Research article

Sulfate removal from acid mine water from the deepest active European mine by precipitation and various electrocoagulation configurations

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ABSTRACT

Sulfate removal from mine or process water is a key issue in the mining industry. In this paper, precipitation with lime (calcium oxide) was integrated with electrocoagulation for sulfate removal from Pyhäsalmi/Finland mine water. Sulfate precipitation with calcium oxide decreased the sulfate concentration from 13,000 mg/L to 1600 mg/L. Various current densities were applied to the pre-treated mine water with various electrodes and aluminium and iron anodes. It was found that 25 mA/cm² was the best tested current density for both anode types. At the second stage, this current density was used for different iron and aluminium anodes in various monopolar and bipolar configurations. It was found that this hybridisation is effective for sulfate removal, and that a bipolar configuration showed better results than the monopolar configuration. The best result was gained from 25 mA/cm² with a two aluminium and two stainless steel anode–cathode configuration and calcium oxide pre-treatment to reach pH 12. The removal efficiency reached 84.4% and 63.8% with aluminium anodes in bipolar and monopolar configurations, respectively. This setup was able to decrease sulfate concentrations from 13,000 mg/L to 250 mg/L, which meets mine water discharge limits. Kinetic studies showed that iron and aluminium anodes obey pseudo-second order kinetic. Finally, the energy consumption was calculated.
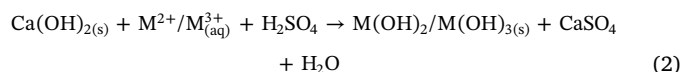
1. Introduction

Sulfate is not considered a toxic pollutant, but high concentrations result in steel and concrete corrosion as well as increasing the salinity of soil and water (Guimaraes and Leao, 2014). Depending on other parameters, 30–419 mg/L of sulfate can change the taste of water. In addition, it was reported that eating 7–8 g of sodium sulfate and magnesium sulfate could cause adult male catharsis. Sulfate concentrations of 1000–1500 mg/L can have laxative effects (World Health Organization, 2004). Restrictions for sulfate discharge are becoming tighter (Jacobs and Testa, 2014) and various regulations have been set for sulfate concentration in water (Table 1).

Sulfate concentrations in mine water range from hundreds to thousands of mg/L (Bowell, 2004; Bai et al., 2013; Tolonen et al., 2015). It is produced by (di-)sulfide oxidation, resulting from the exposure of these minerals to air and water (Stumm and Morgan, 2009). These sulfate concentrations in mine waters of working or abandoned mines are a big challenge for the mining industry (Wolkersdorfer et al., 2015), with more than 70% of mine sites in the world to be manage in

regards to sulfate concentrations (Jacobs and Testa, 2014).

Various technologies have been introduced for sulfate removal, such as gypsum, ettringite or barium sulfate precipitation (Guimaraes and Leao, 2014; Silva et al., 2012; Wolkersdorfer, 2008; Pinto et al., 2016; Johnson and Hallberg, 2005). Because of its economic aspect, chemical saturation and precipitation is the first option on an industrial scale (Guimaraes and Leao, 2014; Bowell, 2004). Lime is a very efficient, cheap and common way to remove metals and sulfate from mine water, commonly resulting in the formation of gypsum (Equations (1) and (2)) (Khorasanipour et al., 2011; Lopez et al., 2009; Fernando et al., 2018; Masindi et al., 2017; Jacobs and Testa, 2014). However, sulfate concentrations by this method can only be decreased to 1200–1800 mg/L (Guimaraes and Leao, 2014; Geldenhuys et al., 2003), due to the gypsum equilibrium (Tolonen et al., 2016).

$$Ca(OH)_{2(s)} \rightarrow Ca^{2+}_{(aq)} + 2OH^-_{(aq)} \tag{1}$$

$$Ca(OH)_{2(s)} + M^{2+}/M^{3+}_{(aq)} + H_2SO_4 \rightarrow M(OH)_2/M(OH)_{3(s)} + CaSO_4 + H_2O \tag{2}$$

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Table 1
Various regulations for sulfate concentration in water.

Organisation	concentration, mg/L	reference
World Health Organisation (WHO)	500	Guimaraes and Leao (2014)
WHO and EPA (drinking water)	250	Fernando et al. (2018)
Europe (drinking water)	250	Council of the European Union (1998)
Europe (groundwater and effluent discharge)	1000	Bowell (2004)
Environmental agencies in mining countries	250 and 500	Guimaraes and Leao (2014)
Surface water discharge – Chile	1000–2000	West et al. (2011)
Ground water discharge – Chile	250–500	West et al. (2011)
Irrigation – Chile	250	West et al. (2011)
General water use and mine water – Australia	1000	West et al. (2011); Arnold et al. (2016)
Drinking water – USA	250	West et al. (2011)
USA (mine water)	10–500	Arnold et al. (2016)
Canada (mine)	65–500	Arnold et al. (2016)
South Africa (mine)	200–400	Arnold et al. (2016)
Finland (mine regulations)	2000	Arnold et al. (2016)

In the ettringite/SAVMIN process, the solution's pH is increased to pH 12 with lime and then aluminium salts are added to form ettringite (Guimaraes and Leao, 2014; Tolonen et al., 2016; Van et al., 2014; Smit, 1999). One of the disadvantages of this process is that the final pH of the solution is very high and needs pH adjustment before discharge.

Precipitation of sulfate by barium salts is expensive and not environmentally friendly (Guimaraes and Leao, 2014; Silva et al., 2012). Other sulfate removal processes, on an industrial scale not commonly used, are sorption by various sorbents such as zeolites, coconut pith or shrimp peelings (Guimaraes and Leao, 2014). Industrial scale processes include membrane-technologies such as reverse osmosis (Guimaraes and Leao, 2014), ion exchange (Guimaraes and Leao 2014; International Network for Acid Prevention (INAP, 2003), biological treatment (Bowell, 2004) and electrocoagulation (Nariyan et al., 2017b). The different processes have advantages and disadvantages: reverse osmosis is energy-intensive, prone to scaling and fouling, has a brine disposal problem (Juby, 1992) and is best used for low sulfate concentrations below 700 mg/L. Also biological sulfate treatment is mainly used for mine water from abandoned mines (Bowell, 2004).

Electrocoagulation is a comparably simple technology in which the sacrificial anodes act as flocculating and coagulating agents. The reaction in the electrocoagulation cell (EC) is more complex than a simple chemical coagulation process (Gupta and Ali, 2013). Various reactions take place inside the EC, such as cathodic reduction, coagulation, electrophoretic movement of particles and electro flocculation by the oxygen and hydrogen produced by the electrodes and other chemical and electrochemical processes. Electrocoagulation has some merits over the other processes like producing an odourless, colourless and clear water with less sludge compared to chemical coagulation. Furthermore, it produces water with lower TDS concentrations and is easy to operate. As no chemicals are used in this process, there is no secondary pollution (Gupta and Ali, 2013; Liu et al., 2010). Electrocoagulation provides neutral pH after treatment, and the sludge is more stable and easy to dewater (Liu et al., 2010). The cost of electrocoagulation (€1.98/m^3 with a current density of 50 mA/cm^2) is less than that of chemical precipitation (€4.53/m^3) for acid mine treatment (Fernando et al., 2018). Therefore, it could be considered for acid mine water treatment as it has not previously received much attention for this purpose.

The reactions of electrocoagulation at the anode and cathode have been reported before (Equations (3)–(6)) (Liu et al., 2010):

Anodic reactions:

$$M_{(s)} \rightarrow M^{n+}_{(aq)} + ne^- \tag{3}$$

$$2H_2O_{(l)} \rightarrow ne^- \rightarrow M_{(s)} \tag{4}$$

Cathodic reactions:

$$M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)} \tag{5}$$

$$2H_2O_{(l)} + 2e^- \rightarrow 2H_{2\,(g)} + 2OH^- \tag{6}$$

Electrocoagulation configurations can be done in different forms of monopolar and bipolar setups. In monopolar configuration, each electrode is connected directly to the power source. This configuration is similar to a single cell consisting of several electrodes and interconnections. However, in the bipolar configuration, the sacrificial electrodes are placed between the pair of parallel electrodes and lack of an electrical connection. This cell configuration provides a simple set up and is easy to maintain (Liu et al., 2010) (Fig. 1 a and b).

In a previous study, it was found that electrocoagulation removes sulfate from mine water (Nariyan et al., 2017b). Yet, it could not
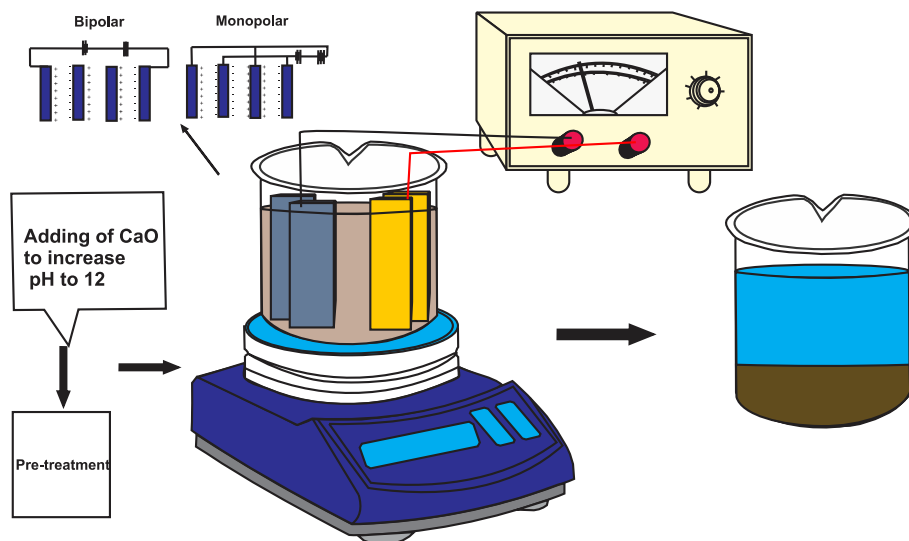
Fig. 1. Schematic diagram of the sulfate removal process with monopolar and bipolar electrocoagulation configurations (adopted from Liu et al. (2010)).

decrease the concentrations below the commonly used regulation limits for the mining industry. In addition, the lime neutralization processes in general cannot decrease the sulfate concentration to below discharge limits for the mining industry.

Sulfate removal is getting a big challenge in mine and process water, and not many publications exist for sulfate removal from mine water with electrocoagulation. However, EC-related publications focus on metal removal from acid mine water. In addition, the effectiveness of electrocoagulation by itself for removing sulfate from mine water was not satisfactory in the previous work (Nariyan et al., 2017b). In this paper, the integration of both technologies (electrocoagulation and precipitation) was tested to verify the effectiveness of this hybridisation in decreasing sulfate concentrations below the discharge limits. The synergetic effect of this hybridisation reduced the sulfate concentration, and the removal efficiency was improved considerably when compared to the previous works (Table 5) (Nariyan et al., 2017b). Precipitation of sulfate as gypsum is in most cases not sufficient enough for decreasing the sulfate concentration, due to the gypsum saturation. In this publication, a model which shows the correlation between treating capacity and mine water flow for electrocoagulation has been introduced.

2. Materials and methods

Calcium oxide and hydrochloric acid were bought from Sigma-Aldrich in high purity. Iron and aluminium as sacrificial electrodes were chosen as anode materials. Calcium salt was applied as pre-treatment in order to increase the calcium concentration in the mine water. Stainless steel was chosen as the cathode material because it does not passivate at high calcium concentration in water (Nariyan et al., 2017b).

The electrode size was 70×50 mm and the experiments were done in different monopolar and bipolar electrode configurations. Hydrochloric acid (0.2 M) and a sand filter were used prior to each experiment for washing and rubbing the electrodes. The electrode distance was set to 0.5 cm to decrease ohmic resistance. A GW INSTEK psp-405 current supply with a current range of 0–5 A and a voltage range of 0–40 V was used for the experiments, and a magnetic stirrer at a speed of 200 rpm (rotations per minute) applied. E_h, corrected to the standard hydrogen electrode (SHE), and pH were measured with Hach intelliCAL™ MTC101 and pHC101 probes attached to a Hach HQ40d (Nariyan et al., 2017b).

The water was collected from the +500 m level at the Pyhäsalmi polymetallic mine, Oulu Province, Finland. This mine has a flow rate of approximately 1 million m³/year and they use lime precipitation for sulfate removal (Kauppila et al., 2013). The collected mine water was stored in a freezer at a temperature of −20 °C. A chemical analysis of this mine water was reported in a previous study, and it can be described as acid mine drainage, with a sulfate concentration of 13,000 mg/L and a pH of 2.86 (Table 2) (Nariyan et al., 2017b).

The volume of the mine water for the electrocoagulation experiments was 500 mL and the current density was set to a predefined constant value during the experiments. Sulfate concentrations of each sample were measured by discrete analyser (Ramboll – now Eurofins – Analytics method RA2087) (Nariyan et al., 2017b) and the sulfate

Table 2
Physio-chemical analysis of the Pyhäsalmi mine, Finland; sampling date 2015-01-12 (Nariyan et al., 2017b).

Parameter	Unit	Value	Moles
pH	–	2.68	2.09×10^{-3}
SO_4^{2-}	mgL^{-1}	13000	1.377×10^{-1}
Electrical conductivity κ (field)	µS cm^{-1}	10657	–
Redox (field, corrected to SHE)	mV	467	–
Temperature (field)	°C	16.7	–
Colour (laboratory)	–	Yellow-brownish	–

removal efficiency was calculated using the following equation:

$$\text{Removal efficiency, } \% = \frac{C_0 - C_t}{C_0} \times 100 \tag{7}$$

2.1. Experimental

Calcium oxide (CaO) was chosen to increase the mine water's pH to 12 as a pre-treatment procedure, as the previous experiments showed that electrocoagulation alone was unable to remove high amounts of sulfate. This caused metal removal from the mine water and lowered the sulfate concentrations from 13,000 mg/L to 1600 mg/L. Electrocoagulation was then chosen as post-treatment for sulfate removal in monopolar and bipolar configuration with two anodes and two cathodes (Fig. 1).

First, the monopolar configuration with one aluminium/iron and one stainless steel electrode were chosen to find the optimum current density. In the second step, various configurations of monopolar and bipolar setups with two anodes and two cathodes were evaluated with a longer reaction time to identify the maximum sulfate removal efficiency to achieve the mine water discharge limits.

3. Results and discussion

3.1. Current density for iron/aluminium anodes

To find the best current density after pre-treatment with calcium oxide (pH 12), various current densities in the range 10–70 mA/cm² were applied to both one iron/aluminium and one stainless steel cathode and up to 120 min of reaction time (Fig. 2 and Fig. 3). The iron anode/stainless steel cathode configuration did not show a substantial increase of the removal efficiency ($\approx 30\%$) above a current density of 25 mA/cm² and, therefore, this current density was chosen for further experiments with this electrode configuration.

In the one aluminium anode/stainless steel cathode configuration, 25 mA/cm² current density showed the highest removal efficiency (52.86%). This higher removal efficiency at 25 mA/cm² current density compared to the lower removal efficiencies at higher current densities might have resulted from passivation of the anode by the potential build-up of an oxide layer on the aluminium anode. In consequence, this would inhibit aluminium dissolution at the anode.

Based on these results, the best current density within 120 min of reaction time is 25 mA/cm² for both iron and aluminium anodes (Figs. 2 and 3). In a previous study without pre-treatment, it was found that the best current density was higher than 25 mA/cm² (Nariyan
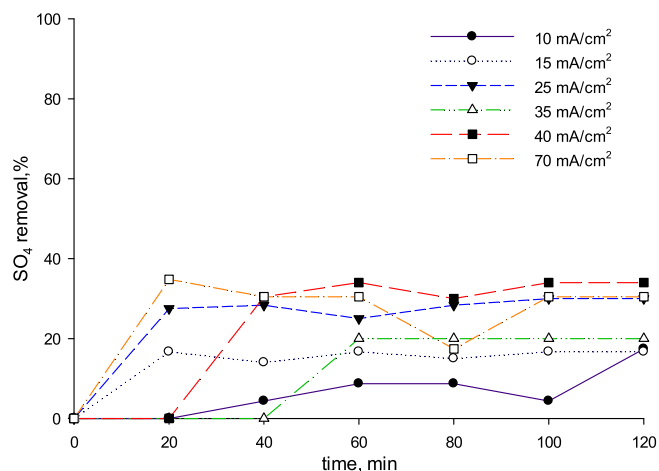

Fig. 2. Effect of different current densities on the removal of sulfate with one iron and one stainless steel electrode after calcium oxide pre-treatment (pH 12).
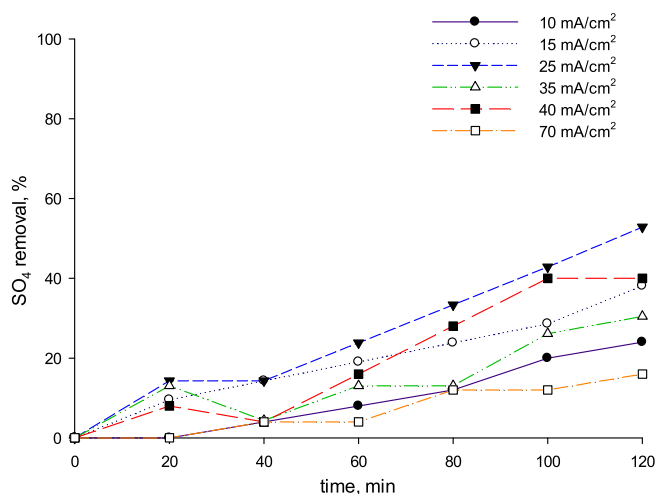
Fig. 3. Effect of different current densities on the removal of sulfate with one aluminium and one stainless steel electrode after calcium oxide pre-treatment (pH 12).

et al., 2017b). Therefore, pre-treatment could decrease the energy consumption of electrocoagulation for sulfate removal. In the next experimental step, 25 mA/cm² current density and the monopolar and bipolar configurations of two anodes and two cathodes were used for evaluating the effect of the electrode configuration on the sulfate removal efficiency.

3.2. Effect of monopolar and bipolar configurations with iron electrodes

In the second step, the selected current densities from the previous experiments were used for two iron anodes and two stainless steel cathodes in different monopolar and bipolar electrode configurations.

The sulfate removal efficiency after 240 min reaction time reached 25% (1200 mg/L) and 81.25% (300 mg/L) in monopolar and bipolar configurations, respectively (Fig. 4a and b). This shows that the electrode configuration has a substantial effect on the sulfate removal efficiency with the bipolar configuration being more effective than the monopolar configuration.

E_h and pH were measured during all experiments to identify potential relations of the removal efficiency and these parameters (Fig. 5 a and b). As can be seen from the results, E_h and pH remained almost constant in the various electrode configurations. None of the observed E_h or pH changes during the various configurations or reaction times can be considered statistically significant, though the pH slightly

increased in the bipolar and decreased in the monopolar configuration.

3.3. Effect of monopolar and bipolar configurations with aluminium electrodes

Two aluminium anodes and two stainless steel cathodes in various monopolar and bipolar configurations were used to evaluate their effect on the sulfate removal. As before, all experiments were conducted at 25 m/cm² current density.

As can be seen, the bipolar configuration was more efficient in sulfate removal. Removal efficiencies reached 63.75% (580 mg/L) and 84.38% (250 mg/L) in monopolar and bipolar configurations, respectively (Fig. 6 a, b). Consequently, a bipolar configuration of two aluminium and two stainless steel electrodes could be effective in lowering mine water sulfate concentrations to discharge limits.

pH decreased from 11.3 to 6.8 in the monopolar and 11.3 to 6.6 in the bipolar configuration (Fig. 7a). This shows that the aluminium anode is slightly better than the iron anode, but both provide a circum-neutral mine water pH, which usually does not need further pH-adjustment. After roughly 120 min of reaction time, the pH stays constant, such as the sulfate concentrations, which is an indication for a so far unidentified equilibrium or buffer mechanism.

Other than the iron electrodes, the aluminium electrodes showed changes in E_h values (Fig. 7b). They fluctuated from 0.48 to 0.37 V in the monopolar configurations, while it was erratic from 0.48 to 0.44 V in the bipolar configurations. In all aluminium anode configurations, the E_h decreased slightly towards the end of the experiments.

3.4. Kinetics

Kinetic models are used to investigate the potential sulfate removal mechanisms encountered during the electrocoagulation process after post-treatment with calcium oxide and in bipolar and monopolar electrode configurations.

q_t was calculated using Equation (8), in which C_0 is the initial concentration of sulfate after pre-treatment (1600 mg/L), C_t the concentration of sulfate after the sulfate removal electrocoagulation process at time t (min), V the volume of the bulk solution in litres (0.5 L) and m the mass of adsorbent (g) (Tan and Hameed, 2017). The adsorbent's mass was calculated from Faraday's law (Equation (9)), in which I is the current (A), t the time (s), M_W the molecular weight of the iron or aluminium electrode (g/mol), n the oxidation number and F Faraday's constant 96485.33289 C/mol (Al-Shannag et al., 2015; Vepsäläinen et al., 2012; Liu et al., 2010). It is worth noting that the calculated mass of the dissolved electrode was multiplied by two,
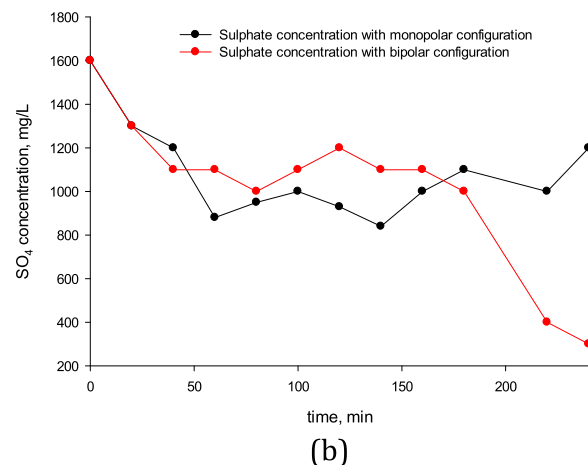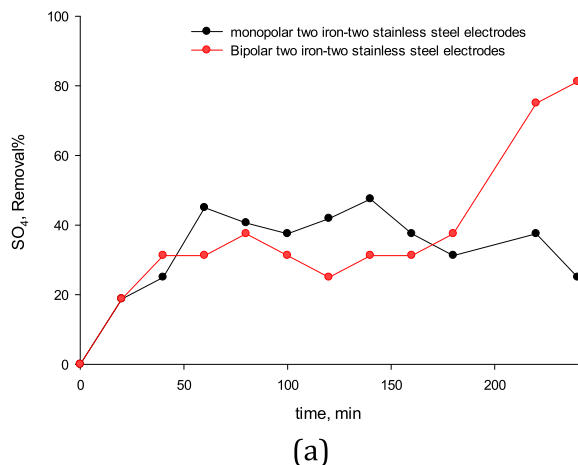

Fig. 4. Sulfate removal efficiency in monopolar and bipolar configurations. (a) Time dependent sulfate removal percentage (b) Time dependent sulfate concentration change (two iron and two stainless steel electrodes).
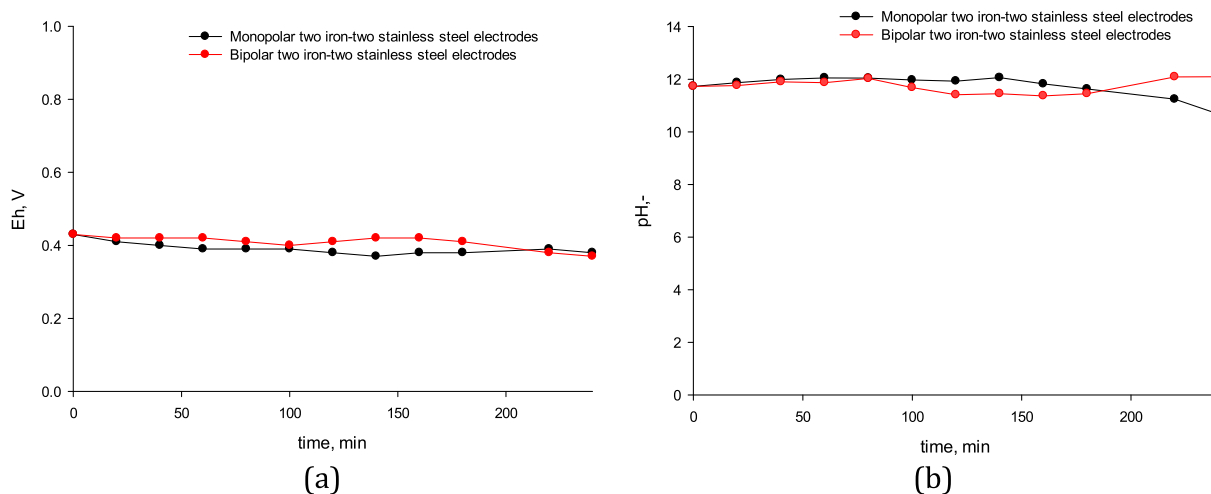
(a)

(b)

Fig. 5. E_h (a) and pH (b) changes over time in monopolar and bipolar configurations (two iron and two stainless steel electrodes).
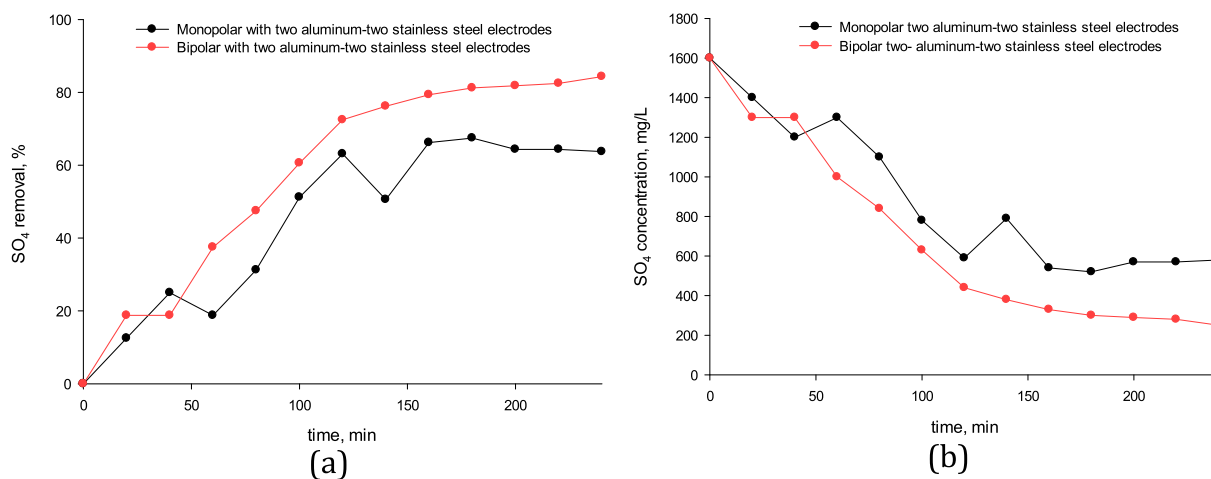

(a)

(b)

Fig. 6. Sulfate removal efficiency in monopolar and bipolar configurations. (a) sulfate removal percentage within time, and (b) sulfate concentration change within time (two aluminium and two stainless steel electrodes).
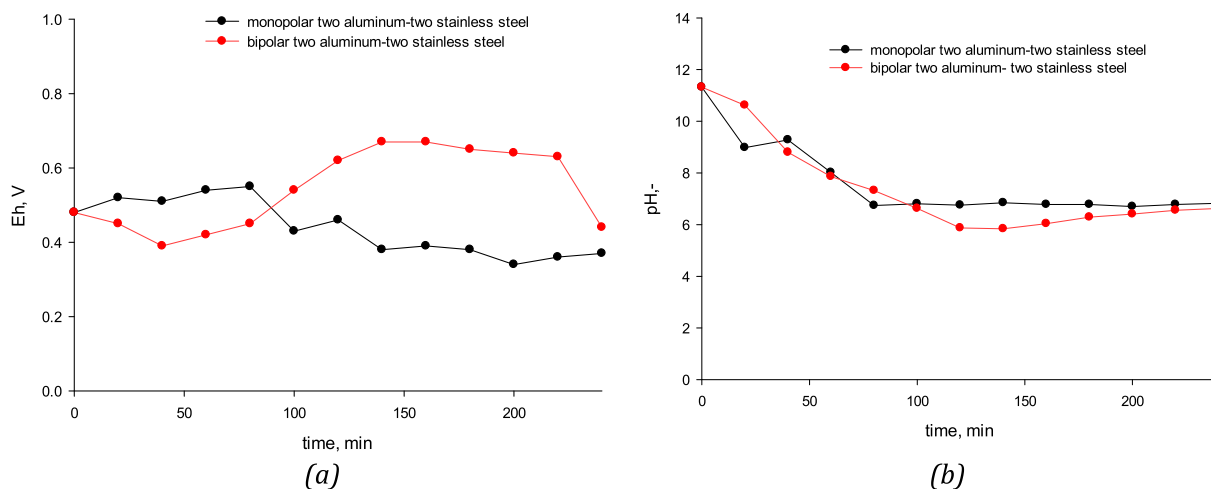

(a)

(b)

Fig. 7. E_h (a) and pH (b) changes during time in monopolar and bipolar configurations (two aluminium and two stainless steel electrodes).

because two anodes in both configurations were applied.

$$q_t = \frac{(C_0 - C_t)V}{m}$$ (8)

$$m = \frac{I \times t \times M_w}{n \times F}$$ (9)

All obtained data were fitted to pseudo-first and -second order kinetic models. The pseudo-first-order kinetic is suitable for describing liquid/solid systems (Equation (10)). In this kinetic model, q_e is the

amount of sulfate removed at equilibrium condition (mg/g) and k_1 (min^{-1}) is the rate constant of the pseudo-first order kinetic (Tan and Hameed, 2017):

$$q_t = q_e(1 - e^{-k_1 t}) \tag{10}$$

The pseudo-second order kinetic assumes that chemical sorption is the main controlling factor for the sorption capacity. In this model, k_2 is the sorption constant rate (g/mg min) (Equation (11)) (Wei et al., 2017):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{11}$$

When the relevance of a model is of concern, the average relative error (ARE) and R^2 should be considered (Equation (12)) (Tan and Hameed, 2017):

$$ARE = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{q_{exp} - q_{cal}}{q_{exp}} \right| \tag{12}$$

It was found that both configurations of monopolar and bipolar with two iron/aluminium and two stainless steel anodes/cathodes obey the pseudo-second order kinetic (Fig. 8 and Table 3). Usually q_e calculated by the pseudo-first order is inferior and is farther from the experimental results than the pseudo-second order (Tan and Hameed, 2017).

Although R^2 for the pseudo-first order kinetic is larger than the one for the pseudo-second order kinetic for two iron and two stainless steel anodes/cathodes, the q_e values do not agree with the calculated ones and the ARE for the pseudo-first order is larger than the pseudo-second order. Therefore, it is concluded that the pseudo-second order model describes the kinetics for the iron anodes better.

Aluminium anodes have a much higher $Q_{e(cal)}$ than the iron anodes in various configurations. For example, $Q_{e(cal)}$ for iron monopolar is 29.94 mg/g and for bipolar 71.43 mg/g, whereas $Q_{e(cal)}$ for aluminium monopolar is 222.22 mg/g and for bipolar 285.71 mg/g. The highest $Q_{e(cal)}$ (285.71 mg/g) is related to the bipolar configuration of two aluminium and two stainless steel anodes/cathodes, which also showed the highest sulfate removal efficiency.

The treating capacity and mine water flow can be correlated based on the following modelling.

$$Q(C_{in} - C_{out}) = r \rightarrow Q(C_{in} - C_{out}) = k \cdot m \cdot q \cdot V \tag{13}$$
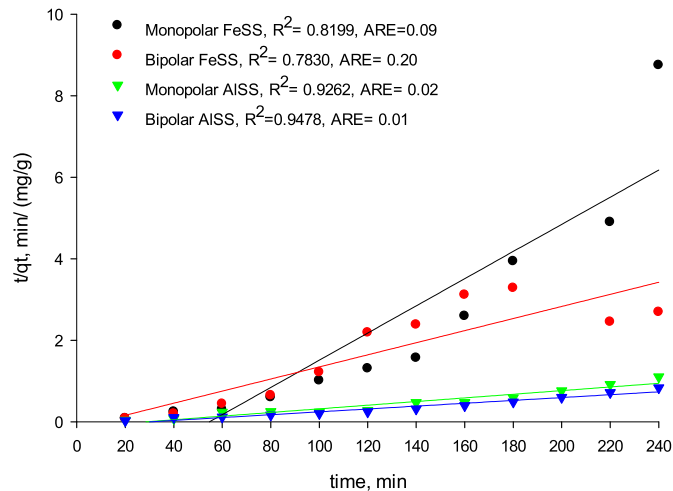

Fig. 8. Fitted diagrams for the most relevant kinetic models (●) pseudo-second order kinetic for monopolar two iron and two stainless steel electrodes, (●) pseudo-second order kinetic for bipolar two iron and two stainless steel electrodes, (▼) pseudo-second order kinetic for monopolar two aluminium and two stainless steel electrodes, and (▼) pseudo-second order kinetic for bipolar two aluminium and two stainless steel electrodes.

Table 3
Kinetic calculations for various electrode types and configurations (calculations done using Sigmaplot 12.0). ARE: average relative error.

| Kinetic model	parameters	Two iron		Two aluminium	
		monopolar	bipolar	monopolar	Bipolar
Pseudo-first-order	$Q_{e\ (cal)}$ (mg/g)	1.16	61.94	24.44	64.08
	$Q_{e(exp)}$ (mg/g)	27.42	89.13	217.11	287.35
	K_1 (min^{-1})	0.0094	0.024	0.0029	0.0038
	R^2	0.9426	0.9167	0.5634	0.6365
	R^2_{adj}	0.9282	0.8958	0.4664	0.5557
	ARE	0.96	0.31	0.89	0.78
Pseudo-second-order	$Q_{e\ (cal)}$ (mg/g)	29.94	71.43	222.22	285.71
	$Q_{e(exp)}$ (mg/g)	27.42	89.13	217.11	287.35
	K_2 (g mg min^{-1})	0.00061	7.97×10^{12}	0.00016	0.00012
	R^2	0.8199	0.7830	0.9262	0.9478
	R^2_{adj}	0.7999	0.7589	0.9188	0.9426
	ARE	0.09	0.20	0.02	0.01
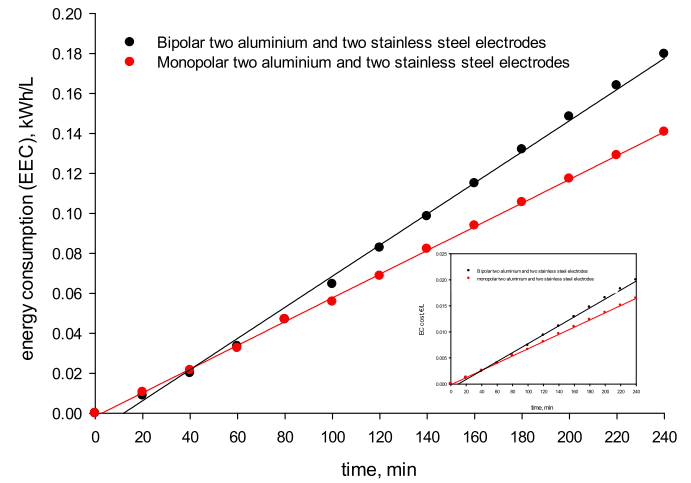
Fig. 9. Energy consumption and cost of monopolar and bipolar aluminium anodes.

In which Q is the water flow rate (assumed $Q_{in} = Q_{out}$), C_{in} and C_{out} are the sulfate concentrations at the beginning and at the end of reaction. r is the adsorption rate, which can be substituted by $k \cdot m \cdot q \cdot V$, in which m is the adsorbent dosage/electro-coagulant dosage (g/L), k is the adsorption kinetic and q is the adsorption capacity (mg/g), while V is the volume of the reactor (0.2 L) (Equation (13)). As both aluminium and iron electrodes obey pseudo-second order kinetic, the final correlation between treating capacity and the mine water flow can be modelled based on Equation (15). The electrocoagulant dosage (g/L) were calculated based on Faraday's law (g) and divided by the reactor volume (0.2 L) to be substituted as g/L in Equation (15).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \rightarrow k_2 = \frac{q_t}{q_e t(q_e - q_t)} \tag{14}$$

$$Q(C_{in} - C_{out})$$
$$= r$$
$$r = k_2 mqV \rightarrow r = \frac{q_t}{q_e \times t \times (q_e - q_t)} \times \left(2 \times \frac{ItM_w}{nF} \times \frac{1}{0.2}\right) \times q_t \times 0.2$$

$$Q(C_{in} - C_{out}) = \frac{q_t}{q_e \times t \times (q_e - q_t)} \times \left(2 \times \frac{ItM_w}{nF} \times \frac{1}{0.2}\right) \times q_t \times 0.2 \tag{15}$$

Table 4
Comparison of various methods for sulfate removal.

Technology	Advantage	Disadvantage	references
lime	Cheap and can be used in industrial scale.	It has high cost for sludge disposal as it produces high amounts of sludge. The treated solution would contain high content of gypsum. Also, it has high maintenance.	Fernando et al. (2018).
limestone	Cheaper than lime treatment with less sludge.	It is not as easy as lime process, because of gypsum saturation and limestone passivation could occur. Therefore, it needs high maintenance. The final sludge is very large amount (sulfate content) and not easy to settle.	Fernando et al. (2018); Moodley et al. (2017).
Precipitation (Barium salts)	Recovery of some components from sludge is possible.	This process is not environmentally friendly because of toxic produced materials (barium sulfate as sludge and hydrogen sulphide gas). Also, it is not cost effective.	Fernando et al. (2018); Moodley et al. (2017)
Anoxic limestone drains	Requires less land, cost and maintenance than constructed wetlands (CWs). It has a good short-term performance.	Hard to maintain anoxic conditions. Possibility of clogging limestone. In the long-term run will fail. Suitable to remove sulfate in low concentrations.	Moodley et al. (2017).
Chemical coagulation	Simple, compact, automation and versatility is easy.	Accumulation of chloride in water	Millar et al. (2016).
Electrocoagulation	Less sludge, smaller footprint (no need of adding chemicals) compared to chemical coagulation. High removal efficiency. More economical than chemical treatment.	Electrocoagulation alone is not efficient enough to remove sulfate. Pre-treatment needed. Power consumption, electrodes (anode and cathode) passivation could issues. Therefore, needs reversing current or on-off the current for avoiding anode passivation and decreasing current consumption, also using stainless steel as cathode to prevent cathode passivation. Aluminium electrodes could be costly.	Semblante et al. (2018); Fernando et al. (2018); Nariyan et al. (2017b).
Wetlands	Less maintenance and does not need chemicals and it is a green technology.	It not very effective for sulfate removal, and is a time-consuming process.	Fernando et al. (2018).
Filtration	Very high removal efficiency. Nanofiltration is very effective for sulfate removal (99%). Reverse osmosis (RO) water quality would be 200–500 mg/L. RO can remove salts up to 10000 mg/L.	Membrane fouling and scaling. Limited lifetime of membranes. Nanofiltration produces brine and it needs pre-treatment. RO needs various steps from pre-treatment to post-treatment. It is energy intensive. Would produce high concentration of sulfate in brine. Therefore, brine management should be considered as the next step that will increase the total cost of this process. Effect of brine circulation and high cross flow in RO is not known. The other disadvantages of RO process is concentration polarization, which is accumulation of the particulate and dissolved material near to the membrane. This will affect the RO performance by higher salt flux and rejection decline, decrease the water flux because of the higher osmotic pressure, precipitation on the membrane surface would be more plausible, cake formation on the membrane by the particulates. RO performance would be decreased by the osmotic pressure and viscosity.	Subramani and Jacangelo (2015); Fernando et al. (2018); Fritzmann et al. (2007); Moodley et al. (2017); González et al. (2017); Fakhru'l-Razi et al. (2009); Morillo et al. (2014).
Adsorption	It is a cheap (wastes can become useful), with high removal efficiency. The other advantages are being fast, economical, flexible, simple, and easy to operate.	It needs more research to be done in this area. Regeneration of adsorbents sometimes is hard. It can be costly in continuous dosing of adsorbent. Depends on the pH of solution and isoelectric of adsorbent. Leaching after adsorption is possible.	Fernando et al. (2018); Acelas and Flórez (2018); Semblante et al. (2018)
Ion exchange	It is a fast, effective and reversible process.	Ion exchangers need to be regenerated because of the limited capacity. Its economical perspective in not known (depends on the resin).	Fernando et al. (2018)
Permeable reactive barriers (PRBs)	Cheap process with prevention of surface water cross contamination and ground water loss. It does not need land and disposal waste.	For high removal efficiency, it needs various substrates implementation. Therefore, the capital cost would get high, especially large barriers required. Each mine site need to be characterized and modelled. It needs specific site for implementation. It can be used only for the less than 20 m below ground. Finally, its performance is not known in long time.	Moodley et al. (2017)
Sulfidogenic bioreactors	Its installation is easy and cheap. It has high efficiency in sulfate removal with a predictable performance.	Due to its various biological reactions, its performance in long run is not known. For running, it needs organic substrates. Finally, its lifetime is limited.	Moodley et al. (2017)
Anaerobic (sub-surface flow) constructed wetlands	Natural and environmentally friendly treatment. Long-term performance is still high. Needs low maintenance. Cost-effective.	It needs large amount of land and is a slow process. Chemical and organic (in remote areas) substrates are costly. In some countries, gravel could be expensive.	Moodley et al. (2017)

Table 4 (*continued*)

Technology	Advantage	Disadvantage	references
Chemical precipitation and EC	High sulfate removal efficiency.	Electricity consumption should be optimized. Energy could be gained from renewable energies such as solar cells. Electrode passivation also should be avoided by optimizing the current density with many factors such as good stirring, reversing current, cathode selection.	(current work)

Table 5

Comparison of EC for sulfate removal.

Sulfate (mg/L)	Removal	Remarks	Reference
2650	40%	180 A/m^2, 60 min.	Jo et al. (2015)
100 sulfide, sulfite, and sulfate (sulfur species)	60%	62 mA cm^{-2} and 10 min, Fe–Al electrodes	Murugananthan et al. (2004)
54	59%	Fe–Al electrodes, current density 47 mA cm^{-2}, treatment time of 20 min.	Murugananthan et al. (2004)
241.5	82.6%	125 A/m^2, 320 min, Sulfate concentration decreased from 241.5 mg/L to 42 mg/L	Drouiche et al. (2007)
3001.9 mg/L (3.125·10^{-2} moL dm^{-3})	80%	acidic conditions (for iron dosages in the range of 0.017–0.090 moL dm^{-3})	Mamelkina et al. (2017)
13000	28.9%	with iron electrode within 120 min, 70 mA/cm^2	Nariyan et al. (2017b)
13000	40.5%	with aluminium electrode within 120 min, 70 mA/cm^2	Nariyan et al. (2017b)
13000	98.1% (250 mg/L) with considering combination processes,	Combination of chemical precipitation with electrocoagulation. Aluminium bipolar anodes with 25 mA/cm^2, 240 min	(Current work)
13000 (1600 mg/L after chemical precipitation)	84.4% (250 mg/L) Electrocoagulation alone	Combination of chemical precipitation with electrocoagulation. Aluminium bipolar anodes with 25 mA/cm^2, 240 min	(Current work)

(Mohammed et al., 2011).

4. Energy consumption and operating cost (OPEX) of electrocoagulation

Power consumption in electrocoagulation is another important factor. Power consumption of the bipolar and monopolar aluminium electrodes were calculated using Equation (16) (Fig. 9). Aluminium electrodes were chosen because they exhibited the highest sulfate removal efficiency compared to the iron electrodes.

In Equation (16), *V*, *I*, *t* are the observed voltage (V), current (A), and time (h), and V_R is the effluent volume (L), for the electrocoagulation process (Nariyan et al., 2017a).

$$EEC = \frac{VIt}{V_R} \tag{16}$$

Based on Golder et al. (2007), the OPEX of electrocoagulation can be calculated (Equation (17), Fig. 9). In this equation, *a* is the cost of the electrical energy price, *b* the cost for the electrode material and *c* the supporting electrolyte consumption (Equation (17)) (Ghosh et al., 2008; Kuokkanen et al., 2015). As no supporting electrolyte was used in the experiments, the cost of the supporting electrolyte can be omitted. Based on the Finland market at 2015, the cost *b* of the aluminium electrodes is 1.60 €/kg Al and the electricity cost *a* is 0.09 €/kWh (Kuokkanen et al., 2015).

$$OPEX = a\,EEC + b\,EMC + c\,SEC \xrightarrow{\text{no supporting electrolyte}} OPEX$$
$$= a\,EEC + b\,EMC \tag{17}$$

It was found that the monopolar configuration uses less energy than the bipolar one with aluminium electrodes, which is in agreement with other studies (Golder et al., 2007). However, monopolar and bipolar configuration energy consumptions were not substantially different: 0.18 kWh/L and 0.14 kWh/L for bipolar and monopolar aluminium anodes after 240 min of reaction time. Based on the cost calculations, just for electrocoagulation and at the end of the 240 min reaction time,

bipolar and monopolar will cost 0.02 and 0.016 €/L, respectively.

Yet, the total cost of a larger scale application would be much smaller. In addition, the applied energy might be from renewable energies, such a solar cells. This could help to reduce the total cost considerably (Kuokkanen et al., 2015). Finally, it is worth mentioning that modern EC plants are using sophisticated electronic controllers that reduce the energy costs substantially if compared to the applications in a normal lab. It is not possible to use the usual lab configurations to estimate the energy costs for modern EC operations reliably.

Different technologies and EC systems for sulfate removal were comapred in order to see the advantages and disadvantages of each technology and show the advantage of current study over other EC studies for sulfate removal (Tables 4 and 5).

5. Conclusions

This research investigated, if sulfate can be removed from mine water by a hybrid technology using electrocoagulation with calcium oxide precipitation as a pre-treatment. It was found that this hybrid set-up removes sulfate from mine water effectively. Current density experiments showed that 25 mA/cm^2 is a good option for both iron and aluminium anodes. The highest sulfate removal achieved with the application of calcium oxide (up to pH 12) with bipolar two aluminium and two stainless steel anodes/cathodes (25 mA/cm^2), which decreased sulfate from 13000 mg/L to 250 mg/L.

Specifically, the sulfate concentration decreased from 13,000 mg/L to 250 mg/L, which meets the discharge limits in most mining companies. The research showed that both, the anode materials and the configuration in electrocoagulation are of relevance. Monopolar configurations in electrocoagulation were less effective in removing sulfate with both iron and aluminium anodes. Aluminium anodes not only showed better efficiency in sulfate removal than iron anodes, but also decreased the pH from 12 to circum-neutral conditions. This is promising, as there will be no need for pH adjustment to discharge the treated water. E_h and pH measurements during the electrocoagulation with various configurations showed that pH and E_h are independent of

the electrode configurations but are a function of the anode type. Specifically, Eh and pH in iron anodes (both configurations) remained almost constant and aluminium anodes in both configurations showed that decreased pH and Eh are erratic during the electrocoagulation process. Kinetic studies showed that iron and aluminium anodes obey the pseudo-second order kinetic in both configurations.

This process needs smaller current density, compared to the previous work has done on same mine water. Also, it was more effective for sulfate removal than other similar works. Therefore, it will be concluded that EC alone would not be effective for sulfate removal, while when it is hybridize with other technologies such as precipitation would be effective for removing sulfate from mine water with high concentrations. As suggestion, this method could be used in mining industry and the cost could be decreased with various techniques such as applying the remote controllers for managing the electrical consumption. Selecting EC configuration should be based on mining company priorities cost (electrical consumption) or removal efficiency. For alleviating the electrical consumption and getting high removal efficiency the combination of both EC configurations could be suggested. Specifically, first the sulfate removal by monopolar configuration and transferring to the bipolar configuration EC cell to get the desired sulfate concentration.

Supplementary video related to this article can be found at https://doi.org/10.1016/j.jenvman.2018.08.095.

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