Int. J. Electrochem. Sci., 9 **(2014)** 6658 - 6667

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Arsenic Removal from Groundwater by Electrocoagulation Process in a Filter-Press-Type FM01-LC Reactor

Omar J. Flores, José L. Nava[*], *Gilberto Carreño*

Universidad de Guanajuato, Departamento de Ingeniería Geomática e Hidráulica, Av. Juárez 77, Zona Centro, C.P. 36000, Guanajuato, Guanajuato, México.
[*]E-mail: jlnm@ugto.mx

Received: 29 May 2014 / *Accepted:* 11 August 2014 / *Published:* 25 August 2014

Treatment of groundwater containing arsenic by electrocoagulation (EC) has been studied in a filter–press–type FM01–LC reactor using 3 cell stack with aluminum as the sacrificial anode. The influence of current density and mean linear flow velocity on the As removal efficiency was analyzed. Groundwater was collected from deep well (320 m deep) located in Guanajuato, Mexico (arsenic 50 μg L^{-1}, carbonates 40 mg L^{-1}, hardness 80 mg L^{-1}, pH 7.5 and conductivity 150 μS cm^{-1}). Prior to EC experiments arsenite contained in groundwater was oxidized to arsenate by addition of 1 mg L^{-1} hypochlorite typically used for disinfection. Arsenate removal by EC might involve adsorption on aluminum hydroxides generated in the process. Arsenate depletion from 50 to 3.9 μg L^{-1} was obtained at current density and mean linear flow velocity of 6 mA cm^{-2} and 1.8 cm s^{-1}, respectively, with energy consumption of 3.9 kWh m^{-3}. The convenience of using the FM01-LC cell as a test reactor, which avoids oxygen evolution reaction during the aluminum electrodissolution, is also discussed.

Keywords: arsenic removal; drinking water; aluminum sacrificial anode; electrocoagulation; FM01–LC reactor.

1. INTRODUCTION

Recently, dissolved As in groundwater in the state of Guanajuato in Central Mexico has been found with concentrations in the order of 50–155 μg L^{-1}. These arsenic levels were caused by arsenic mobilization in mine tailings dams and natural weathering of arsenic containing rocks [1]. Arsenic-contaminated water is a significant problem owing to its toxicity. Long term exposure to arsenic creates chronic health problems such as hyperpigmentation, and keratosis of hands and feet; it also causes bladder, lungs, skin, kidney, liver and prostate cancer [2]. Considering the high toxicity of arsenic, the World Health Organization (WHO) and the U.S. Environmental Protection Agency have set a maximum acceptable level of 10 μg L^{-1} for arsenic in drinking water, which differs from the recommendation of Mexican authorities (25 μg L^{-1}).

The process of As removal from large volumes of water is generally performed by adding chemical coagulants such as aluminum or iron sulphate, using coagulation methods. Electro-coagulation process (EC), where aluminum or iron is dissolved electrolytically, has recently been employed for diminishing the amount of sludge. Flocs of metallic hydroxides remove dissolved species [3–5].

The arsenic species in water from deep wells (at pH ~ 7.5) are innocuous arsenite, $HAsO_2$ and H_3AsO_3 (oxidation state III) and arsenate anion, $HAsO_4^{2-}$ (oxidation state V) [6−7]. The second specie at neutral pH is typically removed by EC [5, 8−9], due to arsenate anion adsorbs on flocs of iron [8−10] and aluminum hydroxides [5, 8, 10].

The electrode materials commonly used for the removal of As by EC are mainly iron [8−10, 12] and aluminum [5, 10]. Kobya et al. (2011) have demonstrated that arsenic removal from drinking water was better with aluminum than with iron electrodes [10, 13].

Literature shows the removal of As by EC process using Al electrodes in solutions containing high arsenic concentrations in synthetically prepared water [10] and groundwater [5]; consequently, these results can differ with regard to those obtained with groundwater because a great number of species that are present in groundwater interfere with the process of arsenic removal, besides reactors operation parameters such as current density, flow rate and reactor geometry.

Studies have shown that phosphates in water samples can interfere with EC arsenic removal using Fe as sacrificial anodes [9]; while silicates and sulphates did not affect As removal. However, reports regarding the effect of dissolved species on As removal by EC using Al electrodes are rather limited. Mohora et al. (2012) reported that natural organic matter is simultaneously removed with As from groundwater by EC using Al anodes [5]. Hu et al. (2014) studied the effect of calcium on arsenate removal by EC using aluminum electrodes; these authors showed that calcium improved the removal efficiency of As (V) owing to calcium forms calcium−arsenate−hydroxide precipitates [14].

In our previous communication we characterized the performance of a continuous filter-press reactor equipped with aluminium electrodes for arsenic removal from underground water [15]. This reactor had a serpentine shape where the electrodes were in a cascade array developing turbulence of the fluid. In that study we put on evidence that the removal of arsenic is dependent of current density and mean linear flow rate, although the experimental aluminium dose was lower than the theoretically calculated owing to massive oxygen evolution and anode passivation.

The purpose of this paper is to evaluate the performance of a well-known scale-able electrochemical reactor, the filter-press-type FM01-LC cell, during the arsenic removal from groundwater (50 μg dm^{-3} As) by EC. The FM01-LC reactor was equipped with 3 cell stack using aluminum as the sacrificial anode. The influence of current density and mean linear flow rate on the arsenic removal efficiency was analyzed. The energy consumption for electrolysis was also estimated. Prior to EC experiments arsenite contained in groundwater was oxidized to arsenate by addition of 1 mg L^{-1} hypochlorite typically used for disinfection.

2. ELECTROCHEMICAL AND CHEMICAL PROCESSES DURING REMOVAL OF AS BY EC

The generation of aluminum cations takes place at the anode, whereas at the cathode, a hydrogen gas production typically occurs. This process generates aluminum hydroxides, which is believed to adsorb As [5, 10, 15]. The mean electrode and chemical reactions in neutral solution (pH ~ 7) are shown below.

At the anode, the electrodissolution of aluminum generates aluminum ions first (Al^{3+}); afterwards, the aluminum ions are transformed to aluminum hydroxides ($Al(OH)_{3(s)}$) and aluminum oxides ($Al_2O_{3(s)}$) in the bulk:

$$Al_{(s)} \rightarrow Al^{3+} + 3e^- \quad (1)$$

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3H^+ \quad (2)$$

$$2Al^{3+} + 3H_2O \rightarrow Al_2O_{3(s)} + 6H^+ \quad (3)$$

The oxidation states of As in water are As(III) and As(V). Typically As(V) is dominant in aerobic surface waters while As(III) is found in anaerobic groundwater. At neutral pH (~7) the predominating species of As(V) present a net negative charge, $HAsO_4^{2-}$, while the species of As(III) generally have no net charge, $HAsO_{2(aq)}$ and $H_3AsO_{3(aq)}$ [6]. The $Al(OH)_{3(s)}$ and $Al_2O_{3(s)}$ flocs are believed to adsorb $HAsO_4^{2-}$ [5, 10, 15]:

$$Al(OH)_{3(s)} + HAsO_4^{2-} \rightarrow [Al(OH)_{3*}HAsO_4^{2-}]_{(s)} \quad (4)$$

$$Al_2O_{3(s)} + HAsO_4^{2-} \rightarrow [Al_2O_{3*}HAsO_4^{2-}]_{(s)} \quad (5)$$

Our group had previously reported the convenience of oxidized arsenite species to $HAsO_4^{2-}$, by the addition of a typical amount of hypochlorite typically used for disinfection purposes to give 1 mg L^{-1} ClO^- in the drinking water [15].

At the aluminum cathode, hydrogen gas is released:

$$3H_2O + 3e^- \rightarrow 1.5H_2 + 3OH^- \quad (6)$$

Typically at the cathode interface the solution becomes alkaline with time. The OH^- migrates and diffuses away from the cathode to the anode, thus favoring water formation, hydroxyl ions reacts with protons of equations (2) and (3), remaining neutral solution:

$$OH^- + H^+ \rightarrow H_2O \quad (7)$$

The major problem of the aluminum anode is its passivation. The passivation can be controlled at low current densities in combination with convection (turbulent flow conditions), which favors Al^{3+} ions transport away from the surface to the bulk solution. In addition, it is recommended to use cathodes of the same material to electro-dissolve $Al_2O_{3(s)}$ by periodic current reversal [5], which allows an even consumption of aluminum electrodes during the process.

3. EXPERIMENTAL

3.1 Solutions

Groundwater employed to electrochemical treatment was collected from deep wells (320 m deep) located in the Bajio region (in Guanajuato, Mexico). Groundwater was characterized using the following parameters: arsenic, carbonates, hardness, conductivity, and pH.

Table 1. Characteristics of the groundwater (320 m deep) samples collected at a depth of 320 m in the Bajío region (Guanajuato, México), after addition of 1 mg L^{-1} ClO^{-}, the concentration typically used for disinfection of groundwater.

Parameters	
As total / µg L^{-1}	59
Carbonates / mg L^{-1}	40
Hardness / mg L^{-1}	80
pH	8.1
Conductivity / µS cm^{-1}	392

Table 1 shows the characteristics of the groundwater. Groundwater that was collected contains 50 µg L^{-1} As total, which exceed the Mexican Norm for arsenic (25 µg L^{-1} As). It is believed that Arsenic (III) is dominant in this anaerobic groundwater. It is important to emphasize that water samples obtained from deep wells were collected before the disinfection process, which is usually made with hypochlorite. Afterwards, 1 mg L^{-1} ClO^{-} was added to the water sample to oxidize arsenite species to $HAsO_4^{2-}$. All electrolyzes presented here were performed after the hypochlorite addition.

3.2. Experimental setup.

Figure 1 shows a scheme of the experimental setup. The system consists of a continuous FM01-LC reactor, where the coagulant is produced. Afterwards, the electrolyte circuit was designed to allow resulting solution (which is a mixture of water and coagulant) is passed to a test jar to induce the flocculation and clarification. Then, the clarified solution is analyzed.

The FM01-LC reactor has been described in the literature with great detail [16–17]. Four aluminum plates with 99.7% purity were fitted into the spacers of the cell to form 3 the cell stack; hence, the electrolyte flowed within the channels. The net spacing between the aluminum electrodes was 0.55 cm, a distance which is given by polypropylene separators. The reactor was switched in monopole configuration. The dimensions of the FM01-LC reactor are presented in Table 2.

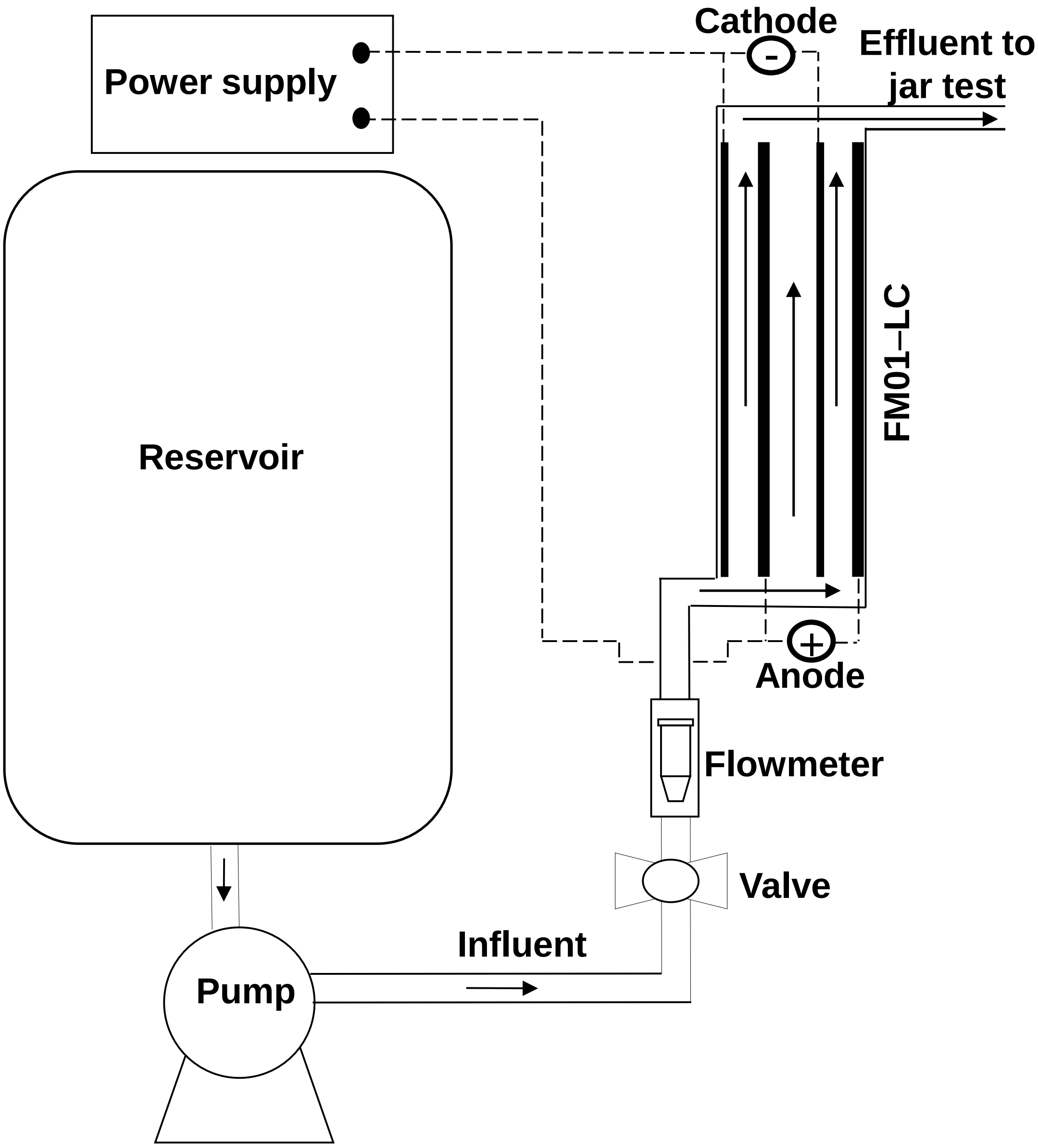

Figure 1. Electrical and flow circuit for the EC process in a filter-press-type FM01-LC reactor.

Table 2. Dimensions of the FM01-LC reactor.

Electrode Length, *L*	16 cm
Electrode height, *B*	4 cm
Electrode spacing, *S*	0.55 cm
Electrode Area in 1 cell, *A*	64 cm^2
Electrode Area in 3 cell stack, *A*	192 cm^2
Hydraulic (equivalent) diameter, $de = 2BS/(B+S)$	0.97 cm

The electrolyte was contained in a 20 L polypropylene reservoir. A magnetically coupled pump of 1/15 hp March MFG, model MDX-MT-3 was used; the flow rates were measured by a variable area glass rotameter from Cole Palmer, model F44500. The electrolyte circuit was constructed from PVC tubing with 0.5 inch diameter; the valves and the three way connectors were made of PVC. A BK precision power supply (model 1090) was used for electrolysis tests. The cell potential was measured using the power supply.

3.3. Methodology

EC studies were carried out using the experimental setup shown in Fig. 1. EC was performed under different hydrodynamic conditions with a mean linear flow rate of 0.9–5.3 cm s^{-1} (giving values of retention time in the FM01-LC reactor between $17.8 \geq \tau \geq 3$ s) and current density of 5.5, 6 and 6.5 mA cm^{-2}. Each resulting solution is passed to a test jar to induce the flocculation and clarification. When the resulting solution was passed to the test jar it was mixed at slow speed (30 rpm) for 15 min for aggregate growth; the aggregates were allowed to precipitate in static solution for approximately 1 h. Arsenic was analyzed in the resulting clarified solution. After dissolution of the floc, aluminum was also analyzed.

3.4. Analytical procedure

Arsenic concentrations in the samples were measured using a standard method [18] with an atomic absorption spectrometer (Perkin Elmer AAnalist 200) equipped with a manual hydride generator at 188.9 nm. The kinetics of aluminum dissolution (aluminum dose) was followed by dissolving the sludge at pH 2 and then quantifying aluminum ions by atomic absorption. The As and Al detection limit was 0.1 μg L^{-1} and 0.15 mg L^{-1}, respectively and the error for triplicate analyses was within 2%. Carbonates and hardness were analyzed according to standard methods [18]. Conductivity and pH measurements were carried out on a waterproof instrument (HANNA model HI 991300). All chemical reagents were of analytical grade. Each individual experiment was performed at least three times and the results were averaged.

4. RESULTS AND DISCUSSION

Fig. 2 shows the residual concentration of arsenic (C_{As}) in fresh groundwater after EC as a function of the mean linear flow rate (u) at 5.5, 6 and 6.5 mA cm^{-2}. The experimental and theoretical aluminum doses are also shown.

At 5.5 mA cm^{-2}, C_{As} linearly increased between 5.5 and 31 μg L^{-1} as a function of u in the interval 0.9–5.3 cm s^{-1} (Fig.2a), indicating that arsenic removal decreases as u increases. This is due to depletion of the experimental Al(III) dose from 43 to 6 mg L^{-1}. It should be noted that C_{As} satisfies the WHO limit of ≤ 10 μg L^{-1} at $u = 0.9$ cm s^{-1} and the Mexican standard of ≤ 25 μg L^{-1} at $u = 0.9$–2.6 cm s^{-1}. The pH after the electrolysis did not change with regard to the initial value (pH~8) as was expected and explained in section 2; at such pH the zeta potential of aluminum hydroxide flocs is positive [19].

This confirms that $HAsO_4^{2-}$ is probably removed by adsorption on $Al(OH)_3$ and Al_2O_3 flocs [5, 10, 15].

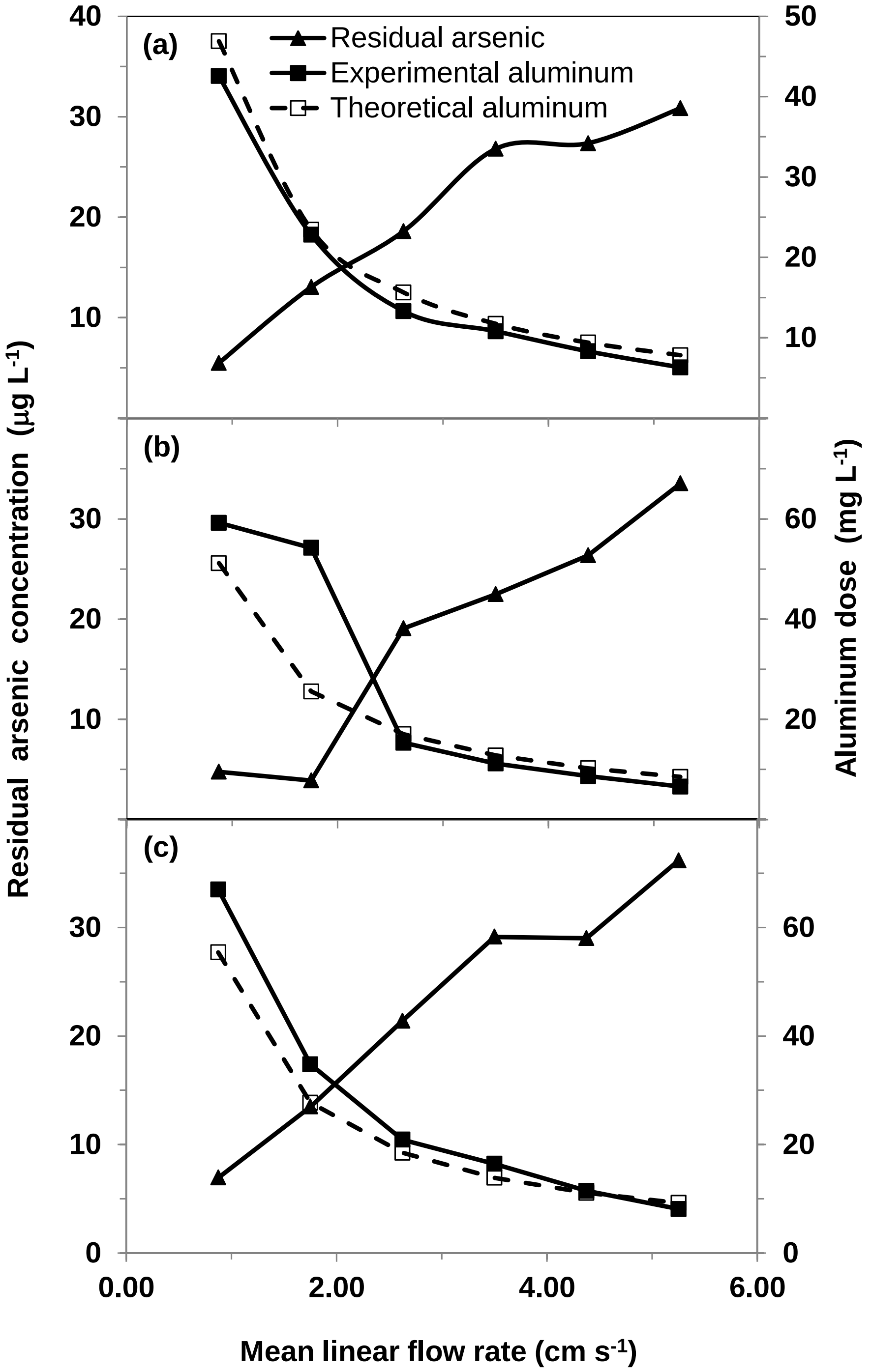

Figure 2. Influence of the mean linear flow rate on the residual arsenic concentration and aluminum dose for groundwater after addition of hypochlorite (initial parameters: arsenic 50 µg L^{-1}, carbonates 40 mg L^{-1}, hardness 80 mg L^{-1}, hypochlorite 1 mg L^{-1}, pH 8.1, conductivity 392 µS cm^{-1}) at a current density of (a) 5.5, (b) 6 and (c) 6.5 mA cm^{-2}. The anode area for 3 cell stack was 192 cm^2.

The experimental aluminum dosage, obtained by analysis of the sludge, was very close to the theoretical amount added, calculated as

$$C_{Al(III)(N)} = \left(\frac{jLMW}{nFSu}\right)(1x10^{6})(N) \tag{8}$$

where $C_{\mathrm{Al(III)}}$ is the 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 (96485 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 1×10^{6} is a conversion factor used to obtain the aluminum concentration in mg L^{-1}.

At 6 mA cm^{-2}, the behavior of C_{As} as a function of u differed for the ranges 0.9–1.8 and 1.8–5.3 cm s^{-1} (Fig. 2b). C_{As} decreased from 4.8 to 3.9 μg L^{-1} at 0.9–1.8 cm s^{-1}, and then C_{As} increased from 3.9 to 34 μg L^{-1} as a function of u in the interval 1.8–5.3 cm s^{-1}. The difference between the experimental and theoretical values of aluminum at $u = 0.91$ and 1.8 cm s^{-1} can be associated with a corrosion of aluminum in addition to its electrodissolution, afterwards at $2.6 \leq u \leq 5.3$ cm s^{-1} the experimental aluminum dose was similar to the theoretical one. The pH after electrolysis was pH~8.

At 6.5 mA cm^{-2}, C_{As} increased from 7 to 36 μg L^{-1} as a function of u in the interval 0.9–5.3 cm s^{-1} (Fig. 2c), indicating that arsenic removal also decreases as u increases at this current density. Again, the difference between the experimental and theoretical values of aluminum at $u = 0.91$ and 1.8 cm s^{-1} can be associated with a corrosion of aluminum, then at $2.6 \leq u \leq 5.3$ cm s^{-1} the experimental aluminum dose was very close to the theoretical one. The pH after EC tests was pH~8.

Table 3. Residual arsenic concentrations after hypochlorite addition satisfying the Mexican standard ($C_{\mathrm{As}} \leq 25$ μg L^{-1}), as well as the aluminum dose ($C_{\mathrm{Al(III)}}$), cell potential and electrolytic energy consumption.

Current density	u (cm s^{-1})	C_{As} (μg L^{-1})	$C_{\mathrm{Al(III)}}$ (mg L^{-1})	E_{cell} (V)	E_{cons} (kWh m^{-3})
5.5 mA cm^{-2}	0.9	5.5	43	11	5.6
	1.8	13	23.4	11.7	3
	2.6	19	13.3	10.9	1.9
6 mA cm^{-2}	0.9	4.8	59	15.9	8
	1.8	3.9	54	15.3	3.9
	2.6	19	15.3	16.6	2.8
	3.5	22.5	11	16.2	2
6.5 mA cm^{-2}	0.9	7	67	15.7	8
	1.8	13	35	17	4.3
	2.6	21	18.5	17	2.9

The highest values of experimental aluminum dose with regard to the theoretical one put on evidence the absence of oxygen evolution during the aluminum electrodissolution in the FM01-LC reactor. These findings are contrary to that obtained by our group in a previous communication in the serpentine shape filter-press reactor, where the experimental aluminium dose was lower than those theoretically obtained, at current densities between 4–6 mA cm^{-2}, due to massive oxygen evolution and anode passivation [15]. In other communication carried out by our group related to current distribution at BDD anode in the FM01-LC reactor we showed the convenience of using the FM01-LC cell as a test reactor due to its uniform current distribution at anode surface avoids oxygen evolution reaction [17].

Table 3 summarizes EC results that satisfy the Mexican arsenic standard of ≤ 25 μg L^{-1}, including the cell potential (E_{cell}) and electrolytic energy consumption, evaluated as

$$E_{\text{cons}} = \frac{E_{\text{cell}}\, I}{3.6\, B\, S\, u} \qquad (9)$$

where I is the current intensity during electrolysis (C s^{-1}), B is the electrode height (cm), S is the electrode spacing (cm) and 3.6 is a conversion factor used to obtain E_{cons} in units of kWh m^{-3}.

Table 3 reveals that EC at 5.5 mA cm^{-2} satisfied the Mexican standard for arsenic at flow rates between 0.9–2.6 cm s^{-1}, corresponding to an aluminum dose of 13.3–43 mg L^{-1}. EC at 6 mA cm^{-2} satisfied the Mexican As standard at flow rates between 0.9 and 3.5 cm s^{-1}, corresponding to aluminum doses of 11–59 mg L^{-1}. EC at 6.5 mA cm^{-2} satisfied the Mexican As standard at flow rates of 0.9–2.6 cm s^{-1}, corresponding to aluminum doses of 18.5–67 mg L^{-1}. The experimental dose of aluminum at each flow rate increased with current density. The cell potential increased with current density and it did not decrease with flow rate.

The best EC in terms of energy consumption was obtained at 5.5 mA cm^{-2} and 2.6 cm s^{-1}, with energy consumption of 1.9 kWh m^{-3} to decrease arsenic from 50 to 19 μg L^{-1}. Data for carbonates, hardness and conductivity are not presented, since these parameters remained almost constant. It should be noted that we did not measure concentrations of phosphates, silicates, sulfates and natural organic matter, 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. Finally, the residual concentration of Al^{3+} in groundwater after all EC tests, at pH=8, was under the detection limit of atomic absorption (0.15 mg L^{-1}). This is attributed to the minimum solubility of aluminum oxides in drinking water, where the residual concentration of Al^{3+} rarely exceeds 2 mg L^{-1} [6].

5. CONCLUSIONS

We systematically investigated arsenic removal from Bajío groundwater by EC using aluminum as a sacrificial anode in a FM01-LC reactor. The influence of current density and mean linear flow rate was analyzed. Arsenic removal was performed after arsenite was oxidized to arsenate by addition of hypochlorite at a concentration typically used for disinfection. Arsenate removal by EC might involve adsorption on aluminum hydroxides generated in the process. The resulting sample meets the Mexican arsenic standard of ≤ 25 μg L^{-1}.

EC investigations revealed that mean linear flow rates between 0.9 and 2.6 cm s^{-1} at current densities of 5.5–6.5 mA cm^{-2} yielded samples that met the Mexican standard for arsenic in water. Under these conditions, aluminum doses of 11–67 mg L^{-1} were suitable. The best EC in terms of energy consumption was obtained at 5.5 mA cm^{-2} and 2.6 cm s^{-1}, with energy consumption of 1.9 kWh m^{-3} to decrease arsenic from 50 to 19 μg L^{-1}.

The agreement between experimental aluminum dose and the theoretical amount added suggest the absence of oxygen evolution during the aluminum electrodissolution in the FM01-LC reactor. This last put on evidence the convenience of using the FM01–LC cell as a test reactor for EC besides its easy scale–up.

ACKNOWLEDGMENTS
We are grateful to CONACYT and CONCYTEG for financial support under the FOMIX GTO-2011-C03-162757 project. We would also like to thank Universidad de Guanajuato for financial support.

References

1. Y. Ramos, F. Ramírez, J. Martínez, D. Muñoz, I. Rodríguez and G. Carreño, *Macla,* 15 (2011) 175
2. A. H. Smith, G. Marshall, Y. Yuan, C. Ferreccio, J Liaw, O. von Ehrenstein, C. Steinmaus, M. N. Bates and S. Selvin, *Environ. Health Perspec.*, 114 (2006) 1293.
3. X. Chen, G. Chen and P.L. Yue, *Chem. Eng. Sci*., 57 (2002) 2449
4. F. Shen, X. Chen, P. Gao and G. Chen, *Chem. Eng. Sci.,* 58 (2003) 987
5. E. Mohora, S. Roncevic, B. Dalmacija, J. Agbaba, M. Watson, E. Karlovic and M. Dalmacija, *J. Hazard. Mater.*, 235-236 (2012) 257
6. M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, NACE, Houston (1974)
7. P. L. Smedley and D. G. Kinniburgh, *Appl. Geochem*., 17 (2002) 517
8. H. K. Hansen, P. Nuñez, D. Raboy, I. Schippacasse and R. Grandon, *Electrochim. Acta*, 52 (2007) 3464
9. W. Wan, T. J. Pepping, T. Banerji, S. Chaudhari and D. E. Giammar, *Water Res*., 45 (2011) 384
10. M. Kobya, U. Gebeloglu, F. Ulu, S. Oncel and E. Demirbas, *Electrochim. Acta*, 56 (2011) 5060
11. J. R. Parga, D. L. Cocke , J. L. Valenzuela, J. A. Gomes, M. Kesmez, G. Irwin, H. Moreno, W. Michael, *J. Hazard. Mater*., 124 (2005) 247
12. A. M. García-Lara and C. Montero-Ocampo, *Water Air Soil Pollut*., 205 (2010) 237
13. M. Kobya, F. Ulu, U. Gebologlu, E. Demirbas and M. S. Oncel, *Sep. Purif. Technol*., 77 (2011) 283
14. Ch.Y. Hu, S. L. Lo and W. H. Kuan, *Sep. Purif. Technol*., 126 (2014) 7
15. O. J. Flores, J. L. Nava, G. Carreño, E. Elorza and F. Martínez, *Chem Eng. Sci*., 97 (2013) 1
16. M. Griffiths, C. Ponce de Leon and F. C. Walsh, *AIChE J*., 51 (2005) 682.
17. T. Pérez, M. I. León and J. L. Nava, *J. Electroanal. Chem*., 707 (2013) 1
18. American Public Health Association/American Water Works Association/Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater*, New York (1995).
19. A. Amirtharajah, M. M. Clark and R. R. Trussell, *Mixing in Coagulation and Flocculation*. AWWARF, Denver (1991)