Removal of arsenic from a deep well by electrocoagulation in a continuous filter press reactor

Ruth Alcacio, José L. Nava, Gilberto Carreño, Enrique Elorza and Francisco Martínez

ABSTRACT

We investigated arsenic removal from groundwater by electrocoagulation (EC) using aluminum as the sacrificial anode in a continuous filter press reactor. The groundwater was collected at a depth of 200 m in the plateau region, in Central Mexico, (As $134 \mu g/L$, Fe $0.3 \text{mg L}^{-1}$, Cd $0.7 \text{mg L}^{-1}$, Na $58 \text{mg L}^{-1}$, pH 6.8). The influence of current density ($J$) and mean linear flow rate ($u$) on As removal was analyzed. EC revealed that $u$ of $0.91 \text{cm s}^{-1}$ (which gives a retention time of 53.4 s) at $J$ of 6 and 8 mA cm$^{-2}$ yielded samples that met the Mexican standard for arsenic ($<25 \mu g/L$). EC at 10 mA cm$^{-2}$ did not improve results any further owing to massive generation of gases and anode passivation. The partial EC removal of arsenic can be attributed to the mixture of HAsO$_2$, H$_3$AsO$_3$ and HAsO$_4^{2-}$. HAsO$_4^{2-}$ is more susceptible to removal by adsorption on Al(OH)$_3$ and Al$_2$O$_3$ flocs. The best EC result was obtained at $6 \text{mA cm}^{-2}$ and $0.91 \text{cm s}^{-1}$, with energy consumption of 0.89 kWh m$^{-3}$, which decreased arsenic from 134 to $14 \mu g \text{L}^{-1}$.

Key words | aluminum sacrificial anode, arsenic removal, electrocoagulation

INTRODUCTION

Historically, mining activities have led to environmental pollution. The main elements in groundwater contamination are heavy metals and metalloids. It is important to mention that in the plateau region in Central Mexico, specifically in the state of Guanajuato, Mexico, dissolved arsenic (As) was recently found in groundwater at concentrations of 50–155 $\mu g \text{L}^{-1}$. This problem was caused by natural weathering of arsenic-containing rocks (Ramos et al. 2011).

Arsenic-contaminated water is a significant problem owing to its toxicity. Long-term exposure to arsenic leads to chronic health problems such as hyperpigmentation and keratosis of the hands and feet; it also causes bladder, lung, skin, kidney, liver, and prostate cancer (Smith et al. 2006). Considering the high toxicity of arsenic, the World Health Organization (WHO) and the US Environmental Protection Agency have set a maximum acceptable level of $10 \mu g \text{L}^{-1}$ for arsenic in drinking water, which differs from the recommendation of the Mexican authorities ($25 \mu g \text{L}^{-1}$).

Removal of arsenic from large volumes of water is generally performed by adding chemical coagulants such as aluminum or iron sulfate. However, owing to low concentrations of dissolved As, this process produces large amounts of sludge because SO$_4^{2-}$ anions consume 50% of the coagulant (Rios et al. 2005). For this reason, electrocoagulation (EC) can be considered as an alternative, in which aluminum or iron, when dissolved electrolytically, supports the coagulation process and decreases the amount of sludge. Nevertheless, EC is still an emerging technology since its application to As removal has only been tested at laboratory and pre-pilot scale. EC is effective in destabilizing dispersed fine particles and anions contained in water (Chen et al. 2002). Flocs of metallic hydroxides are formed and remove dissolved species (Chen et al. 2002; Shen et al. 2003; Mohora et al. 2012; Flores et al. 2013).

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Arsenic species in water from deep wells (pH ~ 7.5) include innocuous arsenite (H\textsubscript{3}AsO\textsubscript{3}, oxidation state III) and arsenate anions (H\textsubscript{3}AsO\textsubscript{4}\textsuperscript{2-}, oxidation state V) (Pourbaix 1974; Smedley & Kinniburgh 2002). Arsenate at neutral pH is more susceptible to EC removal (Hansen et al. 2007; Balasubramanian et al. 2009; Wan et al. 2011; Mohora et al. 2012) because arsenate anions adsorb onto flocs of iron (Hansen et al. 2008; Kobya et al. 2011; Wan et al. 2011) and aluminum hydroxides (Hansen et al. 2008; Kobya et al. 2011; Mohora et al. 2012; Flores et al. 2013). Kobya et al. (2011) demonstrated that aluminum was better than iron electrodes at removing arsenic from drinking water.

The literature shows EC removal of As using Al electrodes in solutions containing high arsenic concentrations in synthetically prepared water (Kobya et al. 2011) and groundwater (Mohora et al. 2012; Flores et al. 2013); consequently, these results differ because a great number of species that are present in groundwater interfere with arsenic removal, in addition to reactor operating parameters such as current density, flow rate and reactor geometry. For the above, the aim of this paper was to study the influence of current density, in addition to reactor operating parameters such as current density, flow rate and reactor geometry. For the above, the aim of this paper was to study the influence of current density, and mean linear flow rate in a continuous EC filter press reactor, equipped with aluminum electrodes, on the removal of As from a deep well (initially As 134 µg L\textsuperscript{-1}, Fe 0.3 mg L\textsuperscript{-1}, Cd 0.7 mg L\textsuperscript{-1}, Na 58 mg L\textsuperscript{-1}, pH 6.8). The energy consumption of electrolysis was also estimated.

### Electrochemical and Chemical Processes During As Removal by EC Using Aluminum Electrodes

EC involves in situ generation of coagulants by electrodissolution of aluminum electrodes. Aluminum cations are generated at the anode and hydrogen gas is evolved at the cathode. This process generates aluminum hydroxide, which is believed to adsorb As (Kobya et al. 2011; Mohora et al. 2012; Flores et al. 2013). The electrode and chemical reactions in neutral solution (pH ~ 7) are shown below. At the anode, electrodissolution generates aluminum ions (Al\textsuperscript{3+}), which are transformed to aluminum hydroxide and aluminum oxide in the bulk:

\begin{equation}
\text{Al(s)} \rightarrow \text{Al}^{3+} + 3\text{e}^{-} \quad (1)
\end{equation}

\begin{equation}
\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3(s) + 3\text{H}^+ \quad (2)
\end{equation}

\begin{equation}
2\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3(s) + 6\text{H}^+ \quad (3)
\end{equation}

The oxidation states of As in water are As(III) and As(V). As(V) is typically dominant in aerobic surface waters, while As(III) is found in anaerobic groundwater. At neutral pH, the predominant As(V) species has a net negative charge (H\textsubscript{3}AsO\textsubscript{4}\textsuperscript{2-}), while As(III) species generally have no net charge (H\textsubscript{3}AsO\textsubscript{2} and H\textsubscript{2}AsO\textsubscript{3}) (Pourbaix 1974). Al(OH)\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3} flocs are believed to adsorb H\textsubscript{3}AsO\textsubscript{4}\textsuperscript{2-} (Kobya et al. 2011; Mohora et al. 2012; Flores et al. 2013):

\begin{equation}
\text{Al(OH)}_3(s) + \text{HAsO}_4^{2-} \rightarrow [\text{Al(OH)}_3\text{HAsO}_4^{2-}]_{(s)} \quad (4)
\end{equation}

\begin{equation}
\text{Al}_2\text{O}_3(s) + \text{HAsO}_4^{2-} \rightarrow [\text{Al}_2\text{O}_3\text{HAsO}_4^{2-}]_{(s)} \quad (5)
\end{equation}

We previously reported that arsenite removal may occur by sweep coagulation, in which interaction occurs between As(III) and Al(OH)\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3} flocs (Hernández 2007). However, reports on the mechanism of As removal by aluminum flocs are rather limited.

At the aluminum cathode, hydrogen gas is released:

\begin{equation}
3\text{H}_2\text{O} + 3\text{e}^{-} \rightarrow 1.5\text{H}_2 + 3\text{OH}^{-} \quad (6)
\end{equation}

The major problem with aluminum anodes is passivation due to Al\textsubscript{2}O\textsubscript{3} precipitation, which leads to high anode and cell potentials and increases the energy consumption and cost of EC (Kobya et al. 2011; Mohora et al. 2012). Passivation can be controlled at low current densities in combination with convection (turbulent flow conditions), which favors Al\textsuperscript{3+} transport away from the surface to the bulk solution. In addition, cathodes of the same material can be used to electrodissolve Al\textsubscript{2}O\textsubscript{3} by periodic current reversal (Mohora et al. 2012), which allows even consumption of the aluminum electrodes during the process.
EXPERIMENTAL

Solutions

The groundwater was collected at a depth of 200 m in the plateau region, in Central Mexico, (As $134 \, \mu g \, L^{-1}$, Fe $0.3 \, mg \, L^{-1}$, Cd $0.7 \, mg \, L^{-1}$, Na $58 \, mg \, L^{-1}$, pH 6.8). Water samples were obtained from the well before the disinfection process.

EC pre-pilot-scale filter press reactor

Figure 1 shows a schematic of the experimental set-up. The system consists of a continuous pre-pilot-scale filter press cell in which the coagulant is produced. The resulting solution (mixture of water and coagulant) is passed to a test jar to induce flocculation and adsorption of arsenic on aluminum flocs. The arsenic is then precipitated and the clarified solution is analyzed.

The connection of current intensity supplied to the electrodes was in monopole configuration. Three aluminum electrodes with 99.7% purity ($3.05 \, cm \times 8.10 \, cm \times 0.30 \, cm$) were used as anodes and four similar electrodes with the same dimensions were used as cathodes. The reactor dimensions are listed in Table 1. The serpentine array induces fluid turbulence, enhancing mass transport of the coagulant from the anode to the bulk.

The reactor was connected to a hydraulic system consisting of a centrifuge pump (model MDX-MT-3) of 0.25 HP and a flow meter (model F-44250LH-8) with a capacity of 0–1 L min$^{-1}$. The PVC pipes connecting the reservoir to the pump were 0.76 cm (0.3 inches) in diameter. The valves and connections were also made of PVC. A BK Precision power supply (model 1090) was used for electrolysis tests.

The cell potential was directly recorded by the annunciator of the power supply. The aluminum electrode potential was measured as the difference between aluminum and a saturated mercurous sulfate reference electrode (SSE; Radiometer model XR200), 0.615 V vs. SHE/V. The potential of this electrode was determined using a high-impedance multimeter (Agilent model 34401A). All electrode potentials are reported with respect to SHE.

Methodology

EC studies were carried out using the experimental set-up shown in Figure 1. EC was performed under different hydrodynamic conditions with a mean linear flow rate of 0.91–4.55 cm s$^{-1}$ (giving values of retention time in the EC pre-pilot-scale filter press reactor between 53.4 $\tau$ 10.7 s) and current densities of 6, 8 and 10 mA cm$^{-2}$. Each resulting solution, after passing through the EC pre-pilot-scale filter press cell, was immediately passed to the test jar and mixed at slow

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Dimensions of the EC reactor</th>
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</thead>
<tbody>
<tr>
<td>Reactor volume $V_r$ (cm$^3$)</td>
<td>88.94</td>
</tr>
<tr>
<td>Height $B$ (cm)</td>
<td>3.05</td>
</tr>
<tr>
<td>Channel length $L$ (cm)</td>
<td>8.1</td>
</tr>
<tr>
<td>Channel width $S$ (cm)</td>
<td>0.6</td>
</tr>
<tr>
<td>Number of channels</td>
<td>6</td>
</tr>
<tr>
<td>Total length of six channels $L_T$ (cm)</td>
<td>48.6</td>
</tr>
<tr>
<td>Anode area in each channel in contact with solution (cm$^2$)</td>
<td>24.7</td>
</tr>
<tr>
<td>Cathode area in each channel in contact with solution (cm$^2$)</td>
<td>24.7</td>
</tr>
<tr>
<td>Cross-sectional area $A_T$ (cm$^2$)</td>
<td>1.83</td>
</tr>
</tbody>
</table>
speed (30 rpm) for 15 min for aggregate growth. The aggregates were allowed to precipitate in static solution for approximately 1 h. As, Fe, Cd and Na were analyzed in the resulting clarified solution. After dissolution of the floc, aluminum was also analyzed. The value of $\tau$ was determined by the ratio $\tau = L_T / u$.

**Analytical procedure**

Arsenic concentrations in the samples were measured using a standard method (APHA 1995) with an atomic absorption (AA) spectrometer (Perkin Elmer AAnalyst 200) equipped with a manual hydride generator at 188.9 nm. The As detection limit was 0.1 $\mu$g L$^{-1}$ and the error for triplicate analyses was within 2%. The kinetics of aluminum dissolution were followed by dissolving the sludge at pH 2 and then quantifying aluminum ions by AA. Fe, Cd and Na were analyzed by AA. All chemical reagents were of analytical grade. Each individual experiment was performed at least three times and the results were averaged.

**ANALYSIS OF RESULTS AND DISCUSSION**

Figure 2 shows the residual concentration of arsenic ($C_{As}$) in groundwater after EC as a function of the mean linear flow rate ($u$) at 6 mA cm$^{-2}$. The experimental and theoretical aluminum doses ($C_{Al(III)}$ and $C_{Al(III)(N)}$ respectively) are also shown. $C_{As}$ linearly increased between 14 and 134 $\mu$g L$^{-1}$ as a function of $u$ in the interval 0.91–4.55 cm s$^{-1}$ (Figure 2), indicating that arsenic removal decreases as $u$ increases and $\tau$ decreases. This is due to depletion of $C_{Al(III)}$ from 71 to 4 mg L$^{-1}$. The $C_{As}$ of 134 $\mu$g L$^{-1}$ at $u = 4.55$ cm s$^{-1}$ ($\tau = 10.7$ s) is due to $C_{Al(III)}$ trended to zero. The $C_{Al(III)}$, obtained by analysis of the sludge, at $u > 0.91$ cm s$^{-1}$ ($\tau < 53.4$ s) was lower than the theoretical amount ($C_{Al(III)(N)}$), calculated as

$$C_{Al(III)(N)} = \frac{(jLMW)}{nFSu}(1 \times 10^6)(N)$$

where $C_{Al(III)(N)}$ is the theoretical aluminum concentration (mg L$^{-1}$), $j$ is the current density (A cm$^{-2}$), $L$ is the length of one channel (cm), $MW$ is the molecular weight of aluminum (26.98 g mol$^{-1}$), $n$ is the number of electrons exchanged ($n = 3$), $F$ is the Faraday constant (96,485 C mol$^{-1}$), $S$ is the channel width (cm), $u$ is the mean linear flow rate (cm s$^{-1}$), $N$ is the number of channels, and $1 \times 10^6$ is a conversion factor used to obtain the aluminum concentration in mg L$^{-1}$.

The difference between the experimental and theoretical values of aluminum at $u = 0.91$ cm s$^{-1}$ ($\tau = 53.4$ s) can be associated with corrosion of aluminum in addition to its electrodissolution, while at $1.82 \leq u \leq 3.64$ cm s$^{-1}$ ($26.7 \geq \tau \geq 13.3$ s) it can probably be explained, on one hand, by oxygen evolution according to Equation (8), which typically occurs simultaneously with Equation (1) (Kobya et al. 2011), and, on the other hand, by anode passivation due to Al$_2$O$_3$ precipitation (Kobya et al. 2011; Mohora et al. 2012).

$$H_2O \rightarrow 0.5O_2 + 2H^+ + 2e^-$$

It is important to remark that the ratio between experimental and theoretical aluminum doses ($C_{Al(III)/C_{Al(III)(N)}} \times 100$ could correspond exactly to the value of the current efficiency, if the aluminum cations, generated at the aluminum anode, were completely incorporated into the bulk. However, Al(OH)$_3$ and Al$_2$O$_3$ precipitate in situ. These precipitates do not lead to exact determination of the current efficiency; for this reason we did not include here current efficiency analysis. On the other hand, the ratio ($C_{Al(III)/C_{Al(III)(N)}}$) obtained here contradicts that obtained...
by Kobya et al. in (2011), who produced ratios slightly higher than unity, during the removal of As by EC using Al electrodes. This improvement can be attributed to the presence of chloride ions in the solution tested by Kobya et al. (2011), owing to chloride corroding Al electrodes, and also forming soluble complexes with aluminum cations.

At 8 mA cm\(^{-2}\), the behavior of \(C_{\text{As}}\) as a function of \(u\) differed for the ranges 0.91–1.82, 1.82–3.64 and 3.64–4.55 cm s\(^{-1}\), (Figure 3). However, the increase in \(C_{\text{As}}\) from 23 to 97 \(\mu\)g L\(^{-1}\) at 0.91–1.82 cm s\(^{-1}\) was significant. The quasi-constant \(C_{\text{As}}\) at 1.82 \(\leq u \leq 3.64\) cm s\(^{-1}\) is due to the low dose of aluminum (\(C_{\text{Al(III)}} < 19\) mg L\(^{-1}\)). The experimental aluminum dose was lower than the theoretical one at \(u > 0.91\) cm s\(^{-1}\) (\(\tau < 53.4\) s).

At 10 mA cm\(^{-2}\), \(C_{\text{As}}\) increased from 42 to 49 \(\mu\)g L\(^{-1}\) as a function of \(u\) and again, the experimental aluminum dose was lower than the theoretical one (not shown here). EC at 10 mA cm\(^{-2}\) did not improve the EC process any further owing to massive generation of electrolytic gases and anode passivation. This last result is in agreement to that reported by other authors (Mohora et al. 2012; Flores et al. 2013).

It should be noted that \(C_{\text{As}}\) satisfies the Mexican limit of \(\leq 25\) \(\mu\)g L\(^{-1}\) only at \(u = 0.91\) cm s\(^{-1}\) (\(\tau = 53.4\) s), at 6 and 8 mA cm\(^{-2}\), but does not meet the WHO limit of \(\leq 10\) \(\mu\)g L\(^{-1}\).

The partial EC removal of arsenic (Figures 2 and 3) can be attributed to the mixture of HAsO\(_2\), H\(_2\)AsO\(_3\) and HAsO\(_3^2\). The third species is probably more susceptible to removal by adsorption on Al(OH)\(_3\) and Al\(_2\)O\(_3\) flocs (Kobya et al. 2011; Mohora et al. 2012; Flores et al. 2013), since these flocs have a positive zeta potential (Amirtharajah et al. 1991). X-ray absorption spectroscopy and X-ray photoelectron spectroscopy would be helpful in investigating the local environment of Al and As in EC flocs generated in groundwater, but this was beyond the scope of the present study.

The electrolytic energy consumption (\(E_{\text{cons}}\)) for the EC results that satisfy the Mexican arsenic standard were 0.89 and 1.19 kWh m\(^{-3}\) for the tests performed at 6 and 8 mA cm\(^{-2}\) (\(u = 0.91\) cm s\(^{-1}\), \(\tau = 53.4\) s). These values were lower than those obtained in other research by our group, employing the same experimental setup, giving values between 1.2 and 5.3 kWh m\(^{-3}\), during the removal of As from groundwater (after the addition of 1 mg L\(^{-1}\) hypochlorite) collected at a depth of 320 m in the Bajio region in Central Mexico (initially As 50 \(\mu\)g L\(^{-1}\), carbonates 40 mg L\(^{-1}\), hardness 80 mg L\(^{-1}\), pH 7.5 and conductivity 150 \(\mu\)S cm\(^{-1}\)) (Flores et al. 2013). It is important to mention that the cell potential (\(E_{\text{cell}}\)) for the electrolysis performed herein remained at a constant value of 6 V. This value was lower than that reported by Flores et al. (2013). The difference in the values of both \(E_{\text{cons}}\) and \(E_{\text{cell}}\) obtained here with those produced by Flores et al. (2013) might be attributed to the chemical composition of each groundwater. The \(E_{\text{cons}}\) was evaluated as

\[
E_{\text{cons}} = \frac{E_{\text{cell}} I}{5.6 BS u} \tag{9}
\]

where \(E_{\text{cell}}\) is the cell potential (V), \(I\) is the current intensity during electrolysis (C s\(^{-1}\)), \(B\) is the channel height (cm), \(S\) is the channel width (cm) and 5.6 is a conversion factor used to obtain \(E_{\text{cons}}\) in units of kWh m\(^{-3}\).

The best EC was obtained at 6 mA cm\(^{-2}\) and 0.91 cm s\(^{-1}\) (\(\tau = 53.4\) s), with energy consumption of 0.89 kWh m\(^{-3}\) which decreased arsenic from 134 to 14 \(\mu\)g L\(^{-3}\). Data for Fe, Cd and Na are not presented, since these parameters remained almost constant.

Studies have shown that several dissolved species present in water samples can interfere with EC arsenic
removal. For example, Mohora et al. (2012) reported that natural organic matter is simultaneously removed with As from groundwater by EC using Al anodes. It should be noted that we did not measure concentrations of natural organic matter and typical anions, such as phosphates, silicates and sulfates, and hence their influence on As removal is not discussed. However, this analysis should serve as a useful starting point and these interferences may be investigated in future research.

The experimental values of aluminum were lower than the theoretical values due to massive generation of electrolytic gases and anode passivation. The random discrepancies for the arsenic removal and experimental dose of aluminum at different current densities, flow rates and retention times indicate a lack of correlation between As removal and experimental dose of aluminum and the current density, flow rate and retention time.

CONCLUSIONS

We systematically investigated arsenic removal from groundwater (As 134 μg L⁻¹, Fe 0.3 mg L⁻¹, Cd 0.7 mg L⁻¹, Na 58 mg L⁻¹, pH 6.8) collected from a deep well (200 m) located in the plateau region (Guanajuato, Mexico) by EC using aluminum as a sacrificial anode in a continuous filter press cell.

EC investigations revealed that a mean linear flow rate of 0.91 cm s⁻¹ (which gives a retention time in the EC pre-pilot-scale filter press reactor of 53.4 s) at current densities of 6 and 8 mA cm⁻² yielded samples that met the Mexican standard for arsenic in water (≤25 μg L⁻¹). Under these conditions, aluminum doses of 71–76 mg L⁻¹ were suitable. EC at 10 mA cm⁻² did not improve the EC process any further owing to massive generation of electrolytic gases and anode passivation.

The partial EC removal of arsenic can be attributed to the mixture of HAsO₂⁻, H₂AsO₃⁻ and HAsO₄⁻. The third species is probably more susceptible to removal by adsorption on Al(OH)₃ and Al₂O₃ flocs. In a given EC reactor geometry the best As removal from 134 to 14 mg L⁻¹ was obtained at 6 mA cm⁻² and 0.91 cm s⁻¹, with energy consumption of 0.89 kWh m⁻³.

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