

Short Communication

Removal of Arsenic and Sulfates from an Abandoned Mine Drainage by Electrocoagulation. Influence of Hydrodynamic and Current Density

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This paper presents a study of arsenic and sulfate removal from an abandoned mine drainage in Guanajuato Mexico (As 24 $\mu\text{g L}^{-1}$, SO_4^{2-} 3567 mg L^{-1} , pH 7 and conductivity 3.56 mS cm^{-1}) by electrocoagulation (EC) using aluminum as the sacrificial anode in a continuous filter press reactor. The concentration of arsenic decreased from 24 $\mu\text{g L}^{-1}$ to 1.8 and 2 $\mu\text{g L}^{-1}$ at current density of 4 and 6 mA cm^{-2} , respectively, at mean linear flow velocity of 1.82 cm s^{-1} , enabling to reach the standard of the World Health Organization for arsenic in water ($C_{\text{As}} < 10 \mu\text{g L}^{-1}$). Sulfate was also partially removed during the EC from 3567 to 1686 mg L^{-1} at 4 mA cm^{-2} and 1.82 cm s^{-1} .

Keywords: Arsenic removal, Electro-coagulation, Remediation of mining water, Sulfate removal.

1. INTRODUCTION

Drinking water supply for a community depends on an adequate knowledge of the environmental conditions in the region. It is very important to identify the pollution sources, as abandoned mines, that could affect negatively water quality and risk the community health. The environment impact assessment requires determining how relevant the abandoned mines drainages are in a local hydrologic context [1].

Guanajuato City population is 110,000 habitants. The city uses as a drinking water source two water reservoirs. These reservoirs supply approximately 40% of the city demand; the difference is pumped from a granular aquifer (alluvial deposits) which is recharged by percolation through fractured rocks in the highlands. To the reservoirs got drainage of abandoned mines. There are more than 20

abandoned mines that drain year round relevant amounts of sulfate waters with a low concentration of arsenic. This problem is extreme during the dry season, when the only water in the creeks is the mine drainage water [2]. This is the reason that, the dissolved arsenic (As) has been found in groundwater and in some water reservoirs, with concentrations in the order of 0.06 mg L^{-1} , caused by arsenic mobilization in mine drainage.

Different arsenic species can exist in bodies of water such as As (III) in a species H_3AsO_3 , or in the form of As (V) whose ionic form in solution is $(\text{H}_2\text{AsO}_4^-)$. It is important to mention that the second species is more susceptible to removal by physico-chemical methods [3].

The process of As removal from large volumes of water is generally performed by chemical coagulants as aluminum or iron sulfate, using coagulation methods. However, due to low concentrations of dissolved As, this process produces a large amount of sludge, since SO_4^{2-} anions consume 50% of the coagulant [4]. For this reason, it has been decided to use EC, where aluminum or iron is dissolved electrolytically, and this enhances the coagulation process and diminishes the amount of sludge. The EC is an effective process to destabilize dispersed fine particles, anions and cations contained in water [5, 6]. Clots of metallic hydroxides are formed and adsorb dissolved species [7].

There are literature reports on EC removal of As using Al electrodes from synthetically prepared water [8, 9] and groundwater [3,10] containing high arsenic concentrations. The result differ because a great number of species that are present in water interfere with arsenic removal, besides reactor operating parameters such as current density, flow rate and geometry. It is important to mention that in the literature As and sulfate removal from abandoned mine drainage by electrocoagulation (EC) are rather scarce.

The goal of this paper is the arsenic and sulfate removal from an abandoned mine drainage in Guanajuato, Mexico, using an EC reactor equipped with aluminum as sacrificed anodes. The influence of hydrodynamics and current density on EC is also discussed.

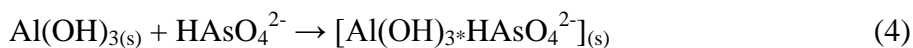
2. ELECTROCHEMICAL PROCESS

EC consists in situ generation of coagulants by electro-dissolution of aluminum electrodes. 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 [3, 9, 11]. The main electrode and chemical reactions in neutral solution ($\text{pH} \sim 7$) are shown below.

At the anode, the electro dissolution of aluminum generates aluminum ions first (Al^{3+}); afterwards, the aluminum ions are transformed to aluminum hydroxides ($\text{Al}(\text{OH})_{3(s)}$) and aluminum oxides ($\text{Al}_2\text{O}_{3(s)}$) in the bulk:



The oxidation state of As in aerated water is As(V). At neutral pH (~7) the predominating species of As(V) present a net negative charge, HAsO_4^{2-} [12]. The $\text{Al}(\text{OH})_{3(s)}$ and $\text{Al}_2\text{O}_{3(s)}$ flocs are believed to adsorb HAsO_4^{2-} [3, 9, 11]:

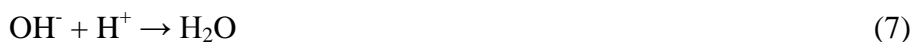


The HAsO_4^{2-} adsorption on $\text{Al}(\text{OH})_{3(s)}$ and $\text{Al}_2\text{O}_{3(s)}$ occurs owing to aluminum flocs at neutral pH has a positive zeta potential favoring the adsorption of arsenates. A similar process might occur with other anions contained in the solution, as is the case of sulfates. Zeta potential analysis may support the aforementioned, although this was beyond of the scope of this paper, but this should serve as a starting point of future research.

At the aluminum cathode, hydrogen gas is released:



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:



The major problem of the aluminum anode is its passivation, due to $\text{Al}_2\text{O}_{3(s)}$ precipitation on the anode, giving high anode and cell potential, increasing the energy consumption and cost of EC [3, 9, 11]. 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 $\text{Al}_2\text{O}_{3(s)}$ by periodic current reversal [11], which allows an even consumption of aluminum electrodes during the process.

3. EXPERIMENTAL

3.1 Water sample

A water sample of 500 liters was taken from an abandoned mine drainage in Guanajuato Mexico ($\text{As } 24 \mu\text{g L}^{-1}$, $\text{SO}_4^{2-} 3567 \text{ mg L}^{-1}$, pH 8.5 and conductivity 3.56 mS cm^{-1}).

3.2 Electro-coagulation reactor

Table 1. Dimensions of the electrocoagulation reactor.

Reactor volume ($V_r=B \times S \times L$) / cm^3	88.9
Weight (B) / cm	3.05
Channel length (L) / cm	8.1
Chanel width (S) / cm	0.6
Total length in 6 channels ($L_T=L \times N$) / cm	48.6
Number of channels (N)	6
Anode area (in each channel) in contact with solution / cm^2	24.7
Cathode area (in each channel) in contact with solution / cm^2	24.7
Cross sectional area ($A_T=B \times S$) / cm^2	1.8

For the electrolysis study an electrocoagulation reactor serpentine type was used at laboratory scale, whose scheme is shown in Fig. 1.

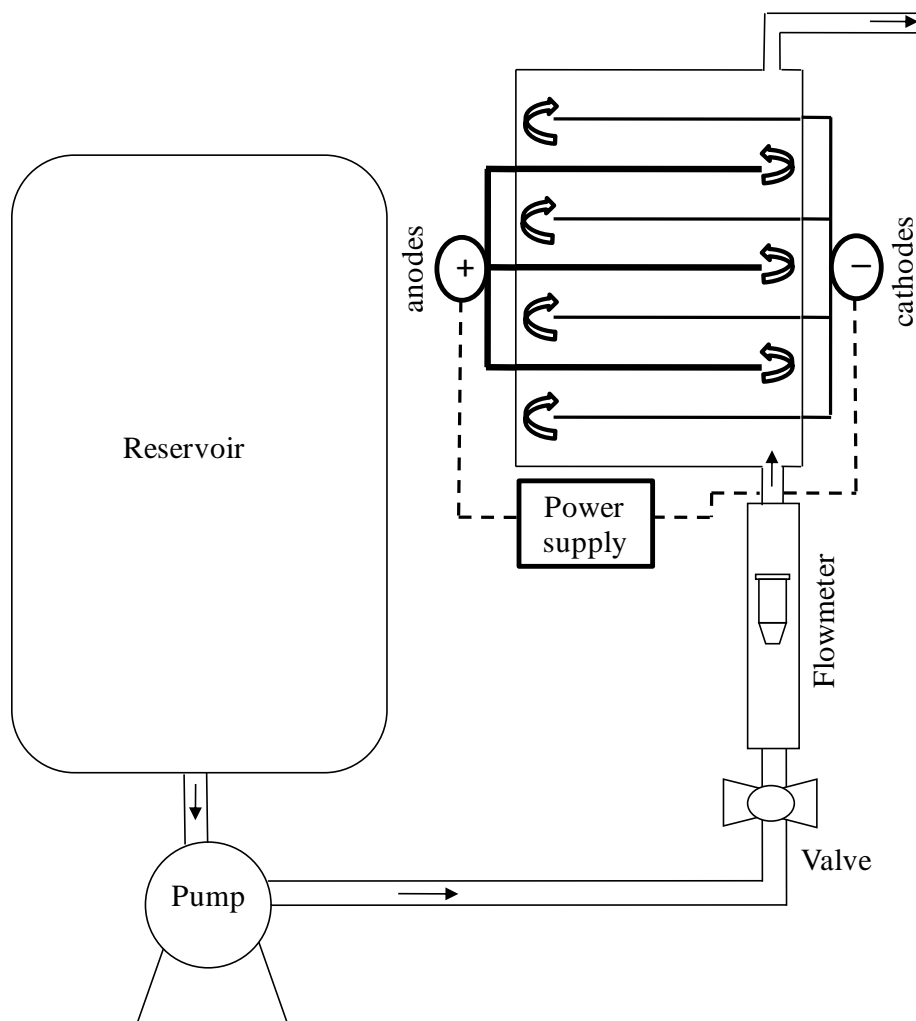


Figure 1. Electrical and flow circuit for the EC process in a filter press reactor

The dimensions of the electrocoagulation reactor are given in Table 1. The system consists of a continuous pre-pilot scale filter press reactor, where the coagulant is produced; consecutively the resulting solution (which is a mixture of water and coagulant) is passed to a test jar to induce the flocculation, with the corresponding adsorption of arsenic on aluminum flocs. Then, the arsenic adsorbed on the aluminum flocs is precipitated, and the clarified solution is analyzed [3].

The reactor was switched in monopole configuration. Three aluminum electrodes ($3.05 \text{ cm} \times 8.10 \text{ cm} \times 0.30 \text{ cm}$) were used as anodes and four similar electrodes were used as cathodes. The electrodes were spaced at 0.60 cm using propylene separators. The serpentine array induces fluid turbulence, enhancing mass transport of the coagulant from the anode to the bulk and avoiding both alumina precipitation and anode passivation. 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 $0\text{--}1 \text{ L min}^{-1}$. The PVC pipes connecting the reservoir to the pump were 0.3 inch 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 measured using the power supply. The aluminum electrode potential was measured as the difference between aluminum and a saturated mercurous sulphate 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.

3.3 Methodology

Trial tests with the water sample at pH of 8.5 were conducted. With these conditions during the EC process, the aluminum electrodes get passive; furthermore, the processes had to be stopped in different occasions to clean the electrodes. In order to avoid the passivation of the aluminum electrodes, the pH of the original sample was adjusted to a value of 7.0, adding HCl at 1.5 %. With this pH all the experiments presented in this work were performed. The pH adjustment let us continue the operation of the reactor and allow getting reproducible results.

The electrocoagulation studies were carried out in different hydrodynamic conditions with a mean linear flow rate ranged between $1.82 \leq u \leq 9.11 \text{ cm s}^{-1}$ at two current densities of 4 and 6 mA cm^{-2} .

Water samples at each electrolysis were taken from the Jar tests equipment. A Jar Test was applied to each sample of water of the effluent, without adding any coagulant. The flocculation in the Jar tests was performed at 100 rpm during 15 minutes. After the Jar test, the water rest for 30 minutes to precipitate the flocs and from the clarified solutions arsenic and sulfates concentrations were analyzed.

3.4 Analytical procedure

Based on the standard method suggested in [13], an atomic absorption (AA) spectrometer (Perkin Elmer AAnalyst 200), equipped with a manual hydride generator at 188.9 nm wavelength was

employed to determine the arsenic concentrations in the samples. The detection limit for this study was $0.1 \mu\text{g L}^{-1}$ of arsenic and analysis of the triplicates was within 2% errors. Sulfates were determined by UV spectroscopy [13]. The kinetics of aluminum dissolution was followed by dissolving the sludge at pH 2; then, aluminum ions were quantified by AA. Conductivity and pH measurements were carried out on a water proof instrument (HANNA model HI 991300). All chemical reagents were of analytical grade. Each individual experiment was performed at least three times, and then the results were averaged.

4. ANALYSIS OF RESULTS AND DISCUSSION

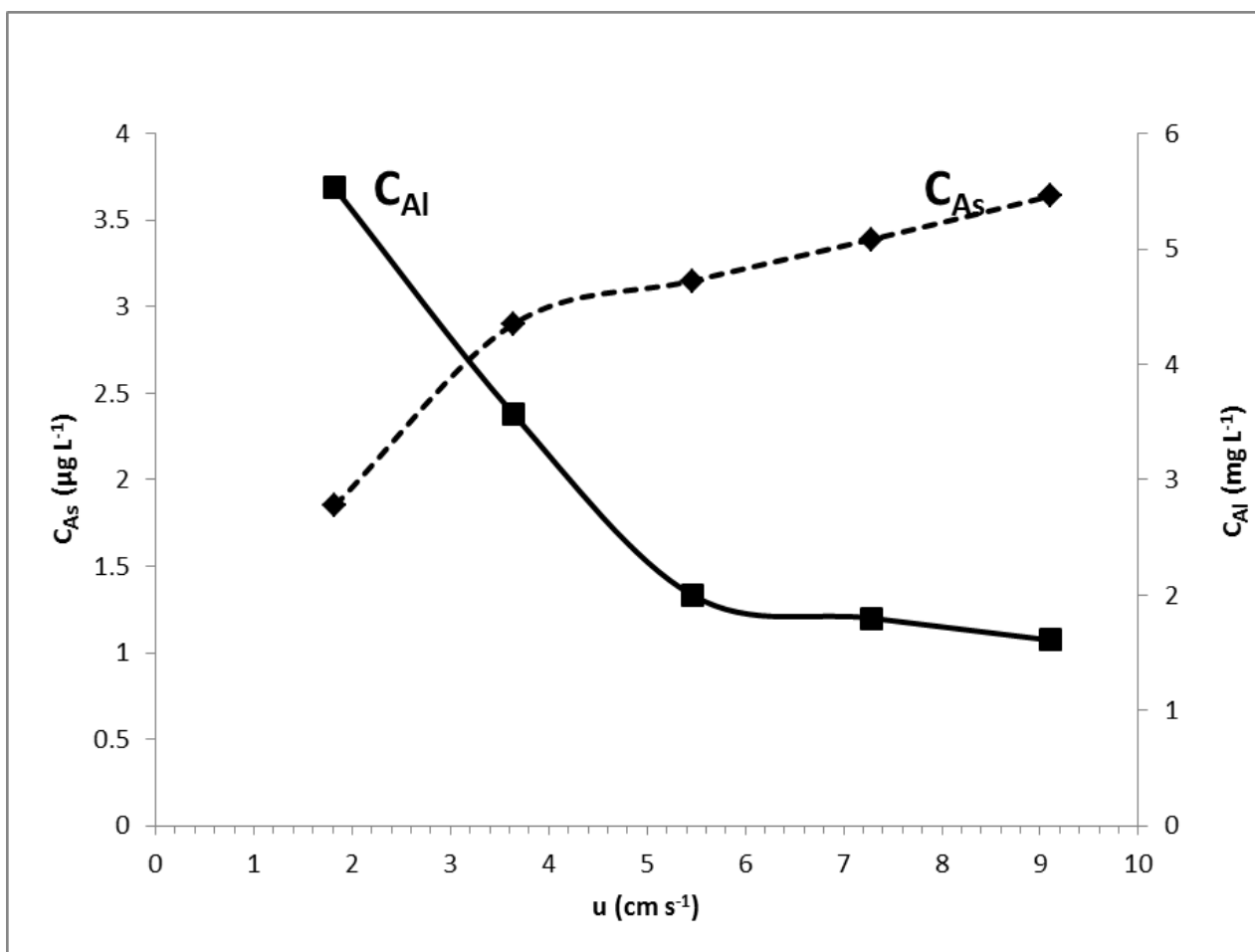


Figure 2. Influence of the mean linear flow rate on the residual arsenic concentration and aluminum dose for water from an abandoned mine drainage (initial parameters: As $24 \mu\text{g L}^{-1}$, SO_4^{2-} 3567 mg L^{-1} , pH 7 and conductivity 3.56 mS cm^{-1}) at current density of 4 mA cm^{-2} .

Figure 2 shows the residual concentration of arsenic (C_{As}) after the EC process as a function of the mean linear flow velocity at constant current density of 4 mA cm^{-2} . C_{As} increases linearly between $1.8 \leq C_{As} \leq 2.9 \mu\text{g L}^{-1}$ at $1.82 \leq u \leq 3.64 \text{ cm s}^{-1}$, due to the depletion of experimental aluminum dose ($C_{Al(III)}$), from 5.53 to 3.57 mg L^{-1} . At $u > 3.64 \text{ cm s}^{-1}$ C_{As} increases linearly between $3.2 \leq C_{As} \leq 3.6 \mu\text{g L}^{-1}$ at $5.46 \leq u \leq 9.11 \text{ cm s}^{-1}$, because of the depletion of $C_{Al(III)}$ from 2 to 1.61 mg L^{-1} . The depletion of

arsenic after EC indicates that As(V) is the predominant specie in the mine drainage and (HAsO_4^{2-}) is probably removed by adsorption on $\text{Al}(\text{OH})_{3(s)}$ and $\text{Al}_2\text{O}_{3(s)}$ flocs [3, 9, 11].

Figure 3 shows the C_{As} after EC at 6 mA cm^{-2} . From the analysis of this Figure we observed four trends for C_{As} , the first one is comprised within $1.82 \leq u \leq 3.64 \text{ cm s}^{-1}$, the second corresponds to $3.64 < u \leq 5.46 \text{ cm s}^{-1}$, the third corresponds to $5.46 < u \leq 7.29 \text{ cm s}^{-1}$, and the final one at $7.29 < u \leq 9.11 \text{ cm s}^{-1}$. In the first section C_{As} remained constant at $2 \mu\text{g L}^{-1}$.

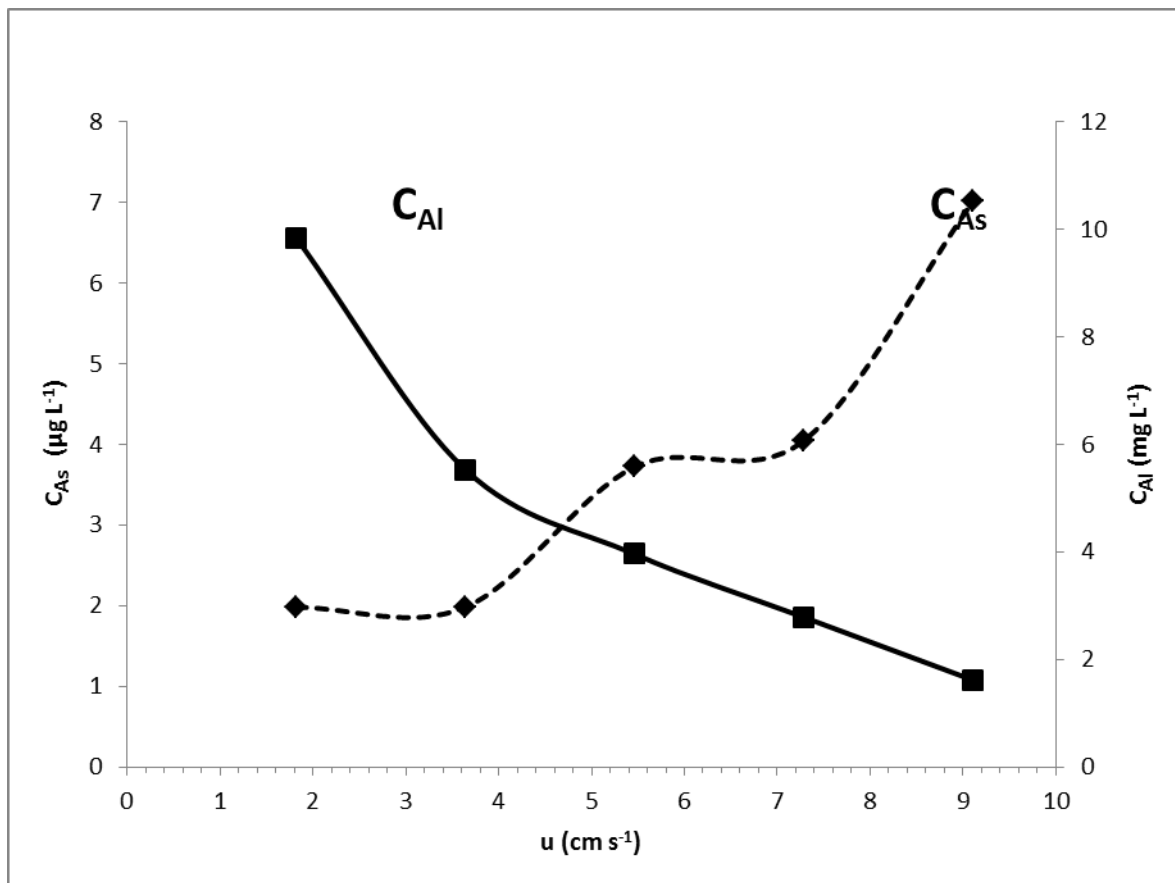


Figure 3. Influence of the mean linear flow rate on the residual arsenic concentration and aluminum dose for water from an abandoned mine drainage (initial parameters: As $24 \mu\text{g L}^{-1}$, SO_4^{2-} 3567 mg L^{-1} , pH 7 and conductivity 3.56 mS cm^{-1}) at current density of 6 mA cm^{-2} .

The increase in C_{As} in the second section from 2 to $3.7 \mu\text{g L}^{-1}$ was significant. In the third section, the increase in C_{As} from 3.7 to $4 \mu\text{g L}^{-1}$ was not significant. Finally in the fourth section, the increase in C_{As} from 4 to $7 \mu\text{g L}^{-1}$ was the most noteworthy. Arsenic removal by EC might involve adsorption on aluminum hydroxides generated in the processes [3, 9, 11]. EC at current densities higher than 6 mA cm^{-2} , not shown herein, did not improve arsenic removal any further, owing to generation of electrolytic gases, which coincides to that previously reported by our group [3, 10].

Table 2 shows the experimental results of aluminum doses, sulfate residual concentration, sulfate percentage removal, also arsenic residual concentration and electrolytic energy consumption. The sulfate percentage removal decrease with current density contrary to that expected. In addition,

sulfate percentage removal decrease with mean linear flow rate. The fact that sulfate removal decreases with current density, may be due to adsorption competition between SO_4^{2-} and $HAsO_4^{2-}$ on $Al(OH)_3(s)$ and $Al_2O_3(s)$ flocs, resulting $HAsO_4^{2-}$ kinetically favored. It is important to highlight that sulfate residual concentration did not meet the WHO standard ($C_{SO_4^{2-}} < 250 \text{ mg L}^{-1}$). The maximum percentage of sulfate removal was obtained at 4 mA cm^{-2} and u of 1.82 cm s^{-1} . The complete removal of sulfates in the presence of arsenic demands the application of other physicochemical technology, which was beyond of the scope of this paper.

Table 2. Residual arsenic and sulfate concentrations as well as the aluminum dose and electrolytic energy consumption. Initial parameters: As $24 \text{ } \mu\text{g L}^{-1}$, SO_4^{2-} 3567 mg L^{-1} , pH 7 and conductivity 3.56 mS cm^{-1} .

$u \text{ (cm s}^{-1}\text{)}$	$C_{As} \text{ (}\mu\text{g L}^{-1}\text{)}$	$C_{SO_4^{2-}} \text{ (mg L}^{-1}\text{)}$	% of SO_4^{2-} removal	$C_{Al(III)} \text{ (mg L}^{-1}\text{)}$	$E_{cons} \text{ (kWhm}^{-3}\text{)}$
4 mA cm^{-2}					
1.82	1.8	1685.6	52.74	5.53	0.49
3.64	2.9	2201.6	38.27	3.57	0.22
5.46	3.2	2464.8	30.89	2.00	0.14
7.29	3.4	2479.2	30.49	1.80	0.10
9.11	3.6	2830.4	20.65	1.61	0.08
6 mA cm^{-2}					
1.82	2.0	2562.4	28.16	9.84	1.92
3.64	2.0	2752.8	22.82	5.53	0.62
5.46	3.7	2034.4	42.96	3.96	0.34
7.29	4.0	2389.6	33.00	2.78	0.23
9.11	7.0	2838.4	20.42	1.61	0.17

Table 2 also shows the energy consumption of electrolysis (E_{cons}), evaluated by means of Equation 8. From the analysis of this Table we observed that E_{cons} increases with current density and drops with hydrodynamic, which is in agreement to that previously reported [3, 10], giving values comprised between $1.92 \leq E_{cons} \leq 0.08 \text{ KWh m}^{-3}$.

$$E_{cons} = \frac{E_{cell} I}{3.6BSu} \tag{8}$$

where I is the current intensity during electrolysis ($C \text{ s}^{-1}$), B is the channel weight (cm), S is the channel width (cm) and the value 3.6 is a conversion factor that allows to obtain E_{cons} in units of kWh m^{-3} .

The best arsenic removal in terms of energy consumption was obtained at 4 mA cm^{-2} and u of 9.11 cm s^{-1} , with 0.08 kWh m^{-3} to decrease arsenic from 24 to $3.6 \text{ } \mu\text{g L}^{-1}$.

5. CONCLUSIONS

We investigated arsenic and sulfates removal from an abandoned mine drainage in Guanajuato (As $24 \text{ } \mu\text{g L}^{-1}$, SO_4^{2-} 3567 mg L^{-1} , pH 7 and conductivity 3.56 mS cm^{-1}) by EC using aluminum as a sacrificial anode in an electrocoagulation reactor serpentine type. The influence of current density, mean linear flow rate was analyzed.

The concentration of arsenic decreased from $24 \text{ } \mu\text{g L}^{-1}$ to 1.8 and $2 \text{ } \mu\text{g L}^{-1}$ at current density of 4 and 6 mA cm^{-2} , respectively, at mean linear flow velocity of 1.82 cm s^{-1} , enabling to reach the standard of the World Health Organization for arsenic in water ($C_{As} < 10 \text{ } \mu\text{g L}^{-1}$). Sulfate was also partially removed during the EC from 3567 to 1686 mg L^{-1} at 4 mA cm^{-2} and 1.82 cm s^{-1} . An increase in the current density (higher than 6 mA cm^{-2}) did not improve the process of EC any further, owing to generation of electrolytic gases.

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