



# Continuous electrocoagulation process for treatment of mining waters

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## Abstract

This research is intended to study the removal of sulfate and other anionic contaminants using continuous electrocoagulation (EC) with iron electrodes. Performances comparison of continuous EC with batch EC and conventional chemical coagulation was performed. Application of the continuous electrocoagulation process with a settler for solid accumulation resulted in a higher sulfate removal and almost complete nitrate elimination. Together with anionic contaminants removal, continuous electrocoagulation was found to be efficient in the depletion of  $\text{NH}_4^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$ . In addition, changes in pH were much lower than those observed in a batch mode.

**Keywords:** sulfate, continuous electrocoagulation, mining water, wastewater treatment

## Introduction

Electrocoagulation is gaining recognition as an effective water treatment technique due to its successful application to remove metals, dyes, oil, suspended solids as well as anionic contaminants. When considering the comparison of electrocoagulation (EC) and chemical coagulation (CC), process performances are not always the same. The reasons for that can be the difference in their dosing methods, excess amount of  $\text{OH}^-$  in the solution during EC and presence of negative counter ions during CC (Canizares 2009); (Harif 2012). Thus, during EC the coagulant is added to the system by electrolytic oxidation of an appropriate anode material when in CC a chemical coagulant is dissolved into solution. These different methods affect greatly the coagulation/flocculation mechanisms and the following floc formation resulting in possible difference in the removal mechanisms of the selected contaminants. Presence of counter ions may influence the formation of hydrolyzed species while excess amount of  $\text{OH}^-$  will result in different pH conditions during EC and CC causing different coagula-

tion mechanisms (Canizares 2009); (Demirbas 2017); (Harif 2012).

Meanwhile, EC operating modes has a great influence on the process performance. Batch EC process is always accompanied by an increasing pH up to the range of 8-10, when continuous EC has slight difference of initial and final pH making operation at the acidic conditions possible. Additionally, energy consumption of a continuous process is relatively low comparing to the batch process for the removal of the same amount of the contaminants. Moreover, operation at continuous mode allows treating of a larger volume of water and possible solid recirculation minimizing the formation of wastes.

Currently, great attention is given to EC as a possible method to treat mining waters. Mining waters are known to have sulfate concentration from hundreds to tens of thousands mg/L, containing nitrate, cyanide, ammonia and different metals. High sulfate concentration may lead to environmental issues such as excess water mineralization, soil and water acidification. Sulfate is toxic to aquatic environment and may be respon-



sible for aggressiveness of water to concrete. Taking everything mentioned into account, high concentration of sulfate in mining water streams is one of the major environmental issues in many countries. Coming regulations and established limits made mining industry find and develop suitable and feasible sulfate treatment technologies.

Until recent years, relatively few papers have been devoted to the removal of sulfate by electrocoagulation. Drouiche (2007) reported on effective application of EC to decrease the sulfate concentration from 241.50 mg/L to 42 mg/L while performing tests with chemical mechanical polishing wastewaters. Murugananthan (2004) have studied the removal of sulfide, sulfate and sulfite from tannery wastewaters by electrocoagulation. The studied concentrations varied from 100 mg/L to 500 mg/L for all three components, and the removal efficiency for the sulfate of 500 mg/L was around 25%. Del Ángel (2014) have conducted electrocoagulation experiments by using aluminum electrodes, and achieved 53 % of sulfate removal from the drainage at an abandoned mine in Guanajuato, Mexico. Radić (2014) reported on over 86% removal efficiency of sulfate with combined CaO/electrocoagulation treatment. Nariyan (2017) affirmed 40.5 % of sulfate removal from mining waters using Al electrodes. However, information about the remediation of sulfate from mining water by electrocoagulation is rather scarce and studies on the continuous electrochemical removal of sulfate are non-existent.

To fill the gap the research on the performance evaluation of batch and continuous EC process for the removal of sulfate from mining waters was studied. Additionally, EC results were compared with those obtained during the chemical coagulation. This paper is dedicated to process performances, removal mechanisms and possible operation conditions for sulfate removal by CC and EC.

## Methods

Electrocoagulation tests were performed in batch and continuous modes (Fig. 1). Batch EC tests were carried out in a lab scale plant described elsewhere (Lacasa 2011). During the continuous EC, the same plant with necessary modifications was used. Detailed set-up and explanations are provided in (Mam-

elkina 2017). Iron electrodes connected in a monopolar arrangement were placed in between of two plastic plates (Lacasa 2011) The dimensions of electrodes with internal deployment were 100×100×2 mm (resulting in total anode area of 168 cm<sup>2</sup>). The current density used during the batch experiments was equal to 30 mA/cm<sup>2</sup> and treatment time was 8 h. Continuous EC experiments were performed at 12.4 A h/dm<sup>3</sup>. A proper mixing of treated water was provided by using a square blade impeller at a speed of 160 rpm (tip speed of 0.84 m/s) and by water circulation using a peristaltic pump at a speed of 90 ml/min.

Synthetic mining waters were prepared based on the average values provided by several Nordic mines. Treated eluent contained sulfate, nitrate, chloride, Cu, Zn and Ni. Levels of each contaminant can be found in the Table1. Treated water was used during the experiments with no conductivity adjustments. Solution pH was adjusted by 0.1 M NaOH and HCl. Metal contents were analyzed with an inductively coupled plasma spectrometer (Liberty Sequential, Varian). Anions concentrations were measured using ion chromatography with a Metrohm 930 Compact IC Flex coupled to a conductivity detector.



Figure 1 Set-up for a continuous electrocoagulation



## Results and Discussion

Prior the electrochemical experiments chemical treatment was performed to find the most suitable range for EC process operation. Chemical coagulation was carried out with the synthetic solution at different pHs and iron coagulant doses. The maximum sulfate removal of 80% was achieved at pH 2 for iron dosage at the range 0.017-0.090 mol/dm. At neutral and alkaline conditions the increase in sulfate removal was observed with the increase in dose of iron coagulant and was as high as 60% at 0.537 mol/dm of iron. Taking into account the highest possible removal of sulfate and lowest possible amount of the coagulant used for elimination, EC operation at acidic conditions was suggested. Possible removal mechanism at acidic conditions during CC may be favored by sulfate precipitation with added iron not excluding other coagulation mechanisms. However, the detailed explanation of the sulfate removal mechanisms during CC is out of the scope of the paper and can be found elsewhere (Mamelkina 2017).

The current density for EC tests was selected based on the production of a specific iron concentration in the liquid face by the electrodisolution of the anode, i.e. a value that allow to generate at least 0.1 mol/dm<sup>3</sup> of iron. Batch and continuous EC experiments were performed at pH 2, 5 and 7.

For batch EC, the maximum sulfate removal from synthetic mining waters was achieved at initial pH 2 and was as high as 20%. Comparing to the results obtained with CC, the significant decrease in the removal of sulfate at initial pH 2 can be explained by the pH increase to the vicinity of 10 during the first hour of treatment. Slight sulfate removal 10% was observed at pH 5, in this case the pH

10 conditions were reached even faster. At pH 7 the EC process was inefficient in terms of sulfate removal. A summary of sulfate treatment efficiencies for different processes and operation modes is given in the Table 1.

From the Table 1 it can be seen that removal of sulfate improved during the continuous EC treatment. One of the reasons for such a behavior is the possibility to maintain the pH almost constant without dropping from acidic to base conditions as it occurred during the batch EC. Among other parameters, affecting the sulfate removal is a dose of added iron that promotes the enmeshment of sulfate into iron hydroxide precipitates. To ensure the desired amount of solids added to the system a novel EC strategy was proposed. 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 results obtained during the continuous treatment of mining waters at pHs 2,5 and 7 are shown in Fig. 2. In agreement with CC treatment the highest removal efficiency of over 60% was achieved at pH 2, illustrating the pivotal role of pH during the process. Accumulation and circulation of solids allowed providing higher solid concentrations ranging from 1.1 to 1.4 mol/dm<sup>3</sup> that favored the enmeshment. Changes in pH profiles were not critical and very much lower than those during the batch EC, making the operation at acidic conditions possible even during the EC.

**Table 1** Removal of selected ions with chemical coagulation (CC), batch and continuous electrocoagulation (EC)

	Mining ww, mg/L	R%, CC	R%, batch EC	R%, continuous EC
SO <sub>4</sub> <sup>2-</sup>	3000	80.0	23.0	63.0
NO <sub>3</sub> <sup>-</sup>	60	10.0	99.9	99.9
NH <sub>4</sub> <sup>+</sup>	30	68.0	99.9	99.9
Cu <sup>2+</sup>	8	5.0	99.9	99.9
Ni <sup>2+</sup>	8	64.0	99.9	99.9
Zn <sup>2+</sup>	15	56.0	99.9	99.9



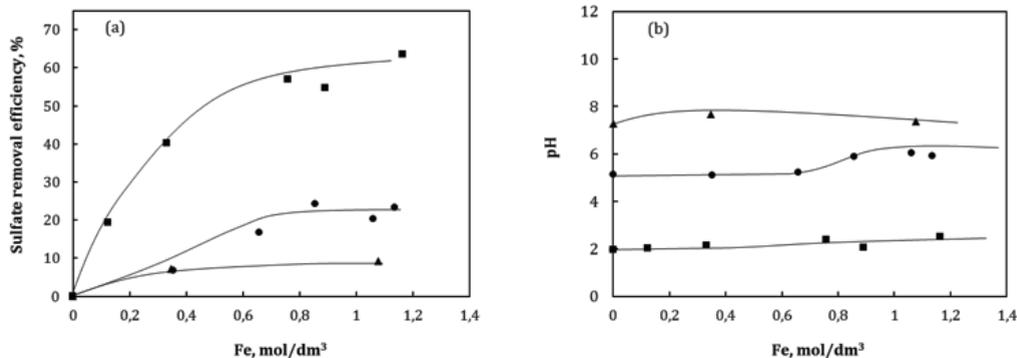


Figure 2 Continuous EC treatment of mining waters

a. sulfate removal efficiency at ■ pH2, ● pH5, ▲ pH7 b. changes in pH

## Conclusion

New design of the EC process resulted in a better sulfate removal than during chemical coagulation and discontinuous EC treatment at the same dosage of iron. Changes in pH were not critical favoring higher sulfate removals obtained with the modified process. Differences in the performance of batch and continuous EC were due to the pH and iron dosing conditions. Continuous EC was found to be efficient because in addition to the elimination of sulfate, it also removed nitrate and selected cations. Moreover, opposite to chemical coagulation, chloride concentration was maintained almost constant, producing an effluent with a higher quality. Continuous operation provides the treatment possibility of sulfur-rich streams of a large volume. Solids recycling allows treatment of process mining water minimizing secondary pollution. Simultaneous removal of anionic and cationic contaminants by EC favours its application as one of the main technique at wastewater treatment plants.

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## ACCEPTABILITY OF PROCESSED MINE WATER

