



Maria Mamelkina

TREATMENT OF MINING WATERS BY ELECTROCOAGULATION



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Abstract

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The mining industry is known to be one of the major contributors to the pollution of aquatic systems. The presence, in mining water, of various contaminants in relatively high concentrations (the most common cations being Fe^{n+} , Al^{3+} , Si^{4+} , Ca^{2+} , Mg^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} , Na^+ , K^+ and anions Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} , HCO_3^-) can cause severe health problems, as well as hindering the reuse and recycling of process water. Currently, there are two approaches used in mining waters management. The first concept aims to reduce the concentrations of harmful dissolved contaminants to acceptable discharge levels. The basis for the second concept is the reuse and recycling of water within the process.

Among treatment methods, electrocoagulation (EC) is receiving more and more attention as an alternative technology to treat mining waters. Eventually, electrocoagulation may replace conventional technologies that require an addition of chemicals and an even higher energy consumption.

To ensure the suitability of electrocoagulation for the treatment of mining waters, the prime objective of this thesis was to investigate the removal mechanisms of sulfate and cyanide involved in EC-processes. Along with the removal mechanisms, parameters affecting the electrocoagulation process were investigated. 3^3 -full factorial design and response surface methodology were implemented in order to systematically study the significance of process parameters (applied current, initial sulfate concentration and initial pH) and their combination on sulfate removal by electrocoagulation. In addition, EC performance using iron and aluminum electrodes was compared. Laboratory tests with both synthetic and real mining waters were performed. In terms of cyanide removal, the electrodes materials and electric charge were the main studied parameters.

Another research question was devoted to the development of a novel treatment concept based on continuous EC operation and solids recirculation. Established process resulted in a more efficient sulfate and metals removal as well as allowed operation at desired initial pH conditions comparing to the batch operation. The performance of this novel continuous treatment concept was compared with batch electrocoagulation and conventional chemical coagulation.

According to the results of this study, removal mechanisms of sulfate are different at neutral/base and acidic conditions, while the removal mechanisms of cyanide vary

greatly, depending upon the material of the electrodes. Iron electrodes are more suitable for the EC-treatment of sulfate and cyanide rich waters. With iron electrodes, partial removal of sulfate and almost complete removal of cyanide were obtained. Under the studied conditions the iron species produced were positively charged favoring the removal of negatively charged ions. Most probably, the lower removal rates of studied contaminants with aluminum electrodes are due to the negatively charged species formed hindering the particle charge neutralization of anions.

In batch operation, the applied current and initial concentration of sulfate are the most critical parameters affecting the removal of sulfate by electrocoagulation, while the effect of initial pH is insignificant and mainly affects the formation of metal species. No matter what the initial pH of the solution, the EC-treatment took place at basic conditions with final pH over 11. On the contrary, the initial pH of the solution had a pronounced effect for continuous EC tests, the initial pH remained constant and operation at acidic conditions improved the removal of sulfate.

In this study, received knowledge on sulfate and cyanide removal prove the suitability of electrocoagulation to treat mining waters. Awareness of the removal mechanisms makes the scale-up of the electrocoagulation process more robust and exact. For further process implementation, at industrial scale, there is a clear need to characterize the solids formed during the EC-process, to develop methods for sludge dewatering and recovery of valuable components from the sludge formed. In addition, there is a need to establish scale-up rules and validate the process at pilot and industrial scales. Having covered these considerations, it will be possible to conclude that electrocoagulation is a sustainable water treatment technology that meets all circular economy principles.

Keywords: electrocoagulation, mining waters, response surface methodology, sulfate, cyanide, scale-up, water treatment, wastewater.

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Maria Mamelkina
January 2020
Lappeenranta, Finland

*This work is dedicated to my parents
Alexander Mamelkin
Irina Mamelkina*

*Посвящается родителям
Мамелькину Александру Николаевичу
Мамелькиной Ирине Юрьевне*

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Abstract

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List of publications

This dissertation is based on the following journal papers. Rights have been granted by the publishers to include the papers in the dissertation. The reprints of the articles are included to the end of the final work.

- I. Mamelkina, M.A., Cotillas, S., Lacasa, E., Sáez, C., Tuunila, R., Sillanpää, M., Häkkinen, A., Rodrigo, M.A. (2017). Removal of sulfate from mining waters by electrocoagulation. *Separation and Purification Technology*, 182, pp. 87-93.
- II. Mamelkina, M.A., Tuunila, R., Sillanpää, M., Häkkinen, A. (2019). Systematic study on sulfate removal from mining waters by electrocoagulation. *Separation and Purification Technology*, 216, pp. 43-50.
- III. Mamelkina, M.A., Vasilyev, F., Tuunila, R., Sillanpää, M., Häkkinen, A. (2019). Investigation of the parameters affecting the treatment of mining waters by electrocoagulation. *Journal of Water Process Engineering*, 32, 100929.
- IV. Mamelkina, M.A., Herraiz-Carboné, M., Cotillas, S., Lacasa, E., Sáez, C., Tuunila, R., Sillanpää, M., Häkkinen, A., Rodrigo, M.A. (2019). Treatment of mining wastewater polluted with cyanide by coagulation processes: a mechanistic study. *Separation and Purification Technology*, 237, 116345.

Author's contribution

Ms. Mamelkina is the principal author and investigator in Articles II and III. The author planned and performed the experiments, analyzed the results and prepare the manuscript. In Article III the model was developed by Dr. Vasilyev while Ms. Mamelkina interpreted and analyzed the modelling results.

In Articles I and IV Prof. Rodrigo was the corresponding author and Ms. Mamelkina designed the experimental set-up, conducted the experiments, performed the analysis and post-processed the experimental data together with the co-authors. In Articles I and IV, the manuscript was prepared by Dr. Cotillas, Dr. Lacasa and Ms. Mamelkina.

Related conference papers and presentations

- I. Mamelkina, M.A., Vasilyev, F., Tuunila, R., Särkkä, H., Lund, C., Lamberg, P., Sillanpää, M., Häkkinen, A. (2016). Sulfate removal by electrocoagulation: Operational conditions and solids characterization. 5th International Congress on Water Management and Mining – Water in Mining 2016, May 18-22, Santiago, Chile. Conference article. In: Wiertz, J., McIntyre, N., ed., *Proceedings of a Conference*. Santiago: Gecamin
- II. Mamelkina, M.A., Tuunila, R., Sillanpää, M., Häkkinen, A. (2016). Removal of sulphate from mining waters by electrocoagulation. 16th Nordic Filtration

- Symposium - Filtration for Circular Economy 2016, August 24-26, Lappeenranta, Finland. Oral presentation.
- III. Mamelkina, M.A., Tuunila, R., Cotillas, S., Lacasa, E., Sillanpää, M., Häkkinen, A., Rodrigo, M.A. (2016). Electrochemical sulphate removal from mining waters using iron and aluminum electrodes. 1st International Conference on Sustainable Water Processing 2016, 11–16 September, Sitges, Spain. Poster presentation.
- IV. Mamelkina, M.A., Tuunila, R., Sillanpää, M., Häkkinen, A. (2017). Electrocoagulation treatment of real mining waters and solid-liquid separation of solids formed. International Mine Water Association Conference 2017, June 25-30, Lappeenranta, Finland. Conference article. In: Wolkersdorfer, C., Sartz, L., Sillanpää, M., Häkkinen, A., ed., *Proceedings of a Conference*. pp. 1070-1075
- V. Mamelkina, M.A., Cotillas, S., Lacasa, E., Tuunila, R., Sillanpää, M., Häkkinen, A., Rodrigo, M.A. (2018). Continuous electrocoagulation process for treatment of mining waters. International Mine Water Association Conference 2018, September 10-14, Pretoria, South Africa. Conference article. In: Wolkersdorfer, C., Sartz, L., Weber, A., Burgess, J., Tremblay, G., ed., *Proceedings of a Conference*. pp. 267-271
- VI. Mamelkina, M.A., Cotillas, S., Lacasa, E., Tuunila, R., Sillanpää, M., Häkkinen, A., Rodrigo, M.A. (2019). Electrochemical Removal of Cyanide from Mining waters. 25th Topical Meeting of the International Society of Electrochemistry 2019, May 12-15, Toledo, Spain. Oral presentation.
- VII. Mamelkina, M.A., Vehmaanperä, P., Tuunila, R., Sillanpää, M., Häkkinen, A. (2019). Electrochemical treatment of mining waters. International Mine Water Association Conference 2019, July 15-19, Perm, Russia. Conference article. In: Wolkersdorfer, C., Khayrulina, E., Polyakova, S., Bogush, A., ed., *Proceedings of a Conference*. pp. 212-216

Nomenclature

Latin alphabet

<i>b</i>	regression modeling coefficient
<i>C</i>	concentration, mg/L
<i>C</i>	electrode consumption, kWh
<i>C</i>	energy consumption, kg
<i>F</i>	Faraday's constant, 96487 C mol ⁻¹
<i>j</i>	current density, A m ⁻¹
<i>I</i>	current, A
<i>M</i>	molecular weight, kg mol ⁻¹
<i>n</i>	number of electrodes
<i>Q</i>	electrical charge passes, A h dm ⁻³
<i>q</i>	flowrate, dm ³ h ⁻¹
<i>R</i>	removal efficiency, %
<i>R</i> ²	coefficient of determination of the goodness of fit criteria
<i>t</i>	time, s
<i>U</i>	cell voltage, V
<i>V</i>	volume of treated water, m ³
<i>w</i>	market price, €/kWh
<i>W</i>	market price, €/kg
<i>X</i>	regression modeling parameter
<i>z</i>	number of electrons involved in the electrode reaction
<i>Z</i>	electrochemical equivalent, g C ⁻¹

Dimensionless numbers

Fo	Fourier number
Re	Reynolds number
We	Weber number

Subscripts

0	initial value
1	initial sulfate concentration
2	initial pH
3	applied current
c	removed contaminant in kg
e	predicted value
el	electrode
en	energy
f	measured value
fe	final experimental value
fp	final predicted value
s	solid
w	treated water in m ³

Abbreviations

AmmEL	ammonia electrochemical treatment
AmdEL	acid mine drainage electrochemical treatment
EC	electrocoagulation
OC	operating costs
Ox	contaminant
Me	metal
NitrEL	nitrate electrochemical treatment
SS	suspended solids
TDS	total dissolved solids
TOC	total organic carbon
TRL	technology readiness level
WAD	weak acid dissociable

1 Introduction

Established restrictions for the discharge of harmful contaminants, limitations in fresh water intake and by-product generation force the mining industry to focus on water treatment technologies that produce the desired water quality for discharge, reuse and recycling, as well as minimizing the environmental footprint of the treatment activities. Electrocoagulation as one of the potential water treatment alternatives can assist the mining industry to comply with these tightening limitations and requirements.

In this thesis, electrocoagulation (EC) refers to the electrochemical method for wastewater treatment, based on the application of an electric current to destabilize suspended, emulsified or dissolved contaminants in an aqueous solution (Moussa et al., 2017). During recent years electrocoagulation has found wide application in the treatment of water from the oil industry (An et al., 2017, Khemis et al., 2005), food industries (de Santana et al., 2018, Chen, Chen & Yue, 2000), tannery facilities (Şengil, Kulaç & Özacar, 2009) and textile production (Khemila et al., 2018, Khorram, Fallah, 2018), as well as pulp and paper operations (Vepsäläinen et al., 2011). At laboratory scale, electrocoagulation is known to be effective for the removal dyes, natural organic matter, arsenic, fluoride, toxic metal and various anionic contaminants (Pajootan, Arami & Mahmoodi, 2012, Akbal, Camcı, 2011, Gatsios, Hahladakis & Gidarakos, 2015, Kobya et al., 2010, Ulu et al., 2014, Vepsäläinen et al., 2009, Lacasa et al., 2011b, Nidheesh, Singh, 2017, Drouiche et al., 2008, Govindan et al., 2015, Sandoval et al., 2019, Moussavi, Majidi & Farzadkia, 2011, Muruganathan, Raju & Prabhakar, 2004, Lacasa et al., 2011c, Pulkka et al., 2014). The suitability of EC-processes for the treatment of mining waters can be fully assessed when possible mechanisms involved in the removal of most common mining waters contaminants are deeply and profoundly understood. Without knowing the removal mechanisms of those contaminants present in mining waters, it is impossible to scale-up the existing laboratory and pilot scale units and bring the technology to the Technology Readiness Level over TRL 7 (EARTO, 2014). The mechanisms of metals, nitrate and phosphate removal from water by electrocoagulation have been already studied and reported (Lacasa et al., 2011c, Lacasa et al., 2011a, Florence, 2015, Oncel et al., 2013).

Thus, this work focuses on the mechanisms of sulfate and cyanide removal as the first, and obligatory, step of the scale-up of the electrocoagulation process. Moreover, in this thesis the suitability of electrocoagulation to treat sulfate and cyanide rich waters is assessed. It is hypothesized that electrocoagulation treatment has a positive effect on the quality of mining waters in general and the removal of sulfate and cyanide in particular. Moreover, it is supposed that more than one removal mechanisms are involved in the EC process. Sulfate removal mechanisms are more likely to be dependent on applied current, electrode material, operational mode, initial concentration of the contaminant and pH of the solution, while cyanide removal mechanisms are more likely to be affected by electrode material and current density.

The main objective in Articles I-III was to investigate the parameters affecting the removal of sulfate from mining waters by electrocoagulation. The effect of operation mode, initial pH and concentration of sulfate, applied current, electrode material as well as water matrix were studied. Additionally, in Article I the performances of chemical coagulation and electrocoagulation were compared in terms of sulfate removal. Moreover, a novel treatment concept, based on continuous electrocoagulation and solids recirculation, was developed and presented in Article I. In Article III, 3³-full factorial design and response surface methodology were implemented to evaluate the significance of the applied current, initial pH, initial sulfate concentration and their interactions on the removal of sulfate from mining waters. The objective in Article IV was to study the suitability of EC-treatment for cyanide rich waters and to describe the mechanisms involved in contaminant removal. The effects of current density and electrode material were investigated. Mechanisms involved in both chemical and electrocoagulation of cyanide removal were compared. Also, various analytical techniques were used to monitor the formation of toxic contaminants during the EC-treatment of mining waters containing cyanide.

This thesis represents a summary of four papers published in international scientific journals. The summary consists of seven chapters. Chapter 1, the Introduction, consists of the research background and motivation as well as explaining the focus of research and objectives. Chapter 2 provides information on the current state-of-the-art of mining waters treatment, using conventional and innovative techniques. Chapter 3 focuses on electrocoagulation theory, process equipment and main operation conditions. Advantages and disadvantages of electrocoagulation, scale-up and design issues as well as economical aspect are covered in Chapter 4. Chapter 5 consists of the description of a water treatment procedure, applying analytical and statistical methods to study the removal mechanisms of sulfate and cyanide from mining waters. The main results and findings of this present research are reported and discussed in Chapter 6. Chapter 7 consists of the conclusions and research perspectives defined by the results achieved during this research.

2 Mining waters

At a mine site, the volumes of water used depend greatly on a type of ore being mined and the size of the mine site. Water is used for mineral extraction and processing, dust suppression, process equipment washing, and cooling, as well as ore and by-product transportation (Wolkersdorfer, 2008, Prosser, Wolf & Littleboy, 2011). For instance, coal mines are known to be one of the largest water users in the mining industry due to the huge amounts of product mined. At metal mines, over 250 million liters of water are required to produce a ton of gold (Prosser, Wolf & Littleboy, 2011).

The term “mine water”, is used to describe any surface or ground waters that are present at the mine site and are involved in mining operations. However, mine water is considered to be only a part of all water used at the mine site, so called “mining waters” (water involved in any of the mining operations). Mining waters include mine water, process water (water from mineral manufacturing with process chemicals as the main contaminants); leaching/drainage water (water that penetrates through solid mine wastes); effluent (discharged water); mine drainage water (flow off water from an active or abandoned mine site) (Lottermoser, 2010, Lapedes, 1974). The main, typical, water streams of a metal mine are shown in Fig. 1. Normally, process dewatering and drainage water arrives at a tailings pond followed by a settling pond from where water is recirculated back to the metals processing or discharged into the environment (Wahlström *et al.*, 2017).

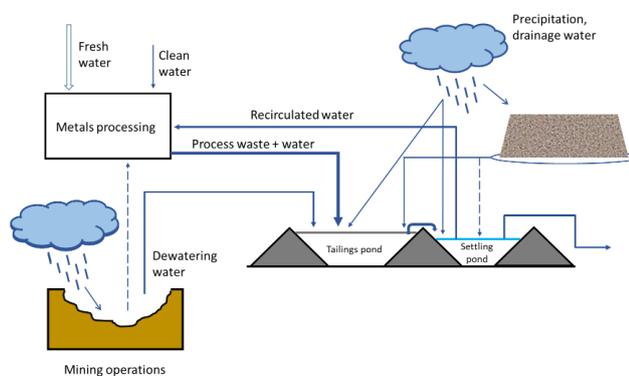


Figure 1. Example of typical water flows of a metal mine. Modified from Wahlström *et al.* (2017).

The composition of mining waters depends greatly on the type of ore being mined and chemicals used in mineral extraction and manufacturing. Also, the potential for water contamination is influenced by several other factors, such as: the type of enrichment processes, weather conditions (climate, rainfalls and drought), the working life of a mine and wastewater management. The most common cations (Fe^{n+} , Al^{3+} , Si^{4+} , Ca^{2+} , Mg^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} , Na^+ and K^+) and anions (Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} , HCO_3^-) as well as

AsO₄³⁻ and other As-compounds could be found from most metal or coal mines (Wolkersdorfer, 2008, Oncel et al., 2013).

During mining operations, the main source of nitrate and other N-compounds in water is a result of incomplete detonation, dissolution of explosives and spillage during blasting activities. Even though nitrate is defined as non-toxic, or only toxic to infants, it contributes significantly to the eutrophication of standing surface water bodies and thus has to be controlled. Nitrate should be eliminated from mining waters due to its detrimental effect on the environment and the reusability of water. Among the most common nitric compounds used during the leaching of silver and gold is cyanide, which is reported as highly toxic for the environment and human being. Cyanide presents in several forms, such as ionic, molecular HCN, salt and metal-complexes.

Increasing attention to sulfate mitigation has been paid during the last few years (Runtti et al., 2018). Even though sulfate has a lower environmental risk, compared to other contaminants presented in mining waters, it contributes to the toxicity of waters, serious pollution of natural water bodies and decrease of the fertility of soils (Fernando et al., 2018, Johnson, Hallberg, 2005). From a mining operations point of view sulfate should be limited because its high concentration may hinder ore processing and metal enrichment, as well as result in the clogging of pipes. Sulfate is regulated in most countries with intensive mining operations. Limit values for sulfate and cyanide are given in Table 1.

Table 1. Limit values for sulfate and cyanide present in discharge waters.

Country	Sulfate discharge level	Cyanide discharge level	References
USA	10-500 mg/L	0.022 mg/L	(Arnold, Gericke & Muhlbauer, 2016, EPA, 2012)
Canada	65-500 mg/L	1 mg/L	(Arnold, Gericke & Muhlbauer, 2016, ECCC, 2018)
Finland	2,000 mg/L	0.4 mg/L	(Wahlström et al., 2017)
South Africa	200-400 mg/L	-	(Arnold, Gericke & Muhlbauer, 2016)
Australia	1,000 mg/L	4 µg/L	(ANZECC, ARMCANZ, 2008, West, Kratochvil & Fatula, 2011)
Russia	500 mg/L	0.07 mg/L	(ГН 2.1.5.1315-03, 2003, ГН 2.1.5.2280-07, 2007)

In the metals mining sector in the Nordic countries, the most regulated species are suspended solids (SS), As, metals such as Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Pb²⁺, nitric compounds

such as NO_3^- , NO_2^- , N tot, CN^- as well as SO_4^{2-} . Common limit values established for SS are in the range from 10 to 20 mg/L. The limits for metals in the discharge water vary considerably between Finnish and Swedish mines. Thus, typical values for the metal's concentration limits at Swedish mines are in the microgram range, while at Finnish mines the limits are set in the range of milligrams (Wahlström et al., 2017). The established limit for sulfate in most mines in Finland is 2,000 mg/L, when worldwide discharge limits for sulfate may vary between 250 and 2,000 mg/L.

2.1 Treatment of mining waters

Despite the diversity in the quality of mining waters, the treatment principles and established techniques are similar from one mine to another. The impact of mining waters on the environment depends greatly on the type of contaminants and their concentrations, as well as the treatment technology applied (Wessman et al., 2014). Considering the results of life cycle assessments, Hengen *et al.* (2014) reported on the greater environmental impact of active, rather than passive, treatment due to the greater energy consumption. Martinez *et al.* (2019) and Masindi *et al.* (2018) reported the greater environmental significance of the reagents and other materials used during treatment over the energy consumption. Nowadays, there is a general recommendation to replace currently used chemical materials, where possible, with environmentally green materials (wood chips, forestry waste), or to use secondary, instead of raw, materials during the construction of treatment facilities and utilize renewable energy (Martínez et al., 2019, Masindi et al., 2018, Hengen et al., 2014). Still nowadays neutralization with lime has been utilized as the main treatment technique to neutralize the acidity of mining waters and remove metals. Among the most critical disadvantages of this technique are the large amount of sludge generated, its long-term chemical stability, as well as poor selectivity, in terms of metals removal (Kauppila, Räsänen & Myllyoja, 2013).

Currently, there are two main water management concepts to deal with the amount of contaminated mining waters. The first aims to bring the concentrations of harmful dissolved contaminants to required discharge levels. The second approach is to treat water only to a level suitable for certain processes rather than to an acceptable discharge level, and in that way allow for water reuse and recycling within the process. In terms of the economical and environmental feasibility of mining operations, the implementation and further development of the reuse-recycling concept is more attractive. A possible drawback of the reuse-recycling concept, at already operating mines, is the requirement to reorganize the plants and their infrastructure (Kauppila, Räsänen & Myllyoja, 2013, Kivi, 2014, Nguyen et al., 2014).

The true cost of mining water treatment depends on the contaminants present in the water to be treated, volumes of water, labor and energy costs as well as the price of the units of treatment equipment. The real cost of treatment activities is mine specific and changes with the needs of a site, therefore; in the USA alone the operational costs of neutralization treatment vary from 1 to 2.5 \$million per year (Gusek, Gusek & Figueroa, 2009). As an

outcome, it might result in greater additional costs to treat generated waters than to develop treatment and control techniques for the minimization of mining waters generation and performing the recycling.

Due to the variety of contaminants present in mining waters some waters are classified as easy to reuse and recycle, whereas others require treatment prior to possible reuse and recycling. Wastewater treatment technologies are generally classified as either established or innovative processes. Additionally, they may be divided into active and passive treatment techniques. Active treatment is based on a continuous addition of chemicals and mixing of reagents with water, involves electrical and mechanical processes as well as requiring staff control and maintenance (Gusek, Gusek & Figueroa, 2009). Active treatment (chemical neutralization and precipitation, biological sulfate-reduction systems, membranes, filters) has been used at many mine sites to minimize the environmental impact of mining-influenced waters (Oncel et al., 2013). However, high investment and operating costs make active technologies an expensive alternative to passive treatment (for example constructed aerobic and anaerobic wetlands, vertical flow systems, limestone ponds and channels). Passive treatment takes advantage of the natural water flow and natural chemical/biological processes to reduce contaminant concentration to acceptable level and to neutralize acidity, it requires infrequent maintenance of the treatment facilities (Wolkersdorfer, 2008).

Innovative techniques exist, with a wide variety of more advanced technologies and generally belong to the active treatment technologies class. Among these are reverse osmosis, membrane treatment, electrodialysis, electrocoagulation, ion exchange, electrolysis, biosorption and bioreactors, limestone reactors, solvent extraction, vertical flow reactors and adsorption (Wahlström et al., 2017). Innovative techniques have been developed to enhance the removal efficiency of contaminants, minimize chemical usage, reduce the volume of sludge generated, enable recycling of process water and divide effluent streams to be treated separately, with better efficiency.

Many of these innovative techniques are not widely adopted for the treatment of mining waters; mainly they are at the exploratory stage, or only used at some individual mine sites. According to Lottermoser (2010), attention should be given to the purposes established and innovative techniques are designed to reduce volume, raise pH, lower dissolved metal and sulfate concentrations and lower bioavailability of metals in solution.

There are several techniques available and commercialized to treat sulfate and cyanide rich streams. The most common ones for the treatment of mining waters with respect to sulfate are biodegradation (Dann, Cooper & Bowman, 2009, Greben et al., 2009) and precipitation, using limestone or aluminum hydroxide (Runtti et al., 2018, Silva, Cadorin & Rubio, 2010, Cravotta III, Trahan, 1999, Amaral Filho et al., 2016). Cyanide is removed by adsorption onto activated carbon or ferrous sulfide, by natural or biological degradation, as well as by alkaline chlorination. The toxicity of cyanide can also be minimized by binding it with various metals (Fe, Cu, Ni, Mn, Pb, Zn, Cd, Sn or Ag) resulting in the generation of soluble and/or insoluble cyanide-metal complexes, which

are mostly non-reactive compounds (Xu et al., 2015, Iakovleva et al., 2018, Kuyucak, Akcil, 2013, Zhao, Zhang & Qu, 2015, Dash, Balomajumder & Kumar, 2009, Seung-Mok, Diwakar, 2009).

2.2 Electrochemical treatment of mining waters

One of the indicators that refers to the maturity level of a technology is the Technology Readiness Level (TRL). TRL indicator levels vary from 1 (when basic principles of a process are observed) to 9 (when a technology is proven in an industrial environment). Currently, the electrochemical treatment of mining waters belongs in the range TRL 5 – TRL 7, meaning that technology has been already validated, demonstrated and system prototypes already exists (EARTO, 2014). Initially, the suitability of electrochemical treatment was studied for the removal of toxic metals (Gatsios, Hahladakis & Gidakos, 2015, Wolkersdorfer, 2008, Oncel et al., 2013, Florence, 2015, Demirbas, Parlak & Yigit, 2010). Later, the technique was further developed to remove nitrate and other nitric compounds (Lacasa et al., 2011c, Koparal, Ögütveren, 2002). Nowadays, in order to bring the technology to a TRL over 5-7, it is critical to study the suitability of electrochemical treatment for sulfate and cyanide removal from mining waters. Without knowledge of sulfate removal effectiveness, as one of the most common components, and cyanide, as one of the most toxic and dangerous impurities in mining waters, it is hard to conclude anything regarding the suitability of electrochemical systems to treat mining waters.

The first patent for electrocoagulation, with aluminum and iron electrodes, was written in the US in 1906 (Hinkson, 1906). The application of electrocoagulation in drinking water treatment was performed extensively in the US by 1946 (Chen, 2004).

While the full-scale industrial application of electrocoagulation for the treatment of mining waters is limited, some pilot units have already been commercialized. One of the latest industrial scale EC-treatment plants was installed in Severnyi Mine, JSC Kola MMC. Iron electrodes were used to remove N-compounds, suspended solids, color and metals (Fe, Cu and Ni) (Makarov et al., 2019). Pilot plants that utilize different electrochemical methods have been designed and tested to remove nitrogen compounds, neutralize water streams and remove toxic metals. Thus, there are several commercialized electrochemical technologies to treat nitrate (NitrEL) and ammonia (AmmEL) rich waters, for example, provided by Current Water Technologies Inc. Also, a solution (AmdEL) to prevent the formation of acid mine drainage using magnesium anodes is also available (Current, 2019). The Outotec EWT process is another commercially available technology that is based on electro-oxidation and electrocoagulation for the removal of toxic metals, arsenic, antimony, selenium and other oxyanions. One module's treatment capacity is from 5 to 40 m³/h, so that the need for the treatment of larger amounts of water can be met by adding more modules. Modular system benefits from the ease of scale-up and reduced quantity of residues formed, when compared to conventional processes, however, the low conductivity and high solid content of treated water may hinder the process significantly (Outotec, 2019). The Hydro 400 is an electrochemical water

treatment unit that is available to treat mining and mineral processing water. One unit is capable of treating 40 m³/h, and the treatment capacity can be increased by adding more units. When testing the Hydro 400 unit, case studies that were performed proved the suitability of EC-treatment to the removal of phosphorous, suspended solids, lead, iron and aluminum from contaminated water. The application of a Hydro 400 unit to treat mining waters resulted in a 15% cost reduction, compared to chemical coagulation and other conventional treatment methods (Hydro Industries, 2019). The Soneco® water treatment system by Power & Waters is based on the combination of ultrasound and electrolysis for the efficient removal of phosphorous and toxic metals, as well as for the neutralization of the acid mine drainage. Soneco® units benefit from a cleaning-in-place tool that provides electrode cleaning by ultrasonic cavitation, prolonging the lifetime of the equipment and affecting dramatically the operation costs (Power & Water, 2019). FCC Aqualia has been recently working on the application of electrocoagulation and bio-electrochemical processes to coprecipitate phosphorus and nitrogen. The main distinction of this process, when compared to the others mentioned, is that it produces biogas as a potential power source and benefits from the possible valorization of generated sludge containing aluminum, phosphorous and nitrogen as a fertilizer (Aqualia, 2019).

Nariyan *et al.* (2018) recently studied the removal of sulfate from mining waters by batch electrocoagulation, using bipolar and monopolar connections. A technology combining calcium oxide precipitation with electrocoagulation resulted in a reduction of sulfate from 13,000 mg/L to 250 mg/L. Electrocoagulation was applied as a post-treatment, with the aim of decreasing the residual concentration of sulfate from 1 500 mg/L to 250 mg/L. The highest sulfate removal by electrocoagulation was achieved using aluminum anodes in bipolar connection at 25 mA/cm². Also, combined CaO/electrocoagulation treatment applied by Radic *et al.* (2014) resulted in over 86% removal efficiency of sulfate from acid mine drainage. Treated water was passed through a set of iron electrode plates followed by aluminum plates at 2.7 mA/cm². A moderate removal of sulfate (53%) from the drainage of an abandoned mine in Guanajuato, Mexico by continuous electrocoagulation with aluminum electrodes at 4 mA/cm² was reported by Del Ángel *et al.* (2014). Cyanide removal of 98% by electrocoagulation operated in both continuous and batch modes using bipolar and monopolar arrangements of electrodes was reported by Moussavi *et al.* (2011a). Application of Fe as an anode and Al as a cathode resulted in the most efficient cyanide removal under condition of continuous operation, with a hydraulic retention time of 140 min. Hassani *et al.* (2011) studied cyanide elimination by electrocoagulation, using iron electrodes connected in a bipolar arrangement. Over 90% removal of cyanide was achieved for an initial cyanide concentration 50 mg/L at 40 V and treatment time of 90 min. However, the data regarding sulfate and cyanide removal were reported without detailed information about the mechanisms involved in EC, and the parameters affecting the contaminant removal. Without knowing this information, further development of the electrocoagulation process and scale-up of the equipment are hindered.

In this thesis, to fill the gap in knowledge and create the whole picture around mining waters treatment by electrochemical technology, the mechanisms of sulfate and cyanide

removal from mining waters were studied. Sulfate removal mechanisms have been determined and a continuous electrocoagulation concept to treat mining waters has been developed and described in Article I. Parameters affecting the electrocoagulation process and their significance were investigated using 3^3 -full factorial design and response surface methodology in Articles II and III. In addition, comparison of synthetic and real mining waters is performed in Article III. Article IV is devoted to explaining the mechanism involved in cyanide removal from mining waters by chemical coagulation and electrocoagulation.

3 Electrocoagulation

3.1 Definition and theory

Electrocoagulation among others, including electroflotation, electrodecantation, electroremediation, electro-oxidation, is one of the electrochemical methods used for wastewater treatment (Sillanpää, Shestakova, 2017). Electrocoagulation is based on the application of an electric current to destabilize emulsified, dissolved and suspended contaminants in an aqueous solution. Electrocoagulation could be defined as an electrochemical method to produce destabilization agents. Those agents induce the neutralization of electric charge for a pollutant removal (Emamjomeh, Sivakumar, 2009). The simplest construction of an electrocoagulation reactor is an electrolytic cell with one anode and one cathode (Emamjomeh, Sivakumar, 2009). Metal ions are released to the system from the anode, while hydrogen gas is produced at the cathode. During electrocoagulation, electrical dissolution of metal ions from electrodes takes place, and thus generation of coagulants *in situ* takes place (Chen, 2004). The electrodes conductive metal plates can be made of the same or different materials (Emamjomeh, Sivakumar, 2009).

Before covering theoretical aspects of electrocoagulation, it is essential to specify some general parameters that are in use to describe the electrochemical processes. These are the applied current, I , [A]; current density, i , [mA cm^{-2}] or [A m^{-2}]; the electric charge, Q , [A h dm^{-3}]. Commonly, an electrical current is defined as a movement of positive and negative ions in opposite directions. Current density is defined as the current per area of electrode, while electric charge refers to the current applied in an hour to treat a volume of 1 dm^{-3} . Generally, all three parameters determine the coagulant dosage rate, bubble production rate and flocs growth, as well as affecting the EC system lifetime and unit size (Koby et al., 2010, Chen, 2004, Chopra, Sharma & Kumar, 2001).

The theory of electrocoagulation is under discussion here, and the process is typically divided into three sequential stages:

- the electrolytic oxidation of the electrode and formation of coagulants
- destabilization of contaminants and the breaking of emulsions
- formation of solids particles, leading to an aggregation of the contaminants.

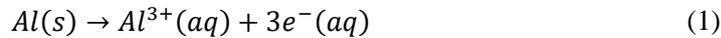
The destabilization mechanism itself consists of several main steps. Firstly, after the current is passed through the solution, an interaction of ions is initiated by dissolution of the sacrificial electrode (anode). Later, a compression of a diffuse double-layer around the charged species occurs. Secondly, the counter ions produced by the electrochemical dissolution of the electrode cause charge neutralization of the ionic species present in the wastewater. Coagulation occurs due to the action of the van der Waals attractions, because the counter ions diminish the electrostatic interparticle repulsion. Thirdly, particle agglomeration occurs due to the formation of a sludge layer that catches and bridges

uncomplexed colloidal particles. The sludge layer is a result of the coagulation process (Mollah et al., 2001, Mollah et al., 2004).

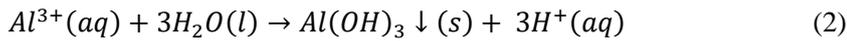
3.1.1 Mechanisms of solids formation

Since aluminum and iron are broadly used in wastewater treatment by conventional electrocoagulation, an explanation regarding the mechanisms involving these two metals is given below (Eqs. 1-14). To produce $Al_n(OH)_{3n}$, firstly, the cationic monomeric species such as Al^{3+} and $Al(OH)_2^+$ are formed during the electrolytic dissolution of the aluminum anode at low pH, which, thereafter, are transformed initially into $Al(OH)_3$ at appropriate pH values (Mollah, et al., 2001). The chemical reactions are as follow (Eqs. 1-6).

For the aluminum anode the reaction is (Chen, 2004)



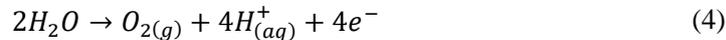
At acidic conditions the reaction is



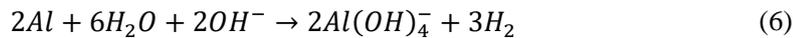
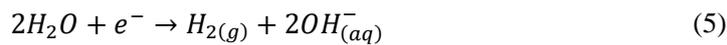
At alkaline conditions the reaction is (Chen, 2004, Mollah et al., 2001)



Formation of oxygen also takes place on the anode (Linares-Hernández et al., 2009)



According to the Linarez-Hernandez et. al. (2009) the main reaction on the cathode is hydrogen evolution. At high pH the cathode is probably attacked by OH^- ions during H_2 formation.

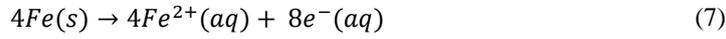


However, other ionic species, such as $Al(OH)_2^+$ and $Al_2(OH)_2^{4+}$ may form in the system, regardless of the pH of the initial aqueous solution. The formation of different species is mainly pH dependent (Mollah et al., 2001).

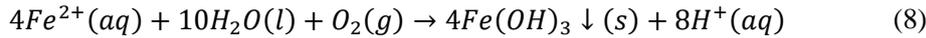
There are two typical mechanisms defined for the production of $Fe(OH)_n$, where $n = 2$ or 3 (Mollah et al., 2001). The chemical reactions are given below (Eqs. 7-14).

First mechanism

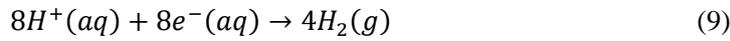
For the iron anode, the reaction is (Mollah et al., 2001).



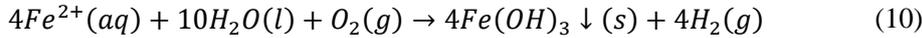
At acidic conditions, both precipitation $Fe(OH)_3$ and oxygen evolution reaction take place.



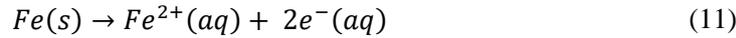
The reaction at the cathode is



The overall reaction is thus


Second mechanism

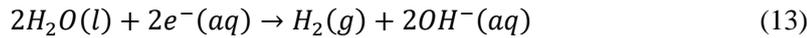
On the iron anode, the following reaction takes place



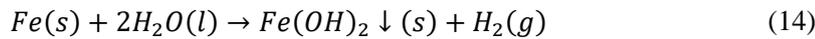
At alkaline conditions, precipitation occurs at the iron anode



On the cathode, hydrogen gas is generated by the following reaction



The overall reaction is thus



The quantity of ions dissolved from an anode can be obtained by weighing the electrodes before and after the test. In addition, it can be calculated using Faraday's law. According to Faraday's law, the quantities of substances liberated at electrodes depend upon the quantity of current passed, time duration of passing the current at a uniform rate and change on the ions being deposited (Ciobanu et al., 2007).

The Faraday's first law of electrolysis says, "The mass of an element liberated on an electrode during electrolysis is directly proportional to the quantity of electricity, which passes through the solution of an electrolyte" (Ciobanu et al., 2007). It means that knowing the current (I , [A]) applied to the cell and the duration (t , [s]) of the process it is

possible to calculate theoretical mass of the substance liberated from the electrodes (Eq. 15).

$$m_f = \frac{Q}{F} \cdot \frac{M}{z} = Z \cdot I \cdot tF, M, z - const, \quad (15)$$

where the Faraday's second law of electrolysis is, "The masses of different substances deposited or liberated, when the same quantity of electricity is passed through different electrolytes, connected in series are proportional to their chemical equivalent masses" (Ciobanu et al., 2007). The equivalent mass of an element presents the ratio of atomic mass of an element and its valence. According to Faraday's law, with an increase in the current density, the production of ions on the anode and cathode is intensified and it leads to better treatment efficiency (Kobyas et al., 2010).

3.1.2 Mechanisms of the contaminant removal

Electrocoagulation of mining waters can be considered successful when contaminants are removed from water and either destroyed or made less soluble due to the action of the reacted and excited state (Mollah et al., 2001). During electrocoagulation, among the mechanisms of contaminants removal can be coagulation, enmeshment, precipitation, adsorption, complexation or charge neutralization of particles (Moussa et al., 2017, Garcia-Segura et al., 2017). These removal mechanisms depend mainly on pH and Redox-potential as well as water composition (Chen, 2004, Linares-Hernández et al., 2009, Martín-Domínguez et al., 2018). Electrode material and applied current are two significant factors that affect the removal mechanisms as well as influencing the process costs and coagulation efficiency (Demirbas, Kobyas, 2017). Schematic representations of removal mechanisms involved in the electrocoagulation process are given in Fig. 2.

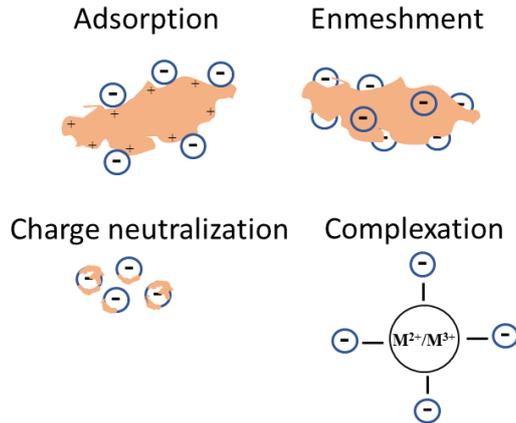
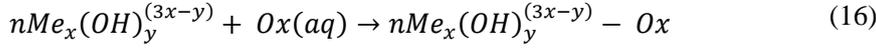
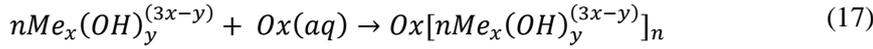


Figure 2. Illustration of possible removal mechanisms involved in the electrocoagulation process. Modified from Garcia-Segura *et al.* (2017).

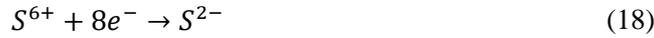
The general equation (Eq. 16) of the adsorption of a contaminant (Ox) on the metal (Me) hydroxides formed during EC is (Koby et al., 2017, Noubactep, Schöner, 2010)



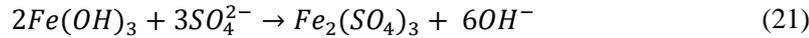
While co-precipitation can be described by (Eq. 17):



Assuming that the reduction of sulfate during the electrocoagulation to sulfide or sulfur occurs (Eqs. 18-20), with the presence of Fe, Ni, Zn and Cu in the solution, the relevant reactions at the RedOx below -0.2 V can be the following (Glinka, 1981)



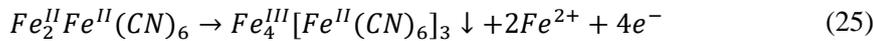
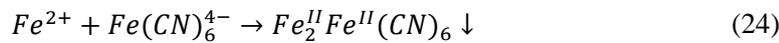
At acidic conditions, the formation of $Fe_2(SO_4)_3$ takes place (Eq. 21) (Glinka, 1981)



Further, electrocoagulation processes at base conditions result in the precipitation of $FeSO_4(OH)$ according to the following reaction (Eq. 22) (Glinka, 1981)



According to the literature, the complexation reactions between iron (II) and free cyanide ions may be described by Eqs. 23-25 (Yu et al., 2016)



The ions produced on the anode neutralize the charge of the particles, thus enabling the coagulation process. There are two typical approaches to the removal of contaminants by the released ions. The first one is the removal by chemical reaction and precipitation. The second is based on the coalescence of colloidal materials, and the removal of these by electrolytic flotation. Moreover, such phenomenon as ionization, electrolysis, hydrolysis and free-radical formation may occur when the water containing colloidal particles, oils or other contaminants is treated by an applied electric field.

Mining waters also contain high concentrations of toxic metals and nitrate. Two main mechanisms for metals removal by electrocoagulation are reported, complexation and electrostatic attraction. Adsorption, electrochemical reduction and precipitation are known as secondary mechanisms. In electrostatic attraction positively charged metal ions are attracted by negatively charged flocs. Due to the ability of the metal to act as ligand, complexation with the hydroxyl ions formed during the electrocoagulation is possible (Garcia-Segura et al., 2017). The primary mechanism for nitrate removal is adsorption, onto freshly formed amorphous coagulant flocs. A further secondary mechanism involved in nitrate removal by electrocoagulation, using aluminum electrodes, is a chemical reaction between nitrate and aluminum to form ammonia, which is subsequently also adsorbed onto the flocs (Lacasa et al., 2011c).

In this study, the removal mechanisms of sulfate were studied and reported in Article I, Article II and Article III. During electrocoagulation with iron electrodes, sulfate was found to be removed by both chemical and physical processes. Different primary mechanisms of sulfate removal were observed at neutral/base and acidic conditions. Article IV is devoted to the mechanisms of cyanide removal by electrocoagulation using aluminum and iron electrodes. Electrode material affected mostly the process performance and energy consumption.

Still today there are discussions about the stages involved in electrocoagulation processes (Mollah et al., 2001, Garcia-Segura et al., 2017, Moussa et al., 2017,). Even though the mechanisms of coagulant agent formation are known, more detailed investigation of the removal mechanisms of different contaminants is required. Thus this work, in particular, is devoted to studying sulfate and cyanide removal mechanisms taking place during the electrocoagulation treatment of mining waters using both iron and aluminum electrodes.

3.2 Process equipment

One of the major distinctions between electrocoagulation reactors are their configurations. Reactor design may be categorized as either a batch or continuous system, as shown in Fig. 3 (Holt, Barton & Mitchell, 2005). On one hand, the advantages of the latter mentioned systems (b) are a continuous feed of wastewater and operation under (pseudo) steady-state conditions. Also, one of the key advantages of continuous systems is that the coagulant demands are substantially fixed. On the other hand, batch systems (a) maintain a fixed wastewater volume per treatment cycle. However, the main disadvantage of batch mode concerns the changes, with time, of operational conditions within the reactor, influencing the mass transfer and flow regime (Holt, Barton & Mitchell, 2005). The selected operation mode mostly affects the performance, reliability and chemical interaction within the EC-process. The reactor design influences such operational parameters as bubble path, flotation effectiveness, floc-formation, fluid flow regime and mixing/settling characteristics (Chopra, Sharma & Kumar, 2001).

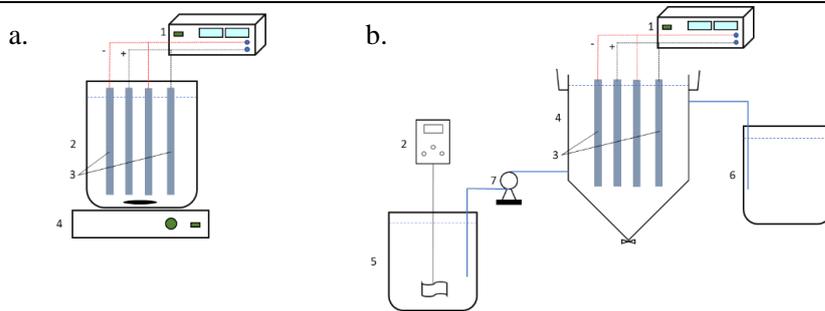


Figure 3. Experimental units for a. batch EC 1-power supply, 2-EC reactor, 3-electrodes, 4-mixer and b. continuous EC 1-power supply, 2-mixer, 3-electrodes, 4-EC reactor, 5-mixing tank, 6-discharge tank, 7-peristaltic pump. Modified from Kobya *et al.* (2010).

As shown in Fig. 3, the simple experimental unit consists of a mixing tank combined with an EC-reactor and a power supply for batch mode operation. While the continuous unit, in addition to the above mentioned, also incorporates a storage/mixing tank, discharge tank and a pump (Chopra, Sharma & Kumar, 2001). The experimental setups also require a resistance box to regulate the current density and a multimeter to read the current value (Mollah *et al.*, 2001).

The configuration of reactors may be with bipolar or monopolar arrangements of multiple pairs of electrodes (Chen, 2004, Emamjomeh, Sivakumar, 2009). Bipolar electrodes are connected in series via the electrolyte, while monopolar electrodes are connected in parallel, via copper bus bar connectors (Jiang *et al.*, 2002). A schematic illustration is given Fig. 4.

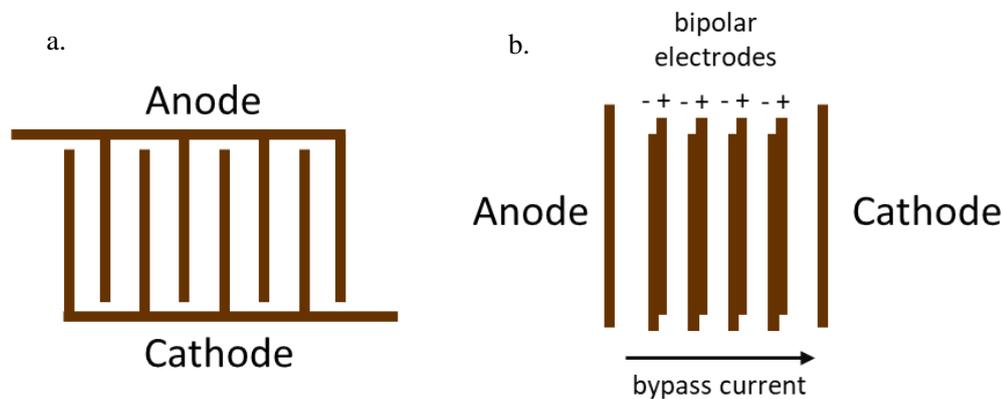


Figure 4. a. monopolar and b. bipolar electrode connections in the electrocoagulation cell. Modified from Jiang *et al.* (2002).

In the case of a serial arrangement of bipolar electrodes, connected via the electrolyte, a voltage $n U$ is supplied between two feeder electrodes, within $n-1$ bipolar electrodes, I

being the equal current that flows across one feeder/solution interface, through the solution, successively into and out of each of bipoles and finally to the second feeder electrode. In a parallel electrode arrangement of monopolar electrodes, an equal voltage U is applied to n pairs of anodes and cathodes, resulting in a current $n I$ passing across the electrode/solution interface via the bulk solution (Jiang et al., 2002).

The main merit of bipolar reactor arrangement relates to easy operation, as only feeder electrodes have to be connected. However, bypassing of the bipolar electrodes may occur due to the large terminal voltage between a pair of feeder electrodes (Jiang et al., 2002).

EC cells connected in series have a higher electrical resistance. In this case, a higher potential difference is needed for an applied current and the same current will flow through all the electrodes. As for the parallel connection, the current will be proportionally divided between all the electrodes according to the resistance of the individual cells (Mollah et al., 2001).

The lack of a systematic approach to electrocoagulation cell design and operation makes it difficult establish typical design and optimal operation conditions (Kumar, Goel, 2010). To find the proper design, and estimate operational parameters, laboratory experiment are of great significance before applying electrocoagulation treatment for pilot or industrial scale. One of the most important parameters being analyzed for every particular application is electrode behavior, depending on the material from which it is made.

3.3 Electrode material

Commonly, the electrode materials used in electrocoagulation processes are iron or aluminum (Mollah et al., 2001). Additionally, magnesium, copper, zinc (Gupta, Ali, 2013), are reported to be used as sacrificial anodes.

During the electrocoagulation process, the anodes dissolve to release Al^{3+} and Fe^{2+} , with further oxidation of Fe^{2+} to Fe^{3+} in acidic or neutral conditions (Linares-Hernández et al., 2009). Ions produced by the anodes form a range of coagulant species that leads to a destabilization and an aggregation of suspended solids and precipitates. Thereby the suspended solids are simultaneously coagulated and floated efficiently with the presence of soluble anodes (Muruganathan, Raju & Prabhakar, 2004). In general, Al and Fe ions are used in the coagulation process due to their trivalent forms (Attour et al., 2014) and low solubility of their hydroxides (Muruganathan, Raju & Prabhakar, 2004). Performance variation, due to the different electrode materials, corresponds to the oxidation potential. For instance, Fe provides a higher oxidation rate than Al, as a consequence of its higher oxidation potential (potential of Fe is -0,447V, of Al – 1,662V).

Linares-Hernandez *et al.* (2009) have reported that the selection of Al electrodes for electrocoagulation processes prevails, due to the introduction of a green to yellow color and turbidity to the treated volume, while Fe electrodes are evolved to the process. Color and turbidity phenomena take place firstly due to the oxidation of Fe^{2+} to Fe^{3+} and

secondly due to the formation of $\text{Fe}(\text{OH})_3$, as a result of the reaction of Fe^{3+} with OH^- (Eq. 10) (Linares-Hernández et al., 2009).

Sometimes a greater removal efficiency of Fe-Al electrode arrangements can be attributed to the higher electrode potential and, consequently, higher oxidation potential between anode-cathode (Linares-Hernández et al., 2009). As a result, the generation of larger coagulant agents and an improvement in contaminant removal may occur (Moussavi, Majidi & Farzadkia, 2011). However, the output of every reaction depends strongly on the type of the contaminants and operational conditions.

The presence of Al and Fe species in solution are pH dependent and affect pollutant removal. The predominant aluminum species associated with the aqueous pH are Al^{3+} at pH less than 3.5, $\text{Al}(\text{OH})_{3(s)}$ for the pH range 4-9.5 and $\text{Al}(\text{OH})_4^-$ when the pH is over 10. The majority of Fe complexes are formed at pH 5-9 and this pH range is considered optimal for the carrying out of electrocoagulation processes. The predominant species over the wide range of pH values is the highly insoluble compound $\text{Fe}(\text{OH})_2$ (Linares-Hernández et al., 2009). At pH around 2, the formation of iron hydroxide complexes is limited by the neutralization of hydroxide ions by H^+ ions.

In an EC cell the amount of coagulant produced by the sacrificial anode into the solution depends on the current density applied to the electrodes (Moussavi, Majidi & Farzadkia, 2011). It is generally accepted that the theoretical concentration, calculated with Faraday's law, is less than the detected concentration of Al or Fe in aqueous solutions. One explanation for the difference refers to the possible promotion of Al and Fe by the cathode. For example, in work by Linares-Hernandez *et al.* (2009), an excess of 50% between calculated and measured concentration of Al^{3+} was reported, while, for Fe^{2+} , the detected concentration was 10% higher than calculated theoretically. According to Mouedhen *et al.* (2008), the current efficiency of aluminum dissolution was about 175%. The author explained this phenomenon by a chemical attack of aluminum cathode induced by hydrogen evolution, resulting in a significant contribution to the total amount of aluminum released.

One of the main problems caused by electrode material is the formation of a passive oxide film on the anode. Passivation of the anode leads to an increase in the applied potential and to a waste of energy during electrocoagulation treatment. Several authors have studied dissolution of the passive film on the surface of aluminum anodes, while processes with iron anodes are poorly explored. An insulating film of alumina (Al_2O_3) is a result of aluminum's natural oxidation with oxygen gas. This film is stable in the range of pH 4-10 in the solution and complicates the release of aluminum cations from the anode surface (Trompette, Vergnes, 2009). It was reported by Mouedhen *et al.* (2008) that treated industrial wastewater containing chloride may provoke the dissolution of the passive film on the anode surface (Mouedhen et al., 2008).

Trompette *et al.* (2009) studied the influence of electrolytes on passive film formation and dissolution. For aluminum electrodes, sulfate ions in the electrolyte were reported to behave as passivating agents, preserving the oxide film formed, while chloride ions at

relatively low concentration, acted as promoters to breakdown the film through pitting corrosion. Also sulfate salt containing electrolytes require a high voltage to break the passive layer. It was found that a decrease of applied voltage is a sign of the presence of a sufficient amount of the corrosive species (e. g. chloride ions) in the solution to be treated. The ratio of $[\text{Cl}^-]/[\text{SO}_4^{2-}]$ should be around, or greater than 0.1 to ensure 6-fold decrease in the applied voltage and the breakdown of the passive film (Trompette, Vergnes, 2009).

Mechelhoff *et al.* (2013) confirmed that the addition of pitting promoters, such as chloride ions, influences positively on the diminishing of the passive layer; however, additional chemicals would result in an increase in complexity, and cost, of electrocoagulation processes. Hence, it was reported that an application of rough aluminum electrodes caused the effect of “spontaneous de-passivation”, thus they were suggested to achieve performance improvement. This phenomenon may be attributed to the hydrolysis of dissolved aluminum (III) ions close to the electrode surface releasing protons, which dissolve the pre-existing passive layer and enhance the release of ions from the anode. Moreover, in case of the rough electrode surface, a presence of cracks in the passivating layer apparently facilitate the dissolution process (Mechelhoff, Kelsall & Graham, 2013).

Iron dissolution was studied by Sasson *et al.* (2009). It was reported that a scientific understanding of iron dissolution during the electrochemical process is much more complex than that of aluminum. There is a scientific dispute about the form of iron dissolution (Fe^{2+} or Fe^{3+}) from the electrode. Incorrect understanding leads to uncertainties and variations in the process, such as:

- 33% uncertainty in the calculated value of the iron-dissolution rate
- differences in hydrolysis and flocculation processes for Fe^{2+} or Fe^{3+}
- oxidation of Fe^{2+} to Fe^{3+}
- independent of the electrochemical process high iron-dissolution of anode at pH 5-7.

Both non-electrochemical and electrochemical iron dissolution was studied by Sasson *et al.* (2009) and their results are summarized in Fig. 5. In both mechanisms, Fe^{2+} ions were declared as dominated, however, there are differences in the direction of motion of the electrons. Electrochemical dissolution results in the movement of electrons out of solution into the anode and the electric wires. Dissolution with no current brings electrons into solution to balance its electric charge. Due to the dual mechanism of iron dissolution, it is hard to predict Fe^{2+} dissolution rates and more investigations are needed.

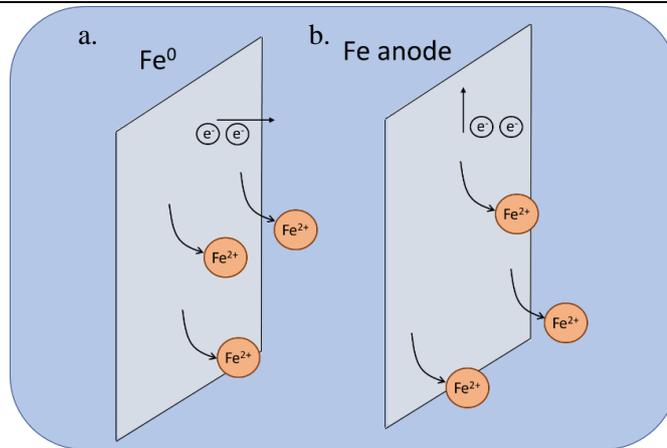


Figure 5. The direction of movement of electrons participating in the iron-dissolution reaction: a. without electrical current, b. with electrical current. Modified from Sasson *et al.* (2009).

3.4 Parameters affecting electrocoagulation processes

The performance of electrocoagulation is known to be affected by electrode material and arrangement, current density, operating time, reactor design, type of electrolyte, pH as well as the combination of these factors (Moussa *et al.*, 2017, Chopra, Sharma & Kumar, 2001, Cañizares *et al.*, 2009, Devlin *et al.*, 2018). Most recent process failures occurred due to an incorrect combination of factors, and misunderstanding of their influence on each other. Thus, at the beginning of process development, its upcoming implementation and scale-up, it is necessary to gain information about the parameters affecting the process.

Electrode material has a great influence on coagulation efficiency, formation of solid species, passivation tendency, process lifetime and operating costs. Generally, mixing and settling characteristics, bubble pass and flotation efficiency are influenced by the reactor design. Anodic dissolution, coagulant dosage, unit size, system lifetime and bubble generation are affected by the current density. Operating time influences the removal efficiency as well as energy and electrode consumptions; while flocs formation as well as power consumption, depend on temperature (Moussa *et al.*, 2017, Chopra, Sharma & Kumar, 2001). Electrolyte nature affects the solid species generation, conductivity of the treated water, destabilization of colloids as well as the formation of the insoluble layer on the surface of electrodes. The pH of the solution contributes mainly to the speciation and solubility of metal hydroxides, thus affecting the process performance.

Some basic relations proposed and confirmed by the variety of studies all over the world may enable the selection of appropriate parameter values in order to achieve better removal efficiency. One of the general recommendations is that among the anions present,

there should be 20% of chloride to ensure a normal operation of EC in water treatment (Trompette, Vergnes, 2009). It was reported that an increase in flow rate or decrease in retention time in continuous operation drives a decrease in the removal of target contaminants (Moussavi, Majidi & Farzadkia, 2011, Emamjomeh, Sivakumar, 2009, Mollah et al., 2004, Kobya et al., 2010).

It was determined that bubbles generated by electrolysis are dependent on pH and current density, with both influencing their size. Typically, with higher current density, the production of small bubbles of hydrogen is faster, thereby also facilitating flotation (Attour et al., 2014). Bubbles are very small and generally vary from 15 to 80 micrometers. It should be taken into consideration that the size of the coagulated solids and the size of electrolytic bubbles are in the same range (Muruganathan, Raju & Prabhakar, 2004).

The distance between two electrodes is inversely proportional to the electrical conductivity. When the distance between electrodes increases the solution becomes more resistant, thus, the solubility of metal into the solution decreases. Consequently, a reduction in removal efficiency takes place with an increase in electrode gap (Attour et al., 2014). Moreover, it was reported by Lacasa *et al.* (2011a) that the counter anion of the metal reagent presented or added fights with negatively charged contaminant present in water for adsorption onto the growing precipitates, thus decreasing the removal rate of the contaminant.

The final pH of the treated solution is generally higher than at the beginning of the process. The reason for this phenomenon is the OH⁻ production at the cathode with time and its appreciable effect of the current density (Attour et al., 2014). The pH value, as well as iron and aluminum concentrations primarily affect the types and amounts of produced species (Lacasa et al., 2011b).

Current density affects the performance of EC-processes, depending on the operational conditions, the type of electrodes and type of the removed contaminant (Moussavi, Majidi & Farzadkia, 2011). An increase in current density leads to anodic oxidation, thus promoting the formation of amorphous metal hydroxide species in the vicinity of the electrode and in the treated solution. Higher current density requires high electrical energy consumption that leads to an increase in the operating costs of the treatment (Kobya et al., 2010, Kobya et al., 2010). Current density in the range of 20-25 Am⁻² was suggested as the most suitable for the long duration of operation without maintenance (Gupta, Ali, 2013). To enhance the removal of the undesirable contaminants, wastewater can be passed through a series of cells with electrodes made from different metals.

Considering the treatment of mining waters by electrocoagulation, it has been reported previously that process performance is mainly affected by the current density, electrode arrangements and materials, reactor design, concentration of the contaminants and initial pH (Oncel et al., 2013, Nariyan, et al, 2017).

This work is devoted to the investigation of process parameters on sulfate and cyanide removal from mining waters. Thus, to study the removal of sulfate the influence of

electrode material, operation mode, electrolyte nature, applied current, initial pH and concentration was reported. Electrode material and current density were studied during the electrocoagulation treatment of mining waters containing cyanide. The main trends and findings are discussed in Section 6.1.

4 Application of electrocoagulation

4.1 Advantages and disadvantages of electrocoagulation

Potentially, electrocoagulation is an economically and environmentally attractive method for the treatment of wastewater (Moussa et al., 2017). This process allows the elimination of various contaminants from water with a minimum of sludge production; however, there is an acute need to understand the effect of operational parameters as well as optimize the process. (Emamjomeh, Sivakumar, 2009). The technique is effective due to the fact that an adsorption of hydroxide onto mineral surfaces is 100 times greater *in situ* rather than with the addition of metal hydroxides as a coagulant (Mollah et al., 2004). Among the main advantages of the method are its cost effectiveness, safety, environmental compatibility, easy operation (Mollah et al., 2004) and possibility of complete automation (Chen, 2004). In comparison with traditional flotation and coagulation, electrocoagulation provides benefits in the removing of small colloidal particles (they have a large probability of being coagulated because of the electric field that sets them in motion). Also, the addition of an excessive amount of coagulants can be avoided, due to their direct formation by electro-oxidation of a sacrificial anode. The flocs formed by EC are more stable and relatively large, containing less bound water (Kumar, Goel, 2010).

Electrocoagulation brings with it a minimal possibility for secondary pollution (Mollah et al., 2004) and the avoidance of the addition of excess amounts of chemicals, in comparison with chemical methods (Mollah et al., 2001). What is more, this method requires low current and it becomes possible to operate the process using renewable (solar, wind) energies (Mollah et al., 2004). Consequently, electrocoagulation could be also beneficial for water treatment in rural areas, where access to electricity is limited.

Moreover, water after the electrocoagulation is clear, colorless and odorless. Formed flocs are similar to chemical flocs, although after electrocoagulation the flocs are generally larger, more acid-resistant and stable and contain less bound water. In comparison with chemical methods, during electrocoagulation an effluent with less total dissolved solids (TDS) content is produced. This leads to the further reduction in water recovery cost (Mollah et al., 2001).

There are numerous advantages, but the method also has its disadvantages, one of the grounds for future research. According to Mollah *et al.* (2001, 2004) the disadvantages are as follow:

- formation of a toxic chlorinated organic compound may take place, if chlorides are present
- formation of trihalometanes occurs with the presence of high concentrated humic and fulvic acid in wastewater
- the incoming wastewater suspension is required to have high conductivity

- electrodes have to be regularly replaced, as they are dissolved into wastewater streams as a result of oxidation
- operating cost increases in those areas where the prices for the electricity are high
- application of the method is restricted with water containing high suspended solids.

One of the operational problems faced during the electrocoagulation process is the formation of a passive oxide film or, in other words, passivation occurring on the surface of anode exhibiting as a white (for aluminum) and red (for iron) layer. The most intensive formation of the layer occurs under the low current densities, while with higher current densities it is less noticeable due to the faster coagulation and settling rate (Attour et al., 2014). Using electrodes with reversible polarity, optimizing reactor design, the addition of chloride ions in the influent and applying mechanical cleaning may prevent anodic passivation (Oncel et al., 2013, Attour et al., 2014).

From the generally accepted understanding, there are more advantages than disadvantages in the application of electrocoagulation as a treatment method. Some of the drawbacks become less critical when developing the EC-treatment of mining waters. For instance, typically high concentration of total dissolved solids brings the conductivity of mining waters to the required level. The concentration of TSS is relatively low, minimizing the deposition of solids on the surface of electrodes. However, high chlorine content and the presence of total dissolved carbon lead researchers to develop and investigate this method more precisely and provide possible optimal operational parameters.

4.2 Scale-up and design issues

One of the requirements of chemical process technology is bringing the technique under development from one scale to another, while, in the ideal case, ensuring similar performances of the processes. One of the tasks in chemical engineering is to determine the relationships between laboratory and full-scale processes by verifying scale-up parameters. There are several reasons why understanding of scale-up might be needed at different stages of process development, such as studying the economic feasibility (pilot plant, demonstration plant), determination of bottlenecks of the technology (miniplant, pilot plant) and commercializing a new process. All in all, scale-up is mainly employed to see if the technology meets the market requirements and expectations (Moulijn, Makkee & Diepen, 2001).

For successful scale-up of the process there is a need to first study the chemical and physical mechanisms involved in the process, to determine the most significant scale-up parameters (where possible and feasible) to merely following the traditional approach in reactor scale-up. However, in most cases, such an approach is very costly and an alternative engineering approach, combining laboratory experiments, miniplants and mathematical simulation of the process can be employed. Therefore, when the process is

relatively novel at the industrial level it is advisable to demonstrate it using a pilot plant (Moulijn, Makkee & Diepen, 2001).

The industrial world, especially the mining industry, is getting more and more attracted to developing water treatment technologies. The ease with which water treatment technology can be brought from lab to industrial scale, along with minimizing the time consumption and costs, is influenced by several factors. Some of these are related to the reactor, process, removal mechanisms, volumes and operating conditions. While others are affected by external factors such as maximum size of the equipment, treatment costs of already established or possible alternative technologies and experience of the company and employees. Possible process scale-up is, firstly, followed by safety and environmental regulations and process feasibility at a larger scale. Some of the limitation are related to the expectations of the process such as high throughput, maximum selectivity and conversion, low overall process costs and ease of scale-up (Perl, 2016).

The possibility to scale-up a process is generally classified using three categories (Harmsen, 2013):

- well-defined, easy and quantifiable process (used, for example, when speaking about adsorption, ion-exchange, heat exchange)
- difficult but quantifiable (related mainly to most of the chemical reactors)
- very difficult and rarely quantifiable (some particular processes).

Electrochemical processes belong to the difficult but quantifiable or very difficult and rarely quantifiable classes. On one hand, the processes are easy to scale-up from the reactor geometry point of view. For example, the scale-up of the most common parallel plate electrochemical cell can be easily performed using modules containing up to 200 parallel placed electrodes (Zhou et al., 2018). On the other hand, the scale-up of electrochemical water treatment processes is hindered by the electrochemical principles involved and especially by the contaminant removal mechanisms (in electrochemical processes normally more than one mechanism is involved).

There are two main rules to consider in the design and scale-up of electrochemical reactors. The first concerns the optimal design of the cell and the other is devoted to the reaction mechanisms involved in the process. Among the most reported and significant scale-up parameters for electrocoagulation process is the relation of the surface area to volume ratio (S/V). The S/V ratio is mainly related to the current density, rate of coagulant dosing and bubble production; however, the flow regime and reactor configuration are not considered. Zolotukhin *et al.* (1989) proposed to use the Reynolds number (Re), Froude number (Fo) or Weber number (We) as main indicators of the fluid regime, buoyancy and surface tension respectively, as well as gas saturation and geometry similarities to guarantee the most appropriate sizing of the equipment.

The cell design used for electrocoagulation processes varies greatly from applying open tanks, parallel plate cells or complex designs with moving electrodes. The choice of

electrode material and shape, reactor configuration, operation mode and electrode arrangement are the key parameters, especially at the initial stage of process development. Electrode material affects the amount, and type, of metal ions in the solution, coagulation efficiency and process costs, while the reactor configuration influences the fluid flow regime, bubble paths, mixing/settling characteristics and mass transfer (Chopra, Sharma & Kumar, 2001). The operation mode influences process performance, energy consumption, while electrode arrangement allows the minimization of energy consumption and improvement in the removal of contaminants (Zhou et al., 2018).

Most of the research to date was performed using a monopolar connection of electrodes, very few studies have been performed using a bipolar connection arrangement. In the latter condition, it is possible to have better performance and lower energy consumption, however, bypassing of electrodes and loss of charge may occur. Nariayan *et al.* (2018) studied the effect of monopolar and bipolar arrangements of iron and aluminum electrodes for the removal of sulfate from mining waters. According to the results reported, a bipolar arrangement improved sulfate removal for both iron and aluminum electrodes.

The major distinctions between different the electrocoagulation reactors are their configuration and operation mode. A design may be presented as a batch or a continuous system (Holt, Barton & Mitchell, 1999). On one hand, the latter mentioned system has, as advantages, a continuous feed of wastewater and operation under (pseudo) steady-state conditions. One of the key advantages of continuous systems is that the coagulant demands are substantially fixed. On the other hand, a batch system maintains a fixed wastewater volume per treatment cycle. However, the main disadvantage is the change with time of operating conditions within the reactor (Holt, Barton & Mitchell, 1999). The operation mode mostly affects the performance, reliability and chemical interaction within the EC-process.

Tank cells (a cylindrical reactor with inner electrodes) are relatively often used for laboratory scale experiments. Its application is attractive, due to the ease of manufacturing and availability of materials, however, among the main drawbacks are the limitation in mass transfer and mixing conditions. Disadvantages in scale-up are poor potential and current distribution, nonuniform mixing patterns as well as challenges in verification of the flow regime and mass transport (Zhou et al., 2018). These tanks are used by several research groups to study the process parameter to eliminate anions from different water streams. Cyanide removal was investigated by Kobya *et al.* (2010b), Moussavi *et al.* (2011a), sulfate removal was reported by Nariyan *et al.* (2018), phosphate removal was studied by Attour *et al.* (2014), Bektaş *et al.* (2004), Kobya *et al.* (2010a) Vasudevan *et al.* (2009).

The commonly used parallel-plate flow cell is another reactor configuration which is mainly constructed with one pair of electrodes (anode-cathode) or with several pairs fixed on a filter press. This type of the reactor provides uniform potential and current distribution. Among the other advantages are the ease of scale-up using a modular system

and better control of the gap between electrodes (Zhou et al., 2018). The application of parallel-plate flow cells is well reported, for example, by Lacasa *et al.* (2011b) for the removal of nitrate, ammonia and phosphate.

Moving three-dimensional electrodes have the advantage of a larger active surface area per unit volume. However, from the scale-up point of view, this type of reactor is not recommended due to the presence of moving parts and thus challenges in the automation of the process. In addition, it provides a non-uniform potential and current distribution (Zhou et al., 2018). Very few results are available regarding the application of moving three-dimension electrodes in electrocoagulation. Sulfate removal from tannery waters was reported by Muruganathan *et al.* (2004), however.

In all cases, the cell design should provide uniform current and potential distributions that promote the optimization of parameters such as energy consumption, coagulant production and process performance. In addition, it is desirable that the equipment should meet the requirements of low cost material for manufacturing, ease of maintenance, installation and operation as well as the possibility for scale-up (Pletcher, 1982).

This work was focused on the principles of transferring an electrocoagulation process from lab scale to pilot plant. Most of the work is related to the investigation of contaminant removal by electrocoagulation. However, the results described in Article I illustrate the author's input in bringing the studied technology to another level. The work focus is on switching from batch operation to continuous, process design and treatment of 200 L of water. In this work both tank (Fig. 3) and parallel-plate flow cells (Fig. 6 and Fig. 7) were utilized for the elimination of sulfate from mining waters. With the application of parallel-plate flow cell, both batch-recycle and continuous single pass modes were tested.

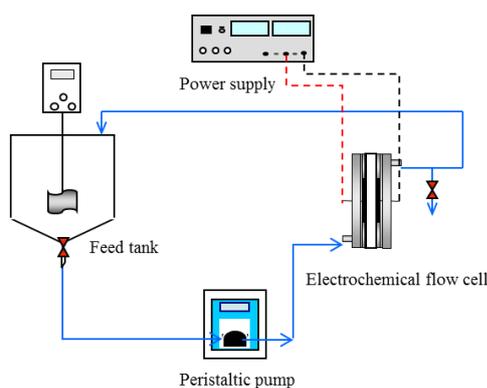


Figure 6. Schematic diagram of an electrocoagulation process operating in batch mode.

A tank cell batch reactor was used mainly to study the effect of electrode material on contaminant removal, pH evolution and performance of the cell for sulfate removal. Within the studied range of initial sulfate concentration, initial pH and applied current the

highest removal of sulfate was 54%. The EC-process was hindered by overheating of electrodes, poor mixing conditions and insulation of electrode surface by solids generated during the process.

When developing a novel process design based on continuous operation and solids recirculation (Fig. 7), the electric charge passing through the system was switched from batch operation to continuous, and this is proposed as one of the scale-up parameters. It should be highlighted that in this arrangement, electric charge depends on the intensity and flowrate but not on time. The electric charge has been calculated using Eq. 27 based on the current density (Eq. 26) that was similar for both batch and continuous operations. The developed process was operated in once-through mode, recirculation of water back to the cell or coagulation tank was not performed, although to increase solids concentration in the tank, solids were recycled.

$$j = \frac{I}{S} \quad (26)$$

$$Q = \frac{j}{q} \cdot S \quad (27)$$

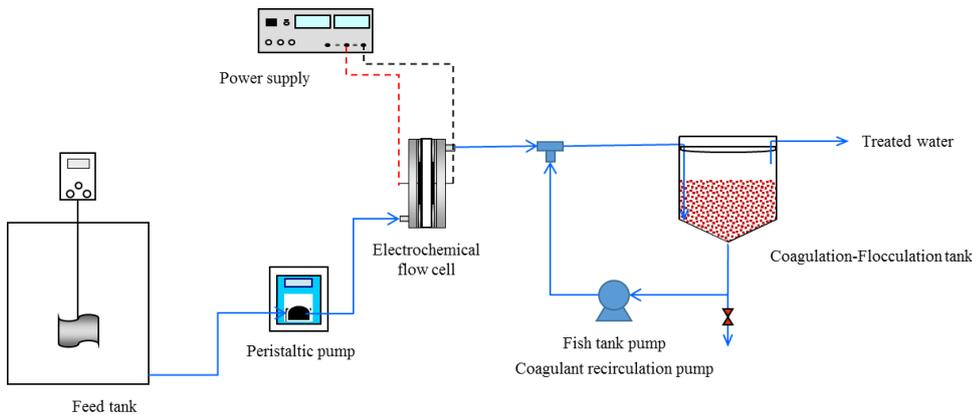


Figure 7. Schematic diagram of a continuous electrocoagulation process with solids recirculation (Article I).

Since most industrial electrochemical processes are based on the parallel-plate electrode configuration, it was obvious to study the performance of EC in batch (Fig. 6) and continuous (Fig. 7) modes using this type of cell. The ease in scale-up makes the utilization of these cells appealing for industrial application.

4.3 Economic aspects

The focus of the present work was on investigation of the mechanism of contaminant removal from mining waters and development of EC-treatment concepts. However, in terms of implementing technology at pilot-scale, as well as future full-scale implementation, one of the critical steps is a techno-economical assessment of the electrocoagulation treatment of mining waters.

Total operating costs (Eq. 28) are considered to combine labor, maintenance and other fixed costs, together with those process specific costs such as energy and electrode consumption (Kabdaşlı et al., 2009, Lacasa et al., 2013).

$$Total\ operating\ costs = OC_c + C_{en,c} + C_{el,c} \quad (28)$$

The operating costs of EC-processes are dependent upon current, treatment time, type of electrode material and arrangement. The nature of the treated water, conductivity and pH may also influence the techno-economical assessment. To provide some preliminary estimation of the process specific operating costs and compare the economic performance of electrocoagulation with other alternative treatments, energy consumption and electrode material were investigated by Kobya *et al.* (2010). Additionally, Golder *et al.* (2007) and Oncel *et al.* (2013a) proposed to include to the cost calculation the cost of added electrolyte, or chemicals where suitable, within the overall cost calculation.

Based on those parameters, costs are calculated as following (Eq. 29)

$$OC_w = w \cdot C_{en,w} + W \cdot C_{el,w} \quad (29)$$

Energy and electrode consumptions for electrocoagulation process are calculated (Eq. 30, 31) based on Faraday's law

$$C_{en,w} = \frac{U \cdot I \cdot t}{V} \quad (30)$$

$$C_{el,w} = \frac{M \cdot I \cdot t}{z \cdot F \cdot V} \quad (31)$$

Generally, from a cost-effective point of view monopolar parallel electrode arrangement and iron electrodes are found to be more suitable for pilot and industrial scale application. However, the choice of process conditions is very site specific and preliminary investigation is always required. The application of aluminum electrodes and bipolar or series arrangement of electrodes may be beneficial when comparing electrocoagulation with other alternative treatment techniques.

5 Materials and methods

5.1 Water samples and chemicals

Synthetic mining waters samples (Articles I-IV) were prepared in accordance with typical Nordic mining waters. Contaminants concentrations were proposed based on the data available from public reports, literature reviews and communication with industry representatives. Analytical grade chemicals were used to prepare the solutions with the desired concentrations of SO_4^{2-} , NO_3^- , Cl^- , Cu^{2+} , Ni^{2+} , Zn^{2+} , NH_4^+ , CN^- . Synthetic mining waters compositions utilized during EC tests and chemical suppliers are given in Table 2. The water pH without adjustment was neutral and, water conductivity varied from 2.5 to 6.7 mS/m. Millipore water was used to prepare these synthetic waters.

Table 2. Compositions of synthetic mining waters used during EC tests and chemical suppliers.

Compound	Concentration, mg/L			Chemicals (I-III)	Chemicals (IV)
	1,000	2,000	3,000		
SO_4^{2-}	1,000	2,000	3,000	Na_2SO_4 (Merck KGaA)	Na_2SO_4 (Panreac Quimica SLU)
NO_3^-	20	40	60	NaNO_3 (Merck KGaA)	NaNO_3 (Panreac Quimica SLU)
Cl^-	100	200	300	NaCl (Merck KGaA)	NaCl (Panreac Quimica SLU)
Cu^{2+}	2	5	8	CuSO_4 (Merck KGaA)	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Panreac Quimica SLU)
Ni^{2+}	2	5	8	NiSO_4 (Merck KGaA)	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Panreac Quimica SLU)
Zn^{2+}	5	10	15	ZnSO_4 (Merck KGaA)	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Panreac Quimica SLU)
NH_4^+	10	20	30	NH_4Cl (Merck KGaA)	$(\text{NH}_4)_2\text{SO}_4$ (Panreac Quimica SLU)
CN^-	-	-	100	-	NaCN (Panreac Quimica SLU)

Electrocoagulation tests were also performed using real mining waters (Article III). Water samples were collected from a tailing pond of the Orivesi mine, Finland. Prior the experiments, intensive agitation was provided to ensure a uniform composition of water used. The values for monitored parameters are presented in Table 3. The initial pH value was 6.2, and conductivity was 5.6 mS/m.

Table 3. Initial concentration of monitored anions and cations of real mining waters (pH=6.2).

Compounds	Units	Concentration
SO ₄ ²⁻		2452.98
NO ₃ ⁻	mg/L	254.33
Co ²⁺		15.29
Ni ²⁺		9.28
Zn ²⁺	μg/L	397.54
Cu ²⁺		11.72
Cd ²⁺		2.09

5.2 Water treatment procedure

Two different electrochemical units, tank cell (Articles II, III) and parallel flow cell (Articles I, IV), were used to perform electrocoagulation treatment. Batch electrochemical tests (Articles II, III) were conducted in a jacketed Plexiglas-tank cell (Fig. 2). During the experiments water was agitated using a plastic curved blade turbine at a speed of 200 rpm, which corresponded to a tip speed of 0.84 m/s. A volume of 1,000 mL of synthetic (Articles II, III) or real (Article III) mining waters was treated during each test. The electrochemical cell was equipped with two pairs of iron (Articles II, III) or aluminum (Article II) electrodes. The total anode area was 168 cm². The distance between the electrodes was 10 mm.

EC-treatment with iron electrodes (Articles II, III) was performed at 1 A, 2 A and 3 A corresponding to the following current densities 6 mA cm⁻², 12 mA cm⁻², 18 mA cm⁻² respectively. Experiments using aluminum electrodes (Article II) were conducted under the currents 3 A and 5.3 A resulting in 18 mA cm⁻² and 31 mA cm⁻² respectively.

Batch (Articles I, IV) and continuous (Article I) electrocoagulation tests were performed in a single compartment parallel plate flow cell. The cell was equipped with one pair of iron (I, IV) or aluminum (Article IV) electrodes. The current densities applied during the batch tests were 30 mA/cm² (Article I) and 1, 10 and 100 A m⁻² (Article IV). Continuous EC tests (Article I) were conducted at 12.4 A h/dm³ and a circulation of solids generated during the process was applied to increase the solids concentration in the tank and enhance the efficiency of sulfate removal. A volume of 3,000 mL of sulfate-rich waters (Article I) and 2,000 mL of cyanide-containing mining waters (Article IV) were recirculated using a peristaltic pump at 90 mL/min (Article IV).

All electrodes were connected in a monopolar arrangement (Articles I-IV). Constant current was maintained using a laboratory power supply PS 3005 (Articles II, III) and Delta Elektronika ES030-10 (Articles I, IV). Before each run, both aluminum and iron electrodes were cleaned with a 4-10% HCl acid solution, followed by rinsing with tap-

and then distilled water. Sodium hydroxide and hydrochloric acid solutions of 0.1 M were used to adjust the pH of waters before EC-treatment.

5.3 Analytical methods

Water samples were allowed to settle, then filtered with a 0.2 μm syringe filter and contaminant concentrations monitored. The concentrations of sulfate, nitrate and chloride were measured with ion chromatography using a Dionex ICS-1100, equipped with an autosampler (Dionex AS-DV). The samples were diluted prior to analysis with an Hamilton Microlab 500 series automated laboratory dilutor (Articles II, III). Anion concentrations were measured using ion chromatography, with a Metrohm 930 Compact IC Flex coupled to a conductivity detector (Articles I, IV). Cyanide concentrations were determined by the silver nitrate titration method originally introduced by Ryan and Culshaw (Article IV).

The amount of solids generated was measured by weighting the electrodes before and after each test using laboratory analytical scales (Article II-III). Total iron concentrations were measured off-line with an inductively coupled plasma spectrometer (Liberty Sequential, Varian) according to standard methods (Articles I, IV). The content of dissolved metals were measured with ICP-MS (Agilent Technologies, Agilent 7900), samples were acidified prior to analysis (Articles II-III). X-ray diffraction (PANanalytical Empyrean XRD) and standard scanning electron microscopy (MERLIN SEM-Zeiss Gemini) were used to analyze the solids (Article III). All analytical data are post-processed using GrainClassifier v1.9, IncaMineral classification software developed at the Luleå University of Technology, for mineral identification, reporting mineral grades and chemical composition of the samples (Article III).

The pH was measured by a pH meter WTW pH 304i and conductivity was measured with a Labor-Konduktometer 703 (Articles II-III). A Sension+ MM150 Portable Multi-Parameter Meter from HACH was used for simultaneous measurements of pH and conductivity (Articles I-IV). The Total Organic Carbon (TOC) was determined using a Shimadzu TOC-VCPH analyzer. Moreover, hypochlorite was analyzed by titration with 0.001 M As_2O_3 in 2 M NaOH.

5.4 Statistical methods

Statistical design of experiments and regression modeling were utilized to investigate the effect of treatment parameters and their interaction on sulfate removal from mining waters by electrocoagulation. 3^k -full factorial design was conducted for the tests with iron electrodes, where k corresponds to the number of factors (Articles II-III) (Brereton, 2007). Three variables: sulfate concentration (X_1), initial pH of the solution (X_2) and applied current (X_3) were selected as study parameters for regression modeling. The levels were equally spaced and dedicated to the high (3 g/L, pH 10 and 3 A), intermediate (2 g/L, pH 7 and 2 A) and low (1 g/L, pH 4 and 1 A) values of the parameters. In total, 39 experiments

were performed, including repetition of combinations at high, intermediate and low factor levels.

The results from tests with synthetic mining waters treated by electrocoagulation with iron electrodes were used to build linear regression models. The regression modeling was performed using MATLAB® software (Jalalvand et al., 2019). Firstly, the results were fitted to the simplest linear regression model (Eq. 32). Secondly, the model was improved by adding interaction and quadratic terms (Eq. 33). Both models were evaluated in terms of their importance and significance applying the analysis of variance (ANOVA). Based on the ANOVA results the final model was developed.

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 \quad (32)$$

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_1X_2 + b_5X_2X_3 + b_6X_3X_1 + b_7X_1^2 + b_8X_2^2 + b_9X_3^2 \quad (33)$$

where Y is the response variable, b gives the coefficients of the model and X is a factor (parameter) variables.

6 Results and discussion

In order to assess the suitability of EC to the treatment of mining waters and study the mechanisms of sulfate and cyanide removal, laboratory scale experiments were performed using different reactor designs, operation modes and experimental conditions. The mechanisms for sulfate removal from mining waters by electrocoagulation were studied and proposed (Articles I-III). Initially, the comparison of batch EC performance for sulfate removal using iron and aluminum electrodes were performed, later the main relationships between sulfate removal and applied current, initial pH and sulfate concentration were obtained (Article II). Based on the results obtained, the model was developed to evaluate the significance of parameters and their interactions. The model was then validated using the results obtained during the treatment of real mining waters (Article III). The following step was the development of a new approach in treatment of sulfate rich water by combining continuous EC and solid particle recirculation (Article I). While investigating the coagulation mechanisms of cyanide removal, in Article IV, the performance of chemical coagulation and batch electrocoagulation were compared.

6.1 Parameters affecting process performance

6.1.1 Electrode material and solids formation

Electrode material is mainly related to the process costs, coagulant dosing and amount, as well as coagulation efficiency. The amount and type of solids formed during EC-treatment are mainly affected by the current applied, pH of the treated solution and nature of the electrolyte. Theoretical and experimental amounts of generated aluminum and iron were compared at different currents; in addition, the electrocoagulation efficiency with iron and aluminum electrodes for sulfate removal was studied (Article II). The amount of generated aluminum species exceeded, by two times, the quantity theoretically predicted by Faraday's law. The formation of iron species was in agreement with the quantity theoretically calculated, when assuming Fe^{2+} formation. At the same amount of coagulant formed, 54% of sulfate was removed during EC with iron electrodes, while the highest sulfate removal achieved with aluminum electrodes was 10%. Sulfate removal with aluminum electrodes at pH over 9 is hindered by the formation of negatively charged hydroxoaluminum ions that make the charge neutralization of negatively charged sulfate ions impossible.

The possible speciation of aluminum and iron containing solid species was investigated (Articles II, III and IV). During the electrocoagulation treatment with iron electrodes, among the possible iron compounds formed within the studied ranges of initial pH, RedOx and sulfate concentration are Fe_3O_4 , $\gamma\text{-FeOOH}$ and positively charged Fe^{3+} , FeOH^+ , $\text{Fe}(\text{OH})_2^+$, the most expected sulfate containing compounds were $(\text{H}_3\text{O})\text{Fe}(\text{SO}_4)_2(\text{H}_2\text{O})_3$ rhomboclase and its modifications (Casas, Crisóstomo & Cifuentes, 2005, Arden, 1951). The initially clear, colorless, solution became turbid with an orange suspension, typical for Fe (III) hydroxides, after 5 min and turned to brown-

green suspension at the end of the treatment. The same change in colors in the presence of sulfate ions was observed by Moreno *et al.* (2007).

Aluminum electrodes showed poor performance in terms of sulfate removal at the experimental conditions studied. Low removal of sulfate could be explained by speciation of aluminum species formed at a pH higher than 10 (Article II). The speciation of aluminum, electrocoagulation efficiency and process performance in terms of sulfate removal were studied by Nariyan *et al.* (2018). During the treatment of mining waters containing cyanide, the observed trajectory allow us to infer the presence of $\text{Al}(\text{OH})_3$ and $\text{Al}(\text{OH})_4^-$, the formation of negatively charged ions make charge neutralization of other negatively charged ions impossible, thus hindering the removal the contaminants studied (Article II, IV). Trajectories of coagulant-pH for iron and aluminum (Fig. 8) were studied for the electrocoagulation treatment of cyanide-rich waters at pH 12 (Article IV). The initially clear colorless solution became turbid, with a white-grey suspension typical for aluminum hydroxides.

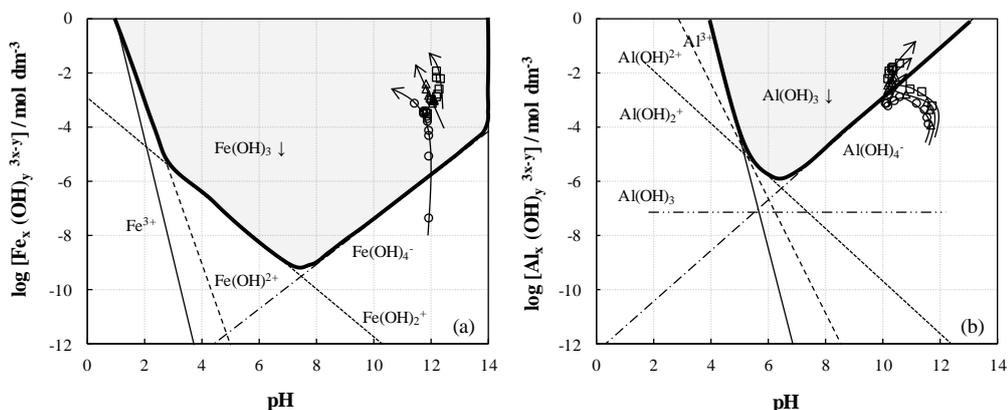


Figure 8. Coagulant-pH trajectory during electrocoagulation of synthetic mining water containing 100 mg CN^- L. Anode/Cathode: Fe/Fe (a), Al/Al (b). Current density: (○) 1 A m^{-2} , (Δ) 10 A m^{-2} , (□) 100 A m^{-2} (Article IV).

50% removal of cyanide is reached for 50 mg dm^{-3} of iron, regardless of the current density applied, whereas 40, 15 and 5% cyanide removal is achieved for the same dosage of aluminum during electrochemical coagulation at 1, 10 and 100 A m^{-2} , respectively. This fact means that iron is much more efficient than aluminum for the removal of cyanide from mining wastewater when coagulants are dosed by a sacrificial anode in the electrochemical coagulation processes, regardless of the current density applied, opposite to the behavior observed during chemical coagulation processes.

6.1.2 Current, pH and initial concentration

The effect of applied current and current density was investigated for sulfate and cyanide removal from mining waters (Articles I-IV). Sulfate removal was improved drastically

with an increase in applied current from 1 to 3 A. This observed trend is probably due to the formation of a greater quantity of solids. Complete cyanide removal using iron electrodes was registered with an almost negligible effect of current density applied. However, cyanide removal was significantly affected by current density during electrocoagulation with aluminum electrodes. Difference in the relationships between cyanide removal and current density when using iron and aluminum electrodes was likely due to the difference in mechanisms involved in the process.

During an electrocoagulation process, pH is a key parameter responsible for speciation and solubility of formed metal species as well as the removal mechanisms of the contaminants. The relationship between pH and removal of sulfate, as well as speciation of solids formed, was studied (Articles I-III). In case of sulfate removal, it was observed that after the first hour of batch EC-treatment, the pH value increased to over 11, regardless of the initial pH of the solution and applied current. Process operation for cyanide removal was limited to pH 12, due to safety reasons, so no effect of pH was studied; however, possible metal species formed during the process were investigated (Article IV).

The amount of coagulant needed was mainly influenced by the initial concentration of the contaminant. The influence of initial concentration on sulfate removal by electrocoagulation and the significance of this factor was studied (Articles I, II). A generally increasing trend, with the initial concentration decreasing from 3,000 to 1,000 mg/L was observed. Such a behavior may be explained by the greater amount of coagulant needed for the removal of sulfate at high initial concentrations.

6.1.3 Electrolyte type

Mining waters are known to contain high concentrations of Ca^{2+} , Mg^{2+} and Cl^- . The presence of Ca^{2+} and Mg^{2+} may result in quick passivation of electrodes and, hence, an increase in energy consumption. On the contrary, chloride ions may postpone passivation of electrodes, by pitting the oxide films formed on the surface of electrodes. To check the suitability of electrocoagulation to the treatment of mining waters, both synthetic and real solutions were used (Article III). The effects of the presence of other contaminants on sulfate removal was investigated during the tests with synthetic mining waters and solutions containing only SO_4^{2-} and Cl^- . With the increase of Cu, Zn and Ni concentration, the removal of sulfate was improved by 20%. This can be explained by the precipitation of metals sulfide within the studied ranges of final pH over 11 and RedOx below -0.2 V (Florence, 2015).

Real mining waters samples were treated by electrocoagulation to evaluate the suitability of electrochemical treatment for the removal of sulfate. According to the results presented in Table 4, electrocoagulation was found to be suitable for the partial removal of sulfate from both synthetic and real mining waters. This study demonstrates that sulfate can be removed to a concentration below current limits established in Finland and Chile (Nariyan, et al., 2018). The presence of Ca^{2+} (369 mg/L) and Mg^{2+} (89 mg/L) at the

concentration presented in the real waters had no notable effect on sulfate removal and process operation.

Table 4. Initial and residual concentration of monitored anions after 5 h of EC-treatment of synthetic and real mining waters (Article III).

Compounds	Source of water	Units	Initial concentration, mg/L	Residual concentration, mg/L		Removal efficiencies, %	
				2 A	3 A	2 A	3 A
SO ₄ ²⁻	synthetic		2052.50	1321.82	1356.07	36	34
SO ₄ ²⁻	mining	mg/L	2968.68	1994.19	2139.34	33	28
NO ₃ ⁻	waters		58.25	<0.5	<0.5	>99	>99
SO ₄ ²⁻	real		2452.98	1766.15	1622.55	28	34
NO ₃ ⁻	mining	mg/L	254.33	9.02	3.59	96	99
	waters						

6.1.4 Operation mode

Electrocoagulation operating modes influence the energy consumption, volumes of treated waters, operation pH and thus affect the process performance. Comparison of electrocoagulation under batch and continuous operation was performed (Article I). Due to poor performances of EC-treatment with aluminum electrodes, it was decided to design the treatment process using iron electrodes (Articles I, II). Considering future scale-up of the equipment, it was agreed to use parallel flow cell, due to its relatively easy sizing and construction.

Initially, it should be highlighted that during batch electrocoagulation the operation pH was increasing rapidly to the vicinity of 10 while, during continuous operation EC, the pH of the solutions remained almost unchanged. This observation allowed conclusions to be made about possible differences in the performance of electrocoagulation while operating in different modes. The highest sulfate removal, of 20%, was observed at pH 2 when operating at batch mode. Removal of sulfate was significantly improved by a novel EC strategy developed, based on continuous operation and solids recirculation. This was achieved through connecting a sedimentation tank to the EC-cell, promoting the flocculation process. This modified electrocoagulation process was based on the coagulation processes typically applied in the treatment of surface water, in which the flocculation enhancement by concentration of coagulants is known to increase the efficiency of the technology. The highest removal efficiency, of over 60%, was achieved at pH 2 (Fig. 9), illustrating the pivotal role of pH during the process. Accumulation and circulation of solids provided higher solid concentrations ranging from 1.1 to 1.4 mol/dm³, promoting enmeshment.

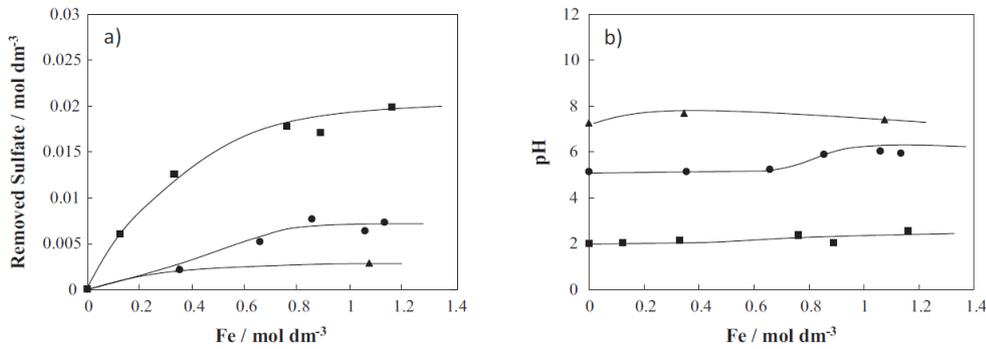


Figure 9. Continuous EC-treatment of mining waters a. removed sulfate at ■ pH2, ● pH5, ▲ pH7 b. changes in pH (Article I).

6.1.5 Repeatability of experiments

An objective of the repeatability tests was to quantify the agreement of the results obtained during the EC tests. The repeatability results support and prove the quality of the whole data set produced during the research work. In this work, the central point (initial sulfate concentration 2,000 mg/L, pH 7, current 2 A) of 3³-full factorial design has been chosen to check the repeatability during the EC experiments with synthetic mining waters. Tests were performed with the repeatability condition of measurement meaning that measurements were performed over a short period using the same operator, same measuring system and same operating conditions.

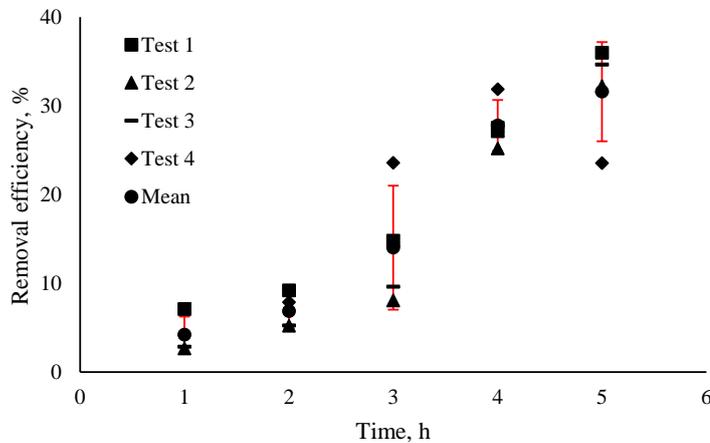


Figure 10. Variation of sulfate removal efficiency during the repeated EC tests with synthetic mining waters $C_0 = 2,000$ mg/L, pH 7, current 2 A and Fe electrodes (Article II).

Results presented in Fig. 10 correspond to sulfate removal efficiency versus time during the repeatability tests. Test 1, Test 2 and Test 3 took place during three subsequent days and new iron electrodes were used as anodes and cathodes, while Test 4 was performed

after 11 more experiments at various operational conditions. The results of Test 1, Test 2 and Test 3 agreed since the behaviour of sulfate removal graphs was repeatable. Possible roughness of the electrode surface and thus the increase of electrode's surface area resulting in more efficient iron dissolution already after 3 h of treatment may result in the discrepancy of results for Test 4 after 3 h of treatment.

6.2 Quality of the regression model

An empirical model to predict the residual sulfate concentrations was developed using response surface methodology (RSM) (Khuri, Mukhopadhyay, 2010). The proposed final model (Eq. 34), valid within the variable range of parameters investigated, is as follows:

$$C_{fp} = 0.44 + 1.16 C_0 - 0.62 I - 0.17 C_0 I - 0.17 I pH_0 + 0.20 I^2 \quad (34)$$

Comparison of modeled and experimental data (Fig. 11) suggests a good prediction of final sulfate concentration by the studied regression model. In a qualitative consideration, it can be seen from the charts that the linear regression model reproduced experimental results well. The goodness of fit criteria, R^2 , was equal to 0.98. The relative difference between the calculated and experimental values did not exceed 10% for most of the experiments.

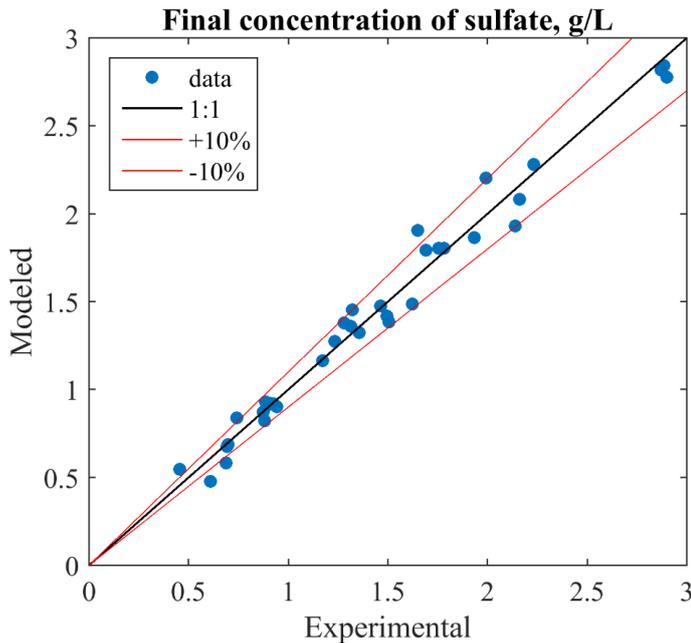


Figure 11. Measured and predicted values of the developed model for final sulfate concentration (Article III).

To verify the model developed using the experimental results obtained with synthetic mining waters, results from the tests with real mining waters were fitted to the model (Table 5). In addition, results of electrocoagulation treatment of real mining waters reported by Nariyan *et al.* (2018) were fitted to the model. Validation of the model, using the results of real mining waters under EC-treatment, demonstrated that the developed model could be used to predict the final concentrations well, especially at high currents, resulting in a decrease in the number of laboratory scale tests required to design equipment.

Table 5. Measured and predicted values of final sulfate concentrations and removal efficiencies obtained during the EC-treatment of real mining waters (Article III).

Current, I , A	3	2
Initial pH, pH_0	6.13	6.25
Initial concentration, C_0 , mg/L	2349.00	2440.00
Final concentration, C_{fe} , mg/L	1623.00	1766.00
Predicted final concentration, C_{fp} , mg/L	1609.79	1795.88
Predicted removal efficiency, R_e , %	31	26
Measured removal efficiency, R_f , %	31	28

6.3 Sulfate removal

Sulfate removal from mining waters was systematically studied using the results obtained from several experimental setups and different process conditions. The effect of applied current, initial pH, initial sulfate concentration and electrode material on sulfate removal by electrocoagulation was investigated (Article II). The significance of factors affecting the electrocoagulation process for sulfate removal from mining waters was studied (Article III). In addition, a comparison of electrocoagulation treatments of synthetic and real mining waters was performed (Article III). A novel concept for sulfate-rich waters treatment by electrocoagulation was developed based on continuous operation and recirculation of solids (Article I).

Table 6. Removed sulfate and final pH values of the solution during EC tests with iron electrodes at different applied currents, initial pH and concentrations (Article II).

Initial pH	Concentration, mg/L	Applied current					
		1 A		2 A		3 A	
		<i>R</i> , %	<i>pH_{fin}</i>	<i>R</i> , %	<i>pH_{fin}</i>	<i>R</i> , %	<i>pH_{fin}</i>
pH 4	1,000	7	11.27	10	11.69	24	10.57
pH 7		10	11.34	29	11.73	28	11.17
pH 10		10	11.31	38	11.84	54	11.78
pH 4	2,000	16	11.89	25	11.97	21	11.95
pH 7		2	10.98	35	12.01	31	11.96
pH 10		10	11.64	37	12.17	40	11.96
pH 4	3,000	1	10.97	24	12.16	51	12.4
pH 7		2	11.22	33	12.21	27	10.02
pH 10		2	11.17	27	12.14	43	12.26

Electrocoagulation treatment for sulfate removal was studied using two reactor configurations: a tank cell and parallel flow cell. Batch operation in both cases resulted in an increase of pH of the treated solution to the vicinity of 10, meaning that process took place under caustic conditions regardless of the initial pH and applied current. Residual sulfate concentration was lowest when current increased up to 3 A, initial pH was 10 and initial sulfate concentration was 1,000 mg/L. Poor process performance was observed at current 1 A and initial sulfate concentration 3,000 mg/L, regardless of the initial pH. The summary of experimental results obtained from experiments in the tank cell is given in Table 6. The influence of pH and iron dosage, as well as change in pH during the electrochemical treatment using parallel flow cell are shown in Fig. 12.

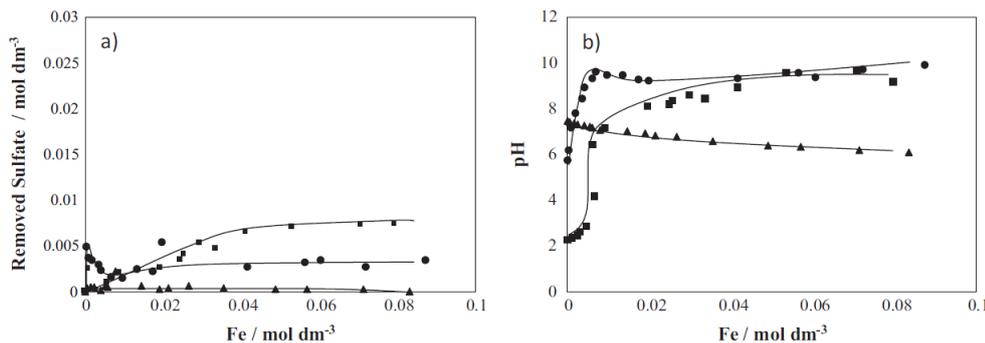


Figure 12. Batch EC-treatment of mining waters a. removed sulfate at ■ pH2, ● pH5, ▲ pH7 b. changes in pH (Article I).

Application of iron electrodes were found to be beneficial for the removal of sulfate. The removal efficiency with aluminum electrodes was 5 times lower, compared to the

performance achieved with iron electrodes (Fig. 13). Among the reasons for such a behavior are the increase in soluble negatively charged hydroxoaluminum ions at pH values higher than 9.

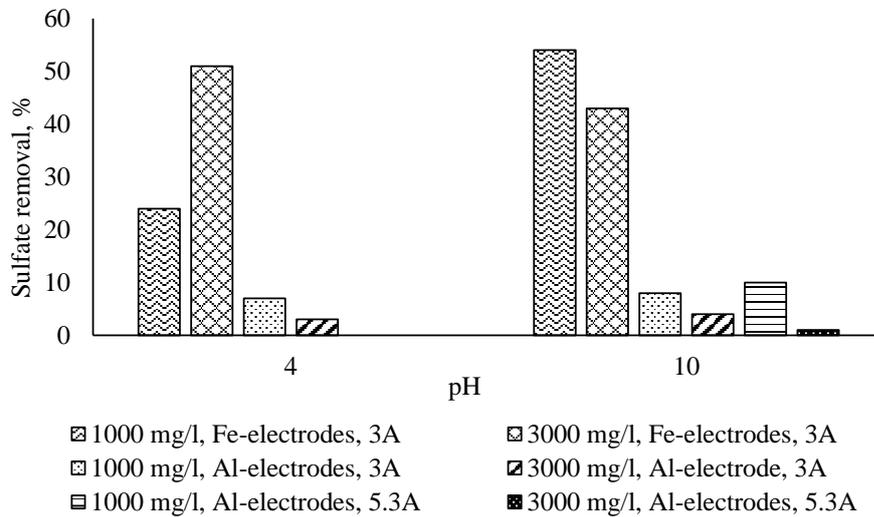


Figure 13. Comparison of sulfate removal from tested waters treated by EC using aluminum and iron electrodes at chosen experimental conditions (Article II).

When developing an empirical model, ANOVA analysis revealed the insignificance of pH_0 during batch operation. The most significant parameters affecting the removal of sulfate from mining waters were initial concentration of the contaminant and applied current, pH_0 was considered as significant only an interaction with applied current. In general, with the increase of the linear term of applied current and interaction terms, the adverse effects were observed resulting in higher removal of sulfate from mining waters. The positive effect of the linear term of initial sulfate concentration and square term of applied current resulted in lower sulfate removal rates with the increase of these factors.

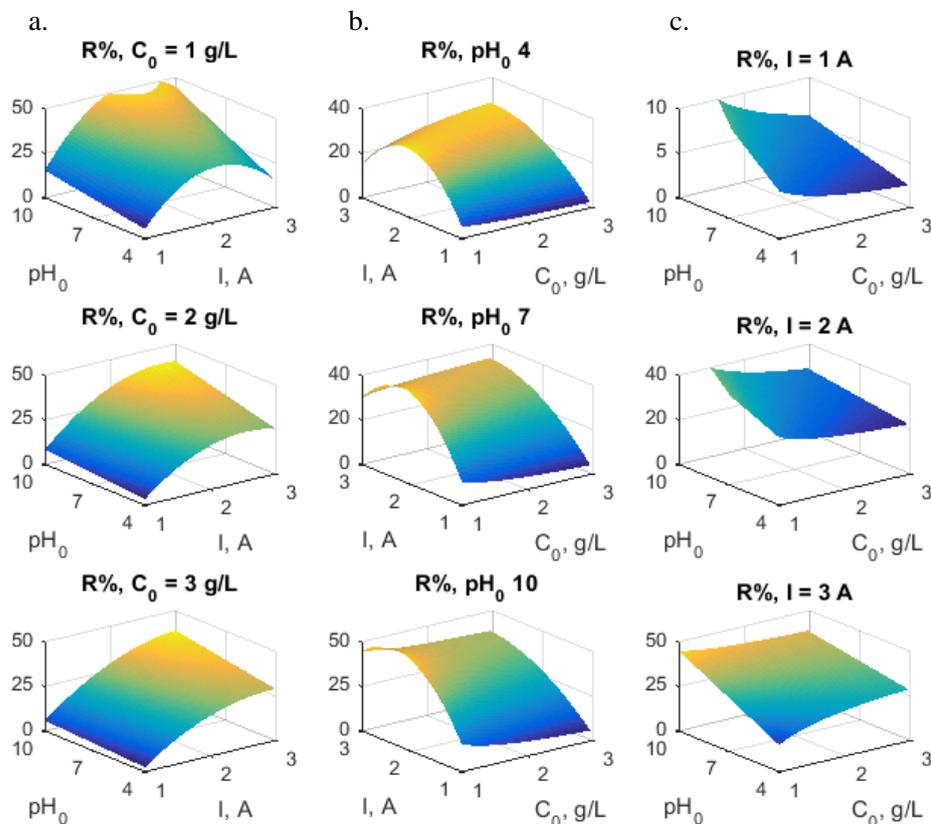


Figure 14. Surface plots of sulfate removal predicted by the developed model at the corner points: a. at fixed initial concentrations, b. at fixed initial pH, c. at fixed applied current (Article III).

Surface plots in Fig. 14a demonstrate that a combination of high applied current and high initial pH resulted in a more efficient removal of sulfate. This is due to the higher quantity of solids formed and the speciation of the metal species generated during electrocoagulation. Surface plots in Fig 14b. demonstrate that sulfate removal with EC was improved at an applied current above 2 A and concentrations lower than 3,000 mg/L. Fig 14c. illustrated that an increase in pH resulted in an improvement of sulfate removal. More efficient sulfate removal for lower concentration at selected applied current may be due to the greater amount of the coagulant available.

6.4 Cyanide removal

To describe in detail the removal mechanism of cyanide involved in the electrochemical treatment process, chemical coagulation and electrocoagulation tests were performed. In

addition, the effect of electrode material, current density and the presence of other contaminants on cyanide removal from mining waters were investigated (Article IV).

When comparing chemical and electrochemical coagulation, performances of the processes differed greatly. Thus, during chemical coagulation the removal of cyanide was limited to 15% and use of an aluminum coagulant resulted in better elimination of cyanide. Results from electrochemical coagulation revealed an improvement in removal of cyanide, with almost complete removal achieved using iron electrodes and 60% removal obtained using aluminum electrodes. Among the reasons describing the enhancement through using electrochemical treatment are the possible mechanisms involved in the process. The primary mechanism of cyanide removal during chemical coagulation was proposed to be adsorption, for both aluminum and iron coagulants, while during electrocoagulation other mechanisms were encountered resulting in significant improvement of cyanide removal from mining waters. Apart from adsorption, other mechanisms involved in cyanide removal were enmeshment into a floc, particle charge neutralization and, in the case of iron electrodes, the formation of metal-cyanide complexes was proposed. Mechanisms of cyanide removal from mining waters by electrocoagulation are drawn schematically in Fig. 15.

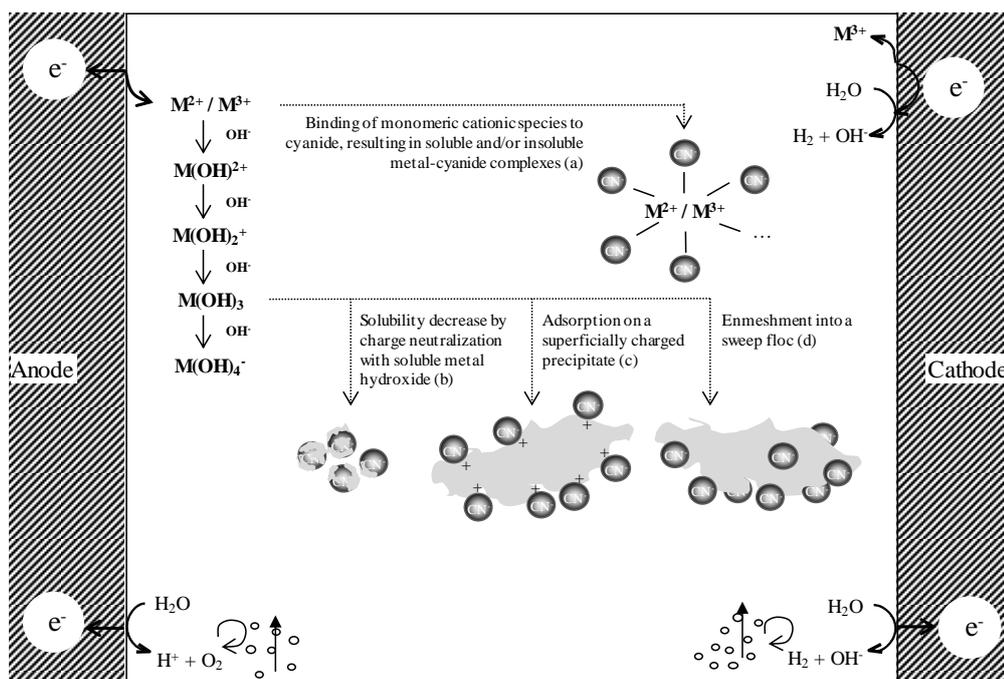


Figure 15. Mechanisms of cyanide removal from synthetic mining wastewater during electrocoagulation. Anode/Cathode: Fe/Fe (a, c, d), Al/Al (b, c, d) (Article IV).

With an increase in current density, the removal of cyanide using iron electrodes was slightly improved, meaning that there was an almost negligible effect of current density. In contrast with electrocoagulation using iron electrodes, the process performance

utilizing aluminum electrodes was found to be current density dependent and cyanide removal decreased with an increase in current density. Iron electrodes were found to be more efficient in terms of cyanide removal, at the experimental conditions studied. The negligible effect of current density when using iron electrodes meant that process operation is possible with low current, leading to low energy consumption.

In the presence of Cl^- and NH_4^+ ions in the mining waters the formation of ClO^- was detected, however, hypochlorite did not undergo further oxidation to chlorate or perchlorate. Chloramines detected in the analyzed water were the products of the chemical reaction of hypochlorite and ammonium. The presence of Cu^{2+} , Zn^{2+} and Ni^{2+} in the treated water might improve the removal of cyanide by complexation. No straight effects of other contaminants on cyanide removal, as well as formation of toxic species such as chlorate, perchlorate or cyanate were detected.

7 Conclusions

The suitability of electrocoagulation for the removal of sulfate and cyanide from mining waters was studied. Sulfate and cyanide removal mechanisms were determined through considering various parameters. Comparisons of chemical coagulation and electrocoagulation were provided in order to deeply understand the removal mechanisms of the contaminants. In addition, to improve the performances of electrocoagulation processes in terms of sulfate removal, a novel approach, combining continuous EC and accumulation/recirculation of solids, was proposed and successfully tested. Special attention was paid to the formation of toxic and harmful contaminants during the removal of cyanide by electrochemical treatment; this aspect of toxic contaminant removal from mining waters is rarely studied.

Considering the main goal of present work, the mechanisms of sulfate and cyanide removal from mining waters was studied. Thus, at neutral and basic conditions, the primary mechanisms for sulfate removal are enmeshment in iron oxide and hydroxide and charge neutralization due to the excess of positively charged iron species. At acidic conditions, sulfate is expected to be primarily removed by charge neutralization, while the secondary sulfate removal mechanism is assumed to be precipitation. Electrocoagulation mechanisms involved in cyanide removal are reduction of cyanide solubility by charge neutralization with aluminum soluble metal hydroxide, adsorption onto a superficially charged metal precipitate and enmeshment into a sweep metal floc. When iron electrodes are used for the treatment of cyanide-containing water the formation of soluble and insoluble iron-cyanide complexes is expected.

The suitability of electrocoagulation to treat mining waters was assessed and the influence of operating parameters studied. The utilization of iron electrodes was found to be more efficient for the removal of both sulfate and cyanide within the range of studied parameters. When operating in batch mode, it was observed that the lower the initial concentration of sulfate, the more efficient the removal, however, the influence of initial pH was found to be insignificant. No significant effect of current density on cyanide removal by electrocoagulation with iron electrodes was observed. Current densities not exceeding 10 A m^{-2} and iron as the electrode material are suggested for further development and assessment of the technique. Generally, electric charge was suggested as one of the main scale-up parameters as it can serve when switching from batch to continuous operation.

A continuous EC-treatment approach, design during this work, with a recirculation of solids allows 70% removal of sulfate at electric charge 12.4 A h dm^{-3} and initial pH 2. For further investigation and techno-economic assessment, continuous electrocoagulation with iron electrodes is suggested.

In general, knowing the removal mechanisms involved in electrocoagulation when treating mining waters for metals, nitrate, sulfate, phosphate and cyanide make it possible to draw conclusions about the suitability and great potential of the technique to treat mining waters in future. However, there are several other aspects to be considered before EC can be used at industrial scale. Among these are studies on the properties of the solids formed during electrocoagulation as well as dewatering, utilization and valorization of the slurry produced. Technoeconomic and environmental assessment is needed to draw conclusions about possible costs, risks, footprints and benefits. Special attention should be paid to the selection of scale-up parameters and process modeling to bring the technology over TRL 7.

It would be valuable to study the effect of particle properties on possible dewatering techniques such as pressure filtration, magnetic-separation, centrifugation or dissolved air flotation. Moreover, recovery of valuable compounds from the slurry formed can be considered as one future research topic. Possible uses of the generated slurry are as one of the components of a fertilizer, concrete or geopolymers. At metal mines, when applying electrocoagulation with iron electrodes, the slurry formed during the process can be reused in the metal production process, making the mining operation sustainable and meeting all the needs of the circular economy.

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Removal of sulfate from mining waters by electrocoagulation



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ABSTRACT

This work focuses on the removal of sulfate from mining waters by using electrocoagulation with iron electrodes. A comparison of the results obtained by electrocoagulation with those obtained with the application of conventional chemical coagulation is provided. The results show that sulfate can be removed from synthetic mining waters by electrocoagulation, and that the pH and coagulant dosage play a very important role. During chemical coagulation under acidic conditions, it is possible to use a low dosage of iron and remove more than 80% of the sulfate present in water. However, chemical coagulation seems to behave as a kind of ion-exchange process (from the viewpoint of effluent quality). Thus, significant concentrations of accumulated chloride (counter ion of iron in the coagulant added) prevents the use of the technology. This problem is avoided by the application of electrocoagulation, which attains good efficiencies that can be even increased by using a continuous process with a flocculation tank. This technology also helps to remove other ionic pollutants contained in the wastewater.

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1. Introduction

The mining industry is the major producer of sulfur-rich wastewater streams [1]. The effluent emanating from mineral excavation and processing contains high sulfate concentrations. Not only, but also sulfur-rich streams come from working and abandoned mines that are continuously discharging mine drainage into surface water and groundwater [2]. The occurrence of sulfate is associated to the oxidation of the sulfur contained in the sulfides (MeS₂) when the drainage is exposed to fresh water and oxygen [3,4].



This drainage contains typically from tens to thousands mg dm⁻³ of sulfate, although its characteristics change as a function of the chemical composition that the water passes through [5,6]. In the literature, the pH of mining drainage has been found to vary, depending on the elements mined and the conditions at the mining sites. In fact, it has been proposed that mine drainage may be divided into three categories according to its acid/base properties

[7]. These categories have been named as acid, neutral and saline mine drainage. Of these, many researchers suggest acid mine drainage as the major problem associated with the mining industry due to its toxicity [2,8].

The presence of high concentrations of sulfate ions can lead to environmental issues, which are also related to many other problems [9]. Sulfate ions are known to be the reason for the aggressiveness of water to concrete [10]. They may also cause laxative effects (associated to the ingestion of water containing more than 500 mg dm⁻³). Because of that, the presence of sulfate ions in water is a major environmental issue in many countries, wherever mining has been practiced on a large scale.

There are several technologies for the treatment of water containing sulfate anions, such as biological degradation [11–13], membrane filtration [14,15], adsorption and/or ion exchange [16–19], and precipitation with limestone [20] or hydrolysed aluminum [9,21]. Several of these technologies are combined with chemical coagulation processes. They are not very efficient, however, because the removal of sulfate ions is not easy due to their high solubility and stability in aqueous solutions.

In this context, electrocoagulation technologies have been proposed as promising technologies for the removal of sulfate anions from industrial wastewater (not mining waters), within a sulfate

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concentration lower than 250 mg dm^{-3} [22–26]. To the present authors' knowledge, the main advantage of this process is the lower amount of counter ions added, compared to the conventional coagulation technology [27]. Thus, the net reagent dosed during electrocoagulation is iron or aluminum hydroxide (metal cations produced at the vicinity of the anode and hydroxide anions produced on the cathode surfaces), which is transformed into many other species in well-known reactions associated to the pH. Still, in the case of chemical coagulation, these hydroxides cannot be added directly because their low solubility would make the addition unprofitable [28,29]. This fact explains the addition of salts as coagulant reagents for conventional coagulation, for which the counter ion may be considered as a pollutant. Then, coagulation for the removal of sulfate behaves in a certain way as an ion exchange process (from the viewpoint of the effluent quality), because the net effect seen is the removal of sulfate and the appearance of the counter ion of iron or aluminum in the added salt.

Other advantages of electrocoagulation are the robustness, easy automation and low energy requirements that allow the processes to be powered by green energy sources such as solar panels, wind mills or fuel cells [30,31]. The primary aim of this work is to evaluate the performance of two electrocoagulation processes for the removal of sulfate from mining waters and to compare the results attained with those that can be obtained by the well-known chemical coagulation processes. Influence of the treatments evaluated on the removal of other ions (such as metals) is also briefly described because they can also be considered as important side processes of the treatment of mining waters, although they are not the goal of this work. To the authors' knowledge, only one previous research has been done to study the possibility of sulfate removal from this type of wastewater with this technology [26]. However, this study is not only focused on the removal of sulfate by electrocoagulation and does not compare the results between chemical and electrochemical coagulation.

2. Material and methods

2.1. Chemicals

The copper sulfate, nickel sulfate, zinc sulfate, sodium sulfate, ammonium chloride, and sodium chloride used for preparing the sample solutions in the study, were of analytical grade and purchased from Panreac Química S.A. (Barcelona, Spain). Double deionized water (Millipore Milli-Q system, resistivity: $18.2 \text{ M}\Omega \text{ cm}$ at 25°C) was used to prepare all solutions. The chloric acid and sodium hydroxide that were used to adjust the pH of the solution, were of analytical grade and supplied by Panreac Química S.A. (Barcelona, Spain). All the chemicals were used without further purification.

2.2. Synthetic mining water

The initial concentrations of ions to prepare synthetic mining wastewater were $3.125 \cdot 10^{-2} \text{ mol dm}^{-3}$ of SO_4^{2-} , $9.677 \cdot 10^{-4} \text{ mol dm}^{-3}$ of NO_3^- , $8.463 \cdot 10^{-3} \text{ mol dm}^{-3}$ of Cl^- , $1.259 \cdot 10^{-4} \text{ mol dm}^{-3}$ of Cu^{2+} , $1.363 \cdot 10^{-4} \text{ mol dm}^{-3}$ of Ni^{2+} , $2.294 \cdot 10^{-4} \text{ mol dm}^{-3}$ of Zn^{2+} and $1.667 \cdot 10^{-3} \text{ mol dm}^{-3}$ of NH_4^+ . These values were selected by taking account of the typical properties of mining waters in several Nordic mines.

2.3. Analytical procedures

Sulfate ions were analysed by using ion chromatography with a Metrohm 930 Compact IC Flex coupled to a conductivity detector.

A Metrosep A Supp 7 – 250/4.0 column was used for anionic separation, and it was packed by polyvinyl alcohol with quaternary ammonium groups. The mobile phase consisted of 85:15 v/v 3.6 mM Na_2CO_3 /acetonitrile, and its flow rate was $0.8 \text{ cm}^3 \text{ min}^{-1}$. The temperature of the oven was 45°C , and the volume injection was $20 \mu\text{L}$. Peaks were identified and quantified by using MagIC Net 3.1. Total iron concentrations were measured off-line with an inductively coupled plasma spectrometer (Liberty Sequential, Varian) according to a standard method [32] (plasma emission spectroscopy).

2.4. Experimental setup

Batch coagulation and electrocoagulation tests were carried out in bench-scale plants described elsewhere [33–35] for the removal of other inorganic species. For continuous electrocoagulation, a modification of the bench scale plant was carried out. This change consisted of concentration of the sludge coming from the flocculation process in a settler in order to enhance the efficiency of sulfate removal. In the latter case, the plant was operated in continuous mode, and pump recycling was used to improve the mixing conditions in the settler (Fig. 1). The interactions between sulfate and the coagulant were favored, and thus the subsequent removal of sulfate.

3. Results and discussion

3.1. Chemical coagulation

In evaluating the performance of electrocoagulation in mining waters, it is important to study first what happens during the chemical coagulation of these effluents, because coagulation is a much simpler process than electrocoagulation and it can give us important information for understanding the electrochemical technology.

It is worth noting that the removal of anions is not a common application in the coagulation treatment, except for cases in which the solubility of the salt resulting from the interaction of the anion with the coagulant reagent is very low. For this reason, its application in mining water treatment is not a highly documented topic. In fact, as pointed out in the introduction, this technology is expected to behave in a certain way as an ion exchange process (from the viewpoint of the effluent quality), because the positive effect searched for (removal of the sulfate anions) is compensated partially with a non-desired effect: an increase in the concentration of the counter ion added with the coagulant [27,36].

As to chemical coagulation, it is a well-known fact that there are two important inputs that influence its efficiency: the pH and dose of the coagulant. Fig. 2 shows the influence of both on the removal of sulfate from the studied synthetic mine wastewater. For the sake of clarity, the five tests carried out (corresponding to different pHs) have been plotted in two separate graphs, one for the acidic conditions (part a) and the other for neutral and alkaline conditions (part b) in order to see the differences obtained with the dosage clearly. FeCl_3 was used as the coagulant, and the time for coagulation, flocculation and sedimentation steps was 1 h for each.

As can be seen in the figure, there is a relevant difference between the results obtained in the range of acidic pHs and those obtained at neutral or alkaline conditions. The increase in the removal of sulfate is progressive in the case of neutral and alkaline wastewater. However, an opposite behavior is observed at pH 2, where a maximum with higher removal of sulfate than that obtained at large doses is observed within a range of low dosage of coagulant. This clearly indicates that two removal mechanisms coexist for the acidic conditions, while for neutral or alkaline con-

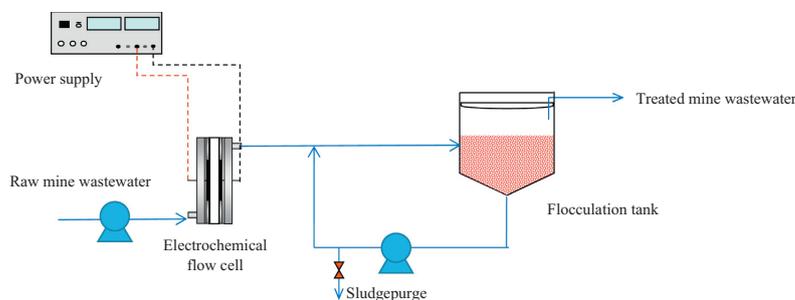


Fig. 1. Continuous electrocoagulation process with enhanced flocculation.

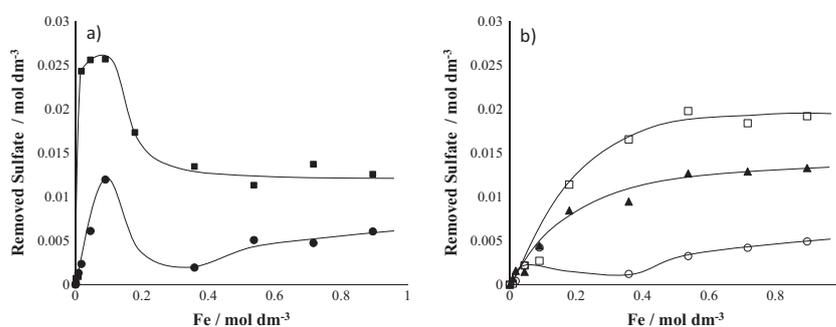


Fig. 2. Influence of the pH and dose of the iron coagulant on the removal of sulfate from synthetic mining water. $[SO_4^{2-}]_0$: $3.125 \cdot 10^{-2}$ mol dm⁻³; (■) pH 2; (●) pH 5; (▲) pH 7; (□) pH 9; (○) pH 12.

ditions only one single mechanism is responsible for the removal of sulfate.

This type of behavior is well-documented for coagulation processes [37–39], and it is explained in terms of iron speciation, which in turn is known to be affected by the pH. At acidic conditions, there are many cationic species that can interact electrostatically with the anions presented in the waste, while at neutral and alkaline pHs, amorphous iron hydroxide precipitates are considered to be the primary coagulant species. These precipitates can be positively or negatively charged by the adsorption of hydroxometallic ions onto the surface, and this surface charge can modify the possibilities for the fixation of sulfate ions significantly.

Taking this expected speciation into account, the maximum removal observed in the tests carried out at acidic conditions (for iron dosages in the range 0.017–0.090 mol dm⁻³) has to be explained in terms of precipitation of the sulfate with the added iron (not excluding other coagulation mechanisms). From the values of the maximum concentrations of sulfate removed from the synthetic mining water (range from 0.011 to 0.025 mol dm⁻³) and from the concentrations of iron required to attain this maximum removal (range from 0.017 to 0.089 mol dm⁻³), it can be drawn that the stoichiometry for this highly-efficient removal is optimum at the iron/sulfate molar ratio ranging from 1:3 to 3:1, which may suggest the formation of different species from Fe₂(SO₄)₃, and also the coexistence of other coagulation mechanisms. Anyhow, the maximum removal obtained at pH 2 was 0.025, which means that more than 80% of the initial sulfate content (0.031 mol dm⁻³) can be removed successfully with iron

coagulants. The decrease in the removal efficiency observed at a higher dose of iron has to be explained in terms of promotion in the formation of hydroxometallic species of iron with a higher solubility at the pH conditions attained.

The more efficient removal with low dosages of the iron coagulant was not observed during the experiments carried out at neutral and alkaline conditions. Only a progressive increase with stabilization in the removal of sulfate in the range of iron dosage from 0.4 to 1.0 mol dm⁻³ was observed. This progressive increase was also noticed in the experiments carried out at acidic conditions at iron dosages over 0.4 mol dm⁻³, where the previously described effects of the neutralization mechanisms seemed to be less important. In this case, bulky iron hydroxide precipitate formation was observed clearly, and hence, the results have to be explained in terms of entrapping of the sulfate ions into the iron hydroxide growing precipitates, either by adsorption or by ion exchange. The higher efficiencies observed for pH 7 and 9 can be explained in terms of a more efficient formation of iron hydroxide precipitates in this range of pHs. On the other hand, the very low efficiency observed at pH 12 can be explained in terms of the expected very negatively charged surface of the iron hydroxide, which in turn is associated with the adsorption of iron hydroxoanions, which prevents the adsorption of sulfate.

One important drawback, pointed out above, was the significant amount of chlorides ions expected to be contained in the effluent of the coagulation tests. Chloride is the counter ion of iron in the added coagulant salt, and this expectation can be seen as confirmed in Fig. 3.

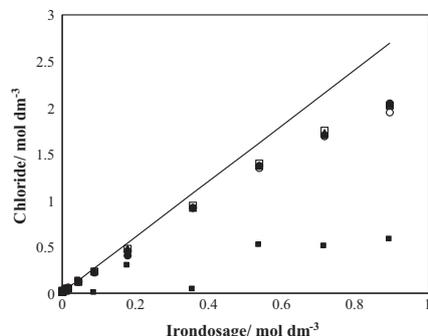


Fig. 3. Chloride concentration in mining wastewater after coagulation tests. (■) pH 2; (●) pH 5; (▲) pH 7; (□) pH 9; (○) pH 12. The continuous line represents the concentration expected according to the dose if no coagulation processes are expected.

As can be seen in the figure, for the five studied pHs, there is an increase in chloride concentration with the increased dosage of the coagulant. This concentration is below the stoichiometric value added (showed by the continuous line), confirming that from the point of view of the occurrence of ions in treated water, chemical coagulation behaves in a certain way as an ion exchange process, because the removal of sulfate is partially compensated with the appearance of chlorides (in a non-stoichiometrical way, which is a very important difference). Hence, chemical coagulation has serious weaknesses for the treatment of mining water from the environmental point of view.

When comparing the effect of the pHs, it can be clearly seen that as the concentration of the dosed iron increases, the difference between the added and measured chlorides is higher at any pH. This may be explained in terms of the adsorption of chloride onto the growing iron hydroxide precipitates. There are no differences within the range of pH 7–12, but it is important to point out the very high removal of chloride at pH 2, which suggests that chlorides may be involved in the removal of sulfates by precipitation with iron species. This helps to explain the variable stoichiometry found between the sulfate and iron for removal at optimum conditions. Regarding other ions contained in the synthetic mine drainage, Table 1 shows their concentration before and after the coagulation treatment with an iron dosage corresponding to the optimum conditions in acidic tests for the removal of sulfate.

As can be seen, there is a significant decrease in the concentration of the selected ions in the mine drainage waste. As expected, the removal is more efficient in the case of cations than in the case of nitrates, and is particularly important for copper and zinc, which is also a clear indicative of the formation of different insoluble salts, and which may help to explain the variable stoichiometry found for the optimum conditions. It is also important to point out that nitrates are removed but at less important concentrations than sulfate.

Table 1
Concentration of selected ions before and after coagulation with 0.089 mol dm⁻³ of iron.

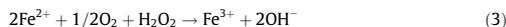
	Raw mine ww	Mine ww coagulated at pH 7	Mine ww coagulated at pH 5	Mine ww coagulated at pH 2
NO ₃ ⁻ /mg dm ⁻³	60.00	50.28	49.54	54.29
NH ₄ ⁺ /mg dm ⁻³	30.00	8.63	8.31	9.62
Cu ²⁺ /mg dm ⁻³	8.00	0.30	0.17	7.62
Ni ²⁺ /mg dm ⁻³	8.00	2.97	3.04	2.85
Zn ²⁺ /mg dm ⁻³	15.00	2.74	4.41	6.60

3.2. Electrochemical coagulation

Having characterized the coagulation process, Fig. 4 shows the removal of sulfate from synthetic waters with initial pHs 2.0, 5.0 and 7.0 in batch electrocoagulation tests carried out at 30 mA cm⁻². At this point, it is worth mentioning that during electrocoagulation, it is not practical to dose large amounts of iron, because sacrifice electrodes can be exhausted very rapidly, and hence, the technology may become less competitive. For this reason, only optimum conditions were looked for. This explains why only tests with acidic wastewater were planned for until iron doses of 0.1 mol dm⁻³ (optimum conditions for sulfate removal during chemical coagulation). The aim was to remove as much sulfate as possible with the lowest amount of iron. In turn, this would produce the lowest amount of sludge and minimize the costs of sludge treatment and solid-liquid separation. Likewise, the current density was selected based on the production of a specific iron concentration in the liquid phase by the electrodisolution of the anode i.e. a value that allow to generate at least 0.1 mol dm⁻³ of iron [40]. However, it is important not to forget that changes in the pH during electrocoagulation are important, and this is one of the most important features of electrocoagulation technology, as compared to the conventional coagulation technology [27,36].

As can be seen in Fig. 4, the pH of the wastewater has a crucial role in the results, and the most efficient treatment was attained when electrocoagulation was applied to the synthetic waters with the initial pH of 2, although, as can be seen in part b, this pH rises rapidly to the vicinity of 10. The same behavior was obtained in the test carried out with synthetic waste with the pH of 5, although in this case the pH 10 conditions were reached in a shorter time. On the other hand, the performance of electrocoagulation at pH 7 was very inefficient, and very low removals were attained.

The experiments were carried out in a discontinuous mode, and as can be seen, after 4 h of operation, no great changes were observed in any of the three tests. This observation indicates that specific electric charges over 3.0 A h dm⁻³ only contribute to increasing the cost unnecessarily, because they promote the formation of higher concentrations of iron and sludge, and in addition, they raise the consumption of energy and treatment time without improving the removal of sulfate. The amounts of iron at the end of the three tests were similar, around 0.08 mol dm⁻³. In addition, it was observed that more than 99.5% were insoluble iron species. On the other hand, taking into account that the charge passed at the end of the tests was 6 A h dm⁻³, the expected faradaic concentration was 0.112 mol dm⁻³, which means an efficiency of 77% in the electrochemical dissolution of iron. This is due to the existence of competitive processes in the electrochemical cell: electrodisolution (Eqs. (1) and (3)) and water oxidation over the anode, favoring the production of oxygen (Eq. (4)).



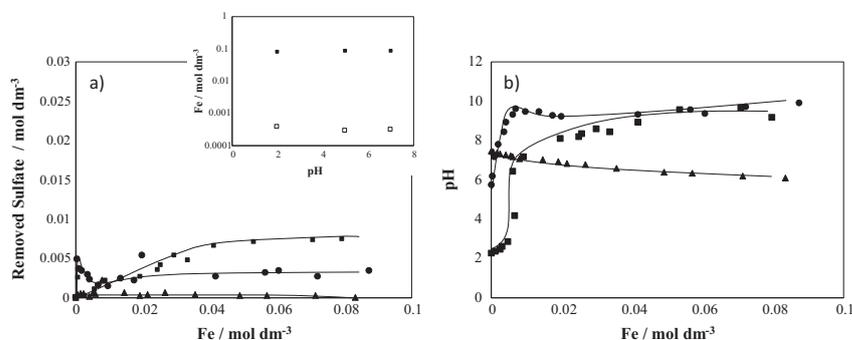


Fig. 4. Removed sulfate (a) and changes in the pH (b) during discontinuous electrocoagulation of synthetic mining wastewaters (initial pHs: ■ pH 2; ● pH 5; ▲ pH 7). Onset in the figure: iron measured at the end of each test (■ total iron; □ suspended iron).

When comparing the results obtained in chemically and electrochemically assisted coagulation, the conclusion can be drawn that both results are in agreement with each other, and confirm that the pH plays a very important role on the final removal efficiency of sulfate. In fact, the lower removal rates achieved during the electrochemically-driven processes can be easily explained in terms of the chemical coagulation results shown in Fig. 1, because of the shift of the pH during the electrochemical process from the initial value up to slightly alkaline values during the tests.

It is worth noting that in these tests, the pH was monitored but not regulated. As has been shown in previous studies [27,36], discontinuous electrocoagulation tends to buffer the pH of the treated wastes in values within the range 8.0–10.0. In many occasions, this range may be even appropriate for discharges into industrial sewers, either alone or mixed with other industrial flows, and hence, the necessity of further neutralization may be avoided. Neutralization of the effluent only will produce an increase in the counter ion added with the acid and diminish the great advantage shown by electrocoagulation, in which no chlorides are added to the treated wastewater, providing much better effluent quality.

Another important point in the treatment of mine waters is to check the effect of the treatment on other pollutants contained in the water. A summary of the results is given in Table 2.

As Table 2 shows, there is a complete removal of all the studied ions (except for chloride), which suggests a much more efficient treatment than the combination of different treatment mechanisms. The complete removal of cations is predictable due to a higher dose of the coagulant and almost complete transformation of iron into precipitates. What seems to be really strange is the removal of nitrate, which is also fully depleted from the system, down to less than 0.01 mg dm⁻³. This depletion can only be understood when considering the chemical reduction of nitrate into ammonium by electrocoagulation processes, a phenomenon that has been described in a previous work [35], and which includes chemical and electrochemical reactions. The concentrations of chloride over the initial value may not be explained in terms of relevant changes, but to be more likely due to the accuracy of the measurement within a highly complex medium.

In the discontinuous electrocoagulation tests without the control of the pH, despite the good removal of cations, the removal of sulfate by precipitation was not as good as in chemical coagulation, because of the final pH reached. In addition, the enmeshment of sulfate into iron hydroxide precipitate was not promoted as well, because of the low doses of added iron. Thus, to promote the removal, another electrocoagulation strategy was required.

This was done by a different design of the electrocoagulation process, consisting of a continuous electrocoagulation tank with a settler in which the solids were concentrated, promoting the flocculation processes (Fig. 1). This modified electrocoagulation process was based on the coagulation processes typically applied in the treatment of surface water, in which the flocculation enhancement by concentration of coagulants is known to increase the efficiency of the technology.

The results obtained during the operation of this new strategy with three synthetic wastes are shown in Fig. 5.

In this continuous electrocoagulation process, the specific electric charge passed depends on the intensity and flowrate but not on time, as has been pointed out elsewhere [41]. Hence, a unique value was obtained for the three tests (steady-state), corresponding to 12.4 A h dm⁻³ which was selected considering the operation conditions that allow a higher sulfate removal. It is important to keep in mind that the unit was operated at a once-through mode, i.e. circulation of water back into the cell was not applied at all, although the sludge was recycled to the settler continuously to favor flocculation. As can be seen in the figure, efficiencies of over 60% were attained by working at pH 2, with a dosage according to Faraday's law of 0.223 mg dm⁻³, which, taking account of the efficiency in the electrochemical dissolution reported previously (77%), was expected to be 0.172 mg dm⁻³.

When comparing the values obtained in the chemical coagulation tests with those of electrocoagulation with the same dosage of iron, almost no differences were found, just a slightly better removal in the electrocoagulation from 0.0172 up to 0.0199 mol dm⁻³ at pH 2, from 0.0050 to 0.0073 mol dm⁻³ at pH 5 and from 0.0015 to 0.0029 mol dm⁻³ at pH 7. The differences in discontinuous electrocoagulation were even higher, because in this case, the maximum removals were 0.0073, 0.0033 and 0, for pHs 2, 5 and 7, respectively.

The improvement can be explained in terms of the higher solid concentrations attained in the sedimentation tank connected to the cell. The expected concentration of iron according to the current charge passed and efficiency in the electrochemical dissolution measured in the discontinuous tests (0.172 mg dm⁻³) was much lower, by more than 6 times, than the value measured in the tank in the steady state, which was in the range 1.1–1.4 mol dm⁻³. In addition, there was another important difference: the amount of soluble iron was much higher in the tests carried out at acidic conditions and much lower in the test carried out at neutral conditions. Regarding the pH, the changes were not critical, and they were much lower than those observed in discontinuous

Table 2
Removal of selected ions with batch electrocoagulation processes (specific electric charge applied 6.0 A h dm⁻³).

	Raw mine ww	Mine ww electrocoagulated at pH 7	Mine ww electrocoagulated at pH 5	Mine ww electrocoagulated at pH 2
Cl ⁻ /mg dm ⁻³	300.00	299.39	281.99	304.87
NO ₃ ⁻ /mg dm ⁻³	60.00	n.d.	n.d.	n.d.
NH ₄ ⁺ /mg dm ⁻³	30.00	n.d.	n.d.	n.d.
Cu ²⁺ /mg dm ⁻³	8.00	n.d.	n.d.	n.d.
Ni ²⁺ /mg dm ⁻³	8.00	n.d.	n.d.	n.d.
Zn ²⁺ /mg dm ⁻³	15.00	n.d.	n.d.	n.d.

n.d. - non detectable.

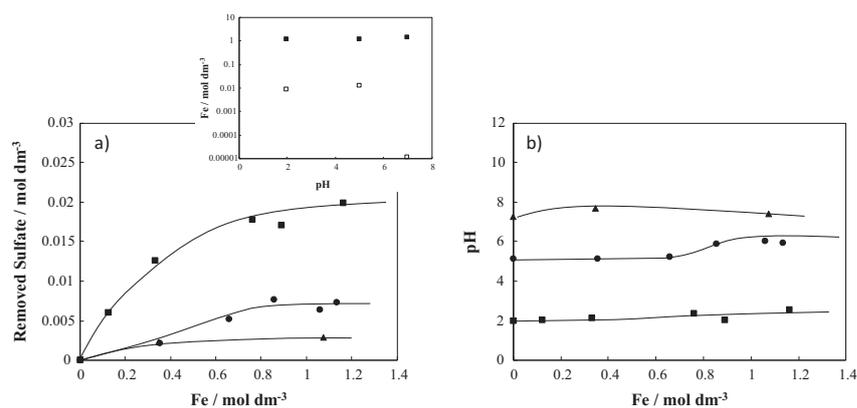


Fig. 5. Removed sulfate (a) and pH (b) during continuous electrocoagulation of synthetic mine drainage (initial pHs: ■ pH 2; ● pH 5; ▲ pH 7). Onset in the figure: iron measured at the end of each test (■ total iron; □ suspended iron).

Table 3
Removal of selected ions with continuous electrocoagulation processes (specific electric charge applied 12.4 A h dm⁻³).

	Raw mine ww	Mine ww electrocoagulated at pH 7	Mine ww electrocoagulated at pH 5	Mine ww electrocoagulated at pH 2
Cl ⁻ /mg dm ⁻³	300.00	299.81	301.44	287.67
NO ₃ ⁻ /mg dm ⁻³	60.00	n.d.	n.d.	n.d.
NH ₄ ⁺ /mg dm ⁻³	30.00	n.d.	n.d.	n.d.
Cu ²⁺ /mg dm ⁻³	8.00	n.d.	n.d.	n.d.
Ni ²⁺ /mg dm ⁻³	8.00	n.d.	n.d.	n.d.
Zn ²⁺ /mg dm ⁻³	15.00	n.d.	n.d.	n.d.

n.d. - non detectable.

electrocoagulation. This can also explain the higher removals obtained with this modified process, because coagulation at acidic conditions was found to be more efficient, as pointed out above.

As for the other two technologies, Table 3 summarizes the removal of other relevant ions contained in water with continuous electrocoagulation. As can be seen, chlorides were not removed, but opposite to chemical coagulation, their concentration was almost maintained during the test (the fluctuations can be explained by experimental error rather than by real changes). As during discontinuous electrocoagulation, all cations including ammonium were depleted down to concentrations below 0.01 mg m⁻³, which is not surprising because of the necessity of compensation of negative charges of sulfate in the flocs and the higher electric current charges applied. Again, nitrate was fully depleted, and the only explanation is in their previous transformation into ammonium ions during the electrocoagulation process [35].

Finally, the results obtained during the novel continuous electrocoagulation process for the removal of sulfate in mining waters reveals that there is a significant improvement not only on the

elimination of sulfate but also on the removal of heavy metals in comparison with other works recently published. In this context, Nariyan et al. [26] affirms that applied current densities of 70 mA cm⁻² (significantly higher than that used in this work) are required to attain an efficient removal of sulfate and heavy metals from mine waters by electrocoagulation. This would imply a higher energy consumption.

4. Conclusions

The following conclusions can be drawn from this study:

- Chemical coagulation with iron salts can be used efficiently to remove sulfate from mining waters. The dosage of iron and the pH have a significant influence on the results, and very effective coagulation in terms of low iron dosage can be attained by working at pH 2. The main drawback of this technology is the accumulation of important concentrations of chlorides in the effluent (counter ion of iron in the coagulant).

- Electrocoagulation attains high removal of sulfate and prevents the formation of chlorides, producing an effluent with a higher quality than chemical coagulation.
- There were relevant differences between the results obtained in batch electrocoagulation and those obtained in a continuous electrocoagulation plant operated with a flocculation tank, which were much better because of the better fit of the pH to the optimum conditions required and the enhanced flocculation.
- Together with sulfate removal, other ionic pollutants were removed by the tested coagulation and electrocoagulation technologies. Electrocoagulation was found to be more efficient because in addition to the depletion of all selected cations, it also removed the nitrates contained in the synthetic mine drainage completely.

Acknowledgments

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Publication II

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Systematic study on sulfate removal from mining waters by electrocoagulation

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Systematic study on sulfate removal from mining waters by electrocoagulation

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ABSTRACT

The mining industry is known to be a major producer of sulfate-rich waters that are harmful to aquatic systems, accelerate acid mine drainage formation and hinder the reuse and recycling of process water. In recent years, many treatment techniques have been studied and developed to treat sulfate-rich streams. One such technique, electrocoagulation (EC), was proposed as a possible alternative to conventional treatment technologies. Electrocoagulation has been used for the removal of nitrate, cyanide and toxic metals from mining waters, but the information about sulfate removal is scarce. In this paper, the results from a systematic study on sulfate removal by EC with iron electrodes applying a 3³-full factorial design are discussed. The results show the leading role of applied current on sulfate removal. In addition, the study concludes that the utilisation of iron electrodes was more efficient in terms of sulfate removal comparing to aluminium electrodes. The removal of sulfate was as high as 54% and 10% using iron and aluminium electrodes respectively. Under the studied experimental conditions, sulfate was proposed to be removed because of particle charge neutralisation and enmeshment of the studied anion in iron oxides and hydroxides.

1. Introduction

Mining waters are often heavily contaminated with anionic and cationic species. Among the most prevalent and harmful compounds are toxic metals [1] and anionic contaminants, such as sulfate, nitrate, chloride, cyanide and fluoride [2]. Concentrations of harmful contaminants are mine-specific, and it is thus difficult to assess the true scale of the environmental impact of mine water discharges accurately. However, it is essential to treat discharged wastewaters and bring the concentrations of harmful dissolved contaminants to acceptable discharge levels [3,4]. Another mining wastewater management concept is to reuse and recycle water within the process sections. Firstly, it makes mining operation more economically and environmentally feasible. Secondly, it allows for treating water only to a level suitable for a certain process rather than to an acceptable discharge level [5].

One of the most common anionic species present in mine wastewaters is sulfate as a final oxidation product of sulfuric minerals [6]. In addition, the use of chemicals, especially sulfuric acid, during the mining processes results in high sulfate concentration in mining waters. The sulfate concentration in mine waters may be from hundreds to several tens of thousands of milligrams per litre [1]. The effluent emanating from mineral excavation and manufacture contains a high

concentration of sulfate ions, but acid mine drainage (AMD) tends to be the main source of sulfate at the mine site [7]. AMD is considered a natural process, but it is accelerated significantly with mining activities. The influence of AMD on the environment is the most severe in closed and abandoned mines, due to an increase of the water tables once pumping is stopped [8].

Requirements and restrictions on the quality of mining waters result in the limitation of discharge concentrations of several anionic compounds. Globally, the discharge limit for sulfate varies from 250 mg/L (USA) to 1000 mg/L (Brazil, Chile) [9,10]. Currently, no general limit is set for the allowed amount of sulfate to be discharged in Finland, although some mine-specific limits for certain mines have been already established and new regulation are expected in future [11]. High concentrations of sulfate result in a high toxicity of waters, serious pollution of natural water bodies and decrease of the reproduction of soils [12].

During recent decades, close attention has been paid to innovative processes enhancing the removal efficiency of contaminants, minimising chemical usage, reducing sludge volume, enabling the recycling of process water and dividing effluent streams to be treated separately with better efficiency. One of such innovative active abiotic techniques is electrocoagulation (EC).

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Electrocoagulation is one of the electrochemical methods used in wastewater treatment. The other methods include electroflotation, electrooxidation and electrodecantation [13]. Currently, all of these methods are under development, and eventually they are aiming at replacing conventional technologies that require an addition of chemicals and even higher energy consumption [14].

Electrocoagulation is based on the application of an electric current to destabilise suspended, emulsified or dissolved contaminants in a solution. The simplest construction of an electrocoagulation reactor is an electrolytic cell with one anode and one cathode [15]. The anode provides metal ions to the system, while the cathode releases hydrogen gas. During electrocoagulation, metal ions are dissolved electrically from electrodes, generating coagulants *in situ* [16].

Among the advantages of EC are its comparatively low investment and maintenance costs, lower, comparing to other treatment techniques, sludge production and the possibility to operate by solar energy [14]. Moreover, EC, when compared to chemical coagulation, benefits from the avoidance of harmful anions added during the treatment, operation at wider pH range and more stable flocks that allow the possible separation by settling [17,18]. Finally, compared to other chemical methods, during electrocoagulation, effluent with a lower total dissolved solids (TDS) content is produced, and that leads to a reduction in the further water recovery costs [19].

The electrodes or conductive metal plates can be made of the same or different materials [15] and can be arranged in a mono-polar or bipolar mode [16]. The electrode materials commonly used in electrocoagulation processes are iron or aluminium, and titanium has also been mentioned [19]. Furthermore, the application of graphite plates, copper, zinc [20] and dimensionally stable anodes (DSA) made of a thin layer of noble metal oxides on titanium substrate [16] has been reported. Most commonly, Al and Fe ions are used in the electrocoagulation processes due to their trivalent forms [21] and the low solubility of their hydroxides [22].

The behaviour of electrodes in different electrolytes has a pivotal role in the formation of a passive oxide film on the anode. The passivation of the anode leads to an increase in the applied potential and to waste of energy during the electrocoagulation treatment. The dissolution of the passive film on the anode surface may be provoked by the presence of corrosive species (e.g. chloride) [23–25]. In the case of sulfate presence, the desired ratio of $[Cl^-]/[SO_4^{2-}]$ should be around 0.1 to ensure a sixfold decrease in the applied voltage and the breakage of the passive film [25].

In addition, the application of electrodes with rough surfaces and frequent current reversals are suggested for the efficient dissolution of the anode [23].

Besides the material of the electrodes, there are other parameters that affect the EC process, such as the reactor design, electrode type, arrangement, current density, operation time, pH and temperature [16,26]. The lack of information on sulfate removal by EC requires detailed laboratory-scale studies before its application on the pilot and industrial scales.

EC as a treatment technique of mining waters is gaining attention due to its successful application for the removal of other typical mining waters contaminants, such as nitrate, sulfate, cyanide, toxic metals, etc. [27–34]. The treatment of mining waters by batch electrocoagulation has been recently studied by Nariyan et al. [35,36]. Mamelkina et al. reported on continuous electrocoagulation concept development for sulfate removal [37]. Del Ángel et al. have conducted electrocoagulation experiments by using aluminium electrodes, and they achieved 53% of sulfate removal from the drainage from an abandoned mine in Guanajuato, Mexico [38]. Radic et al. report over 86% removal efficiency of sulfate from acid mine drainage with combined CaO/electrocoagulation treatment [12]. However, the data regarding sulfate removal was reported without detailed information about the processes involved in EC and the parameters affecting the sulfate removal.

Electrocoagulation treatment of sulfate and mechanisms of

contaminant removal during the process are rarely studied. Without knowledge on sulfate removal as one of the main components of mining waters it is hard to conclude about the suitability of electrocoagulation to treat mining waters. To fulfil the gap and create the whole picture about mining water treatment by electrocoagulation, there is an acute need to evaluate the suitability of electrocoagulation as a sulfate removal technology.

This paper is dedicated to the investigation of the removal efficiency of sulfate from synthetic mining water depending on the applied current, the initial pH and the initial sulfate concentration in the solution. The aim of the study is to examine the suitability of treating sulfate-rich waters with electrocoagulation. In addition, the comparison of process performances using iron and aluminium electrodes is provided.

2. Materials and methods

2.1. Materials

Synthetic sulfate-rich waters were prepared in order to analyse the removal of sulfate by electrocoagulation. The synthetic water composition was proposed based on the discussions with industrial partners, literature review and public reports available from mines. Synthetic waters contained SO_4^{2-} , NO_3^- , Cl^- , Cu^{2+} , Ni^{2+} , Zn^{2+} , NH_4^+ . Sulfate values were chosen based on the average sulfate concentration in Finnish and Swedish mines. Extreme cases were not taken into account. The stock solutions with a sulfate concentration of 1000, 2000 and 3000 mg/L were prepared by using Na_2SO_4 , $NaNO_3$, $NaCl$, $CuSO_4$, $NiSO_4$, $ZnSO_4$ and NH_4Cl (Merck KGaA). The pH of the solutions was adjusted to a desired level by either 0.1 M NaOH (Merck KGaA) or 0.1 M HCl (Merck KGaA), depending on the conditions in each test. NaCl was added to prevent the quick passivation of the anode. The amount of NaCl required was calculated according to the expression $[Cl^-]/[SO_4^{2-}] = 0.1$. All of the chemicals were of analytic grade, used without further purification and supplied by Merck KGaA, Germany. The conductivity of the solution was measured and reported on without any adjustments.

2.2. Experimental equipment and procedure

Electrochemical tests were performed in a jacketed Plexiglas-reactor (Fig. 1). The treated volume of sulfate-rich water was 1000 ml. The electrochemical cell consisted of four iron or aluminium electrodes connected to the power source by using a monopolar arrangement. The electrode dimensions were 6×7 cm and the electrode surface area was 84 cm^2 per plate (two sides), resulting in 168 cm^2 of total anode area. The gap between the electrodes was 10 mm. Constant current was maintained by using laboratory power supply (PS 3005).

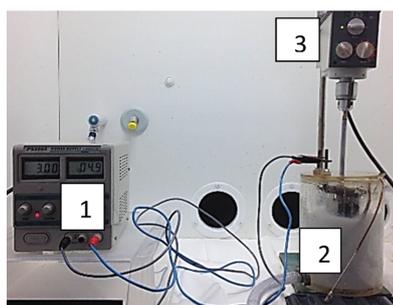


Fig. 1. Picture of the experimental setup taken during the EC-test with aluminium electrodes at 3A: (1) power supply, (2) electrochemical cell, (3) mixer.

The applied current during EC-treatment with iron electrodes was 1 A (6 mA/cm²), 2 A (12 mA/cm²) and 3 A (18 mA/cm²). Preliminary tests were also performed at range 0.1 to 5 A, however, the noticeable sulfate removal was observed at applied current from 1 to 3 A. Tests with aluminium electrodes were performed at 3 A and 5.3 A (31 mA/cm²). The first three experiments were conducted at a current of 3 A providing the same current density as in the case of using iron electrodes. The rest of the experiments were conducted at a current of 5.3 A resulting in the same amount of solids formed as in the case of using iron electrodes at a current of 3 A. A plastic curved blade turbine was used to provide proper mixing of the treated solution during each test at a speed of 200 rpm, which corresponded to the tip speed of 0.84 m/s. Treatment over 5 h makes the technology less competitive, leads to high energy consumption and increase the amount of solids formed. The pre-treatment of iron and aluminium electrodes was performed with a 10% and 4% HCl acid solution, respectively, and after treatment they were rinsed with tap- and distilled water before each run.

A sample of 20 ml was taken with a syringe from the centre part of the reactor once per hour. Straight after the sample was taken, 10 ml were filtered with a 0.45 µm syringe filter to enable particle separation, and for the rest of the sample, pH and conductivity measurements were performed.

2.3. Design of experiments

The experiments with iron electrodes were performed according to the 3³-full factorial design [39]. This was then supplemented with four repetitions of central point and two repetitions of corner points with the minimal and maximal values of the factors thereby totaling a total of 35 experiments. Independent factors were the initial pH of the solution, the initial concentration of sulfate ions in the solution and the current applied to the system. The experimental conditions for EC-tests with iron electrodes as well as the initial concentrations of water contaminants are given in Table 1. Six additional experiments with aluminium electrodes were performed to study the influence of electrode material on sulfate removal. The experiment with aluminium electrodes were only performed at the experimental conditions that favoured the highest removal of sulfate using iron electrodes.

The initial pH was selected to study the effect of pH on the efficiency of the electrocoagulation process and to observe the differences between the initial and final pH. The initial concentration of sulfate ions was selected to investigate the efficiency of the electrocoagulation process within the high concentration ranges of sulfate, as concentrations up to 500 mg/L had been studied previously [22]. Moreover, sulfate concentration in mining waters is an important factor due to its variation from one to tens of thousands of milligrams per litre [1]. The applied current controls the electrochemical reactions occurring on the electrode surface and results in the amount of solids formed during the process.

The measured responses were the residual concentration of sulfate ions in the solution, the final pH of the solution, conductivity and the

Table 1
Mining water content and experimental conditions used during EC-treatment with iron electrodes.

Parameters	Levels		
	1	2	3
Current, I (A)	1	2	3
Initial pH	4	7	10
Initial concentration, (mg/L)			
SO ₄ ²⁻	1000	2000	3000
NO ₃ ⁻	20	40	60
Cu ²⁺	2	5	8
Zn ²⁺	5	10	15
Ni ²⁺	2	5	8
Cl ⁻	100	200	300
NH ₄ ⁻	10	20	30

mass of electrodes. Based on the collected data, the removal efficiency of sulfate, the weight loss of electrodes and pH changes during treatment were calculated.

2.4. Analysis procedure

The sulfate concentrations were measured with ion chromatography by using Dionex ICS-1100 equipped with autosampler Dionex AS-DV. The samples were diluted prior the analyses with an automated laboratory dilutor Hamilton Microlab 500 series. Amounts of iron and aluminium were evaluated by weighting the electrodes before and after each test using the laboratory analytical scales. The pH was controlled by pH meter WTW pH 304i and conductivity was measured with Labor-Konduktometer 703.

3. Results and discussion

3.1. Summary of the laboratory results

Synthetic mining waters were treated by electrocoagulation in a 1L batch reactor using iron and aluminium electrodes. The influence of EC operating parameters on sulfate removal was investigated. A summary of the main results obtained during the EC-tests with iron and aluminium electrodes are given in Tables 2 and 3, respectively.

Presented data make it already possible to establish some general relationships observed during the systematic studies on sulfate removal. For instance, the removal of sulfate increases with the increase in applied current. Another finding is the utilisation of iron electrodes for more efficient sulfate removal at the studied concentration ranges. Moreover, the final pH of the treated solutions was caustic regardless the initial pH and electrode material. The detailed discussion about the effects of applied current, initial pH and concentration using iron electrodes applying 3³-full factorial design is provided in Sections 3.2 and 3.3. Sections 3.4 corresponds to the effect of electrode material on sulfate elimination and Section 3.5 provides information about the repeatability of the experiments.

3.2. Effect of applied current

The applied current is one of the most significant factors affecting the electrocoagulation process. This parameter has a significant effect on the dissolution of electrodes, the energy consumption of the process, the change in pH and conductivity as well as the amount of solids generated [16,26,29]. In this study, the experiments with iron electrodes were carried out at three different currents, namely 1, 2 and 3 A, tests were performed according to the statistical design of experiments. It was observed that increasing the current from 1 to 3 A increased the

Table 2
Removed sulfate and final pH-values solution during EC-tests with iron electrodes at different applied currents, initial pH and concentrations.

Initial pH	Concentration, mg/l	Applied current					
		1 A		2 A		3 A	
		R, %	pH fin	R, %	pH fin	R, %	pH fin
pH 4	1000	7	11.27	10	11.69	24	10.57
pH 7		10	11.34	29	11.73	28	11.17
pH 10		10	11.31	38	11.84	54	11.78
pH 4	2000	16	11.89	25	11.97	21	11.95
pH 7		2	10.98	35	12.01	31	11.96
pH 10		10	11.64	37	12.17	40	11.96
pH 4	3000	1	10.97	24	12.16	51	12.4
pH 7		2	11.22	33	12.21	27	10.02
pH 10		2	11.17	27	12.14	43	12.26

Table 3
Removed sulfate and final pH-values solution during EC-tests with aluminium electrodes at different applied currents, initial pH and concentrations.

Initial pH	Concentration, mg/l	Applied current			
		3 A		5.3 A	
		R, %	pH fin	R, %	pH fin
pH 4	1000	7	9.99	–	–
pH 10		8	10.63	10	10.81
pH 4	3000	3	9.95	–	–
pH 10		4	9.94	1	10.36

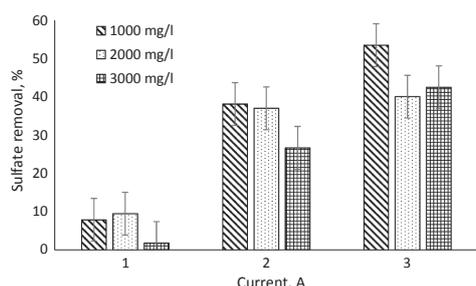


Fig. 2. EC-process performance in sulfate removal at different currents and initial sulfate concentrations for initial pH 10, iron electrodes.

removal of sulfate. A summary of the EC performance in sulfate removal at different currents and various initial sulfate concentrations for initial pH 10 are shown in Fig. 2. The maximum removal efficiencies were 16%, 38% and 54%, respectively, at 1, 2 and 3 A, influenced also by the initial concentration. In case of iron electrodes, better removal at higher currents is likely because of the more intensive release of iron ions from the anode surface, resulting in the formation of greater amount of insoluble iron precipitates. Among the possible precipitates

with the presence of sulfate in electrolyte are Fe_3O_4 , $\alpha\text{FeO}(\text{OH})$, $\gamma\text{FeO}(\text{OH})$, $\text{FeSO}_4(\text{OH})$ and positively charged iron hydroxides [31,40,41]. Thus, higher removal may occur due to the more efficient enmeshment of sulfate in iron oxide and hydroxide and possible charge neutralisation by the excess amount of positively charged iron ions. Other researchers have observed the enmeshment of sulfate ions in porous metal precipitates [22]. Moreover, the adsorption on the precipitates and charge neutralisation as a removal mechanism for other anions have been investigated by several researchers [29,32,42].

Results obtained using 3^3 -full factorial design allow to conclude that the highest removal efficiency with iron electrodes was achieved at different combinations of factors at various initial sulfate concentrations; however, the main parameter in the process was the applied current. Thus, highest sulfate removal efficiencies were registered at 3 A regardless the changes in initial concentration and pH.

The highest removal efficiencies for the solutions with sulfate concentrations 1000, 2000 and 3000 mg/L treated at the current 3 A were 54% (pH 10), 40% (pH 10) and 51% (pH 4), respectively. Based on the difference in the removal efficiencies, it may be concluded that other operating parameters, such as initial pH and sulfate concentrations affect the performance of EC-treatment of sulfate-rich solutions.

3.3. Effect of initial pH and concentration

The pH as one of the parameters affecting the EC-process is mainly responsible for speciation and solubility of metal oxides and hydroxides as well as contaminant removal mechanisms. Effect of solution pH on the performance of EC-process with iron electrodes was evaluated at various initial pH-values 4, 7 and 10 using statistical design of experiments. The pH profile in Fig. 3 shows that after 1 h of treatment at current 3 A pH was around 11.2 regardless of the initial pH of the solution. This indicates that after 1 h, electrocoagulation treatment of sulfate took place at base conditions. The upward trend is typical for final pH with an increase in the current [32]. During the first hour of treatment the initial pH changed dramatically, and the changes in pH varied inversely to the increase in the initial pH. A sharp increase in pH for low initial pH and comparatively slight change in pH for high initial pH was also observed by İrdemez et al. [43]. The increase in pH during the EC-treatment has been explained in terms of OH radical evolution

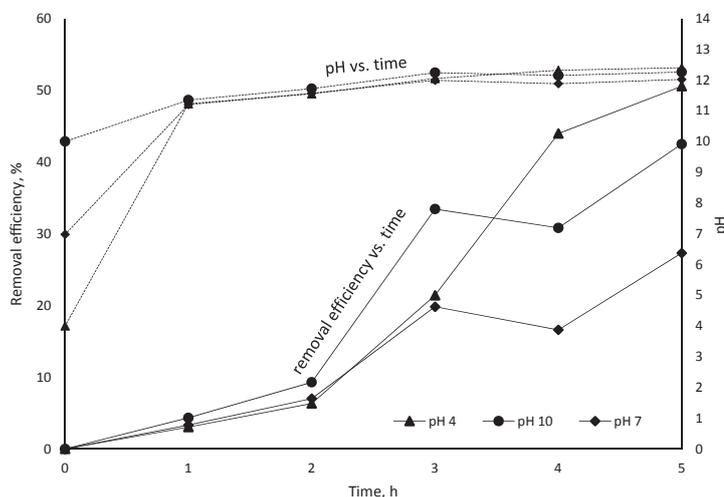


Fig. 3. Variation of removal efficiency and pH of electrocoagulation-treated samples as a function of time at C = 3000 mg/L, current 3 A, iron electrodes.

from the cathode and water oxidation at the anode [32]. Moreover, rapid changes from pH 4 to pH over 11 is explained by faster production and slower consumption of OH radicals. The stabilisation of pH around 11 is likely because of the buffering effect of the iron oxides/hydroxides mixture.

The removal efficiencies of sulfate for the solution containing 3000 mg/L of sulfate treated under the current of 3 A with varying pH values are shown in Fig. 3. According to the results shown in Fig. 3, poor sulfate removal was observed after the first hours of treatment, but the sulfate started to be removed significantly after two hours of treatment when pH stabilised at about 12 and the calculated amount of generated solids was 9 g/l. The high removal efficiency at low pH seems to be promising for the industrialisation of the method, as it is not necessary to adjust the initial pH of mine water, or it requires just slight adjustment to obtain partial removal of sulfate.

Another parameter influencing the removal rate during the EC is initial concentration of the contaminants. To study this phenomenon, experiments with initial sulfate concentrations of 1000, 2000 and 3000 mg/L and initial pH values 4, 7 and 10 were performed. As an example the relationships between removal efficiency of sulfate and treatment time at pH 10 is plotted in Fig. 4. The observations make it possible to conclude that an increase in initial sulfate concentration results in a lower removal of sulfate. A general decreasing trend in sulfate removal with the initial increasing sulfate concentration at the range of 1000–3000 mg/L is in agreement with earlier reported studies on sulfate removal from synthetic waters with sulfate concentrations varying from 100 to 500 mg/L [22]. Such a behaviour may be explained by the lower concentration of iron-coagulant required for the removal of sulfate at lower initial concentrations. The content of synthetic mining waters, especially the $[Cl^-]/[SO_4^{2-}]$ ratio, may also affect the process efficiency [25].

According to the results with iron electrodes, the highest sulfate removal of 54% was achieved when the applied current was 3 A, the initial pH of the solution was 10, and the initial sulfate concentration in the solution equalled 1000 mg/L. The highest sulfate removal from the solution with the initial sulfate concentration 3000 mg/L was 51% at the applied current of 3 A and the initial pH of 4. At a current of 2 A, the highest removal efficiency achieved was 38% at pH 10 for the initial sulfate concentration 1000 mg/L.

The initial water conductivity was mainly affected by the initial concentration of studied contaminants. It equalled 2.27, 4.23 and 6.20 mS/m, respectively, to the change in concentration from 1000 mg/L to 3000 mg/L. However, the final conductivity of the EC-treated samples depended greatly on the applied current, and consequently on the presence of iron and other ions in the solution. A higher applied current led to higher change in water conductivity during the EC-process. An increase in conductivity during anion removal by EC is also reported and explained by Kumar et al. and Moussavi et al. [17,33]. Vepsäläinen

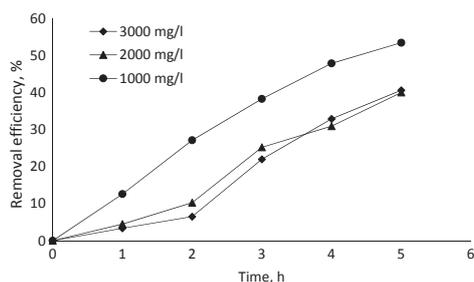


Fig. 4. Effect of the initial sulfate concentration on the final sulfate removal of electrocoagulation-treated samples at pH 10, current 3A, iron electrodes.

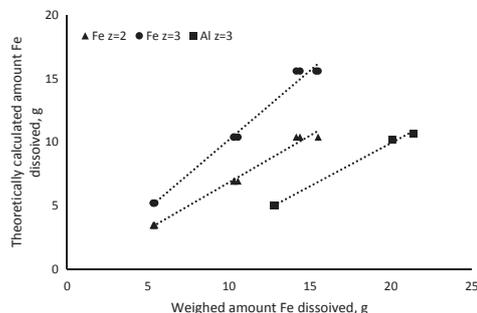


Fig. 5. Correlation between theoretically calculated and experimentally obtained amount of iron and aluminium generated at various currents during the electrocoagulation treatment of sulfate solutions, pH 10, current 1, 2 and 3 A for Fe, 3 and 5.3 A for Al.

et al. observed a decrease in conductivity with the increase of current during EC-experiments with mechanically treated water in a paper mill [18].

3.4. Effect of electrode materials

Electrode material in EC is mainly responsible for the amount and type of metal ions in the solution, coagulation efficiency and process costs. In this study, iron and aluminium electrodes were tested and the loss of electrode weight was investigated during the experiments. The obtained results presented in Fig. 5 show that the generation of iron and aluminium from the anodes was repeatable and affected by the applied current. The amount of generated solids increased proportionally to the current.

Theoretical and experimental amounts of generated iron were compared at currents 1, 2 and 3A. Experimentally generated amounts of iron at different currents correlated with the theoretical amounts based on the calculation (Faraday's law) when the number of electrons transferred (z) equalled to 2, while with $z = 3$ excess formation of iron of up to 50% during the experiments could be observed. The literature reports on iron dissolution of around 100% [16] or lower than 100% [44]. According to this, the formation of Fe^{2+} was expected during the present EC-experiments. Moreover, the literature proposes various mechanisms of iron generation and solids formation during the EC-process. A detailed summary is given by [40].

Experimental amounts of generated aluminium were two times higher than those theoretically predicted. Such a behaviour can be explained by a chemical attack of aluminium cathode induced by hydrogen evolution resulting in a significant contribution to the total amount of aluminium released. For example, Linares-Hernandez et al. reported of an excess of 50% between the calculated and measured concentrations of Al^{3+} [45]. According to Mouedhen et al., the current efficiency of aluminium dissolution was about 175% [24]. The exceeded experimental amounts of generated aluminium can be additionally explained by the presence of chloride in the mining waters. In this case, operating at relatively high current densities, chloride acts as a pitting agent promoting the breakage of the passive layer and increasing the dissolution efficiency of the aluminium electrodes [46].

The effect of electrode materials on sulfate removal was studied using two different approaches. Based on the results obtained during the EC using iron electrodes, the most suitable conditions for the highest removal of sulfate within the range of studied parameters were chosen. According to these results, EC-tests using aluminium electrodes were performed, firstly, by applying the same current densities and, secondly, by generating the same amount of solids. The results of the

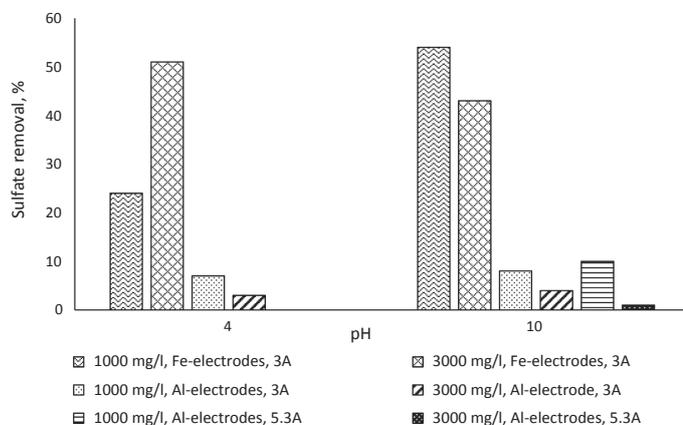


Fig. 6. Comparison of sulfate removal from tested waters treated by EC using aluminium and iron electrodes at chosen experimental conditions.

EC-process performance, in accordance with the different electrode materials, are shown in Fig. 6.

It can be seen in Fig. 6 that the application of iron electrodes resulted in more efficient sulfate removal with the highest of 54%, while for aluminium electrodes the highest removal efficiency obtained was 10%. The reason for the poor sulfate removal could be the final pH of the solution, which was around 10. The most probable species that are responsible for electrocoagulation efficiency with aluminium are polymeric hydroxoaluminium ions and the aluminium hydroxide precipitates [25,47]. At a pH higher than 9, the formation of aluminium precipitates decreases [44] and the formation of negatively charged hydroxoaluminium ions is expected [23] making the charge neutralisation of negatively charged sulfate impossible. Poor sulfate removal using aluminium electrodes at a pH higher than 10 is in accordance with the results reported by earlier researchers [22].

In general, the partial removal of sulfate ions from the solution can be explained in terms of the good solubility of aluminium and iron sulfate in aqueous media, electrocoagulation operation at caustic conditions and low amount of positively charged ions to neutralise the charge of negative bivalent ions.

3.5. Repeatability of experiments

Repeatability refers to the variation in the results obtained from repeated experiments on the same subject under identical conditions [48,49]. The objective is to quantify the agreement of the results obtained by the studied method. Among the reasons to repeat the

experiments are the verification of results, data collection for statistical analysis of the results as well as the development of skills of an operator. Good repeatability gives confidence in the quality of the whole data set produced during the research work. To check the repeatability during the electrocoagulation treatment of sulfate-rich solution, four independent experiments were performed. The initial conditions for the repeatability tests were chosen to be the central points with initial sulfate concentration 2000 mg/L, pH 7 and current 2 A. Tests were performed with the repeatability condition of a measurement meaning that measurements were performed over a short period of time using the same operator, same measuring system and same operating conditions [49].

The behaviour of pH (Fig. 7a) and sulfate removal efficiency (Fig. 7b) versus time during the repeatability tests is considered. Test 1, Test 2 and Test 3 with iron electrodes were conducted one after the other in three days with totally new iron electrodes used as anodes and cathodes, while Test 4 took place after 11 more experiments performed at different operational conditions.

The results of Test 1, Test 2 and Test 3 were in agreement since the changes in sulfate removal followed the same pattern, and the pH-graphs were repeatable. The obtained results are repeatable over a short period of time. The discrepancy of results for Test 4 after 3 h of treatment may tell about the poor reproducibility of the results that may be, over an extended period of time, caused by the possible roughness of the electrode surface and thus the increase of electrode's surface area resulting in more efficient iron dissolution already after 3 h of treatment.

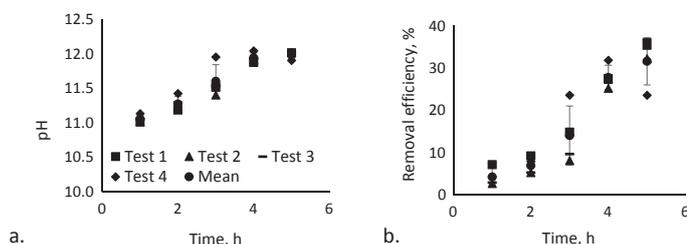


Fig. 7. Variation of (a) pH and (b) removal efficiency of sulfate, as a function of time obtained during repeated electrocoagulation tests with sulfate solutions at $C = 2000$ mg/L, pH 7, current 2 A, iron electrodes.

4. Conclusion

The conducted research on the electrocoagulation treatment of sulfate-rich streams has provided an understanding of the phenomenon occurring during the process. The results illustrated that sulfate removal is a current dependent process, and an increment of applied current favours the contaminant removal. However, the contaminant removal was still found to be challenging at higher sulfate concentrations. The highest removal rates were attained with iron electrodes. For most of the experimental conditions, the sulfate removal rate was moderate. Most probably, this happened because of the good solubility of iron and aluminium sulfate, operation of electrocoagulation at base conditions and possible passivation of electrodes in the presence of sulfate in the solution. The electrocoagulation removal mechanism of sulfate was proposed according to the pH of the treated solution and speciation of solids formed during the process. The removal of sulfate is due to its enmeshment on iron oxides and hydroxides as well as ion charge neutralisation by positively charged iron hydroxocomplexes. Once we have a more detailed explanation of sulfate behaviour during the treatment, electrocoagulation could be considered as a suitable auxiliary process for the removal of sulfate, while treating other compounds, but not the main sulfate treatment technology. In addition to the performed systematic studies, to ensure the suitability of electrocoagulation for sulfate removal the real mining waters should be treated. Potentially, moderate sulfate removal will enable the reuse and recycling of process water and minimise the effect of mining waters on the environment.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2019.01.056>.

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Publication III

Mamelkina, M.A., Vasilyev, F., Tuunila, R., Sillanpää, M., Häkkinen, A.

**Investigation of the parameters affecting the treatment of mining waters by
electrocoagulation**

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Investigation of the parameters affecting the treatment of mining waters by electrocoagulation

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ABSTRACT

Recently electrochemical methods have been studied as an alternative to conventional methods to treat industrial and municipal waters. One such water, the mining water, has been mainly treated previously by electrocoagulation (EC) to remove metals. Few studies have been performed on the removal of sulfate, nitrate and cyanide from mining waters. In this paper, results from 39 lab-scale experiments on the elimination of sulfate by electrocoagulation with iron electrodes are presented. Significance of parameters affecting the removal of sulfate by EC was studied using response surface methodology (RSM). Also, results from kinetic studies and comparison of synthetic and real mining waters are reported. According to kinetics studies, it was suggested that both physical and chemical mechanisms are involved in sulfate removal. At the same test conditions, sulfate removal from both synthetic and real mining waters followed the same pattern. The study concludes that the most significant parameters in sulfate removal are initial sulfate concentration and applied current when initial pH was insignificant in batch operation. From a technology development perspective, this study enhances knowledge about the significance of process parameters and their interactions as well as allows further scale-up of the process

1. Introduction

Electrochemical water treatment is mainly represented by electrochemical oxidation and reduction, electrocoagulation, electroflotation and electro dialysis [1]. Among others, electrocoagulation (EC) is a promising technique for the removal of various contaminants, such as dyes [2], toxic metals [3–5], natural organic matter [6–8], arsenic [9,10], fluoride [11–13], cyanide [14], sulfate [15–17], nitrate [18] and other anions [19]. Currently, at laboratory scale, electrocoagulation has been successfully applied to treat water streams from oil [20], tannery [21], textile [22,23], paper [24,25] and food productions [26,27], mining [15,28,29] and polishing operations [30,31] as well as from municipal waters [32,33]. Some studies report that a potential application of EC could be the removal of toxic metals, sulfate and nitrate removal from mining waters at different stages of mining operations [15,28,29].

Electrocoagulation of mining waters can be considered to be successful when contaminants are removed from water and destroyed or made less soluble with the application of the reacted and excited state [34]. Possible mechanisms of contaminants removal can be coagulation, precipitation, enmeshment, complexation, adsorption or charge

neutralization of particles [35,36]. The removal mechanisms depend on the water composition, pH as well as Redox-potential [37–39]. Another significant factor affecting the removal mechanisms and electrocoagulation process is the electrode material that mainly influences the coagulation efficiency and process costs [40].

However, electrode material and subsequently the predominant species formed are not the only parameters affecting the electrocoagulation process. Hence, reactor design, applied current, operating time, presence of other contaminants, pH, temperature as well as the combination of factors may affect the process performance significantly [36,41–43]. To study the significance and possible contribution of factors and their interactions to the process performance, detailed research should be conducted. Incorrect combination of factors and misunderstanding their influence on each other may lead to the failures of the process. Thus, at the beginning of the process development and its upcoming implementation, it is necessary to gain information about the parameters affecting the process. For instance, reactor design generally influences the mixing and settling characteristics, bubble pass and flotation efficiency. Applied current mainly affects anodic dissolution, system lifetime, unit size, coagulant dosage and bubble generation. Removal rate and energy consumption depend on operating

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time; while temperature influences current efficiency, flocs formation as well as power consumption [36,42]. Considering the electrocoagulation treatment of mining waters, it has been reported by several researchers that process performance is mainly affected by the reactor design, electrodes arrangement, current density, initial pH, electrode material and concentration of the contaminants [15,28,29].

In the modern world of mining operation high sulfate concentrations, operational process requirements and established discharged limits make it obligatory to develop and implement new sulfate removal technologies [44]. One such technology, the electrocoagulation, has gained much attention from the scientific and industrial world. The scientific literature lacks information regarding the design and scale-up of EC reactors. Only few studies are devoted to the scale-up and commercialization of electrochemical processes [45–48]. Thus, Cameselle et al. [45] have reported on a successful scale-up of electrochemical decolorization of a textile dye process from 1 L to 20 L, when Garcia-Segura et al. [46] have provided a comprehensive review on scalability and commercial application of electrochemical removal of nitrate from groundwaters and industrial waters. Souza et al. [47] have investigated the effect of stacking single electrochemical cells on the energy efficiency and process performance of treatment of pesticide containing water. Martín de Vidales et al. [48] compared the performances of both bench-scale and pilot plant electrolysis for treatment of urban waters. It compels researchers to start from the laboratory scale studies once developing an EC process intended to eliminate contaminants that have been rarely, incompletely and unsystematically studied before [8–10,15,18]. One of the systematic approaches, a response surface methodology (RSM) [47] is frequently used to formalize laboratory-scale studies of process performance. The methodology helps to check the significance of the effect of different factors on the responses and to predict response values for given values of factors [47,48]. Previously, RSM has been applied to investigate the effect of various parameters on electrocoagulation processes for the removal of natural organic matter [8], uranium [49], fluoride [50], nitrate [51] and copper [52]. A comprehensive review of the modeling approaches for electrocoagulation can be found from [53]. Lacasa et al. [54] have performed the modeling of electrocoagulation for the elimination of anions from water.

In this paper, RSM was employed to study the effects of initial pH, applied current and initial sulfate concentration on sulfate removal efficiency. Full factorial design [55] that results in detailed information about the significance of factors and their interactions, as well as their influence on the responses, was applied herein. Such an approach makes future implementation and sizing of EC treatment possible and brings technology to another level of operation. Additionally, the behavior of the EC process during the treatment of synthetic and real mining waters was investigated and compared to evaluate if the synthetic waters can be used for small laboratory tests before actual treatment at the mine site. Moreover, kinetic studies were performed to confirm the possible removal mechanisms of sulfate. This work is supported by other studies on sulfate elimination where continuous treatment concept was developed [15], removal mechanisms, different electrodes arrangement and a combination of EC with precipitation have been studied [17,56].

2. Materials and methods

2.1. EC equipment and procedure

Electrocoagulation experiments were conducted in a batch mode using 1000 mL jacketed Plexiglas-reactor. Detailed information about the equipment is available from elsewhere [56]. The reactor was equipped with two pairs of iron electrodes connected in a monopolar arrangement. Total anode area was equal to 168 cm². The applied current was maintained constant at 1 A (6 mA/cm²), 2 A (12 mA/cm²) or 3 A (18 mA/cm²). The duration of each test was 5 h, samples of

20 mL were taken every hour, allowed to settle and then filtered with a 0.2 µm syringe filter to produce a particle free sample. A plastic curved blade turbine maintained proper mixing conditions at a speed of 150 rpm, which corresponded to the tip speed of 0.60 m/s. Electrodes were cleaned with 10% HCl (Merck KGaA) solution and rinsed with distilled water before each run.

Contents of the dissolved metals were measured with ICP-MS (Agilent Technologies, Agilent 7900), residual sulfate, chloride and nitrate concentrations were analyzed with ion chromatography (Dionex ICS-1100 equipped with autosampler Dionex AS-DV). The mineralogical phases were all identified using the PANalytical HighScore PLUS 3 software and the Crystallography Open Database (COD). All the analytical data are post-processed using GrainClassifier v1.9, IncaMineral classification software developed at the Luleå University of Technology for mineral identification, reporting mineral grades and chemical composition of the samples.

2.2. Materials

Electrocoagulation tests were performed using both synthetic and real mining water. Contaminants and their concentrations to prepare synthetic mining waters have been chosen considering the real mining water compositions available from the reports and literature. Compositions of synthetic mining waters used during EC-tests are given in Table 1 [57]. The initial pH of synthetic mining waters equaled to 4, 7 and 10 depending on the experimental conditions. Sodium hydroxide and hydrochloric acid solutions of 0.1 M were used to adjust the pH of waters before EC-treatment.

Beside sulfate, mining waters are known to be heavily contaminated with metals (Cu²⁺, Ni²⁺, Zn²⁺, Mg²⁺, Ca²⁺) and anions (NO₃⁻, Cl⁻). Presence of these ions may affect the EC-performance and efficient removal of sulfate by electrocoagulation. The effect of the presence of NO₃⁻, Cu²⁺, Zn²⁺ and Ni²⁺ were also studied. Experiments were performed according to the experimental procedure described above using synthetic mining waters and Na₂SO₄/NaCl solutions.

In this study, the real mining water sample was collected from one of the mines located in Finland and the initial concentrations of the monitored compounds are given in Table 6 in Section 3.4. There was no need to adjust the pH or conductivity of the initial sample due to the suitable pH value of 6.5 and high concentrations of anions bringing the conductivity to the desired level of 5.6 mS/cm.

2.3. Experimental design and modeling

Regression modeling was performed in MATLAB® [58] using the results from tests with synthetic waters. Three variables sulfate concentration (X₁), initial pH of the solution (X₂) and applied current (X₃) were selected as study parameters for regression modeling. The levels were equally spaced and dedicated to the high (3 g/L, pH 10 and 3 A), intermediate (2 g/L, pH 7 and 2 A) and low (1 g/L, pH 4 and 1 A) values of the parameters. A total number of the experiments according to the full factorial design was 3^k, where k corresponds to the number of

Table 1
Compositions of synthetic mining waters and chemical suppliers.

Compound	Concentration, mg/L			Chemicals
	Low	Medium	High	
SO ₄ ²⁻	1000	2000	3000	Na ₂ SO ₄ (Merck KGaA)
NO ₃ ⁻	20	40	60	NaNO ₃ (Merck KGaA)
Cl ⁻	100	200	300	NaCl (Merck KGaA)
Cu ²⁺	2	5	8	CuSO ₄ (Merck KGaA)
Ni ²⁺	2	5	8	NiSO ₄ (Merck KGaA)
Zn ²⁺	5	10	15	ZnSO ₄ (Merck KGaA)
NH ₄ ⁺	10	20	30	NH ₄ Cl (Merck KGaA)

Table 2
Full factorial design matrix of three factors along with experimental and predicted concentrations of sulfate using the final empirical model (Eq. (4)).

Run	Initial values		Measured responses		
	Initial sulfate concentration, C_0 , mg/L X_1	Current, I , A X_2	Initial pH, pH_0 X_3	Final sulfate concentration, C_{fe} , mg/L (experimental) Y	Final sulfate concentration, C_{fe} , mg/L (predicted) Y
1	2052.5	2	6.98	1321.82	1454.01
2	1939.79	2	7.00	1314.92	1362.48
3	1961.35	2	7.00	1281.70	1379.99
4	1976.16	3	7.01	1356.07	1333.91
5	954.8	1	3.95	941.99	881.42
6	970.11	1	4.00	910.08	896.24
7	975.22	1	7.00	874.68	907.40
8	977.05	1	10.02	883.20	915.38
9	982.95	1	4.03	885.79	908.67
10	975.74	1	3.97	899.33	901.69
11	976.61	1	4.00	891.54	902.53
12	971.96	1	4.01	928.76	898.03
13	975.64	1	4.00	911.06	901.59
14	1970	2	6.97	1506.18	1387.01
15	2942.98	3	10.05	1692.20	1776.94
16	2960.74	3	10.00	1756.80	1788.60
17	2918.03	1	4.03	2886.19	2781.40
18	2942.82	1	7.02	2870.85	2811.60
19	2953.19	1	9.98	2900.55	2827.84
20	1956.51	2	4.00	1463.29	1468.77
21	1959.67	2	10.11	1234.38	1282.51
22	2948.41	2	9.99	2161.97	2089.19
23	2946.95	2	3.99	2232.93	2273.42
24	2968.68	2	6.86	1994.19	2202.38
25	974.67	2	3.95	694.14	672.95
26	976.61	2	6.85	689.61	584.90
27	986.33	2	10.20	610.30	489.27
28	2923.83	3	6.98	2139.34	1957.28
29	1957.62	3	9.98	1173.37	1131.38
30	1971.48	2	4.00	1463.29	1489.08
31	2948.26	3	4.00	1457.52	2100.48
32	1971.48	2	4.00	1622.38	1489.08
33	981.37	3	4.00	742.16	839.70
34	1886.11	3	3.98	1497.19	1420.64
35	972.72	3	6.91	699.52	688.57
36	979.43	3	9.77	455.29	549.78
37	1970.13	1	3.95	1651.23	1907.47
38	1979.76	1	7.01	1934.62	1865.97
39	1967.79	1	10.03	1781.70	1803.76

factors [55]. In total 39 experiments were performed including the repetition of combinations at high, intermediate and low factor levels. Table 2 shows experimental runs that were performed according to full factorial experimental design including the initial values of parameters as well as experimental and predicted values of the final concentration of sulfate. Measured values were obtained after 5 h of EC-process after each run while predicted values were calculated using the Eq. (4) proposed by the final model. The analysis of variance (ANOVA) was used to assess the importance and significance of the model and its parameters. Kinetic models for sulfate removal were developed using the results obtained during the tests performed according to the full factorial design of experiments. Results were fitted to first (Eq. (5)) and second-order (Eq. (6)) models to study mechanisms involved in sulfate removal by electrocoagulation.

3. Results and discussion

3.1. Summary of laboratory results

Before applying the RSM to study the influence of different parameters on the sulfate removal by electrocoagulation, some laboratory results that provide more profound understanding of the models and

approaches described in this article are presented. During the EC, the removal rate of sulfate varied from 1 to 54% depending on the operational conditions. The summary of changes in final sulfate concentration is given in Fig. 1. The increase in pH during the first hour of treatment was observed regardless of the initial pH and applied current. Thus, the pH after the first hour of treatment varied from 11 to 12.17 resulting in EC-process operation at alkaline conditions. The increase in pH is due to the water oxidation at the anode and evolution of OH radical from the cathode. A buffering effect of the iron oxides/hydroxides mixture is mainly responsible for the stabilization of pH over 11 [55,59].

In addition to sulfate removal, elimination of chloride was observed. Thus, chloride removal at 2 A was as high as 41% for initial chloride concentration of 200 mg/l with the presence of 2000 mg/l of sulfate and initial pH 10.11. At 3 A chloride removal was as high as 63% for initial chloride concentration of 300 mg/l with the presence of 1000 mg/l of sulfate and initial pH 9.7. No chloride removal was observed at 1 A. The decrease in chloride concentration can be explained by the formation of its intermediates such as chlorine/hypochlorite and chloramines. Downward trend in chloride elimination with a decrease in current density is in agreement with the results reported by Llanos et al. [33] and Souza et al. [47].

Applied constant current of 1, 2 and 3 A resulted in the electrode consumption of 1, 2 and 3 g per liter of treated water per hour, respectively. The generation of iron was repeatable and increased with the increase in the applied current. The weight loss from electrodes was consistent with the theoretical amounts calculated based on the Faraday's law, assuming the release of Fe^{2+} from the anode. The initially clear colorless solution became turbid orange suspension typical for Fe (III) hydroxides after 5 min and turned to brown-green suspension at the end of the treatment. According to literature, among the possible iron compounds formed within the studied ranges of initial pH (4, 7, 10), RedOx (0.2 to -0.2 V) and sulfate concentration are Fe_3O_4 , γ - $FeOOH$ and positively charged Fe^{3+} , $FeOH^+$, $Fe(OH)_2^+$, the most expected sulfate containing compounds were expected to be $(H_3O)Fe(SO_4)_2(H_2O)_3$ rhomboclase and its modifications [60]. The detected XRD pattern of a synthetic magnetite/amorphous FeO was obtained by the reflections originated from the corresponding natural magnetite. The XRD results confirmed the formation of Fe_2O_4 and Fe_3O_4 as the main products of EC-treatment.

More phases containing sulfate were determined from the solid samples using SEM. Results from SEM demonstrated the formation of banded and granulated species containing Fe, O and S. Fig. 2 shows a backscattered SEM image of solid sample taken after the EC test at 3 A. In Fig. 2, light gray color denotes the iron oxide, gray color corresponds to the phase containing sulfate and dark gray color turns to phase with the presence of chloride.

To evaluate the effect of co-existing ions, separate tests were performed using synthetic mining waters (Table 1) and solutions containing only SO_4^{2-} and Cl^- anions. After 5 h of treatment at initial sulfate concentrations 1000 and 2000 mg/L, final concentrations of sulfate were comparable within the 5% range. No significant effects of the presence of other contaminants on sulfate removal were observed. However, differences in final sulfate concentrations for 3000 mg/L with the presence of 8 mg/L of Cu, Zn and Ni is probably due to possible precipitation of metals sulfide within the studied ranges of final pH over 11 and RedOx below -0.2 V [61]. Similar trends were observed within the studied ranges of initial pH (4, 7) and applied current (1 A, 3 A). As an example, the results from EC-tests at 2 A and pH 10 are presented in Fig. 3.

3.2. Regression modeling of sulfate removal by electrocoagulation

Firstly, the simplest linear regression model (Eq. (1)) predicting the final sulfate concentration in EC treated solution was used to study the main parameters affecting the process performance. Obtained results show the primary influence of initial sulfate concentration in the

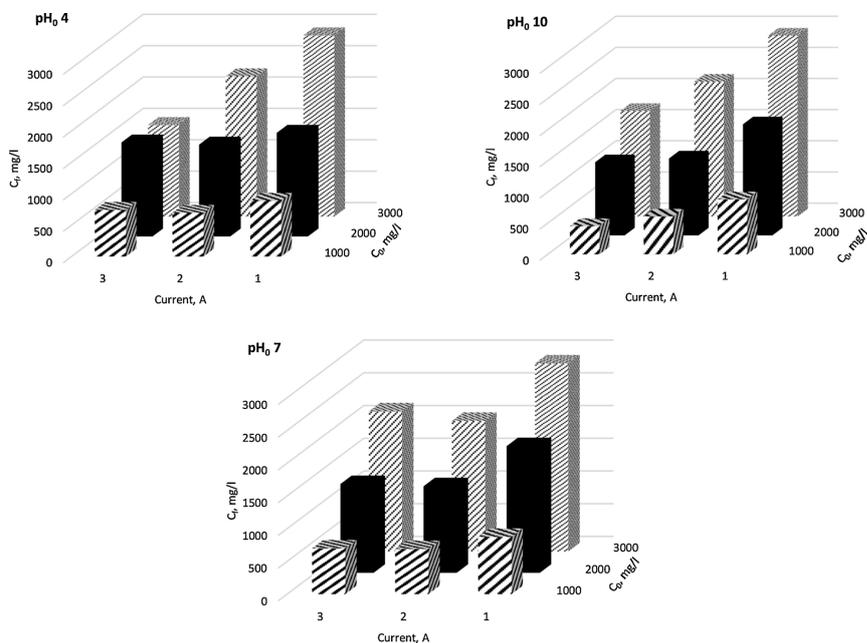


Fig. 1. Effect of applied current and initial sulfate concentration (C₀) on final sulfate concentration (C_f) at various initial pH (pH₀) during the electrocoagulation treatment of synthetic mining waters.

solution and applied current. No effect of the initial pH was observed. Secondly, the simplest model has been improved by adding interaction and quadratic terms (Eq. (2)).

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 \tag{1}$$

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_1X_2 + b_5X_2X_3 + b_6X_3X_1 + b_7X_1^2 + b_8X_2^2 + b_9X_3^2 \tag{2}$$

The analysis of variance (ANOVA) was performed to evaluate the importance and significance of the model. Analysis of ANOVA results was performed with respect to a p-value that is commonly compared to a widely acceptable significance level of 5%. ANOVA results revealed that some terms were insignificant and only parameters with the p-values less than 0.05 were included in the final model. Results observed in Table 3 illustrate that all p-values of linear terms, C₀I, IpH₀ and I² terms were less than 0.05 that explained the significance of these

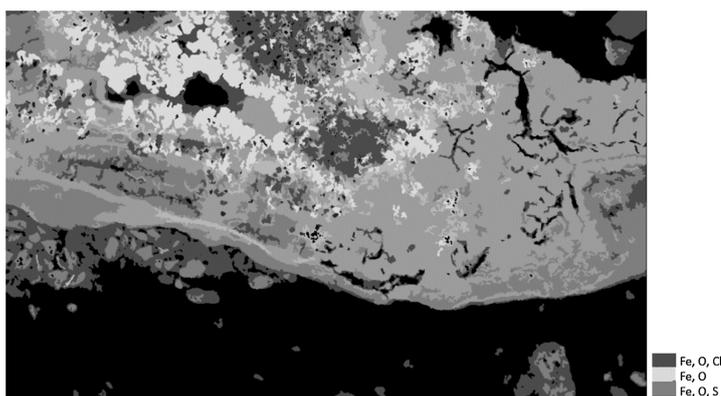


Fig. 2. Backscattered SEM image of solids generated during the EC process (C₀ = 3000 mg/l, pH 10, 3 A), magnification 100, EDS measurement is done to find out their elemental composition.

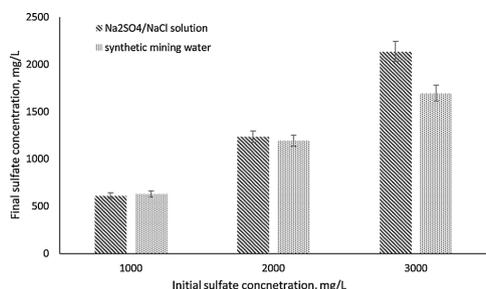


Fig. 3. Effect of co-existing ions on final sulfate concentration at initial pH 10 and current 2 A during the electrocoagulation treatment of synthetic mining waters (Table 1) and Na₂SO₄/NaCl solutions.

Table 3 ANOVA of the model containing linear, interaction and quadratic terms for the prediction of the final sulfate concentration after 5 h of EC treatment.

	SumSq	DF	MeanSq	F	p-value
<i>C₀</i>	13.504	1	13.504	1288.387	2.53E-24
<i>I</i>	1.278	1	1.278	121.919	1.63E-11
<i>pH₀</i>	0.118	1	0.118	11.274	0.002
<i>C₀I</i>	0.263	1	0.263	25.083	2.98E-05
<i>C₀pH₀</i>	0.001	1	0.001	0.133	0.718
<i>IpH₀</i>	0.122	1	0.122	11.672	0.002
<i>C₀²</i>	0.0067	1	0.007	0.651	0.427
<i>I²</i>	0.313	1	0.312	29.848	8.79E-06
<i>pH₀²</i>	0.0002	1	0.0002	0.0236	0.879
Error	0.283	27	0.283	1	0.5

variables and showed their significant influence on the sulfate elimination by EC. The rest of the variables were considered insignificant due to the high p-values and were expected to have the least effect on final sulfate concentration.

Even though ANOVA results showed the significance of term *pH₀* ($p = 0.002 < 0.05$), in the regression model, the coefficient of this parameter was of minor significance with the p-value equaled to 0.068 (the results are not presented here), that was higher than 0.05 threshold. Additionally, it was observed in experiments that regardless of the initial pH, the pH of the solutions increased up to 12 after 1 h of treatment meaning that the electrocoagulation took place at alkaline conditions. Based on these findings, the term *pH₀* was removed from the final regression model. The influence of initial pH was taken into account in interaction term *IpH₀* of the model. After the deletion of insignificant terms, the model became:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_1X_2 + b_4X_2X_3 + b_5X_2^2 \quad (3)$$

According to the experimental data, the final empirical model valid within the variable range of parameters investigated can be described as follows:

$$C_{fp} = 0.44 + 1.16C_0 - 0.62I - 0.17C_0I - 0.17IpH_0 + 0.20I^2 \quad (4)$$

The measured and predicted final sulfate concentrations obtained during the EC treatment of synthetic mining waters are shown in Table 2. Comparison of experimental and modeled data suggests the reasonably good prediction of final sulfate concentration after EC treatment by the suggested final model. The goodness of fit criteria, *R*² was equal to 0.98.

Table 4 presents the coefficients of the final model and their t- and p-values. The t-value showed the significance of the regression

Table 4 Coefficients of the final model (Eq. (3)) for the prediction of the final sulfate concentration after 5 h of EC treatment.

Term	Coefficient	SE	tStat	pValue
Constant	0.438	0.141	3.100	0.004
<i>C₀</i>	1.163	0.054	21.495	< 0.001
<i>I</i>	-0.615	0.147	-4.195	< 0.001
<i>C₀I</i>	-0.174	0.027	-6.434	< 0.001
<i>IpH₀</i>	-0.017	0.004	-4.404	< 0.001
<i>I²</i>	0.202	0.036	5.549	< 0.001

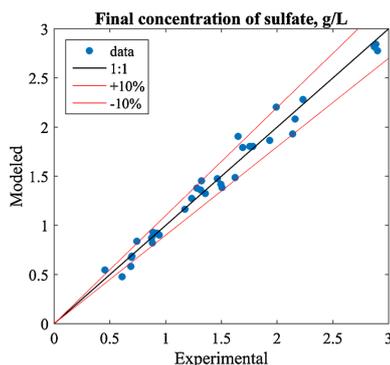


Fig. 4. Measured and predicted values of the developed model for final sulfate concentration.

parameters. The higher the absolute t-value was, the greater was the influence of the parameter. The adverse effects of the linear term of applied current and interaction terms were observed resulting in lower final sulfate concentration with the increase of these variables. The positive effect of the linear term of initial sulfate concentration and square term of applied current resulted in higher final sulfate concentrations with the increase of these factors.

Since the final concentration of a contaminant is a controlled value in current regulations and established discharge limits, it was decided to mainly study the final concentration as a response. The measured and predicted values of the final sulfate concentration achieved during the EC-treatment with iron electrodes are shown in Fig. 4. Measured values of final sulfate concentration were measured after 5 h of EC treatment and predicted values of final sulfate concentration were obtained by applying the developed model (Eq. (4)). Comparison of modeled and experimental data suggests a good prediction of final sulfate concentration by the studied regression model. In a qualitative consideration, it can be seen that the linear regression model well reproduced experimental results. The relative difference between the calculated and experimental values did not exceed 10% for most of the experiments.

In addition to the final sulfate concentration, the effect of studied factors on the removal efficiency as one of the process performance parameters was investigated. Here removal efficiency was calculated based on the predicted final concentrations of sulfate and the influence of the studied parameters was demonstrated. Nine surface plots as a function of two factors (initial pH, *pH₀*, and applied current, *I*, *A*; applied current, *I*, *A* and initial sulfate concentration, *C₀*, *g/L*; initial pH, *pH₀*, and initial sulfate concentration, *C₀*, *g/L*) were built to illustrate the relationship between various EC operation parameters and sulfate removal. The third factor was fixed at the corner points (initial sulfate

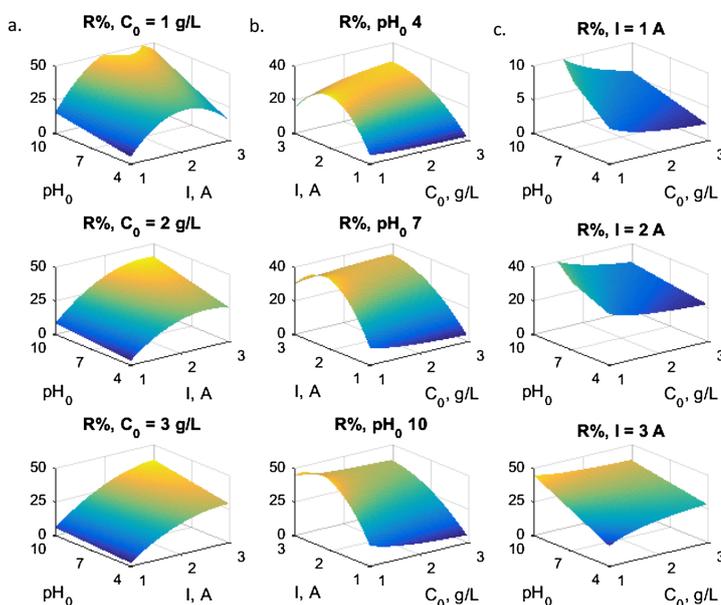


Fig. 5. Surface plots of sulfate removal predicted by the developed model at the corner points: a. at fixed initial concentrations (C_0), b. at fixed initial pH (pH_0), c. at fixed applied current (I).

Table 5
Summary of results obtained by using first and second-order kinetic models.

Initial sulfate concentration	Current	First-order model	Correlation coefficient	Second-order model	Correlation coefficient	Removal efficiency
C_0 , mg/L	I , A	k_1 , min^{-1}	R^2 , -	k_2 , $(\text{mg/L})^{-1} \text{min}^{-1}$	R^2 , -	R , %
2943	3	0.0021	0.8908	9.80E-07	0.8903	43
1958	3	0.0020	0.9814	1.34E-06	0.9754	40
979	3	0.0027	0.9940	4.36E-06	0.9980	54
2948	2	0.0014	0.9019	5.80E-07	0.8923	27
1960	2	0.0020	0.9195	1.36E-06	0.9080	37
986	2	0.0016	0.9371	2.18E-06	0.9107	38
2953	1	0.0001	0.3998	2.29E-08	0.3977	2
1968	1	0.0003	0.9032	1.79E-07	0.8974	9
977	1	0.0003	0.9980	3.26E-07	0.9976	10

concentration, C_0 , g/L, initial pH, pH_0 , and applied current, I , A). No significant effect of pH on sulfate removal at low current was observed; however, pH had an essential effect on the process efficiency with an increase in current. This finding is illustrated on the surface plots in Fig. 5a demonstrating that a combination of high applied current and high initial pH resulted in more efficient removal of sulfate. This is due to the speciation of the metal species generated during the EC-process at different pH condition. Surface plots in Fig. 5b reflected that sulfate removal with EC improved at an applied current above 2 A and concentrations lower than 3000 mg/L. Fig. 5c illustrated that sulfate removal increased with pH increasing. In both cases (Fig. 5b, c) more efficient sulfate removal for lower concentration at selected applied current may be due to the greater amount of the coagulant available.

3.3. Kinetic study

In this work, the kinetic study for the sulfate removal was performed for various applied currents and initial sulfate concentrations. First and

second-order kinetic models were tested to study the removal rate and electrocoagulation mechanisms. Rate constants were determined using linearized time-dependent concentration equations of first (Eq. (5)) and second-order (Eq. (6)) models [62]:

$$\ln C = \ln C_0 - k_1 t \tag{5}$$

$$1/C = 1/C_0 + k_2 t \tag{6}$$

where C (mg/L) is the concentration of sulfate in the solution at the end of treatment, C_0 (mg/L) is the initial sulfate concentration, k_1 (min^{-1}) and k_2 ($(\text{mg/L})^{-1} \text{min}^{-1}$) are the first and second order constants. Correlation coefficients were gained by plotting linear trend lines and rate constants were obtained as slopes of these lines. The goodness of the kinetic model was described using the correlation coefficient, R^2 . The values of the rate constants and the correlation coefficients are summarized in Table 5.

As can be seen, sulfate obeys relatively well both first and second order kinetics, suggesting that both physical (enmeshment) and

Table 6
Initial and residual concentration of monitored anions after 5 h and cations after 1 h of EC-treatment of real mining water.

Compounds	Source of water	Units	Initial concentration	Residual concentration		Removal efficiencies, %	
				2 A	3 A	2 A	3 A
SO ₄ ²⁻	synthetic mining water	mg/L	2052.50	1321.82	1356.07	36	34
SO ₃ ²⁻			2968.68	1994.19	2139.34	33	28
NO ₃ ⁻			58.25	< 0.5	< 0.5	> 99	> 99
SO ₄ ²⁻	real mining water	mg/L	2452.98	1766.15	1622.55	28	34
NO ₃ ⁻			254.33	9.02	3.59	96	99
Co ²⁺	real mining water	ug/L	15.29	0.08	0.12	99	99
Ni ²⁺			9.28	0.33	0.29	96	97
Zn ²⁺			397.54	< 0.8	< 0.8	> 99	> 99
Cu ²⁺			11.72	0.41	0.37	96	97
Cd ²⁺			2.09	< 0.08	< 0.08	> 99	> 99

Table 7
Measured and predicted values of final sulfate concentrations and removal efficiencies obtained during the EC-treatment of real mining water.

Current, <i>I</i> , A	3	2
Initial pH, <i>pH</i> ₀	6.13	6.25
Initial concentration, <i>C</i> ₀ , mg/L	2349.00	2440.00
Final concentration, <i>C</i> _f , mg/L	1623.00	1766.00
Predicted final concentration, <i>C</i> _{fp} , mg/L	1609.79	1795.88
Predicted removal efficiency, <i>R</i> _p , %	31	26
Measured removal efficiency, <i>R</i> , %	31	28

chemical (co-precipitation) reactions are involved in the removal mechanisms [62]. Values of k_1 and k_2 increase when the applied current increases and concentration decreases. The negligible removal rate of sulfate could be the reason for the small correlation coefficient at current 1 A and initial sulfate concentration of 2953 mg/L. Studying electrochemical treatment of mining waters, Nariyan et al. [17] proposed that sulfate follows the second-order kinetic model; however, reported values for correlation coefficients are close to each other and no decision on the model can be made only based on the correlation coefficient. Additionally, it should be mentioned that obtained values for k_1 and k_2 were in agreement with the reported study [17]. Higher R^2 values and removal efficiencies illustrated that experimental conditions proposed in the present research were more suitable for sulfate removal.

3.4. EC treatment of real mining waters

To evaluate the treatment performance of electrocoagulation method for sulfate removal, electrochemical tests were performed also with a real mining water sample. The removal efficiencies at two test conditions were compared with the results obtained for synthetic mining water treatment at the same conditions by applying the currents of 2 and 3 A. EC-treatment at current 1 A was not performed due to negligible removal rates achieved during the tests with synthetic waters. Sulfate concentration was monitored, and sulfate removals were compared with those obtained during the tests with synthetic mining waters. In addition to sulfate elimination, nitrate and metals' removals were also monitored.

According to the results presented in Table 6, electrocoagulation was found to be suitable for the partial removal of sulfate from synthetic waters and real mining waters. Almost complete removal of studied metals was achieved after 1 h of treatment, while over 90% removal of nitrate was observed only after 5 h of treatment. This study demonstrates that sulfate can be removed to a concentration below current limits established in Finland and Chile (Nariyan, et al., 2018b). Multi-stage electrocoagulation treatment, as well as a combination of

electrocoagulation with other treatment technologies, allow efficient removal of sulfate from mining waters below the current discharge limits in most parts of the world.

To predict the removal efficiencies during the treatment of real mining waters, the developed model was used. Firstly, predicted final concentrations were calculated and used to estimate the removal efficiencies. The comparison of the experimental and predicted values is given in Table 7.

Additionally, to verify the model, experimental results reported by Nariyan et al. [17] were used and the following conditions were fitted to the model: current 3.25 A, initial pH 12, initial sulfate concentration 1600 mg/L, iron electrodes and monopolar arrangements. The predicted removal efficiency was 45%, which was in agreement with the experimental results reported (40% removal of sulfate after 2.5 h of treatment). Validation of the model by using the results of real mining water EC-treatment demonstrated that the developed model could be used to predict the final concentrations especially at high currents.

4. Conclusion

The performed study on parameters affecting the sulfate removal from mining waters by electrocoagulation provided knowledge on the significance of the parameters and their interactions. That makes future implementation and scale-up of the process possible. The highest removal could be achieved at the highest applied current, highest pH and lowest initial sulfate concentration. With the increase in initial pH from 4 to 10 no significant influence of initial sulfate concentration was observed. In general, the increase in applied current and initial pH favors the removal of sulfate. The most significant parameter in sulfate removal was its initial concentration in water; the increase in concentration challenged the sulfate elimination. Kinetic studies proposed that both physical and chemical mechanisms are involved in sulfate removal from mining waters by electrocoagulation. The tests with the real water sample prove the suitability of EC-treatment for the sulfate removal from real mining waters. The model developed using the results of synthetic water treatment successfully predicted the final concentration of sulfate after EC-treatment of real mining waters. In addition to sulfate, the removal of nitrate, Co²⁺, Ni²⁺, Zn²⁺, Cu²⁺ and Cd²⁺ from real mining waters was observed. After the theoretical background on sulfate removal is gained, the next important process development step is the determination of the scale-up parameters, sizing of the equipment and economic evaluation of the technique.

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Publication IV

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Treatment of mining wastewater polluted with cyanide by coagulation processes: A mechanistic study



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ABSTRACT

In this work, coagulation and electrocoagulation for the removal of cyanide ions contained in synthetic mining wastewater were evaluated paying particular attention to the elucidation of the coagulation mechanisms. Iron and aluminum salts with concentrations ranging from 0.01 to 10 000 mg dm⁻³ metal were used in chemical coagulation. Experimental data were properly fitted to Freundlich isotherm to elucidate that the main mechanism to remove cyanide during chemical coagulation was adsorption onto coagulant flocs although a maximum cyanide removal percentage of only 25% was attained. Then, electrochemical coagulation with iron and aluminum electrodes was evaluated at 1, 10 and 100 A m⁻², obtaining completely different results. Iron electrochemical coagulation leads to the complete cyanide removal regardless of the current density applied, although the TOC removal was much lower than expected. On the contrary, only 60% of cyanide removal was reached by aluminum electrochemical coagulation and its efficiency was found to be highly dependent on the current density applied. Furthermore, no cyanate or hazardous inorganic chlorine species were detected during both electrocoagulation processes. However, chloride was oxidized to hypochlorite and then, it reacted with ammonium ions (contained in mining wastewater or produced by chemical reduction of nitrate by aluminum) to form chloramines. A proposal of coagulation mechanisms during the electrochemical process that explains experimental results was developed which involved the formation of iron-cyanide complexes, charge neutralization, adsorption on a superficially charged metal precipitate and/or enmeshment into a sweep metal floc.

1. Introduction

Free cyanide may be contained in industrial wastewater such as mining, metallurgical, petrochemical or coking wastewater [1–4]. About 13% of the 1.1 million metric tons of hydrogen cyanide produced annually worldwide is consumed by mining and metallurgical processes [5]. In mining processes, cyanide solutions are primarily used for the extraction of gold and silver from crushed ores. In addition, also they may be used to recover other metals such as copper, lead and zinc. The pH of cyanide solutions is a key parameter because free cyanide can be in the form of cyanide anion or volatile hydrocyanic acid, this last form being the predominant species for pH values below 8.5. Cyanide is considered a very toxic substance, because it can inhibit oxygen transfer to the cells due to its ability to bind iron in the blood by forming complexes and then, it can cause suffocation in animals and humans. The oral cyanide dose that is lethal to 50% of the exposed population

ranges between 1 and 3 mg/kg of body weight.

The cyanide removal from industrial wastewater by conventional technologies has been widely reported during the last decade. Thus, cyanide may be degraded to ammonia by microorganisms under aerobic conditions [1] or it may be oxidized to less toxic cyanate by strong oxidizing agents such as hydrogen peroxide, hypochlorite and ozone [6]. In addition, it may be adsorbed on clays, feldspars and organic carbon, react with sulfur to form the seven-times less toxic thiocyanate and it may also strongly bind with various metals such as Fe, Cu, Ni, Mn, Pb, Zn, Cd, Sn or Ag to generate soluble and/or insoluble cyanide-metal complexes which are mostly non-reactive compounds [2,3,7–10].

Electrochemical technologies have recently emerged for industrial applications thanks to their simple equipment and easy automation in different environments and scales [11–16]. Furthermore, these technologies can be considered as environmentally friendly because no

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addition of chemicals is needed and they can also be easily powered with green energy sources such as solar panels, windmills or fuel cells [17–20]. Among others, electrochemical oxidation, electro-Fenton and electrochemical coagulation have been reported to remove cyanide from industrial wastewaters. Both electrochemical oxidation and electro-Fenton leads to the oxidation of cyanide to cyanate and then, cyanate is mineralized to carbon dioxide and nitrogen. At this point, electrochemical oxidation attained around 90% of cyanide removal by using several anode materials such as mixed metal oxides, platinum, PbO₂ or boron doped diamond [21–23]. Likewise, electro-Fenton with reticulated vitreous carbon as cathode material reached over 90% of cyanide oxidation to cyanate by electrochemically generated hydrogen peroxide [24]. On the contrary, electrochemical coagulation is mainly based on the release of coagulants from a sacrificial anode. These species reduce the solubility of free cyanide in solution by different mechanisms. In literature, efficiencies over 90% for the removal of cyanides were reported by using electrochemical coagulation with iron electrodes, although no in-depth studies on removal mechanisms were found [25–27].

In this context, this paper mainly focuses on the development of coagulation mechanisms both in chemical and electrochemical coagulation processes to remove 100 mg dm⁻³ of cyanide in synthetic mining wastewater at alkaline pHs. To do this, standard jar test experiments were carried out by using iron and aluminum salts. Likewise, iron and aluminum electrodes inserted in a flow-by electrochemical reactor were tested under several current density values. Finally, the chemical reactivity of organic and inorganic species contained in solution was studied in order to rule out the formation of hazardous species.

2. Material and methods

2.1. Chemicals

Sodium cyanide and mining wastewater compounds [12] were of analytical grade and purchased from Panreac Química SLU. Chemicals to analyze cyanide were purchased from Merck and other chemicals used in several analyses were purchased from Sigma Aldrich, and each one was also analytical grade. Double deionized water of Millipore Milli-Q system with a resistivity of 18.2 MΩ cm at 25 °C was used to prepare each solution.

2.2. Experimental procedures

Chemical coagulation experiments were developed by using the standard Jar-test technique. Each flask was filled with a volume of 500 mL of mining wastewater intensified with 100 mg CN⁻ dm⁻³. Then the selected iron or aluminum chloride concentration was added, followed by the dosing of NaOH solution used for pH adjustment to a value of 12. After that, the mixture underwent 3 min rapid mixing and 12 min slow mixing. Then, after settling for 30 min, the supernatant liquid was filtered through a 0.20 μm filter and then, cyanide concentration was measured.

Electrochemical coagulation experiments were carried out in a single compartment flow cell working under batch operation mode [28,29]. The electrodes placed in the electrochemical cell were made of iron and aluminum, and both anode and cathode materials were the same at each experiment. The electrode dimensions were 10 cm × 10 cm and the net spacing between electrodes was 0.9 cm. The electric current was applied by using a Delta Electronika ES030-10 power supply characterized by the ranges 0–10 A and 0–30 V, and the current flowing through the cell was measured with a Keithley 2000 digital multimeter. Each experiment was carried out under galvanostatic conditions and the current densities applied were 1, 10 and 100 A m⁻². A volume of 2.0 L of mining wastewater intensified with 100 mg CN⁻ dm⁻³ (at initial pH of 12) were introduced into a glass tank and then, recirculated through the electrochemical cell using a

peristaltic pump. Samples of 75 mL were collected each time and after settling time of 30 min, the supernatant liquid was filtered through a 0.20 μm filter for the determination of cyanide and other inorganic ions. TOC measurements were carried out without filtration. The chemical coagulation tests were performed during 15 min whereas electrochemical coagulation experiments were carried out during 540 min each one.

The chemical composition of the synthetic mining wastewater used has been previously reported elsewhere [12].

2.3. Analytical procedures

Cyanide concentrations were determined by silver nitrate titration method, which was initially introduced by Ryan and Culshaw [30]. The silver nitrate (AgNO₃) titration bases on the reactions produced by this salt in a cyanide media, where soluble silver cyanide complex (Ag(CN)₂⁻) is firstly formed (Eq. (1)), after which, the excess Ag⁺ ions complex with rhodanine turning the color from a yellow to a pale pink. Further addition of AgNO₃ yields solid argentocyanide (AgCN) (Eq. (2)). In this study, a modified standard method was used. AgNO₃ stock solution was further diluted to yield 0.00125 and 0.000125 M AgNO₃ solutions for the titrations. Stronger AgNO₃ solution was used for samples containing more than 10 mg dm⁻³ of cyanide whereas more dilute was used for samples containing 1–10 mg dm⁻³ of cyanide. The indicator solution was prepared by dissolving 0.03 g 5-(4-Dimethylaminobenzylidene)-rhodanine in 0.1 dm³ acetone and stored in a dark bottle. The titrations were carried out with 0.005 dm³ of cyanide solution to which four drops of rhodamine indicator solution were added, after which the sample was titrated to a color change. Finally, the concentration of CN⁻ was calculated using Eq. (3), where M is the molar mass (g mol⁻¹), V is volume (10⁻³ dm³), and factor of reagent is 0.012255 for 0.00125 M AgNO₃ solution and 0.0012255 for 0.000125 M AgNO₃ solution.



$$\text{CN}^-(\text{mg dm}^{-3}) = \frac{M(\text{NaCN}) \cdot V(\text{AgNO}_3)}{M(\text{CN}^-) \cdot V(\text{sample})} \cdot \text{factor of reagent} \cdot 10000 \quad (3)$$

In addition, ion chromatography by using a Metrohm 930 Compact IC Flex coupled to a conductivity detector was used to determine inorganic ions. The column Metrosep A Supp 7 located in an oven at 45 °C with a mobile phase of 85:15 v/v 3.6 mM Na₂CO₃/acetone were used to analyze anions whereas cations were analyzed by using the column Metrosep C6 250 at 30 °C with a mobile phase of 1.7 mM HNO₃ and 1.7 mM 2,6-pyridinedicarboxylic acid. The flow rates of mobile phases were 0.8 and 0.9 cm³ min⁻¹ to determine anions and cations, respectively. In both cases, 20 μL was the volume injection of each sample.

The total iron or aluminum concentration was measured off-line using an inductively coupled plasma Liberty Sequential Varian system according to the standard methods. The pH and conductivity were simultaneously measured using a Sension + MM150 Portable Multi-Parameter Meter from HACH. The Total Organic Carbon (TOC) was determined using a Shimadzu TOC-VCPH analyzer and the theoretical TOC was calculated according to Eq. (4) where [CN⁻] is referred to free cyanide that remains in solution, AW_C is the atomic weight of carbon (12 g mol⁻¹) and MW_{CN⁻} is the molecular weight of cyanide (26 g mol⁻¹). In addition, hypochlorite was analyzed by titration with 0.001 M As₂O₃ in 2 M NaOH [31,32].

$$\text{TOC}_{\text{th}} = [\text{CN}^-] \cdot (\text{AW}_C/\text{MW}_{\text{CN}^-}) \quad (4)$$

Finally, the sludge generated during both conventional and electrochemical coagulation was characterized by X-Ray Diffraction (XRD) analysis using a Philips PW-1710 instrument with Ni-filtered Cu Kα radiation (λ: 1.5404 Å). Samples were scanned at a rate of 0.02° step⁻¹

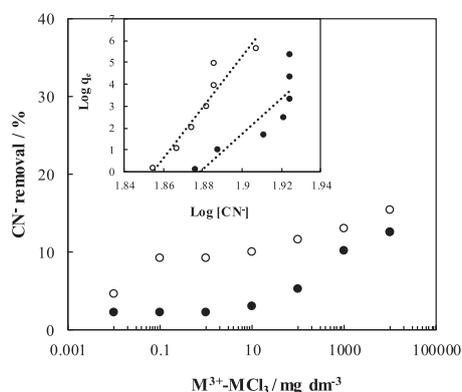


Fig. 1. Cyanide removal percentage as a function of coagulant dosages during chemical coagulation of synthetic mining wastewater intensified with $100 \text{ mg CN}^- \text{ dm}^{-3}$ at pH of 12. Inorganic coagulants: Fe^{3+} - FeCl_3 (full symbols), Al^{3+} - AlCl_3 (empty symbols). The inset shows data fitted to Freundlich isotherm.

within the range $10^\circ \leq 2\theta \leq 90^\circ$ and the diffractograms obtained were compared with the JCPDS-ICDD references.

3. Results and discussion

Fig. 1 shows the percentage of cyanide removed during the chemical coagulation of 100 mg dm^{-3} of cyanide in mining wastewater. Every test was developed at pH 12 to ensure the stability of cyanide ion in aqueous solution avoiding the release of HCN. Thus, after the addition of the coagulant with the corresponding decrease in the pH, this parameter was rapidly modified up to 12.0. The coagulants tested were inorganic salts of iron (FeCl_3) and aluminum (AlCl_3) within the wide range $0.01 - 10\,000 \text{ mg dm}^{-3}$. Ferric iron (Fe^{3+}) was selected as iron salt because the pH conditions used leads to a rapid oxidation of ferrous iron (Fe^{2+}) to ferric form in water [33].

As it can be seen, both reagents can help to remove cyanide, although the efficiency is not very high and cyanide removal percentages during chemical coagulation are always below 15%, even for the highest coagulant dosage of $10\,000 \text{ mg dm}^{-3}$. This last value generates a large amount of sludge in the final effluent and, for this reason, no higher coagulant doses were used. In addition, the percentage of cyanide removed is higher with the aluminum than with the iron coagulant dosages.

Initially, adsorption of the cyanide onto the growing hydroxide precipitates is the expected primary mechanism to explain the removal of this pollutant. To confirm this and, thus, to elucidate the possible mechanisms which control the removal of cyanide in mining wastewater by using chemical coagulation processes, experimental data were fitted to Freundlich isotherm (Eq. (5)) as shown in the inset of Fig. 1. The Freundlich isotherm is an adsorption curve which relates the equilibrium concentration of a solute adsorbed onto the surface of a solid through chemisorption, physisorption or both (q , $\text{mg CN}^- \text{ adsorbed/g M-MCl}_3$) with the concentration of the solute in the solution (CN^- , mg dm^{-3}). The models obtained for iron and aluminum adsorbents are shown in Eqs. (6) and (7), respectively. As observed, fitting of the experimental data to the model is not perfect and suggests that, in addition to adsorption, other processes must be contributing to the removal of cyanide. Thus, experimental data are observed to fit the Freundlich isotherm during aluminum chemical coagulation with a regression coefficient of 0.9047 whereas for chemical coagulation with iron, data fit the Freundlich isotherm with a lower regression coefficient

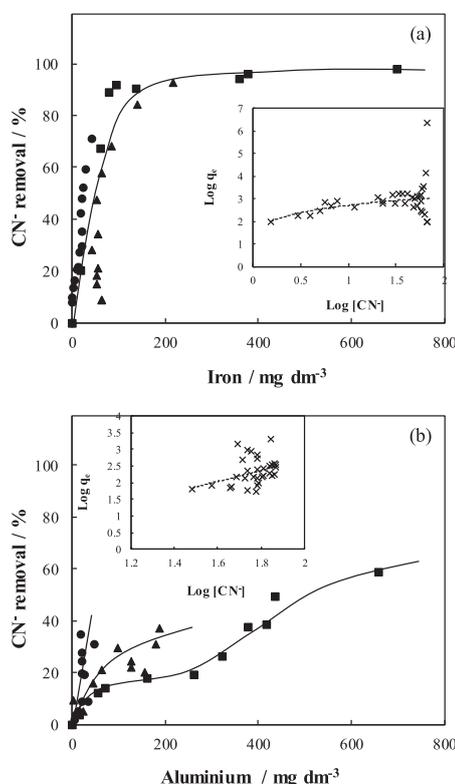


Fig. 2. Cyanide removal percentage as a function of electrogenerated coagulant concentration during electrochemical coagulation of synthetic mining wastewater intensified with $100 \text{ mg CN}^- \text{ dm}^{-3}$ at initial pH of 12. Anode/Cathode: Fe/Fe (a), Al/Al (b). Current density: (●) 1 A m^{-2} , (▲) 10 A m^{-2} , (■) 100 A m^{-2} . The insets show data fitted to Freundlich isotherm.

of 0.7585. This fact supports the hypothesis made regarding that cyanide in mining wastewater is removed by adsorption onto aluminum or iron flocs formed during the chemical coagulation process. However, the extremely low values obtained for Freundlich's constant (K_F) indicates a low adsorption capacity from adsorbents added during chemical coagulation to remove cyanide from mining wastewater in comparison with other K_F values reported in literature [34–37] and the co-existence of other processes, most probably complexation processes.

$$q_e = K_F \cdot C_e^{1/n} \quad (5)$$

$$q = 4 \cdot 10^{-154} \cdot [\text{CN}^-]^{81.67} \quad (6)$$

$$q = 3 \cdot 10^{-216} \cdot [\text{CN}^-]^{116.25} \quad (7)$$

Coagulation and electrocoagulation technologies differ significantly in the way in which the coagulants are added to the wastewater and it is reported that this type of addition of inorganic coagulants in solution may significantly affect the pollutant removal efficiency of the coagulation process [38,39]. The chemical coagulation process involves the addition of inorganic salts, mainly iron or aluminum salts, as coagulants which alters the physicochemical composition of the solution by increasing its conductivity. On the contrary, the electrochemical

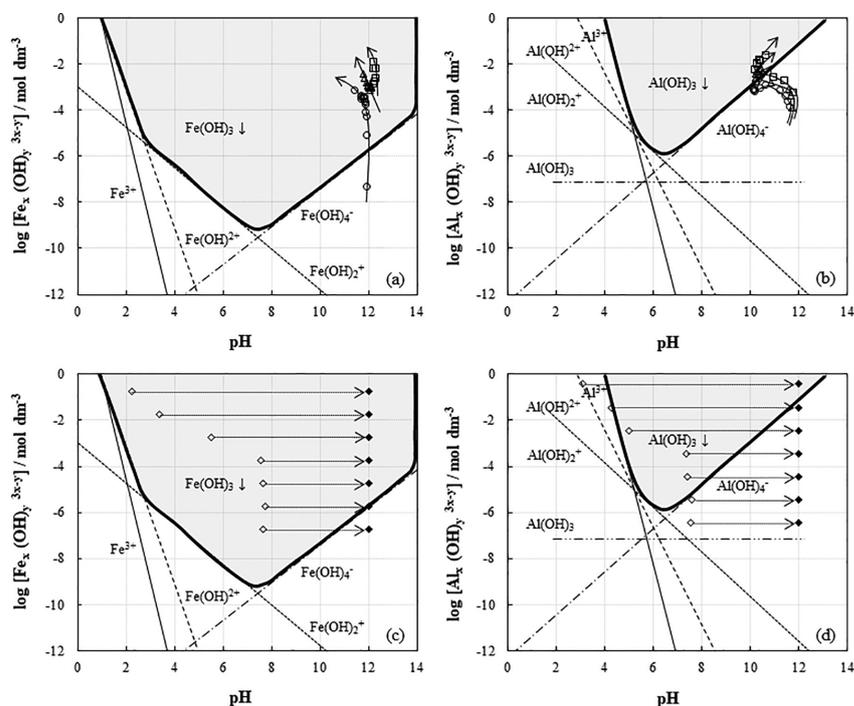


Fig. 3. Coagulant-pH evolution during chemical and electrochemical coagulation of synthetic mining wastewater intensified with $100 \text{ mg CN}^- \text{ dm}^{-3}$. Electrochemical coagulation: anode/cathode: Fe/Fe (a), Al/Al (b); current density: (○) 1 A m^{-2} , (Δ) 10 A m^{-2} , (□) 100 A m^{-2} . Chemical coagulation: coagulant salts: FeCl_3 (c), AlCl_3 (d); pH correction: initial pH (○), corrected pH (●). Arrows indicate the trends in pH during the process.

coagulation process involves the in-situ generation of coagulants through the electro-dissolution of a sacrificial anode, which is usually made of iron or aluminum. At this point, Fig. 2 shows the cyanide removal from mining wastewater during electrochemical coagulation with iron (Fig. 2a) and aluminum (Fig. 2b) electrodes. The electrochemical coagulation processes were developed within the range of current densities $1\text{--}100 \text{ A m}^{-2}$ and no passivation phenomena were observed for all the tests carried out with both electrode materials.

Surprisingly, cyanide is completely removed from mining wastewater during electrochemical coagulation at initial pH of 12 by using iron electrodes with almost negligible influence of current density applied. However, less than 60% of cyanide removal is attained for electrochemical coagulation with aluminum electrodes. In addition, a significant influence of the current density on cyanide removal is clearly observed with this electrode. Then, 50% of cyanide removal is reached for 50 mg dm^{-3} of iron, regardless the current density applied whereas 40, 15 and 5% of cyanide removal is achieved for the same dosage of aluminum during electrochemical coagulation at 1, 10 and 100 A m^{-2} , respectively. This fact means that iron is much more efficient than aluminum for the removal of cyanide from mining wastewater when coagulants are dosed by a sacrificial anode in the electrochemical coagulation processes, regardless of the current density applied, opposite than the behavior observed during the chemical coagulation processes. Furthermore, the higher current density applied, the lower is the cyanide removal efficiency observed during aluminum electrochemical coagulation processes.

For comparison purposes, and in order to know more about

mechanisms, data obtained during the iron and aluminum electrochemical coagulation processes were also fitted to a Freundlich isotherm and plots are shown in the insets of Fig. 2a and b, respectively. In both cases, the theoretical Freundlich isotherm line does not fit well experimental data as a high dispersion of experimental points can be observed with regression coefficients of only 0.1269 for iron (Eq. (8)) and 0.1158 for aluminum (Eq. (9)). This fact confirms that the main mechanism to remove cyanide from mining wastewater during electrochemical coagulation is not adsorption onto iron or aluminum flocs as hypothesized during chemical coagulation.

Here, it is noteworthy to point out that iron or aluminum speciation significantly depends on the dosage form, the pH of the solution and their concentration [38]. In this context, it is important to bear in mind that the pH was fixed at 12 for the chemical coagulation using the standard jar test experiments and corrected after the addition of the coagulants to reach again the same pH value (because the salts behave as Lewis acids) whereas for the electrochemical tests, pH was initially fixed at 12 and then, monitored along electrochemical coagulation processes without further changes, as in this case the net reagent dosed is iron or aluminum hydroxide, which does not behave as a Lewis acid. Thus, Fig. 3 shows the evolution of coagulant-pH in the speciation maps for the removal of cyanide in mining wastewater during the iron (Fig. 3a) and aluminum (Fig. 3b) electrochemical coagulation processes within the range of current densities from 1 to 100 A m^{-2} , and during chemical coagulation tests with iron (Fig. 3c) and aluminum (Fig. 3d) salts. Initial pH was adjusted before start the experiments to a value of 12. In the case of chemical tests, this adjustment was carried out again

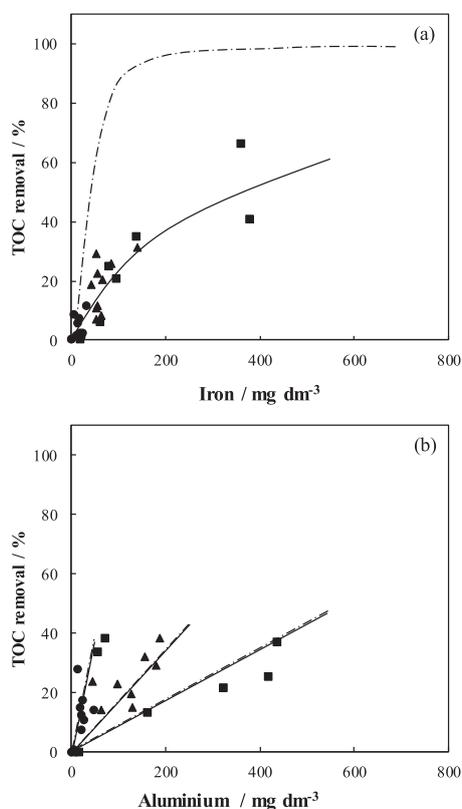


Fig. 4. TOC removal percentage as a function of electrogenerated coagulant concentration during electrochemical coagulation of synthetic mining wastewater intensified with $100 \text{ mg CN}^- \text{ dm}^{-3}$. Anode/Cathode: Fe/Fe (a), Al/Al (b). Current density: (●) 1 A m^{-2} , (▲) 10 A m^{-2} , (■) 100 A m^{-2} . Dashed lines represent theoretical TOC removal according to experimental data.

after adding the coagulant since aluminium and iron salts decrease the solution pH.

$$q = 121.43 \cdot [\text{CN}]^{0.59} \quad (8)$$

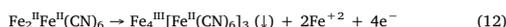
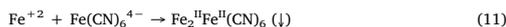
$$q = 0.32 \cdot [\text{CN}]^{1.61} \quad (9)$$

The pH is observed to be maintained in values close to 12 during iron electrochemical coagulation regardless the current density applied and under these conditions, the electrodisolved Fe^{+2} may be quickly oxidized and hydrolyzed to iron precipitate $\text{Fe}(\text{OH})_3$ as the main ionic monomeric species in solution. Opposite, pH is observed to decrease down to 10 throughout aluminium electrochemical coagulation and this decrease is faster at lower current density values. Here, two different phases can be distinguished depending on pH evolution. Firstly, the soluble ionic monomeric species $\text{Al}(\text{OH})_4^-$ and $\text{Al}(\text{OH})_3$ are the main aluminium species in solution when pH decreases from 12 to 10 and secondly, the aluminium precipitate $\text{Al}(\text{OH})_3$ is the dominant aluminium species when pH is maintained constant in a value of 10. Then, different pH behavior is observed depending on coagulation process as pH was maintained in a constant value of 12 during chemical coagulation at standard jar test experiments and, as a consequence, different iron or

aluminium species are present in solution depending on coagulation process. Regarding the chemical coagulation tests, it can be seen how the initial addition of the coagulant acidifies the mining wastewater from the initial value of 12 to a value which decreases with the increasing coagulant dose and how during the tests, this acidification is compensated with the addition of sodium hydroxide to reach pH 12 again, leading to a very different expected speciation, which is much less efficient than that obtained by the electrochemical process naturally. In addition, because of the expected high solubility of aluminium hydroxide at pH 12, the presence of other precipitates should be expected, which protects the insoluble product formed during the initial addition of the coagulant.

At this point, it is worth to take in mind that the bonding properties of cyanide ion make it a very strong-field ligand for several transition metals [40]. Among others, cyanide ion is capable of forming hexacyanides with titanium, vanadium, chrome, manganese, iron or cobalt, tetracyanides with nickel, palladium or platinum and dicyanides with copper, silver or gold. In this way, Fig. 4 shows the TOC removal percentage as a function of iron (Fig. 4a) and aluminium (Fig. 4b) electrogenerated concentrations for the electrochemical coagulation treatment of synthetic mining wastewater intensified with 100 mg dm^{-3} of free cyanide, in order to study the possible formation of soluble cyano metal complexes. TOC present in synthetic mining wastewater comes from the carbon in cyanide ion. In addition, the theoretical TOC removal calculated from Eq. (4) has also been plotted here.

Regarding the evolution of TOC removal percentage during the iron electrochemical coagulation, the result obtained is much lower than the expected value and no influence of the current density is observed. At the end of each experiment, the experimental TOC removal percentage is expected to be up to 100% vs. less than 60% of TOC removal percentage monitored. This fact suggests that free cyanide is not totally removed from solution and it could still remain as soluble cyano iron complexes in wastewater. According to literature, the complexation reactions between iron (II) and free cyanide ions may be described by Eqs. (10)–(12) [11]. Iron (II) is firstly electrodisolved from an iron electrode during electrochemical coagulation process and then, iron (II) reacts with free cyanide to form soluble ferrocyanide complex ($\text{Fe}(\text{CN})_6^{4-}$) as shown in Eq. (10). When the amount of ferrous ions increases throughout experimental time, $\text{Fe}(\text{CN})_6^{4-}$ may be immobilized as an insoluble ferrocyanide ($\text{Fe}_2^{\text{II}}\text{Fe}^{\text{II}}(\text{CN})_6$) which can be quickly oxidized to form insoluble ferric ferrocyanide ($\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$). However, the presence of soluble $\text{Fe}(\text{CN})_6^{4-}$ in solution is much less toxic than free cyanide and its formation is essentially nontoxic except under UV-irradiating condition [41].



On the other hand, TOC removal percentage overlaps with theoretical TOC removal percentage during aluminium electrochemical coagulation processes which means an almost null formation of any soluble cyano aluminium complexes. In addition, a significant influence of the current density is observed. The lower current density applied the higher TOC removal efficiency is attained. Nevertheless, the maximum TOC removal percentage reached is below 40%, regardless of the current density applied.

In this context, the mechanisms proposed for free cyanide removal from synthetic mining wastewater by means of both iron and aluminium electrochemical coagulation processes is schematically drawn in Fig. 5. It is important to consider that the release of Fe^{+2} from an iron plate anode leads to the formation of soluble and/or insoluble metal-cyanide complexes during the iron electrochemical coagulation process. The presence of soluble metal-cyanide complexes allows the toxicity of solution to drastically decrease in comparison with the initial toxicity of

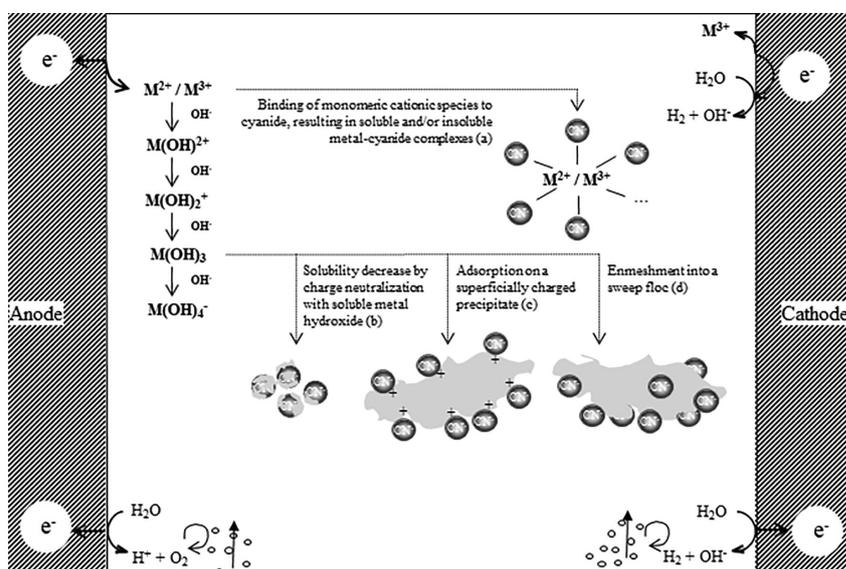


Fig. 5. Mechanisms proposed for cyanide removal from synthetic mining wastewater during electrochemical coagulation. Anode/Cathode: Fe/Fe (a, c, d), Al/Al (b, c, d).

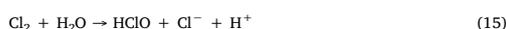
free cyanide. On the other hand, free cyanide is removed by charge neutralization with soluble $\text{Al}(\text{OH})_3$ during the aluminum electrochemical coagulation process. Finally, free cyanide may also be removed thanks to its adsorption on a superficially charged metal precipitate and its enmeshment into a sweep metal floc in both electrochemical coagulation processes.

The mechanism proposed for cyanide removal may be supported by the characterization of the sludge generated after the coagulation treatment (shown in Fig. 6). The XRD analysis of the resultant sludge from chemical coagulation treatments with FeCl_3 (Fig. 6a) shows the main diffraction goethite ($\text{Fe}^{3+}\text{O}(\text{OH})$) peaks (1 1 0), (1 3 0), (0 2 1), (1 1 1), (1 2 1), (1 4 0), (2 2 1), (1 6 0), (2 5 0) and (0 6 1) at $2\theta = 21.1^\circ$, 33.3° , 34.7° , 36.6° , 39.9° , 41.2° , 53.2° , 59.1° , 61.4° and 64.1° , respectively. However, the XRD analysis for the sludge generated during electrochemical coagulation with iron electrodes (Fig. 6c) confirms not only the presence of the magnetite ($\text{Fe}^{2+}(\text{Fe}^{3+})_2\text{O}_4$) peaks (2 2 0), (3 1 1), (4 0 0) (5 1 1) and (4 4 0) at $2\theta = 30.1^\circ$, 35.4° , 43.0° , 57.1° and 62.7° , respectively, but also the appearance of the ferric ferrocyanide ($\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$) peak (3 2 1) at $2\theta = 28^\circ$. This fact could justify the formation of the cyano iron (II) complexes (Eqs. (10)–(12)) in solution as a significant mechanism to remove free cyanide during electrochemical coagulation with iron electrodes, in comparison to its removal by adsorption onto iron (III) oxide-hydroxide. On the other hand, Fig. 6b shows a mixture of bayerite ($\alpha\text{-Al}(\text{OH})_3$) peaks (0 0 1), (1 0 1), (1 1 1) and (1 1 2) at $2\theta = 18.7^\circ$, 27.9° , 40.6° and 53.2° , respectively, and gibbsite ($\gamma\text{-Al}(\text{OH})_3$) peaks (1 1 0) and (0 2 3) at $2\theta = 20.3^\circ$ and 45.4° for chemical coagulation with AlCl_3 . However, only the bayerite ($\alpha\text{-Al}(\text{OH})_3$) peaks (0 0 1), (1 0 1), (1 1 1) and (1 1 2) at $2\theta = 18.7^\circ$, 27.9° , 40.6° and 53.2° , respectively, are observed for the electrochemical coagulation with aluminum electrodes in Fig. 6d. Here, the difference between gibbsite and its other polymorphs, such as bayerite, consists of a slightly different arrangement of hydroxyl groups which make bayerite more efficient for the removal of free cyanide.

In order to go more in-depth, the chemical and/or electrochemical

reactivity has also been studied for the different species involved in mining wastewater ($3000 \text{ mg SO}_4^{2-} \text{ dm}^{-3}$, $300 \text{ mg Cl}^- \text{ dm}^{-3}$, $60 \text{ mg NO}_3^- \text{ dm}^{-3}$, $30 \text{ mg NH}_4^+ \text{ dm}^{-3}$ and $100 \text{ mg CN}^- \text{ dm}^{-3}$) in order to determine the possible formation of hazardous species.

Regardless of the possible oxidation of cyanide to form cyanate (CNO^-), CNO^- has been not detected by ionic chromatography along with any electrochemical coagulation tests. Anyway, CNO^- is well known to quickly decompose as shown in Eq. (13). Regarding the formation of other hazardous inorganic species, it is especially important to focus on the chlorine species because chloride may be electro-oxidized to chlorine (Eq. (14)) and thus, it disproportionates to hypochlorite (Eqs. (15)–(16)) or is further oxidized to other chlorine compounds in higher oxidation state, such as chlorate or perchlorate (Eqs. (17)–(19)) [42]. These high oxidation state chlorine compounds are reported to be hazardous to human health [43,44]. For this reason, the evolution of chlorine species has been monitored along with iron and aluminum electrochemical coagulation processes as shown in Fig. 7a and b, respectively.



Chloride is observed to be transformed into hypochlorite which behaves as a reaction intermediate. The higher the current density applied, the higher is the hypochlorite concentration regardless of iron or aluminum electrochemical coagulation processes. The maximum

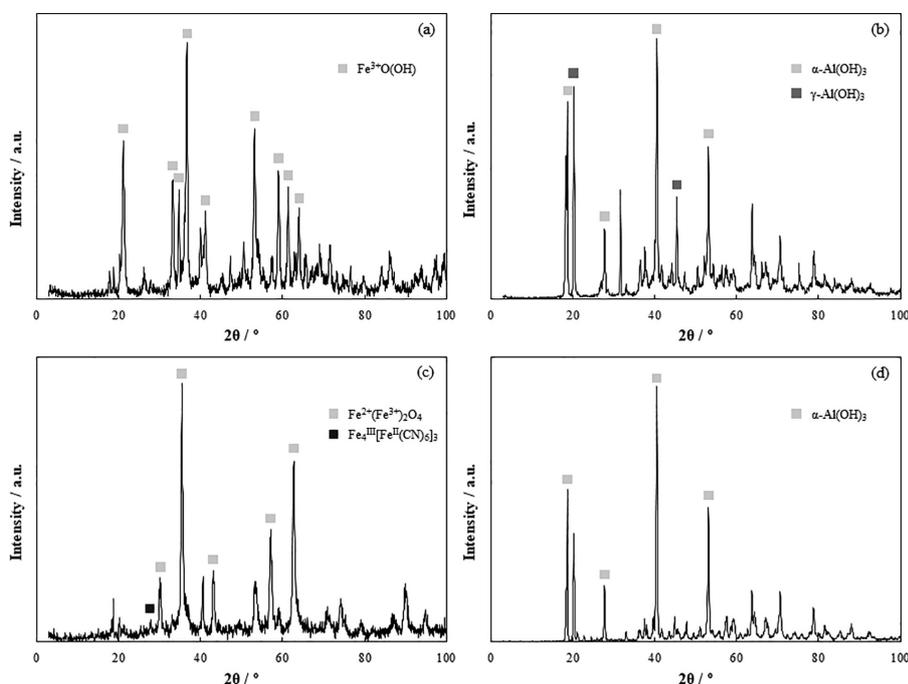


Fig. 6. XRD analysis of the sludge generated after the coagulation treatment of synthetic mining wastewater intensified with $100 \text{ mg CN}^- \text{ dm}^{-3}$: (a) chemical coagulation with $1000 \text{ mg FeCl}_3 \text{ dm}^{-3}$, (b) chemical coagulation with $1000 \text{ mg AlCl}_3 \text{ dm}^{-3}$, (c) electrochemical coagulation with Fe electrodes at 100 A m^{-2} , (d) electrochemical coagulation with Al electrodes at 100 A m^{-2} .

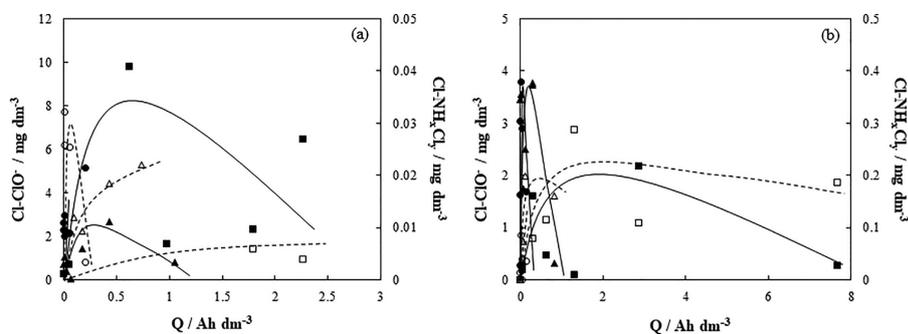


Fig. 7. Hypochlorite (full symbols) and chloramines (empty symbols) concentrations as a function of applied electric charge during electrochemical coagulation of synthetic mining wastewater intensified with $100 \text{ mg CN}^- \text{ dm}^{-3}$. Anode/Cathode: Fe/Fe (a), Al/Al (b). Current density: (●) 1 A m^{-2} , (▲) 10 A m^{-2} , (■) 100 A m^{-2} .

hypochlorite concentration detected in solution is up to $10 \text{ mg Cl-CIO}^- \text{ dm}^{-3}$ for iron electrochemical coagulation although it is below $4 \text{ mg Cl-CIO}^- \text{ dm}^{-3}$ for aluminum electrochemical coagulation. Opposite to it could be expected, hypochlorite does not undergo further oxidation to hazardous chlorine species such as chlorate or perchlorate because these chlorine species have been not detected in solution along with any electrochemical coagulation tests. On the contrary, hypochlorite is well known to chemically react with ammonium ions and

then, it results in the production of inorganic chloramines as shown in Eqs. (20)-(22) [45,46].



As can be observed, the presence of chloramines in solution is

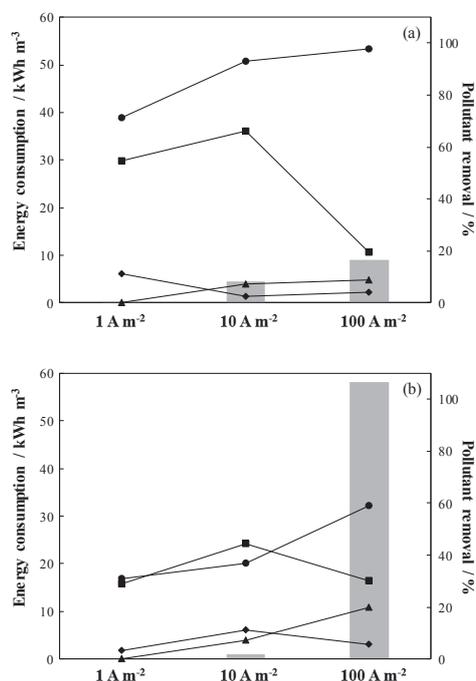
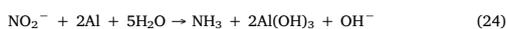
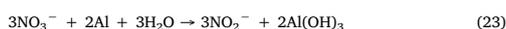


Fig. 8. Influence of current density on energy consumption (bars) for pollutants removal (points) during electrochemical coagulation of synthetic mining wastewater intensified with $100 \text{ mg CN}^- \text{ dm}^{-3}$. Anode/Cathode: Fe/Fe (a), Al/Al (b). Pollutant species: (●) CN^- , (▲) NO_3^- , (■) NH_4^+ , (◆) SO_4^{2-} .

influenced by current density applied. The concentration of chloramines ranges from 0.01 to 0.03 mg dm^{-3} during iron electrochemical coagulation and this concentration increases up to 10 times for aluminum electrochemical coagulation. This fact may be explained bearing in mind the chemical reduction of nitrate to ammonium ions by aluminum as shown in Eqs. (23) and (24) [47,48]. This confirms the higher concentration of chloramines during aluminum electrochemical coagulation, in comparison with their concentration during iron electrochemical coagulation because of the increase of ammonium ions in solution with aluminum electrodes.



Finally, Fig. 8 shows the energy consumption as a function of the current density ($1\text{--}100 \text{ A m}^{-2}$) for the removal not only of the target organic pollutant cyanide but for the inorganic pollutants presented in mining wastewater such as nitrate, ammonium ions and sulfate during both iron and aluminum electrochemical coagulation processes.

As expected, the energy consumption increases with current density, regardless of the electrode material tested in electrochemical coagulation. However, at the highest current density 10 kWh m^{-3} are required to remove 100% of cyanide from mining wastewater during iron electrochemical coagulation, whereas 60 kWh m^{-3} are only able to attain 60% of cyanide removal for aluminum electrochemical coagulation. The higher energy consumption with aluminum electrodes may be explained by the higher cell potential needed to electrochemically release the coagulant due to its passivation layer. Likewise, inorganic species

from mining wastewater are also removed during both electrochemical coagulation processes although in a much lower range than the target pollutant. Thus, at 10 A m^{-2} the removal percentage of nitrates is 7.5 and 7.2%, for ammonium ions is 66.2 and 44.4% and for sulfates is 2.4 and 11.0% during iron and aluminum electrochemical coagulation, respectively. The results obtained for the removal of nitrates are in agreement with previous works reported in the literature [48], where the same amount of nitrate removal was obtained for the same reagent dose using both iron and aluminum anodes. Nitrate removal can be explained by adsorption onto growing metal hydroxide precipitates. Moreover, the lower removal of ammonium ions with aluminum electrodes than with iron ones may be explained due to their production by the chemical reaction between nitrates and aluminum which increases their concentration in solution [47]. Finally, the removal percentages for sulfates are very low because sulfate may be efficiently removed from mining wastewater by coagulation although at acidic pHs [12].

4. Conclusions

From this work, the following conclusions can be drawn:

- Chemical coagulation at pH of 12 leads to a maximum cyanide removal percentage from mining wastewater of 15%. Although it is not the unique, adsorption onto metal flocs is the primary mechanism that explains results. Experimental data are fitted to Freundlich isotherm with correlation coefficients of 0.7585 for Fe- FeCl_3 and 0.9047 for Al- AlCl_3 .
- Electrochemical coagulation with iron electrodes leads to the complete cyanide removal from mining wastewater at initial pH of 12, regardless of the current density value applied. However, a maximum cyanide removal of 60% is attained during electrochemical coagulation with aluminum electrodes at the highest current density value tested (100 A m^{-2}). The cyanide removal does not fit well to Freundlich isotherm with low correlation coefficients ($r_{\text{Fe}}^2 = 0.1269$, $r_{\text{Al}}^2 = 0.1158$) which means that the main coagulation mechanism is not an adsorption process in this case.
- Electrochemical coagulation with iron electrodes allows the formation of soluble and/or insoluble iron-cyanide complexes due to the release of Fe^{+2} from the iron plate anode. In electrochemical coagulation with aluminum electrodes, cyanide decreases its solubility by charge neutralization with aluminum soluble metal hydroxide. Likewise, cyanide may also be removed by adsorption on a superficially charged metal precipitate and enmeshment into a sweep metal floc in both cases.
- Chemical and/or electrochemical reactivity of cyanide and inorganic species from mining wastewater is also studied. A null detection of cyanate or inorganic chlorine hazardous species such as chlorate or perchlorate is found through electrochemical coagulation tests. However, chloride oxidizes to hypochlorite and hypochlorite concentrations up to 10 and 4 mg dm^{-3} are measured for iron and aluminum electrochemical coagulation, respectively. Likewise, hypochlorite behaves as intermediate because it chemically reacts with ammonium ions (contained in mining wastewater or produced by chemical reduction of nitrate by aluminum) to form chloramines in a concentration up to 0.3 mg dm^{-3} during aluminum electrochemical coagulation.
- The energy consumption required to remove 100% of cyanide from mining wastewater is 10 kWh m^{-3} during iron electrochemical coagulation at the highest current density value, whereas 60 kWh m^{-3} only attains 60% of cyanide removal along with aluminum electrochemical coagulation. In addition, other inorganic species from mining wastewater may be simultaneously removed during electrochemical coagulation processes.

Declaration of Competing Interest

Author declares that there is no conflicts of interest.

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