

Electrocoagulation treatment of real mining waters and solid-liquid separation of solids formed

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Abstract This research was aimed at studying the possibility of mining water treatment using electrocoagulation and pressure filtration. Batch experiments took place at 1L and 70L reactors. Filtration properties of the slurries were studied using a laboratory scale Nutsche filter. The highest sulfate removal was obtained using Al electrodes after 5h treatment, while for nitrate after 3h. Most metals were removed almost completely after 1h. Cake formed during filtration had high porosity and moisture content. It is worth mentioning that not only the treatment of waters, but also residue processing is an important issue once talking about sustainable water treatment technologies.

Introduction

Electrocoagulation finds its wide application for treatment of wastewaters generated during tannery, electroplating, dairy and textile processes (Chen 2004). Electrocoagulation (EC) enables efficient treatment of wastewater containing metals, anionic contaminants, foodstuff, organic matter, polymeric wastes, oil wastes, textile dyes, lignin, chemical and mechanical polishing wastes, phenolic wastes and aqueous suspensions containing ultrafine particles (Emamjomeh 2009; Lacasa 2011). Currently, with the successful application of electrocoagulation in different fields a rising interest is given to it as a possible technique for treatment of mining waters containing sulfate, nitrate, cyanide, various metals and other harmful contaminants.

EC can be classified as an active, abiotic water treatment technique. EC is defined as an electrochemical method to produce destabilization agents (most commonly Al^{3+} or Fe^{2+} ions). Two simultaneous processes occurring during the EC are metal ions are generated on an anode and hydrogen gas was released on an inert cathode. The driving force of the EC process is current density that influences energy and electrode consumption, process performance and costs. EC operates at both batch and continuous modes resulting in different water flow regimes, chemical interaction, concentration gradients, flocs formation and mixing/settling characteristics during the process (Mollah 2004; Jenke 1984; Holt 2005).

During EC process sludge is formed. This sludge mainly contains metal oxides and hydroxides with contaminants removed by the EC. Sludge properties have a significant effect on the down-stream processes such as sludge dewatering and disposal, as well as possible reuse of the slurry. To prevent the toxic contaminants to be improperly disposed and to enable the recovery of valuable compounds, there is a need to design further dewatering processes and determine operational conditions.

One of the possible dewatering processes is cake filtration that means solid-liquid separation by passing the liquid through a thin permeable filter medium. Initially, a solid layer ap-

pears on the face of the filter media and later solids deposit on the cake itself while the filter medium acts as a support. Depending on the driving force, cake filtration can be classified as pressure, vacuum or centrifugal. Pressure filtration is based on the liquid removal and solid retention in the form of cakes under the positive pressure above the semi-permeable separating surface (Svarovsky 1981; Tarleton 2008). When talking about EC slurries, among other possible dewatering techniques are centrifugation (Holt 2005), electrodeewatering (Shin 2006) and magnetic separation (Shin 2004).

The purpose of this research was to study the possibility of efficient treatment of real mining waters using electrocoagulation and pressure filtration technologies. The effect of current density and equipment sizing on the pollutant removal was evaluated. Filtration properties of the slurries formed during EC were also investigated.

Methods

Electrocoagulation tests were performed in 1 L (fig. 1a) and 70 L (fig. 1b) Plexiglas batch reactors. Reactors were equipped with two pairs of aluminum or iron electrodes connected in a monopolar arrangement. The dimensions of electrodes with internal deployment were 60×70×2 mm (resulting in total anode area of 168 cm²) and 300×300×5 mm (resulting in total anode area of 3600 cm²). The current density used during the experiments was equal to 6, 12 and 18 mA/cm² and treatment time was 5 h. 20 ml samples were taken once every hour during the tests in 1 L reactor, once every 15 min during the first hour and then once every hour of treatment in 70 L reactor. A proper mixing of treated water was provided by using a curved blade turbine at a speed of 200 rpm (tip speed of 0.84 m/s) and 155 rpm (tip speed of 1,6 m/s).

Solids formed during the EC process in 70 L reactor were left to settle for 24 hours. Treated water was removed by decanting; solids remained at the bottom of the reactor. Slurry was mixed well and filtered using laboratory Nutsche filter (fig. 1c). Used filtration pressures were under 2, 4 and 6 bar. No pH and temperature adjustments took place. Sample volume was 200 ml/batch.

Mining water was provided by Orivesi mine, Finland. Water was used during the experiments with no pH and conductivity adjustments. Metal contents were analyzed with ICP-MS (Agilent technologies, Agilent 7900), sulfate and nitrate concentrations were measured using ion chromatography (Dionex ICS-1100).



Figure 1 a. EC reactor 1L b. EC reactor 70 L c. Nutsche filter.

Results and Discussion

Elimination of harmful contaminants by electrocoagulation can be influenced by the current density, electrode material, operation mode and reactor design, pH of treated water, presence of other contaminants as well as the speciation of solids formed and their solubility. Summary of the results on anion removal as well as other significant process parameters is given in the table (tab 1.). Based on the results obtained during the experiments with real mining waters with 1L and 70L treated volumes, the removal of sulfate with aluminium electrodes is higher compared to that with iron electrodes. Nitrate is equally well removed with aluminium and iron electrodes. The effect of reactor design and electrode material is observed when comparing the removal efficiencies of anions at different treated volumes at 12 mA/cm². Nitrate removal in 70L reactor is 50% less than with aluminium electrodes in 1L reactor and over 60% lower once treated with iron electrodes. Sulfate is removed over 30% less when the bigger reactor is used. These observations can be explained in terms of mixing conditions, electrode material and its purity, difference in final pH and amount of dissolved metals. Thus, mixing conditions influence the particle size and water flow and final pH affects mainly speciation of oxides and hydroxides formed when the decrease in the amount of dissolved metals reduces the dosage of formed solids per 1L of treated volume. All these parameters affect the removal mechanisms of nitrate by adsorption and sulfate by particle charge neutralization and co-precipitation (Lacasa 2011; Mamelkina 2017).

Table 1 Process operation parameters and anion removal from real mining waters by EC

Electrode material	Parameter	Current density, mA/cm ²			
		6*	12*	18*	12**
Al	R NO ₃ ⁻ , %	87.69	97.61	99.69	45.52
	R SO ₄ ²⁻ , %	47.18	44.91	45.08	29.46
	pH final	10.12	9.97	9.81	9.09
	æ final, mS/cm	4.14	4.05	3.87	4.66
	U, V	2.85	4.62	6.78	8.54
	m, g/L	2.82	5.80	8.69	1.75
Fe	R NO ₃ ⁻ , %	90.71	96.72	98.58	37.52
	R SO ₄ ²⁻ , %	18.90	27.61	30.92	9.80
	pH final	11.91	11.85	11.60	10.31
	æ final, mS/cm	5.41	5.32	4.74	5.25
	U, V	2.30	3.85	5.27	8.54
	m, g/L	5.04	10.30	15.82	2.84

*- 1 L reactor; ** – 70 L reactor

R – removal efficiency, æ – conductivity, U – voltage, m – amount of dissolved electrode

When talking about the current density as one of the scale up parameters it turns out that with the treated volume increasing there is supposed to be a decrease in electrode consumption per one litre of treated volume. That results in a lower dosage of adsorbent, hence, decreasing the removal of nitrate. In case of nitrate, dosage of solids can be suggested as one of the scale up parameters. With the data available, it is difficult to conclude about the lower removal rates for sulfate. Among other suggestions can be the lack of positively charged ions to neutralize sulfate as these positively charged ions may be more rapidly involved to other concomitant reactions occurring during the EC process. More detailed explanation of this phenomenon is out of the scope of present research.

Energy consumption during the batch EC process rises with the increase in current density and treated volume as well as the gap between electrodes. In accordance with the design features of 70L reactor the gap between electrodes was increased from 1 cm to 1.7 cm resulting in an increased voltage and energy consumption.

In addition to anions removal, the elimination of Cu, Zn, Ni and Al was studied using two different reactors (fig. 2). The effect of electrode material and current density on metal removal was investigated. No significant effect on metal removal was observed using different reactor configuration meaning successful equipment sizing using current density as a scale up parameter. When 70 L reactor with aluminium electrodes was used, 90, 96 and 99% removal of nickel, copper and zinc was achieved after 15 min of EC treatment, respectively. With iron electrodes removal efficiencies were 98, 90 and 99% removal of nickel, copper and zinc after 15 min of treatment. In 1h almost completely removal of aluminium, nickel and zinc was observed. In 1L reactor metals were almost completely removed after 1h treatment time regardless the electrode material and current density.

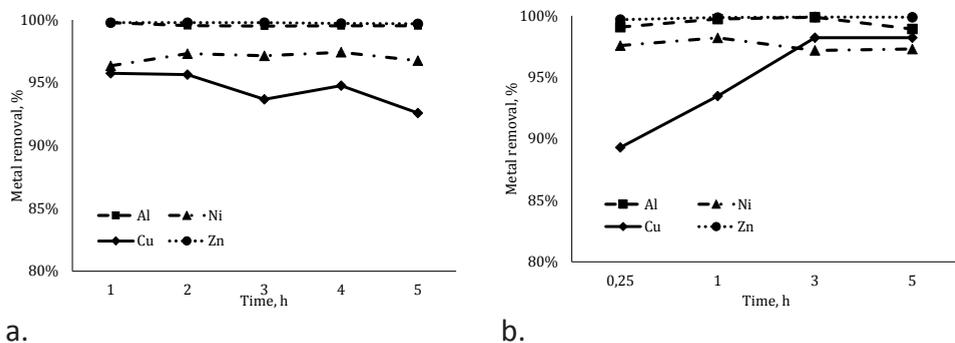


Figure 2 Metal removal efficiency by EC using iron electrodes at a. 1L reactor, b. 70L reactor (initial pH 6.4, κ 5.56 mS/cm, current density 12 mA/cm²)

In terms of metal removal, treatment of a larger volume of water applying the same current density benefits from minimizing the electrode consumption. Thus, for efficient metal removal at 70L reactor the loss of electrode was 0.35 and 0.57 g/Lh while in 1L reactor the loss equalled to 1.16 and 2.06 g/Lh for aluminium and iron electrodes, respectively.

During pressure filtration stage the effect of pressure, current density and electrode material on sludge dewatering was investigated. Cakes formed during filtration differed based on their moisture content and porosity (fig. 3). In general, cakes with high porosity and moisture content were obtained. Highly flocculated solids and presence of charged particles in the slurry can most probably explain this behavior. Pressure did not affect the porosity and moisture content, however, influenced the filtration time. Current density mainly affected cake thickness, slurry density and amount of filtrate.



Moisture content, -	0.762	0.947	0.65
Solid content, -	0.04	0.01	0.05
Porosity, -	0.903	0.982	0.89
Current density, mA/cm ²	12	12	18
Pressure, bar	2	2	4
Filtration time, min	20.0-30.0	14.2-16.7	7.0-11.0
Electrode material	Fe (real water)	Al (real water)	Fe (synthetic water)

Figure 3 Cakes formed during the dewatering of EC sludge formed using iron and aluminium electrodes

Conclusion

EC tests performed in 1L and 70L reactors demonstrated almost complete removal of metals and nitrate, when partial removal of sulfate was achieved. According to the results, aluminium electrodes are suggested to work with for further development and investigation of EC treatment of real mining water. No significant effect of current density, reactor configuration and electrode material on metal removal was observed within the variable range investigated. Sulfate and nitrate removal declined with the increase in treated volume. When current density can be used as a scale up parameter, handling of larger volumes will result in decrease of electrode consumption per one liter of treated volume.

Formation of highly porous cakes with high moisture content challenges the dewatering process. According to the results, it is worth mentioning that not only the treatment of waters, but also residue processing is an important issue once talking about the development of efficient and sustainable water treatment technologies. The treatment techniques should be studied together with up and down stream processes to have a possibility in prediction of possible problems at different stages of operation.

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