Short Communication

Sulfate Ions Removal from an Aqueous Solution Modeled on an Abandoned Mine by Electrocoagulation Process with Recirculation

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This paper shows the feasibility of sulfate ions removal by electrocoagulation (EC) with recirculation, which includes flocculation and clarification stages. The electrocoagulation stage uses aluminum as a sacrificial anode in a continuous filter-press reactor. Sulfate removal from synthetic water with chemistry modeled on an abandoned mine (3500 mg L^{-1} SO_4^{2-}, in 1.5 mg L^{-1} $NaClO$ at pH = 6.77 and conductivity 6.56 mS cm^{-1}) was tested. This solution resembles water from abandoned mines in Guanajuato City, Mexico. We analyzed the influence of current density (j) and linear flow velocity in the electrocoagulation reactor (u_r) on the sulfate removal efficiency. The EC tests were carried out at $0.91 \leq u_r \leq 3.64$ cm s^{-1} and $4 \leq j \leq 6$ mA cm^{-2}. The first configuration (single EC process) did not meet the Mexican standard limit for sulfate ($SO_4^{2-} \leq 400$ mg L^{-1}), due to the produced floc being saturated by an excess of sulfate ions. The second EC (two recycles of the EC process) satisfied the Mexican standard after the second recirculation, with a residual sulfate concentration of $SO_4^{2-} = 270$ mg L^{-1}, obtained at $u_r = 0.91$ cm s^{-1} and $j = 6$ mA cm^{-2}, giving a theoretical aluminum dose of $C_{Al^{3+}} = 149.34$ mg L^{-1}. SEM, EDA-X analyses were performed to confirm the presence of sulfate ions in the flocs. XRD patterns confirm the presence of an aluminum hydroxide (Boehmite) that causes the sulfate removal via sulfate adsorption on the aluminum flocs. The flocs (sodium sulfate-aluminum hydroxide) presented sizes below 2 μm.

1. INTRODUCTION

Water supply is an essential need for a community, so it is important to identify the pollution sources, like mining operations that could affect negatively the water quality and cause human health problems [1]. In Guanajuato City, Mexico there are more than 20 abandoned mines that drain significant quantities of sulfate ions into the water sources producing sulfate concentrations beyond the permissible level recommended by the World Health Organization (WHO) and by the Mexican authorities (NOM-127-SA1-1994), that is 500 and 400 mg L^{-1}, respectively. Concerns in relation to health effects of sulfate in water have been heightened due to reports of diarrhea may be associated with water containing high levels of sulfate.

Sulfate can derive directly from the dissolution of some acid minerals, but most sulfate is originated from the oxidative dissolution of pyrite (FeS_2) and other sulfide minerals under a complex cycle of reactions [2, 3]. The main problem related to abandoned mine water occurs when they contain sulfide minerals that can oxidize and generate acid mine water [4], which have high concentrations of sulfates. Sulfate content in water is toxic since SO_4^{2-} ions hydrolyze to form H_2SO_4 that is highly corrosive. Abandoned mine water may contain high concentrations of heavy metals, including Co, Cr, Cd, Mn, Ni, Pb, Cu and Zn [5, 6], as well as common inorganic salts such as calcium, magnesium, potassium, and sodium. One important point will be to quantify the effects of such ions and heavy metals above mentioned on sulfate removal in water.

Sulfate ions removal from water is a complicated problem due to the high solubility and stability of these anions in aqueous solutions. Physical-chemical and biological methods such as chemical precipitation [7] (partial removal, adding a neutralizing chemical, such CaO to increase water pH and to precipitate compounds as hydroxides and carbonate phases), electrocoagulation technique [1, 8-9] (generation of coagulant in situ by dissolving sacrificial anodes such as aluminum), and sulfate-reducing bacteria [10] (use of sulfate as terminal electron acceptor in anaerobic treatment, transforming the soluble anion to H$_2$S or HS$^-$) have been used to remove sulfate ions from abandoned mine water.

Electrocoagulation (EC) technique is based on the electrolytic oxidation of anode materials and the generation in-situ of coagulant. EC has been contemplated as an effective option to removing several pollutants in water treatment, including sulfate, because this technique lowers the volume of sludge and also offers some considerable advantages, such as quite compact and easy operation, no chemical additives needed, and high flow rates [11]. Aluminum and iron are commonly used as sacrificial anodes in electrocoagulation researches. Several studies that use the electrocoagulation technique to diminish contaminants concentrations in water can be found in the literature [1, 11 - 13]. However, this technique and its applications have been only performed in the lab and at the pre-pilot scale.

In a previous paper carried out by our group we described the performance of a continuous filter-press reactor fitted with aluminum electrodes for sulfate removal from abandoned mine drainage

(SO_4^{2-} 3567 mg L^{-1}, pH 7 and conductivity 3.56 mS cm^{-1}). In that paper, we conclude that sulfate ion was just partially removed during the process reaching a residual sulfate concentration of 1686 mg L^{-1}, which did not satisfy the Mexican standard for sulfate [1].

Hence, this paper deals with the electrocoagulation process (EC) with recirculation, to remove sulfate ions from synthetic water, that contains a similar sulfate concentration to that present in water from abandoned mines in Guanajuato City, Mexico (3500 mg L^{-1} SO_4^{2-} in 1.5 mg L^{-1} $NaClO$ at pH = 6.77 and conductivity 6.56 mS cm^{-1}), in order to meet a value that satisfy the International and Mexican regulations. The influence of heavy metals was not included in this paper. The entire electrocoagulation process is conformed of a continuous filter-press reactor equipped with aluminum electrodes coupled with a jar test to induce the formation of the flocs, with the subsequent decantation of the flocs. Current density and mean linear flow rate influence on the sulfate removal efficiency was analyzed.

2. SULFATE ION REMOVAL BY ELECTROCOAGULATION PROCESS.

EC involves in-situ generation of coagulants by electrodissolution of aluminum electrodes. Aluminum cations are produced at the anode and hydrogen gas emerges at the cathode, as shown in Figure 1.

The principal reactions involved are:

At the anode:

$$Al^0 \rightarrow Al^{3+} + 3e^- \tag{1}$$

At the cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2}$$

During the electrodissolution of Al, various aqueous aluminum species are generated. At pH between 6 - 7, the aluminum cations are converted to polymeric species and form $Al(OH)_3$ precipitate

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \tag{3}$$

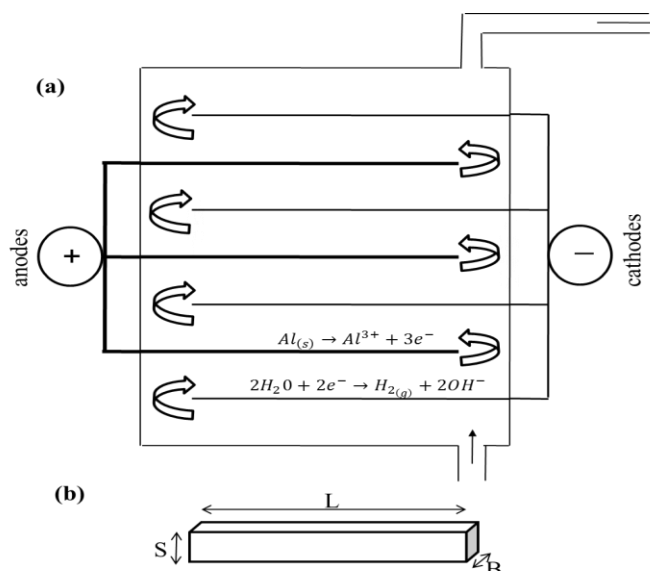These aluminum species, $Al(OH)_3$, act with the contaminants to form large size flocs [14].

Figure 1. (a) Graphic representation of the filter-press reactor. (b) 3D view of a single channel of the reactor: length *L*, width *S*, height *B*.

The sulfate removal mechanism by EC is carried through by adsorption in which aluminum hydroxides flocs entrap an SO_4^{2-} ion according to equation (4). There is no chemical interaction between these ions and metal hydroxyl compounds, but it suggests an electrical interaction [17].

$$SO_4^{2-}{}_{(aq)} + Al(OH)_{3(s)} \rightarrow Al(OH)_2 \cdot SO_4^{-}{}_{(s)} + OH^{-}{}_{(aq)} \qquad (4)$$
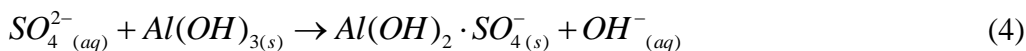
The most important problem with aluminum anodes is the passivation due to $Al(OH)_3$ and Al_2O_3 precipitation, which conducts to the high anode and cell potentials and therefore, the energy consumption increase and the cost of electrolysis tests raise [15, 16]. Passivation can be avoided using a combination of low current densities and turbulent flow conditions. This last helps to move Al^{3+} away from the anode surface to the bulk solution. In addition, the aluminum cathodes can be used to electro-dissolve the aluminum hydroxide and alumina by periodic current reversal [15] which permits even the same diminution of the aluminum electrodes during the EC process.

3. EXPERIMENTAL.

3.1. Solution

Synthetic water with chemistry that resembles water on an abandoned mine from Guanajuato City was used in the current work. The synthetic water for EC process was prepared artificially to obtain 3500 mg L^{-1} SO_4^{2-} in 1.5 mg L^{-1} $NaClO$ at pH = 6.77, giving an electrical conductivity of 6.56 mS cm^{-1}. Hypochlorite was added into the testing solution in order to prevent the Al_2O_3 precipitation

and consequently the anode passivation. Heavy metals were not included in this research. All chemical reagents were of analytical grade.

3.2. Electrocoagulation process

Figure 2 shows the design of the first experimental set-up. The scheme contains a continuous filter-press reactor where the coagulant is produced. The resulting aqueous solution (a water/coagulant blend) is passed through a jar test to provoke flocculation of aluminum flocs. These tests were performed in a 0-300 RPM Multiple Agitator (model AM-6).
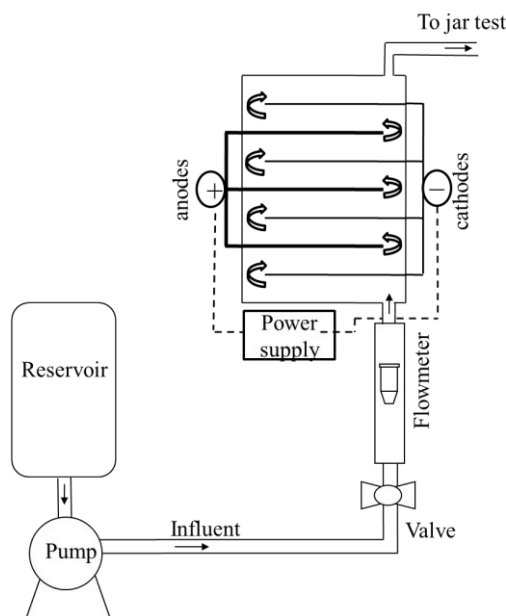

Figure 2. Diagram of the experiment, filter press cell coupled to a flocculation-clarification stage (jar test).

Table 1. Dimensions of the EC reactor.

	Reactor
Volume, V (cm^3)	88.94 ($B_T \times L \times S_T$)
Height, B (cm)	3.05
Chanel width, S (cm)	0.6
Channel length, L (cm)	8.1
Number of channels	6
Total length, L_T (cm)	48.6
Anode area in each channel (cm^2)	24.7
Cathode area in each channel (cm^2)	24.7
Cross-sectional area, A_T (cm^2)	1.83

Three electrodes (aluminum 99.7% purity) with dimensions of 3.05 cm × 8.1 cm × 0.3 cm were

employed as anodes and four similar electrodes were employed as cathodes. The electrodes were separated at 0.60 cm using propylene separators. Anodes and cathodes were connected in a monopole configuration. The EC reactor dimensions are recorded in Table 1. This electrocoagulation cell was built up in our laboratory to remove different pollutants from synthetic solutions and real water. To enhance mass transport of the coagulant from the sacrificial electrode (anode) to the bulk solution and therefore prevent both alumina precipitation and anode passivation, a serpentine arrangement in the EC reactor was used. This kind of layout induces fluid turbulence.

The EC reactor was joined to a hydraulic system consisting of a magnetically coupled, 1/10 hp pump (Little Giant model 4-MD-HC) that was used to supply electrolyte flow. A $0.1 - 1.0$ L min^{-1} White industries flowmeter model F44250 was used to measure the volumetric flow. The pipes, valves and connections were made of PVC. Pipes connecting the reservoir (water supply) to the pump were 0.3-inch diameter. A BK Precision power supply model 1621A DC was used to perform the electrolysis tests. The cell potential was directly registered by the power supply indicator.

3.3. Methodology

Figure 2 shows the experimental set-up for EC studies. EC process was carried out under different hydrodynamic conditions established by volumetric flow rates (0.1–0.4 L min^{-1}). These volumetric flow rates produce mean linear flow rates and retention times in the EC reactor of $0.91 \leq u_r \leq 3.64$ cm s^{-1}, and $13.35 \leq \tau_r \leq 53.36$ s, respectively. The resulting solution, after electrocoagulation stage, was immediately sent forth to the flocculation and clarification unit (jar test), this solution was mixed for 15 min at moderate speed (30 rpm) to form flocs. Then, these aggregates were permitted to precipitate in a motionless solution for 1 hr. Sulfates ions were examined in the clarified solution (after flocculation and clarification stage). The EC process was performed at current densities of 4, 5 and 6 mA cm^{-2} at each mean volumetric flow rates.

After the first EC process, the clarified solution was newly treated in the same EC system. The second (first recirculation) and third (second recirculation) EC processes were performed to meet the WHO standard (< 400 mg L^{-1} SO4^{2-}). The flocculation-precipitation methodology, for the first and second recirculation tests, was the same to that employed in the single EC process. Residual sulfate concentration of treated solutions and the analysis of the flocs were analyzed.

3.4. Analytical procedure

Sulfate ions concentrations in the samples were measured by the turbidimetric method according to the Active Standard ASTM D516 Standard Test Method for Sulfate Ion in Water, using a Perkin Elmer spectrophotometer Lambda 35 UV/VIS model.

Conductivity and pH measurements were carried out on a Thermo Scientific Orion Versa Star benchtop meter, with pH/ISE/mV, using a conductivity cell (Orion 013005MD), and a ROSS Ultra pH/ATC triode (Orion 8157BNUMD).

The Scanning Electron Microscopy (SEM) analysis was performed in a high-performance Analytical Scanning Electron Microscope Jeol JSM-6010PLUS/LA. This microscope is used for fast characterization and imaging of fine structures on both small and large samples.

The Energy Dispersive Analysis of X-rays (EDA-X) was carried out in a Jeol detector. This analytical technique is used for chemical characterization of a sample. The detector is integrated in the SEM microscope. A small quantity of the samples was placed on graphite tape which was supported on an aluminum sample holder. Analysis of the samples was carried out in a vacuum.

X-ray diffraction analyses (XRD) of precipitates formed during electrocoagulation technique were carried out in a Rigaku X-ray Diffractometer Ultima IV model. XRD patterns were measured using Cu Kα_1 radiation, applied at 30 kV and 30 mA of voltage and current, respectively. Each pattern was collected in the diffraction angle range of 10–100° in 2θ and scanned at 4.5° min^{-1}.

4. RESULTS AND DISCUSSION

Figure 3 shows residual sulfate concentration ($C_{SO_4^{2-}}$), and the theoretical aluminum dose, using the first configuration (single EC process). The curves are presented as a function of mean linear flow rates in the EC reactor (u_r), at different current densities of 4, 5 and 6 mA cm^{-2}, respectively. We observed that the sulfate removal increased with current density.

The theoretical aluminum dose in the EC reactor has been theoretically calculated as [13]:

$$C_{Al^{3+}} = (N)\left(\frac{j \cdot L \cdot MW}{z \cdot F \cdot S \cdot u_r}\right)\left(10^6\right) \tag{5}$$

where 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}), Z is the number of electrons exchanged (z=3), F is the Faraday constant (96485 C mol^{-1}), S is the channel width (cm), u_r is the mean linear flow rate (cm s^{-1}), N is the number of channels (N=6), and 10^6 is a conversion factor used to obtain the aluminum concentration in mg L^{-1}.

At current density of 4 mA cm^{-2}, $C_{SO_4^{2-}}$ increased linearly between 1800 and 1900 mg L^{-1}, as a function of u_r in the interval 0.91–1.82 cm s^{-1}, and at $u_r > 1.82$ cm s^{-1} $C_{SO_4^{2-}}$ it increased linearly between 2000 and 2750 mg L^{-1}, due to a diminish in the experimental aluminum dose caused by the increment of mean linear flow. It should be noted that sulfate removal efficiency just reached 48.6% (1800 mg L^{-1}), with a theoretical aluminum dose of 33.2 mg L^{-1}. An increment in the sulfate removal efficiency might be achieved by increasing the aluminum dose, which can be obtained if the current density is higher.
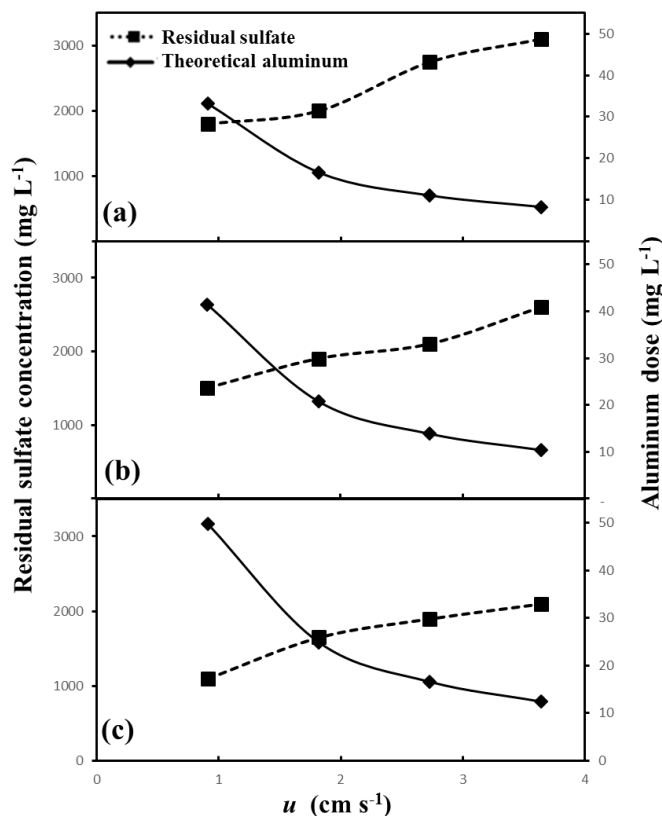
Figure 3. Effect of the mean linear flow rate on the residual sulfate concentration and the theoretical aluminum dose for synthetic water after single EC process at a current density of (a) 4, (b) 5 and (c) 6 mA cm^{-2}, (initial parameters: sulfate 3500 mg L^{-1}, hypochlorite 1.5 mg L^{-1}, pH = 6.77 and conductivity 6.56 mS cm^{-1}).

At 5 mA cm^{-2} and u_r of 0.91 cm s^{-1}, $C_{SO_4^{2-}}$ achieved a value of 1500 mg L^{-1}, then, at $u_r > 1.82$ cm s^{-1} $C_{SO_4^{2-}}$ increased linearly between 1900 and 2600 mg L^{-1}, due to a decrease in the aluminum dose. At this current density, the sulfate removal efficiency reached 57.1% (1500 mg L^{-1}), with a theoretical aluminum dose of 41.48 mg L^{-1}.

Finally, at 6 mA cm^{-2} and u_r of 0.91 cm s^{-1}, the residual sulfate concentration, $C_{SO_4^{2-}}$ reached a best value of 1100 mg L^{-1}, with a theoretical aluminum dose of 49.8 mg L^{-1}. The sulfate removal efficiency was 68.6%. From $0.91 < u_r < 1.82$ cm s^{-1} sulfate concentration increased linearly between 1100 and 1650 mg L^{-1}, then, at $u_r > 1.82$ cm s^{-1} $C_{SO_4^{2-}}$ increased linearly up to 2100 mg L^{-1}. It has previously been shown that the experimental and theoretical aluminum doses are similar in the same conditions, for each of the current density values giving current efficiencies between 89.2% and 97.0% [11].

The best sulfate removal by EC, using this first configuration, was at mean linear flow $u_r = 0.91$ cm s^{-1}, retention time $\tau_r = 53.36$ s and theoretical aluminum dose $C_{Al^{3+}} = 49.78$ mg L^{-1}, but an optimal value was not achieved according to the Mexican official standard (< 400 mg L^{-1}). It was probably due to the overload of sulfate ions onto the aluminum flocs, since the sulfate concentration was much higher than the concentration of aluminum produced by the working electrodes ($8.30 < C_{Al^{3+}} < 49.78$ mg L^{-1}). Del Ángel et al. [1] presented similar results using real abandoned mine water (SO_4^{2-} 3567

mg L^{-1}, pH 7 and conductivity 3.56 mS cm^{-1}), the sulfate ion concentration after the electrocoagulation process reached a value of 1686 mg L^{-1} (52.7%).

At higher current density (> 6 mA cm^{-2}), secondary reactions like oxygen evolution reaction (OER) may occur, equation (6) [11 - 13]:

$$H_2O \rightarrow 0.5O_2 + 2H^+ + 2e^- \qquad\qquad (6)$$

The OER enter into competition with equation (1), resulting perhaps in a lower aluminum dose, causing poor sulfate removal. Since residual sulfate concentration, after EC trials did not meet the Mexican standard limit $C_{SO_4^{2-}}$ ($\leq$ 400 mg L^{-1}), we decided to recirculate the clarified solution to the EC process making a first and second recirculation.

The clarified solution after the first EC process was recirculated inside the electrochemical reactor followed by the jar tests, under the same experimental conditions (explained in section 3.2.). EC tests were performed under hydrodynamic conditions imposed by volumetric flow rate at 0.1 L min^{-1} (u_r = 0.91 s^{-1}) and current density of 6 mA cm^{-2}. Sulfates were analyzed in the resulting clarified solution.

Table 2. Residual sulfate concentrations for the best EC test after the single EC and recirculation trials together with the theoretical aluminum dose ($C_{Al^{3+}}$), cell potential (E_{cell}) and energy consumption ($E_{s, vol.}$). 6 mA cm^{-2} and u_r of 0.91 cm s^{-1}. Initial parameters (3500 mg L^{-1} SO_4^{2-} in 1.5 mg L^{-1} $NaClO$ at pH = 6.77 and conductivity 6.56 mS cm^{-1}).

Configuration	$C_{SO_4^{2-}}$ (mg L^{-1})	$C_{Al^{3+}}$ (mg L^{-1})	E_{cell} (V)	$E_{s, vol.}$ (KWh m^{-3})
Single EC	1100	49.78	3.66	0.51
First recycle	611	99.56	5.75	0.80
Second recycle	270	149.34	6.24	0.86

Table 2 summarizes the residual sulfate concentration and the theoretical aluminum dose, for the EC test performed at 6 mA cm^{-2} and u_r of 0.91 cm s^{-1}, for the single EC and the recirculation trials. The residual sulfate concentration ($C_{SO_4^{2-}}$) after the first EC recirculation achieved a value of 611 mg L^{-1} (sulfate removal efficiency 82.6%), which did not satisfy the Mexican standard limit (< 400 mg L^{-1}). Then, the second EC recirculation reached a value of 270 mg L^{-1}, and the sulfate removal efficiency was 92.3%.; here the WHO and Mexican standard limits for sulfates were met. Further depletion of the residual sulfate concentration in the EC recirculation trial is attributed to an increase in the aluminum floc production.

Sulfate ions removal studies by electrocoagulation process are very limited specially from abandoned mine water (with high concentrations of sulfate). For example, Sharma and Chopra analyzed the effect of current density, electrocoagulation time, inter-electrode distance among others

on the removal of sulfate in municipal wastewater (SO_4^{2-} = 133 mg L^{-1}), the maximum efficiency of sulfate ion removal was approximately 80% in batch mode using two aluminum electrodes [18]. Basha and coworkers removed sulfate from copper smelting industrial effluent (SO_4^{2-} = 49.13 mg L^{-1}) by a combined method, electrodialytic separation in coupling with anion-exchange membranes followed by electrocoagulation using stainless steel as cathode and mild steel as anode reaching a sulfate removal efficiency of 72.7% [19]. While Mahvi et al. removed sulfate ions from synthetic water by electrocoagulation process using six plate aluminum electrodes attached in monopolar configuration in batch mode, (SO_4^{2-} = 350 and 700 mg L^{-1}) barely reaching 70% of sulfate removal efficiency [20]. Worthy mentioning that the EC process with recirculation, as stated in this paper, offers better sulfate removal efficiencies particularly with high initial concentration (3500 mg L^{-1} SO_4^{2-}, in 1.5 mg L^{-1} *NaClO* at pH = 6.77 and conductivity 6.56 mS cm^{-1}).

Table 2 also shows the cell potential (E_{cell}), and energy consumption by electrolysis ($E_{s,vol}$). $E_{s,vol}$ which were evaluated by means of equation (7) [13].

$$E_{s,vol} = \frac{E_{cell} \cdot I}{3.6 \cdot S \cdot B \cdot u_r} \qquad (7)$$

Where $E_{s,vol}$ is the energy consumption, I is the current intensity during electrolysis (C s^{-1}), E_{cell} is the cell potential (J C^{-1}), B is the channel height (cm), and 3.6 is a conversion factor used to obtain $E_{s,vol}$ in units of kWh m^{-3}.

Scanning Electron Microscopy (SEM) experiments were carried out to inspect the morphology and size of the flocs obtained from the EC tests. Typical SEM images of the flocs formed during the EC process obtained from single EC process [4 (a) and 4 (a′)], first [4 (b)] and second [4 (c)] recirculation, at 6 mA cm^{-2} and u_r of 0.91 cm s^{-1} are shown in Figure 4. Flocs from the first EC are composed of particle agglomerates of up to around 80 μm, Figure 4 (a). Several well-formed sodium sulfate crystals of up to 5 μm are shown in Figure 4(b). On the first recirculation, the produced flocs are composed of particle agglomerates of up to around 50 μm, Figure 4 (c). Finally, Figure 4 (d) shows that the flocs formed after the second recirculation, are particle agglomerates consisting of elements with sizes of around 2 μm.

SEM image of flocs obtained from electrolysis confirms that the growth of aluminum flocs is responsible for the increased adsorption (sulfate removal). To explain the influence of current density and mean linear flow rate on the floc size, microfilm analysis of the flocs growing during EC process can be useful. This analysis was beyond of the scope of this paper.

To analyze the elemental constituents of flocs, Energy Dispersive Analysis of X-rays (EDA-X) was performed. Table 3 recaps typical composition of the flocs for each EC and it validates the presence of O, Al, S, Na and Cl elements. This analysis shows the presence of sulfur, and it confirms that the Al flocs ensnare the sulfate ion.

EDA-X results clearly show that *adsorption process* is the major process that affects the sulfate removal efficiency, an ion exchange competition between anions (such as Cl^-) did not affect the process because of their small concentration in the synthetic solution (1.5 ppm).

Table 3. Composition of the flocs determined by EDAX.

	Single EC process	First recycle	Second Recycle
Element	Average at. %	Average at. %	Average at. %
O	57.02	67.51	54.40
Al	3.25	14.71	23.23
S	15.03	8.85	8.07
Na	24.70	8.93	12.02
Cl	0.0	1.49	2.29

XRD analysis were performed to provide information about crystalline compounds, including identification and quantification of phases. Figure 5 shows the XRD patterns of the flocs obtained from the single EC (a), first (b) and second (c) EC recirculation trials at 6 mA cm^{-2} and u_r of 0.91 cm s^{-1}. In Figure 5 (a), only peaks corresponding to sodium sulfate, file number in Crystallography Open Database (COD), 1011184, were identified.
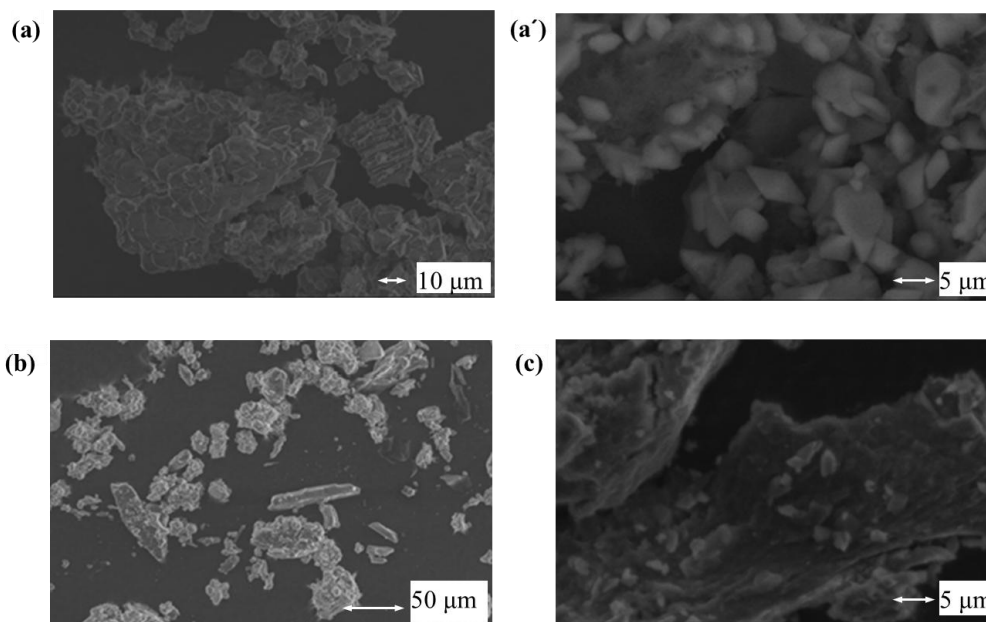

Figure 4. SEM image of flocs obtained during single EC process [(a) and (a´)], first recirculation (b) and second (c) recirculation at 6 mA cm^{-2} and u_r of 0.91 cm s^{-1}.

In Figure 5 (b) and (c), peaks corresponding to two sodium sulfates, COD files 1011184 and 1010522, were identified. They are represented as Na_2SO_4 (I) and Na_2SO_4 (II), respectively. Also, one aluminum hydroxide, Boehmite, file number 0013998 in American Mineralogist Crystal Structure Database, AMCSD, was identified. In Table 3, it can be seen that in the first EC sample Al content is 3.25 at. %, while Al content increases to 14.71 at % and to 23.23 at %, in the first and second EC

recirculation samples, respectively. This increase of aluminum is related to the recirculation of EC process. The Al content correspond to the aluminum hydroxide showed in XRD patterns in Figure 5 (b) and (c).
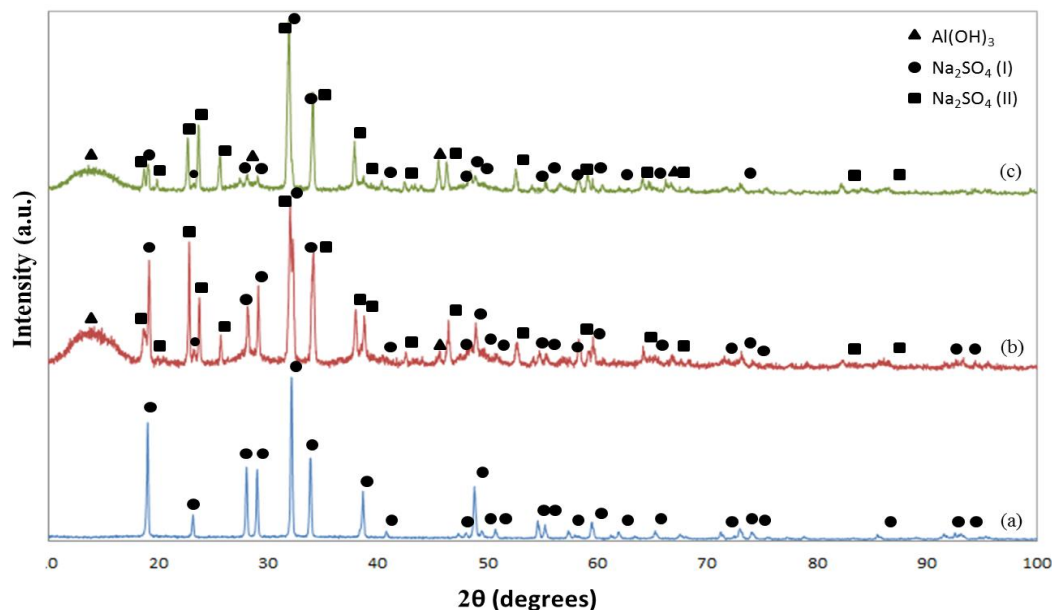

Figure 5. XRD patterns analysis of the dried flocs obtained from EC tests at 6 mA cm^{-2} and u_r of 0.91 cm s^{-1}. Single EC process (a), first (b) and second (c) recirculation.

5. CONCLUSIONS

In this study, sulfate removal using an electrocoagulation process with recirculation from synthetic water (3500 mg L^{-1} SO_4^{2-} in 1.5 mg L^{-1} *NaClO* at pH = 6.77 and conductivity 6.56 mS cm^{-1}) that resembles water from abandoned mines in Guanajuato City, Mexico has been investigated. The EC technique was carried out at a current density, j = 6 mA cm^{-2} and mean linear flow velocity, u_r = 0.91 cm s^{-1}, achieving a residual sulfate concentration of 270 mg L^{-1} (sulfate removal efficiency of 92.3%) after second recirculation. This value satisfied the WHO (< 500 mg L^{-1}) and Mexican (< 400 mg L^{-1}) standards for sulfate.

Studies have shown that sulfate removal is a bit complicated specially for higher initial concentrations and may not be a suitable single-stage process. EC technique with recirculation is an alternative to reach better sulfate ions removal efficiencies.

SEM analyses showed some well-formed sodium sulfate crystals and particle agglomerates of up to around 50 μm. EDA-X analysis confirms the presence of O, Al, S, Na, and Cl, which means that the aluminum flocs entrap the sulfate ions. XRD analysis showed peaks corresponding to sodium sulfate in single EC process. XRD analysis of the flocs after the first and second recirculation EC processes showed two sodium sulfates phases and Boehmite (aluminum hydroxide).

As far as we know, this is the first time that an EC process with recirculation has been successfully performed for sulfate removal. This experimental characterization should serve as a basis in which real water from abandoned mine would be later included.

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