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Electrochemical reduction of As(III) and As(V) in acidic and basic solutions

D. BEJAN and N.J. BUNCE*
Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1
*(*author for correspondence, fax: +519 766 1499, e-mail: bunce@chembio.uoguelph.ca)*

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Abstract

The removal of As(III) and As(V) from acidic and basic solutions by electrochemical reduction was studied using a reticulated vitreous carbon cathode and a IrO_2/Ti anode in an electrochemical reactor that could be operated divided or undivided. By using a cascade of 7–9 plug flow reactors, residual concentrations of arsenic less than 20 ppb were achieved upon reduction of 100 ppm As(III) in either acidic or alkaline solutions and for 100 ppm As(V) in acidic solution. The reduction of As(V), generally considered electrochemically inactive in alkaline solutions, was proved possible, but was much less efficient. In all cases, the only product of electrochemical reduction was arsine. A moderate improvement in reduction efficiency was achieved under conditions of electrocatalytic hydrogenation using 5% Pd on alumina as catalyst.

1. Introduction

The chemistry of arsenic has recently seen a great revival of interest, not least because of the widespread incidence in Asia of human disease resulting from arsenic contamination of drinking water [1–3]. A vigorous search for inexpensive methods of removal of arsenic from water is under way, with novel technologies such as adsorption to basic yttrium carbonate [4] and treatment with zero-valent iron [5, 6] having been proposed. Electrochemical methods of arsenic removal have been suggested, including electrodialysis [7] and electrocoagulation [8], in which concurrent dissolution of an iron anode in the presence of H_2O_2 generates Fe(III) hydroxide, which sorbs arsenic compounds.

The electrochemical reduction of inorganic As(III) and As(V) in aqueous solutions has also been examined preparatively [9–11], with the objective of maximizing the yield of elemental arsenic at the expense of the highly toxic gas arsine, AsH_3. In contrast, the electrochemical removal of As(III) or As(V) from waste waters has received little recent study. Houlachi and Claessens [12–14] claimed a method for removing arsenic from wastes produced in the electrorefining of copper. The application of a periodic reversed current (PRC) or a periodic interrupted current (PIC) achieved codeposition of arsenic, copper and other metallic elements (e.g., Sn, Bi) onto the cathode with minimal production of arsine. Twardowski [15] reported a method for removal of As(III) from mineral acids by electrochemical reduction to arsenic, which was deposited on a three-dimensional carbon cathode, using a divided cell and cathode potentials that disfavoured over-reduction to arsine. In this system As(V) was inactive and could only be removed electrolytically by prior chemical reduction to As(III).

The present issues surrounding the electrochemical removal of arsenic from waste water are as follows:

(a) if the objective is to maximize the yield of elemental arsenic at the expense of the highly toxic arsine, strict control of the cathode potential is needed. This is undesirable industrially where constant current operation is preferred. Since moreover, the production of arsine cannot be suppressed completely [12–14], provision must be made for its capture and transformation into a solid product [16]. A further problem with this approach is that As(0) is poorly conductive; its deposition inactivates the cathode, which must be regenerated by polarity reversal or chemical dissolution of arsenic. In addition, flow-through cathodes such as reticulated vitreous carbon (RVC) or carbon cloth are vulnerable to clogging by the solid arsenic.

(b) none of the electrochemical reduction techniques described in the extant patents decreased the arsenic concentration to levels acceptable in drinking water, presently 50 ppb, with the Environmental Protection Agency's 10 ppb standard to be implemented in the US by 23 January 2006 [17].

(c) the majority of proposals involve divided cells, and sometimes the recirculation of electrolyte or special electrochemical techniques. The ideal would be an undivided cell that would remove arsenic efficiently in a single pass at constant current.

(d) research to date has focussed only on the reduction of As(III) and mainly on acidic solutions. As(V) is generally considered to be electrolytically inactive, and to require chemical reduction to As(III) prior to electrolysis. Tomilov et al. [18] concluded that 'the results of research into the electrode behaviour of pentavalent arsenic compounds are extremely contradictory and fail to lead to unambiguous conclusions as to the mechanism or even the feasibility of a direct cathodic reduction of the arsenate ion'.

Our objective in this paper is to reexamine the electrochemical reduction of As(III) and As(V) in acidic and alkaline solutions in the context of the foregoing problems. Secondarily, we plan to use this study as fundamental research in support of the goal of removing arsenic from acid mine drainage (AMD) [19–21].

2. Experimental details

2.1. *Materials*

Sodium m-arsenite, $NaAsO_2$ purity 96.7% and sodium arsenate heptahydrate, $NaH_2AsO_4 \cdot 7H_2O$, assay 101.5% were supplied by Sigma. Solutions were prepared using deionized water; pH was adjusted using ACS reagent grade sulfuric acid or sodium hydroxide, both supplied by Fisher. The catalyst used in catalytic hydrogenation was 5% Pd on alumina (Aldrich).

The material used for the three-dimensional cathode was reticulated vitreous carbon, RVC 100 ppi (pores per inch), supplied by Electrosynthesis Company Inc. This material offers a high specific electrode area ($A_e = A/V_e = 65.57\ \mathrm{cm^2\ cm^{-3}}$, where A is the electrode area and V_e is the volume of electrode), in addition to acting as a turbulence promoter thus increasing the mass transfer coefficient, k_m [22].

2.2. *Apparatus*

For cyclic voltammetry experiments an 273A EG&G potentiostat was employed with a conventional three-electrode glass cell. The working electrode (WE) was a RVC 10 ppi rectangular solid with dimensions: 54 mm × 15 mm × 4.4 mm. The counter electrode (CE) was a IrO_2/Ti grid and the reference electrode (RE) was a saturated calomel electrode (SCE).

The electrolysis experiments were performed with a Plexiglas electrochemical reactor built in our laboratory. The reactor consisted of two compartments each having dimensions 58 mm × 15 mm × 4.5 mm, and separated by a DuPont Nafion® 424 cation exchange membrane supplied by Electrosynthesis Company Inc. The three-dimensional cathode was incorporated in a 'flow-through' mode and had dimensions 54 mm × 15 mm × 4.4 mm, affording a gross volume of 3.56 $\mathrm{cm^3}$, representing 91% of the total volume of the cathode compartment, and surface area 235 $\mathrm{cm^2}$, calculated using information supplied by the manufacturer. The dimensionally stabilized anode (DSA) was made of Ti coated with IrO_2 (∼7.2 $\mathrm{cm^2}$). The two electrodes were fitted in a vertical electrode configuration, and employed pieces of Pt wire (Aldrich) as electrode feeders. Power to the electrochemical reactor was supplied by a EG&G model 363 potentiostat/galvanostat.

2.3. *Experimental procedures*

The reactor was operated in plug flow mode, with separate solutions passed through the cathode and anode compartments at equal flow rates. The catholytes were aqueous solutions of arsenic compounds and the anolyte was a 0.0187 M solution of H_2SO_4. Flow rates ranging from 0.1 to 1.3 mL $\mathrm{min^{-1}}$ were obtained using Masterflex C/L or Fisher Scientific peristaltic pumps. Typically, the reactor was operated in single pass mode; in experiments involving batch recycle operation, both catholyte and anolyte were recirculated. In some experiments, the reactor was operated as an undivided cell, by removing the ion exchange membrane and sealing the inlet and outlet on the anode side. In order to eliminate the influence of dioxygen, the solutions were deaerated with argon before use as catholytes and kept free of oxygen during the experiments. The outlet catholyte was collected in a four-neck gas disengagement flask from which the gaseous products, hydrogen and arsine, were swept through a U-tube containing 10.00 mL of 0.1001 N iodine (Aldrich). Residual iodine was titrated against $Na_2S_2O_3$ (Aldrich), according to the method described by Smirnov et al. [9]. In order to check for complete absorption of arsine, the gas stream from the U-tube was passed through a second U-tube containing silver diethyldithiocarbamate (Aldrich) and morpholine (Aldrich) in chloroform (Fisher) which would give a red coloration if arsine were present [23]. In experiments in which the concentration of arsine was not measured, the gases were purged into a fume hood. The anolyte was vented through the anodic outlet along with the gaseous oxygen that was formed. The pH of the solutions was measured with a IONcheck 10 standard pH-meter.

Concentrations of arsenic in solution were determined by Nicholas Schrier of the Laboratory Services Division, University of Guelph, using a Varian Vista-Pro inductively coupled plasma spectrometer, or a Perkin-Elmer 5100 ZL graphite furnace atomic absorption spectrometer.

In order to achieve a high overall conversion, a modified cascade of flow reactors was used: after each pass, the collected outlet catholyte (less the sample for analysis) was used as the inlet catholyte for the next pass through the same reactor. This protocol involved discontinuance of the flow of electrolyte, which is normally continuous for a cascade of reactors. All electrolyses were carried out at constant current, with the electrical circuit including also an ammeter and a voltmeter.

3. Results and discussion

3.1. *Cyclic voltammetry*

Cyclic voltammograms (CV) for 1 mM As(III) were recorded in both acidic (pH 1.9) and basic solutions (pH 12.1) at a scan rate of 20 mV s^{-1}. The voltammograms are presented in Figures 1 and 2. The initial potential of arsenic formation was taken to be that at which the current measured on the working electrode in the presence of sodium m-arsenite began to exceed the current measured in the solvent alone: −0.25 V vs SCE in acidic solution and −0.49 V vs SCE in basic solution. In the case of sodium arsenate, the voltammograms for solution and for solvent alone were indistinguishable.

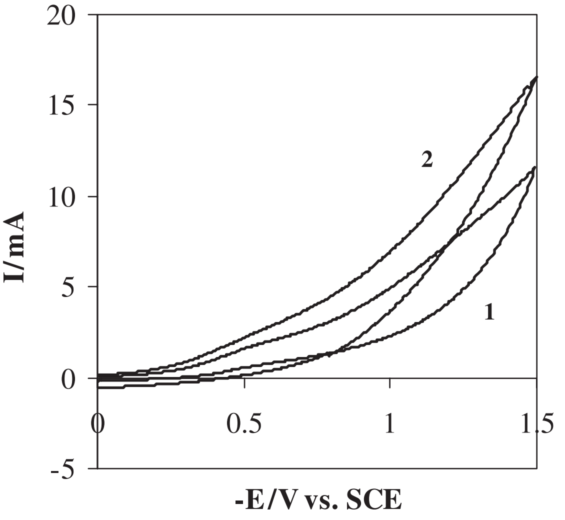

Fig. 1. Cyclic voltammogram of As(III) in acidic solution. Key: **(1)** 0.0187 M H_2SO_4; **(2)** 0.0187 M H_2SO_4 + 10^{-3} M $NaAsO_2$. WE: RVC 10 ppi; RE: saturated calomel; CE: IrO_2/Ti.

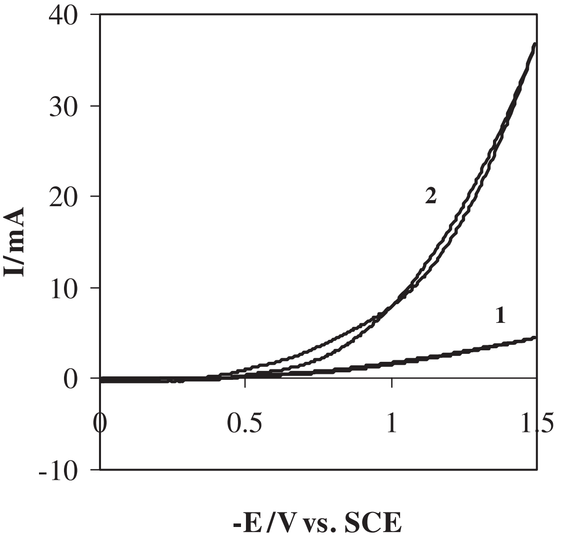

Fig. 2. Cyclic voltammogram of As(III) in basic solution. Key: **(1)** 0.1 M NaOH; **(2)** 0.1 M NaOH + 10^{-3} M $NaAsO_2$. WE: RVC 10 ppi; RE: saturated calomel; CE: IrO_2/Ti.

3.2. *Electrochemical reduction of As(III) and As(V) in acidic solution*

3.2.1. *Electrochemical removal of As(III)*

The speciation of trivalent arsenic in aqueous solution is principally AsO_2^- at pH > 10, $HAsO_2$ or As_2O_3 at 0 < pH < 10, and AsO^+ at pH < 0 [24]; hence in acidic solution (0.0187 M H_2SO_4), electrochemical reduction will involve the neutral molecule:

$$\begin{aligned} &\text{Cathode} \quad 2\,H^+ + 2\,e^- \rightarrow H_2 \\ &\qquad\qquad As(III) + 3\,e^- \rightarrow As(0) \\ &\qquad\qquad As(0) + 3\,e^- + 3\,H^+ \rightarrow AsH_3 \\ &\text{Anode} \quad H_2O - 2\,e^- \rightarrow 1/2\ O_2 + 2\,H^+ \end{aligned}$$

To restore charge balance protons migrate from the anode compartment to the cathode compartment.

A single pass of 100 ppm As(III) solutions through the reactor at current densities 2.55, 5.1 and 10.2 A m^{-2} led to the removal of 83, 89 and 94% of As(III), respectively (Figure 3, curves 1). The current efficiency (CE) was 6.96, 3.75 and 1.99% respectively. Higher overall conversions were obtained using the cascade of plug flow reactors mode of operation. On the second pass a further 75, 82 and 84% of As(III) removal was achieved with a current efficiency of 1.11, 0.38 and 0.1%, respectively. After the third pass the corresponding As(III) concentrations in the spent catholyte were 1.7, 0.8 and 0.4 ppm. The dependence of the removal efficiency on the current suggests that even at these high conversions, diffusion-limited reduction had not

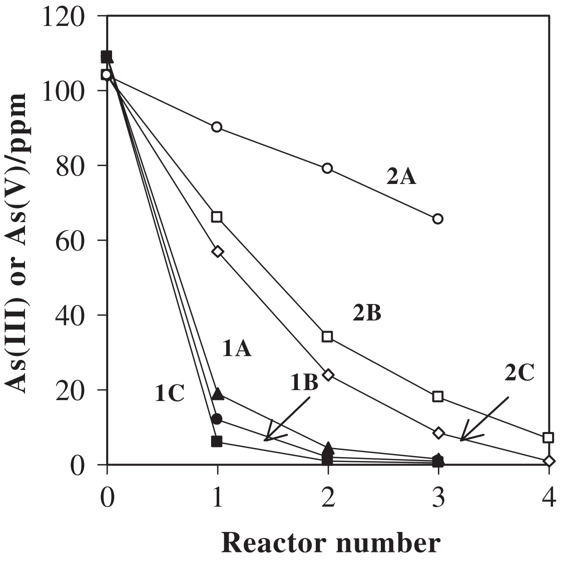

Fig. 3. Electrochemical reduction of As(III) (curves **1**) and As(V) (curves **2**) in acidic solutions using a cascade of plug flow reactors. Flow rate 0.36 mL min^{-1}. Key: (**1A**) 2.55, (**1B**) 5.1, (**1C**) 10.2, (**2A**) 5.1, (**2B**) 10.2 and (**2C**) 15.3 A m^{-2}.

completely been attained. Following Twardowski [15] we suggest that this effect may be due to gas evolution within the small interstices of the RVC cathode. Analysis showed that arsine accounted for all of the As(III) removed, and consistent with this, no deposit of As(0) was noticed on the cathode.

3.2.2. *Electrochemical removal of As(V)*

The speciation of As(V) in aqueous solution as a function of pH is AsO_4^{3-} at pH > 12.4; $HAsO_4^{2-}$ at 7.2 < pH < 12.4; $H_2AsO_4^-$ at 3.6 < pH < 7.2 and H_3AsO_4 at −2 < pH < 3.6 [24]. The solution to be electrolysed was prepared by dissolving $NaH_2AsO_4 \cdot 7H_2O$ in 0.0187 M H_2SO_4; under these conditions the neutral molecule predominates:

$$\begin{aligned} &\text{Cathode} \quad 2\,H^+ + 2\,e^- \rightarrow H_2 \\ &\qquad\qquad As(V) + 2\,e^- \rightarrow As(III) \\ &\qquad\qquad As(III) + 3\,e^- \rightarrow As(0) \\ &\qquad\qquad As(0) + 3\,e^- + 3\,H^+ \rightarrow AsH_3 \\ &\text{Anode} \quad H_2O - 2\,e^- \rightarrow 1/2\ O_2 + 2\,H^+ \end{aligned}$$

A single pass of the As(V) solutions through the reactor at current densities 5.1, 10.2 and 15.3 A m^{-2} led to the removal of 14, 37 and 45% of As(V), respectively (Figure 3, curves 2) at a current efficiency of 0.72, 0.98 and 0.81%. Higher overall conversions were again obtained by operating in a cascade of reactors. For example, at 15.3 A m^{-2}, four passes of the arsenic(V) lowered the residual arsenic to 0.83 ppm. Analysis showed that arsine accounted for all of the As(V) removed, and consistent with this, no deposit of As(0) was noticed on the cathode. Thus reduction of As(V) is an 8-electron process that affords arsenide anions without the formation of detectable quantities of arsenious acid or elemental arsenic:

$$H_3AsO_4 + 8\,e^- + 8\,H^+ \rightarrow AsH_3 + 4\,H_2O$$

This conclusion, which is consistent with those of Chernykh et al. [11], indicates that the transfer of the first electron requires a more negative potential than the transfer of subsequent electrons.

3.2.3. *Influence of the flow rate on As(V) removal in acidic solution*

The flow rate through a plug flow reactor determines by how much the concentration of substrate is reduced: Equation 1 [22, 25]. High values of the mass transfer coefficient k_m, the specific electrode area A_e, and the volume of the three-dimensional electrode V_e, and low flow rates q promote efficient conversion of reactant to product.

Table 1. Influence of the flow rate on the electrochemical reduction of As(V) in 0.0187 M H_2SO_4 using a cascade of three-plug flow reactors; j = 10.2 A m^{-2}

Flow rate /mL min^{-1}	As(V) concentration /ppm			
	Initial	Reactor 1	Reactor 2	Reactor 3
1.3	103.0	93.7	82.5	72.2
0.36	104.0	66.0	34.0	17.8
0.1	103.0	14.4	1.5	0.1

$$\frac{C(\mathrm{out})}{C(\mathrm{in})} = \exp\left(\frac{-k_m A_e V_e}{q}\right) \qquad (1)$$

The influence of flow rate was studied for the removal of As(V) from acidic solutions at a current density j of 10.2 A m^{-2} (Table 1).

3.2.4. *Use of an undivided reactor for removal of As(III) and As(V) in acidic solution*

Undivided reactors are preferable for industrial applications because of their lower construction and maintenance costs. Both As(III) and As(V) could be removed from acidic condition using an undivided cell but at the expense of considerably lower efficiency (Table 2).

3.3. *Electrochemical reduction of As(III) and As(V) in basic solution*

3.3.1. *Electrochemical removal of As(III)*

In the electrochemical reduction of As(III), the catholyte was a solution of $NaAsO_2$ in 0.0125 M NaOH (pH = 12.1) and the anolyte was 0.0187 M H_2SO_4, and a Nafion® 424 cation exchange membrane was used to divide the cell. The reactions involved in the reactor are as follows:

$$\begin{aligned} &\text{Cathode} \quad 2H_2O + 2\,e^- \rightarrow H_2 + 2\,HO^- \\ &\qquad\qquad As(III) + 3\,e^- \rightarrow As(0) \\ &\qquad\qquad As(0) + 3\,e^- + 3\,H^+ \rightarrow AsH_3 \\ &\text{Anode} \quad H_2O - 2\,e^- \rightarrow 1/2\ O_2 + 2\,H^+ \end{aligned}$$

Table 2. Comparison between electrochemical reduction of As(III) (5.1 A m^{-2}) and As(V) (10.2 A m^{-2}) in acidic solution using a cascade of divided and undivided plug flow reactors; flow rate: 0.36 mL min^{-1}

Position	As(III) concentration /ppm		As(V) concentration /ppm	
	Divided	Undivided	Divided	Undivided
Initial	109.0	98.2	104.0	103.3
Reactor 1	12.0	50.7	66.0	76.3
Reactor 2	2.1	37.8	34.0	58.1
Reactor 3	0.8	27.9	17.8	43.2

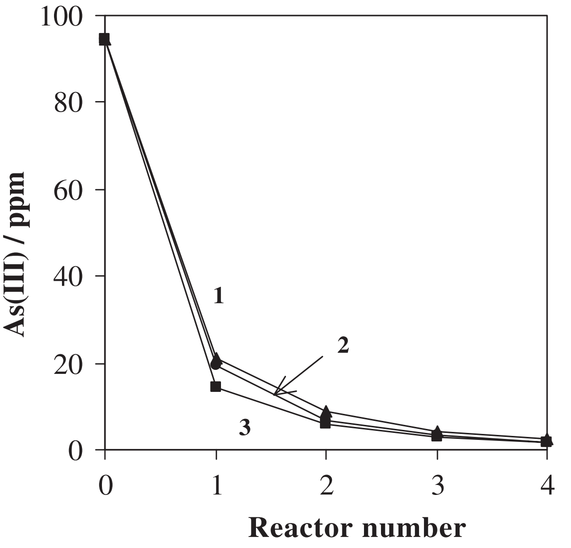

Fig. 4. Electrochemical reduction of As(III) in basic solutions using a cascade of plug flow reactors. Flow rate 0.36 mL min^{-1}. Key (**1**) 2.55, (**2**) 5.1, (**3**) 10.2 A m^{-2}.

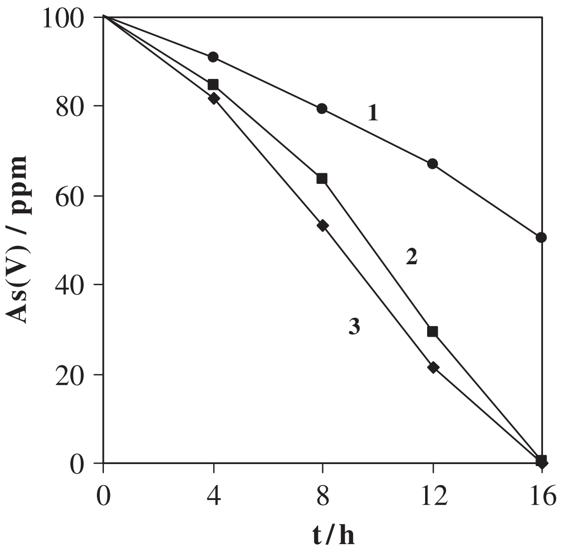

Fig. 5. Electrochemical reduction of As(V) in basic solutions using a plug flow reactor in batch recirculation mode of operation. Flow rate 0.36 mL min^{-1}. Key: (**1**) 5.1, (**2**) 10.2 and (**3**) 15.3 A m^{-2}.

A single pass of 100 ppm As(III) solutions at current densities 2.55, 5.1 and 10.2 A m^{-2} led to the removal of 78, 80 and 85% of As(III), respectively (Figure 4), with current efficiencies 5.66, 2.91 and 1.55%. A second pass achieved further As(III) conversions of 59, 65 and 59% with CE at 0.96, 0.48 and 0.16%, respectively, and after four passes the residual As(III) concentrations were 2.5, 1.7 and 1.6 ppm. No deposition of arsenic on the electrode was observed visually, and arsine was formed quantitatively.

3.3.2. *Electrochemical removal of As(V)*

In 0.0125 M NaOH (pH 12.1), the predominant form of As(V) is $HASO_4^{2-}$ [24]. Under conditions similar to those for the reduction of As(III) in basic solution, 100 ppm of As(V) was electrolysed at 5.1 and 10.2 A m^{-2} in the divided reactor. The reactions involved in the reactor are as follows:

$$\text{Cathode} \quad 2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,HO^-$$

$$As(\text{v}) + 2\,e^- \rightarrow As(\text{III})$$

$$As(\text{III}) + 3\,e^- \rightarrow As(0)$$

$$As(0) + 3\,e^- + 3\,H_2O \rightarrow AsH_3 + 3\,HO^-$$

$$\text{Anode} \quad H_2O - 2\,e^- \rightarrow 1/2\ O_2 + 2\,H^+$$

Conversions were much lower in this system: only 38.6% for 10.2 A m^{-2} and 18.2% for 5.1 A m^{-2} after seven passes of 100 ppm As(V) through the reactor. Because an impractical number of passes would be required to achieve a low residual concentration of arsenic, we investigated the use of a plug flow reactor in batch recirculation mode. The reservoir external to the reactor served as the gas disengagement vessel and was kept under a flow of nitrogen. The flow through the cell was adjusted so that the whole volume of solution passed through the cell in 1 h. Operation of the cell for 16 h gave final concentrations of As(V) 0.03, 0.6 and 50.6 ppm for current densities 15.3, 10.2 and 5.1 A m^{-2} (Figure 5), but the current efficiencies were very low, 0.11, 0.16 and 0.16%.

3.4. *Electrochemical reduction of low concentrations of As(III) and As(V)*

We carried out a series of reactions in which the starting concentration of arsenic was only 1 ppm. Using the plug flow mode of operation, residual concentrations of 20 ppb (the detection limit for our analytical instrumentation) was possible with four passes through the reactor for As(III) in acidic or basic solution and for As(V) in acidic solution (Figure 6).

3.5. *Electrocatalytic hydrogenation*

The controversy over whether As(V) is or is not reducible electrochemically led us to explore the possibility that the actual mechanism of reduction of this species may be electrocatalytic hydrogenation. This would make the efficiency of the process highly dependent on the electrode. These experiments employed a flow-through batch cell built in our laboratory and described elsewhere [26]. In all experiments the cathode was RVC 80 PPI (36 mm dia. 5 mm thickness), with a glass enclosed copper wire feeder, and the anode was a IrO_2/Ti grid with a copper wire feeder. The catholyte solution had a volume of 75 mL and the anolyte a volume of 20 mL, with the two compartments separated by a Nafion® 424 cation exchange membrane. The catholyte solution and catalyst powder (5% Pd on alumina) were forced through the RVC cathode by

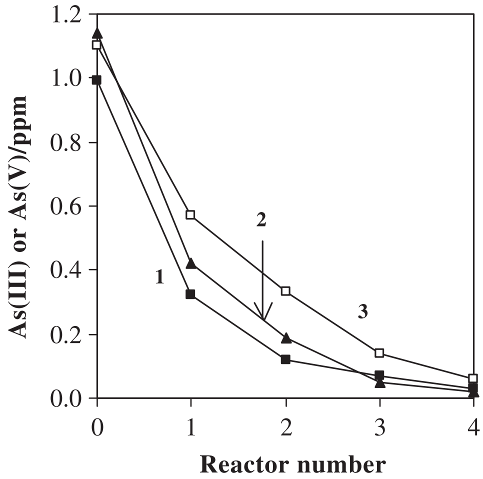

Fig. 6. Electrochemical reduction of As(III) and As(V) at starting concentration around 1 ppm using a cascade of plug flow reactors. Key: (**1**) As(III), acidic solution, $j = 5.1$ A m^{-2}, flow rate 0.36 mL min^{-1}; (**2**) As(III), basic solution, $j = 5.1$ A m^{-2}, flow rate 0.1 mL min^{-1}; (**3**) As(V), acidic solution, $j = 10.2$ A m^{-2}, flow rate 0.36 mL min^{-1}.

stirring, using a cross-shaped stir bar causing the impregnation of catalyst powder in the cathode.

The catalytic effect on the removal of As(III) from both acidic and alkaline solutions was more pronounced in the early stages of the reaction, as shown by comparing reactions in the same cell with and without catalyst (Figure 7). For example, in acidic solution, after 5 min of electrolysis 23.7% of As(III) was removed in the absence of catalyst (37% CE) and 63.6% in its presence (99.3% CE). Reduction of As(V) was much slower and the effect of catalysis was less pronounced, especially in basic solution (Figure 8). These results suggest that further exploration of electrocatalytic hydrogenation as a means of reducing arsenic species may be worthwhile.

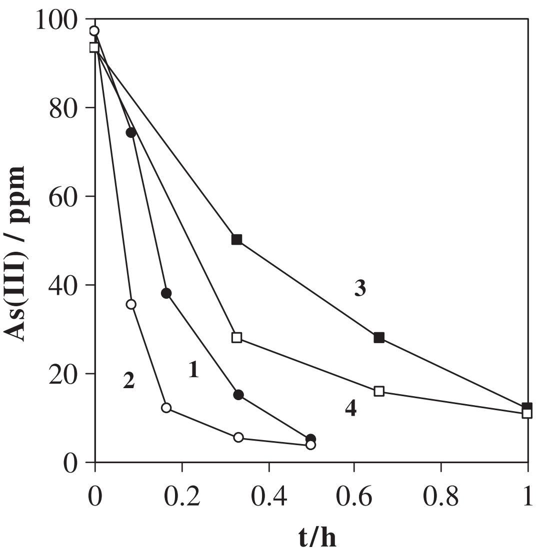

Fig. 7. Electrochemical reduction of As(III) in the cell used for electrocatalytic hydrogenation; $j = 4.24$ A m^{-2}. (**1**) acidic solution, no catalyst; (**2**) acidic solution, 200 mg of catalyst; (**3**) basic solution, no catalyst; (**4**) basic solution, 200 mg of catalyst.

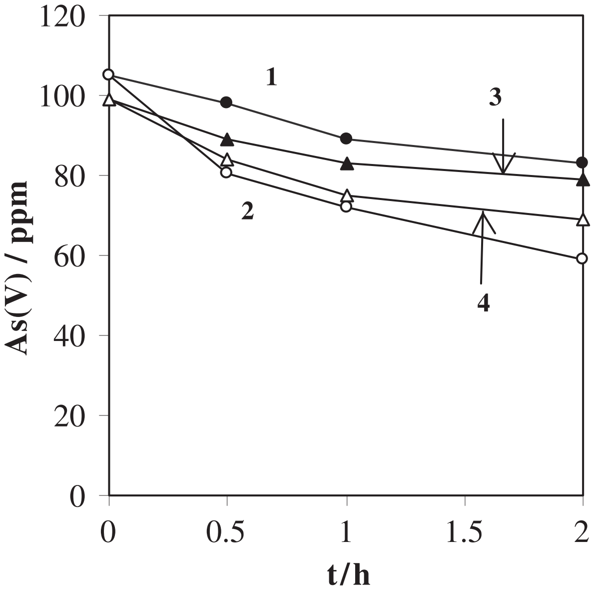

Fig. 8. Electrochemical reduction of As(V) in the cell used for electrocatalytic hydrogenation; $j = 4.24$ A m^{-2}; (**1**) acidic solution, no catalyst; (**2**) acidic solution, 200 mg of catalyst; (**3**) basic solution, no catalyst; **(4)** basic solution, 200 mg of catalyst.

4. Conclusion

Both As(III) and As(V) can be reduced electrochemically in acidic or alkaline solution using an RVC cathode in a plug flow reactor, giving arsine as the exclusive product. RVC is a useful cathode material because of its very high surface to volume ratio (65.57 cm^2 cm^{-3}) and its ability to promote turbulent mass transport conditions. The rate of removal of arsenic depended on both the flow rate and the current density. By using a cascade of 7–9 plug flow reactors, residual concentrations of arsenic below 20 ppb were achieved for As(III) in both acidic and alkaline solutions and for As(V) in acidic solution. The removal of As(V) from alkaline solutions was shown to be possible, but the efficiency was low. Although divided cells were used in most of our experiments, we demonstrated proof of concept for using an undivided cell, again at considerable sacrifice in efficiency. In terms of developing a technology, additional work is required to optimize cell design, especially with respect to limiting As(III) oxidation at the anode. Electrocatalytic hydrogenation significantly raised the rate of removal of As(III) in both acidic and basic solutions, but had only a modest effect in the case of As(V). All systems studied yielded AsH_3 rather than elemental arsenic as the exclusive reduction product. From the technical perspective, this is advantageous in that arsenic forms a nonconducting deposit on the cathode surface. The formation of arsine represents a technical challenge due to its toxicity, but its trapping on a large scale has been described [16]. Under laboratory conditions venting the product gases into a fume hood or trapping with iodine are both effective.

Acknowledgements

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