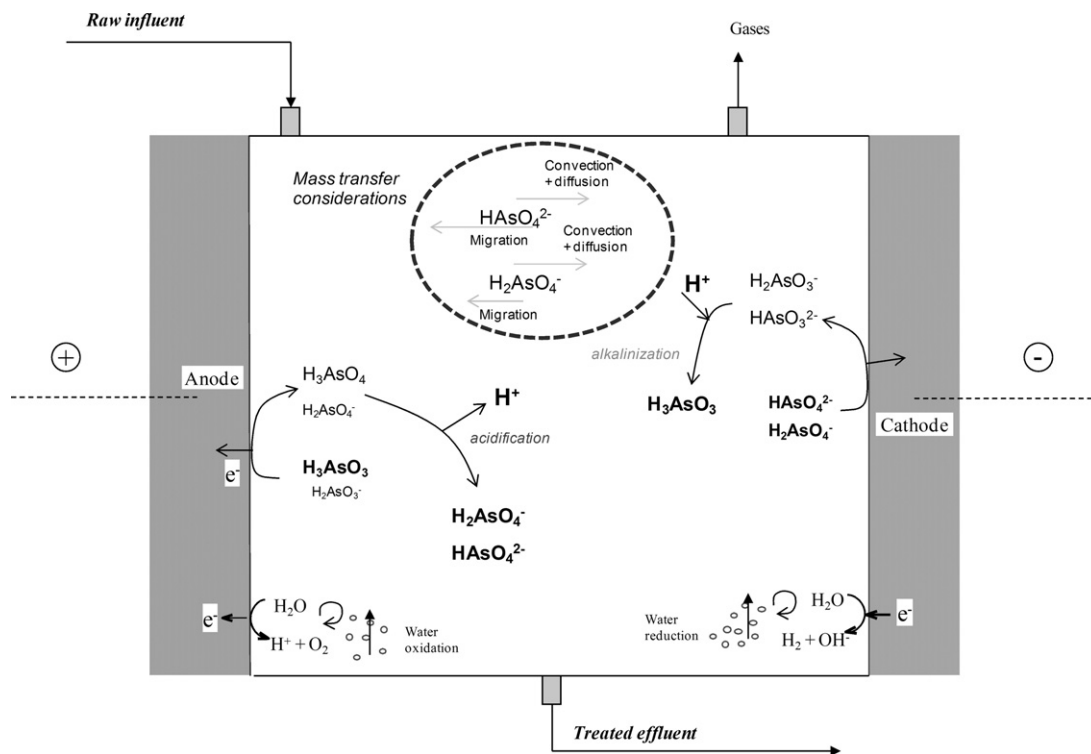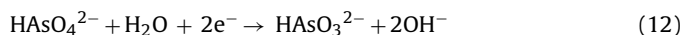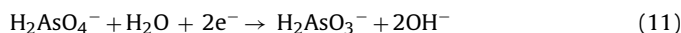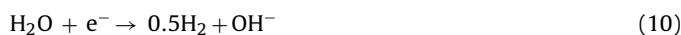
Fig. 4. Scheme of the arsenic-species transformations.

pH observed later in the reaction. It should be noted that no net pH change is expected to occur from the electrolytic process in the mono-compartment cell, as the production of protons and hydroxyl anions is the same.

$$H_2O + e^- \rightarrow 0.5H_2 + OH^- \tag{10}$$

$$H_2AsO_4^- + H_2O + 2e^- \rightarrow H_2AsO_3^- + 2OH^- \tag{11}$$

$$HAsO_4^{2-} + H_2O + 2e^- \rightarrow HAsO_3^{2-} + 2OH^- \tag{12}$$

In the cathodic processes, the primary product species (once the dissociation equilibria is established) should be the non-ionic H_3AsO_3 and oxo-anionic $H_2AsO_3^-$, which means that the pH would also be perturbed by the later protonation of the electrochemically produced species. This process explains both the observed pH increase when the As(V) to As(III) reaction became significant during the second stage of the electrolyses and the final pH value at the end of the treatment being close to the initial value of the raw solution (measured prior to the electrolysis).

Hence, although no net changes in the pH are expected from the electrochemical point of view, the hydrolysis constants of the acids coupled with the electrochemical reactions help to explain the pH changes shown in Fig. 3. The less extensive water oxidation and reduction processes during the electrolyses at lower current densities (as a consequence of the more efficient arsenic oxidation and reduction on the respective electrodes) help to explain the abrupt changes observed under these conditions.

Importantly, the reaction in Eq. (12) should not be favourable compared to the reaction in Eq. (11) due to mass transfer considerations. The mass transfer coefficient (k_m) of the electrochemical cell within the fluid dynamic conditions used (400 dm³ h⁻¹, 298 K) is 1.28×10^{-5} m s⁻¹ (measured by a typical ferro-ferricyanide test, as reported in Cañizares et al. [31,32]). The current density limit can be calculated using Eq. (13), where n is the number of electrons involved in the redox process (2 mol e⁻/mol As) and F is the Faraday constant (96,485 C/mol e⁻).

$$i_{\lim}(t) = nFk_m[As] \tag{13}$$

Based on this equation, the current limit for the cell and hydrodynamic conditions used in the electrolyses is 0.659 A m⁻² for an As(V) concentration of 20 mg dm⁻³, meaning that the process is always under mass transport control. One of the more important transport mechanisms is migration. Due to electrostatic considerations, the migration of a bivalent anion ($HAsO_4^{2-}$) towards the cathode is less favourable than the migration of a monovalent anion ($H_2AsO_4^-$). This difference may explain the sole promotion of electrochemical As(V) reduction under more acidic conditions (which promotes the less negatively charge oxo-anion, $H_2AsO_4^-$) and the observation that the efficiency of this reaction decreased with increasing pH, finally reaching a As(V)/As(III) ratio plateau for all of the electrolyses in the study. This hypothesis clearly explains the strange shape of the product distribution during the As(III) electrolyses as summarize the scheme shown in Fig. 4.

Similar results were obtained with each anode material. Initially, the oxidation occurring on the DSA surface was assumed to be weaker than that on the CDA due to the supposed production of a hydroxyl radical, which would complement the direct oxidation processes. Because of the short life time of the hydroxyl radicals this oxidation process take place near the anode. In the literature [33], it has been reported that large quantities of radicals are formed during the electrolysis of aqueous solutions using CDA electrodes and that these radicals are responsible for the oxidation seen at this anode. In the case of the DSA [34], however, the radicals generated are chemisorbed and transformed into chemical oxides, which are assumed to be responsible for the direct oxidation and reduced efficiency of the process. It was observed that the residual arsenite concentrations for the two electrodes were low, although the lowest arsenite concentration was reached during the CDA electrolyses.
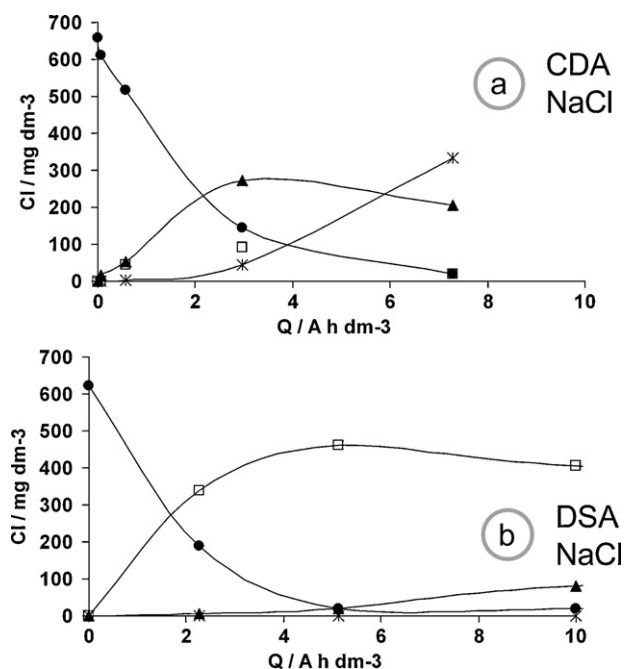
Fig. 5. Concentration profile of the chlorine-intermediates detected during the electrolysis of 20 mg dm^{-3} As(III) solutions in sodium chloride (1000 mg dm^{-3}) with a CDA (part a) and a DSA (part b) at a current density of 30 mA cm^{-2}. (●) Cl–Cl$^-$, (□) Cl–ClO$^-$, (▲) Cl–ClO$_3^-$, (✳) Cl–ClO$_4^-$.

The effect of the anode material should also be important for producing other oxidants that can mediate electrolytic processes. Fig. 5 shows the main chlorine intermediates found in the electrolytic media during the electrolysis with the CDA and DSA electrodes at a current density of 30 mA cm^{-2}. Hypochlorite and chlorate were formed at both electrodes, whereas perchlorates were formed only at the CDA [35]. Initially, these strong oxidative agents can indirectly oxidise arsenite to arsenate, making the arsenite oxidation process more efficient in the presence of sodium chloride and accounting for the improved As(V)/As(III) ratio obtained at larger current densities, as the production of the oxidant is promoted under these conditions.

From the kinetic point of view, hypochlorite is a notably more efficient oxidant than chlorates and perchlorates, although its prevalence in the electrolyses with the DSA (chlorates and perchlorates are the primary species in the CDA electrolyses) did not lead to a greater efficiency in the oxidation of As(III) to As(V) but rather to the CDA being more efficient. In addition, the As(III) to As(V) conversion was obtained mainly in the first stage, where the concentration of the chlorine oxo-anions was not of great importance. Therefore, the mediating reagents are complementary to the direct oxidation and are not the controlling oxidation mechanisms.

Fig. 6 shows the effect of the electrolyte on the As(III) oxidation for both anode materials when using a current density of 30 mA cm^{-2} applied to the non-divided electrolytic cell. As previously stated, a CDA is much more efficient than a DSA in the same electrolyte, and chloride has a significant effect on the oxidation process. Thus, the most efficient electrolysis used CDA electrodes and chloride media, and the least efficient process used a sulphate electrolyte with a DSA. The differences in the behaviour between these two inorganic salts may be due to the species being formed by the respective electro-oxidation reactions. No oxidants were detected in the sulphate media, although it has been reported in the literature [36] that under the same operational conditions, the electrolysis of a sulphate solution with a CDA yields persulphates, which may have reacted during the electrolyses, giving them a
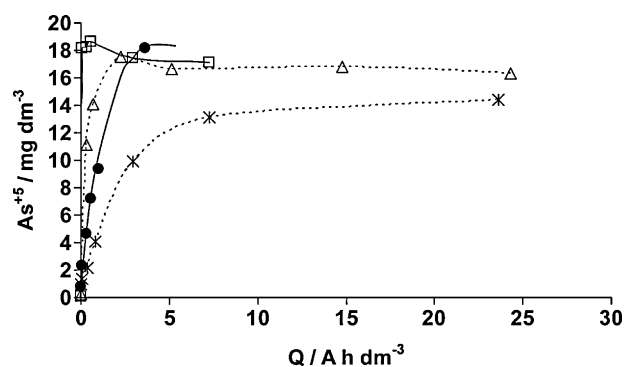

Fig. 6. A comparison of the effects of the anode material and supporting electrolyte on As(III) oxidation in non-divided electrochemical cells at $j = 30$ mA cm^{-2}. (●) CDA – 1000 mg dm^{-3} Na$_2$SO$_4$; (□) CDA – 1000 mg dm^{-3} NaCl; (✳) DSA – 1000 mg dm^{-3} Na$_2$SO$_4$; (△) DSA – 1000 mg dm^{-3} NaCl.

minimal effective concentration throughout the process, as they were immediately reduced.

From the previous results, it seems clear that due to reversibility, it is not possible to completely convert As(III) into As(V) in a single compartment electrochemical cell unless As(V) is continuously removed. In addition, the worst As(V)/As(III) ratio results were obtained at low current densities, which advises against using lower current densities in non-divided electrolytic processes. This restriction is a significant drawback, as lower current densities lead to more efficient processes due to lower rates of water oxidation and cell voltage.

To study As(III) to As(V) oxidation while avoiding the reverse reaction, a double-compartment cell equipped with a cationic exchange membrane was used to separate the anodic and cathodic compartments. Fig. 7 compares the results obtained with both types of cells when using both anodes and a current density of 30 mA cm^{-2}. The effect of the anode material remained the same in the two-compartment cell, with the CDA being more efficient than the DSA. However, the more significant observation is that in the double-compartment cell, the As(III) was fully oxidised to As(V).

The effect of the supporting electrolyte in the oxidation process remained the same when working with a double-compartment cell (Fig. 8). It can also be seen that in every case, the system reaches a steady state even when working at low current densities, where the process was not recommended for single-compartment cells due to the greater effect of the As(V) reduction. These conditions are more energy efficient, and they are also similar to those typically used in electro-coagulation processes. This result implies that the electro-coagulation of As(III) salts may be more efficient than conventional
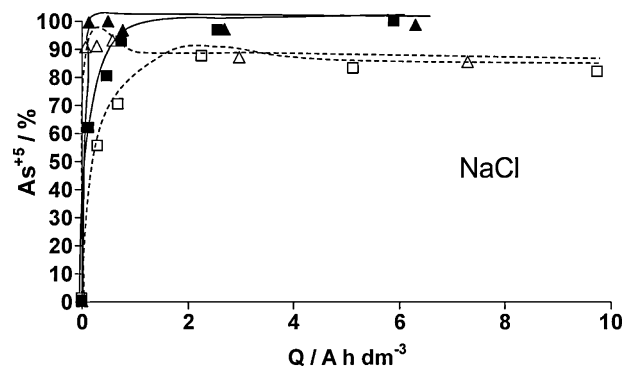

Fig. 7. Effect of cell compartmentalisation (using a cationic membrane) on the oxidation of a 20 mg dm^{-3} As(III) solution in sodium chloride (1000 mg dm^{-3}), into As(V) at a current density of 30 mA cm^{-2}. (▲) CDA, two compartment; (△) CDA, one compartment; (■) DSA two compartment; (□) DSA, one compartment.
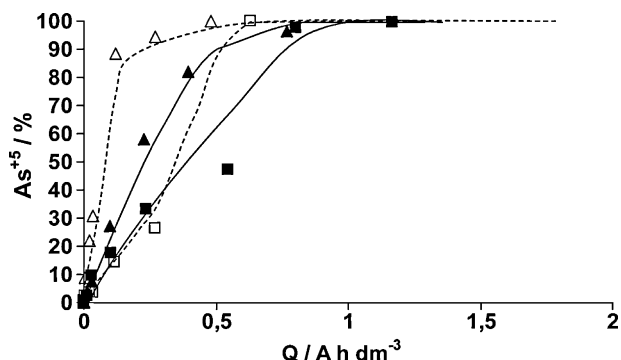
Fig. 8. Effect of the supporting electrolyte and anode material on the oxidation of a 20 mg dm^{-3} As(III) solution into As(V) in a two-compartment electrochemical cell at a current density of 1.5 mA cm^{-2}. (▲) DSA, chloride; (△) CDA, chloride; (■) DSA, sulphate; (□) CDA, sulphate.
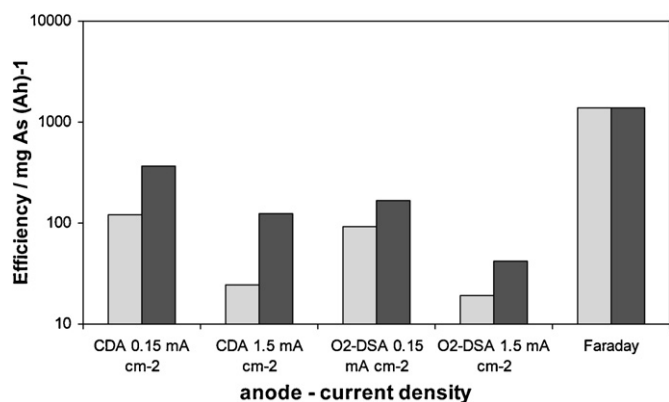

Fig. 9. The maximum efficiencies obtained for the oxidation of arsenic at low current densities in the two-compartment electrochemical cell.

coagulation due to the partial conversion of As(III) to the easier to coagulate As(V). The high efficiencies of the electrolytic processes and the high yield of the electro-coagulation of As(V) suggest using of a sequential electrolysis/electro-coagulation process for treating As(III)-polluted waters rather than the direct electro-coagulation of As(III).

Fig. 9 shows the maximum efficiencies obtained in the oxidation of As(III) at low current densities in the two-compartment electrochemical cell. The efficiencies were significantly higher when chloride was used. Notably, the efficiency values were higher when working with lower current densities, as oxygen evolution is not favoured under these conditions.

4. Conclusions

From the results obtained in this work the following conclusions can be drawn.

- The electrochemical oxidation of As(III) with dimensionally stable and conductive diamond anodes leads to the formation of significant concentrations of As(V) species. The electrochemical oxidation of As(III) to As(V) is reversible; consequently, the conversion is only complete in divided cells equipped with cationic exchange membranes. For non-divided cells, conversion rates ranging from 70 to 90% can be obtained using the current densities typical of environmental electrolytic processes.
- Both direct and mediated electrochemical processes are involved in the oxidation of As(III). Only small differences are seen between a DSA and a CDA in a chloride media. These differences are greater

in sulphate media. In every case, CDA electrolysis is more efficient. The oxidants produced at both electrodes are distinct.
- Current density is a significant parameter. Due to the action of mediation oxidation, using large values is recommended in non-divided cells to obtain a favourable As(V)/As(III) ratio. Lower values can be used in divided cells, yielding a more efficient process.
- The oxidation in a discontinuous system shows two different stages: a first stage in which the production of As(V) is efficient, and a second stage in which the process reverses. The dissociation constants of the different acids involved are important for explaining the mechanisms of the process, particularly the high first dissociation constant value of the H$_3$AsO$_3$.

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