Electrochemical treatment of mining waters

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Abstract

This research is intendent to study the removal of cyanide, sulfate, chloride and nitrate from mining waters using electrochemical treatment. Tests were performed in batch and continuous modes with real and synthetic mining waters. Electrolysis and electrocoagulation with different electrodes materials (iron, aluminum for electrocoagulation, Ti-coated and carbon for electrolysis) resulted in favouring of anions removal. Additionally, performances comparison of electrolysis and electrocoagulation for cyanide removal was completed. Sulfate removal of 95% was achieved using electrocoagulation with iron anode and aluminum cathode. Electrocoagulation favored the almost complete removal of nitrate regardless the electrodes material tested, when electrooxidation was found to be inefficient for treatment of nitrate-rich waters. Cyanide concentration decreased from 100 mg/L to 1 mg/L during the electrocoagulation with iron anode in 5 min treatment time. A review on total suspended solids (TSS) removal from waters by electrochemical techniques is also provided.

Keywords: anions, TSS, electrochemical treatment, mining water

Introduction

Mining waters are often heavily contaminated with anionic and cationic species. Among the most prevalent and harmful compounds are toxic metals and anionic contaminants, such as sulfate, nitrate, chloride and cyanide. Moreover, high concentration of total suspended solids (TSS) may hinder the downstream processes. It is essential to treat discharged water and bring the concentrations of dissolved contaminants and TSS to acceptable discharge levels. Another mining water management concept is to reuse and recycle water within the process sections. Firstly, it makes mining operation more economical and environmental friendly. Secondly, it allows for treating water only to a level suitable for a certain process rather than to an acceptable discharge level.

Generally, high concentration of nitrate results in detrimental effect on the environment and the usage of water in industry. Nitrate is described as non-toxic or only toxic to infants as it causes the blue-baby syndrome. Nitrate has to be removed due to possible contribution to the eutrophication of standing surface water bodies. According to the European Environmental Commission (EEC) recommendations for drinking water the maximum allowable concentration of nitrate is 50 mg/L. Nitrate concentration in mining waters may vary from tens to hundreds milligrams per liter. One of the main sources of nitrate in the water is the utilization of nitrogen-based explosives. Water contamination with nitrates and other N-compounds is a result of incomplete detonation, dissolution of explosives and spillage during blasting activities. However, the real source of nitrate in mining waters is questionable doubtful. Many mines are surrounded by human settlements, thus other sources of nitrate that contribute to an increase in its concentration are human and animals wastes as well as fertilizers. Despite the real source of nitrogen, it is obligatory in most countries to bring the nitrate concentration to a desire level. Recently, electrochemical water treatment methods are developed to treat nitrate-rich waters. Lacasa et al. (2011) reported nitrate elimination from groundwater by electrocoagulation, continuous electrochemical treatment of drinking and mining water was studied by Kumar et al. (2009) and Mamelkina et al. (2017), and the performance of electrocoagulation and electroreduction was compared by Koparal et al. (2002).

High sulfate concentration contributes to substantial pollution of water bodies, challenges the reproduction of soils and hinders the process operations. In the world of mining, sulfate is defined as a final oxidation product of sulfuric minerals. Globally, the discharge limit for sulfate varies from 250 mg/L (USA) to 2,000 mg/L (Finland) (Nariyan 2018). Mining waters typically contain from hundreds to several tens of thousands of milligrams per liter of sulfate. The level of sulfate in mining waters is increasing through the use of sulfuric acid during the mining processes. However, the main source remains to be an acid mine drainage. One of the main reasons for treatment of sulfate-rich waters is to meet the discharge requirement or enable the reuse and recycling of water within the process. Among possible promising techniques to eliminate sulfate is electrochemical treatment. The performance of electrocoagulation process using bipolar and monopolar arrangement of electrodes was described by Nariyan et al. (2018), whereas Mamelkina et al. (2017; 2019) studied batch and continuous electrochemical treatment. Fernando et al. (2018) provided a comprehensive review on possible challenges and opportunities of treatment of sulfate-rich mining waters. Pulkka et al. (2014) provided a broad review on sulfate, nitrate as well as other anions removal by electrochemical methods.

Cyanide is defined as a carbon/nitrogen compound reported as highly toxic for the environment and harmful for people health. Cyanide presents in several forms, such as ionic, molecular HCN, salt and metal-complexes. Regulated limit for WAD-cyanide at one of the Finish mines is 0.4 mg/L. One of the main sources of cyanide in mining waters is its utilization during the leaching of gold and silver. Among other industries releasing cyanide with the effluent are automobile, photography and pharmaceuticals manufacturing. Electrochemical oxidation and electrocoagulation were tested in order to prevent the release of cyanide to water bodies (Perez 2017); (Moussavi 2011). Kuyucak et al. (2013) delivered a comprehensive review on cyanide removal from effluents emanating from gold mining and metallurgical processes.

Another water quality indicator is the presence of total suspended solids. Total suspended solids (TSS) are usually defined as particles with the size over 2 microns presented in water. TSS refer to all suspended solids, organic and inorganic, by mass. On the one hand, excessive amount of suspended solids in water may increase flooding risks, deteriorate water quality for aquatic and human life as well as hamper navigation. On the other hand, in mineral processing the presence of suspended solids in water flows favors flotation of minerals. However, the ranges of optimal concentration of TSS in process water is still questionable and more investigation is required to obtain the concentration range that facilitate the flotation process. The concentration of TSS in the discharged waters at Finish and Swedish mines is regulated. The discharge limits vary from 5 to 20 mg/L. The TSS level can be as high as 240 mg/L (Ledo coal mine) and may increase up to several thousands. TSS removal by coagulation mechanism was studied by Irfan et al. (2013); continuous and batch electrocoagulation was tested by Azarian et al. (2018) and Sardari et al. (2018); electroflotation was proposed for removal of TSS from water streams by Mohtashami et al. (2019).

This paper is dedicated to the removal of cyanide, sulfate, nitrate and TSS using electrochemical treatment. The effects of electrode material, treatment time, operation modes and applied current were studied. In addition, the performance comparison of electrocoagulation and electrooxidation for cyanide and nitrate is provided.

Materials and methods

Electrocoagulation tests to remove sulfate were previously performed in batch (Mamelkina 2019) and continuous (Lacasa 2011, Mamelkina 2017) modes. Electrocoagulation and electrooxidation tests to remove nitrate and cyanide were performed with artificial mining waters using batch EC-reactors. Treated volume of mining waters was 1 L. The following combinations of electrodes (anode/cathode) were tested Fe/Fe, Al/Al, Fe/Al, Al/Fe, Fe/C, Al/C, Fe/Ti, Al/Ti, Ti/Ti, C/C, Ti/C, C/Ti (anode/cathode). The removal of nitrate, ammonia, total nitrogen and cyanide was monitored. The applied current was 0.3 A (0.18 mA/cm^2), 1 A (6 mA/ cm^2) and 3 A (18 mA/ cm^2). The operating pH values were 3, 7 and 11. The duration of the experiments varied from 30 min to 5 hours.

Synthetic mining waters were prepared using pure water and analytical grade chemicals. Based on the average values provided by several Nordic mines, treated eluent contained sulfate 1000 mg/L, nitrate 10 mg/L, chloride 150 mg/L and cyanide 100 mg/L. Cyanide was analyzed using titration by silver nitrate solution with rhodanine as an indicator. Concentrations of sulfate, nitrate and chloride were measured using ion chromatography with a Metrohm 930 Compact IC Flex coupled to a conductivity detector.

Results and discussions

The performance of electrochemical treatment is mainly affected by the current density, reactor design, process operation mode, pH of treated waters, electrodes' material and arrangement as well as by presence of other contaminants. Summary of the results on sulfate removal by electrocoagulation is given in the table (tab 1.). Obtained results prove the suitability of electrocoagulation to treat mining waters. It can be seen that elimination of sulfate is the highest at batch mode when Fe anodes and Al cathodes are used. Continuous operation allowed 70% removal of sulfate at acidic pH. High removal of sulfate during batch operation was achieved regardless the initial pH whereas continuous treatment was only efficient at pH 2. The reason for high performance at pH 2 can be the excess amount of positively charged ions presented in treated water. These ions (Fe^{3+}, $Fe(OH)_2^+$ and $FeOH^+$) are the most common ones at acidic pH and favors the removal of sulfate by surface charge neutralization.

To study the removal of nitrate the variety of electrode combinations were tested at three different pH 3, 7 and 11. Electrocoagulation was performed using Al and Fe as anodes while the electrochemical oxidation was tested using Ti-coated and carbon (both inert) electrodes. The results of nitrate elimination presented in Fig. 1. showed high performance of electrocoagulation. Almost complete removal of nitrate was obtained after 30 min of treatment using Al/Fe. Additionally, results showed that the electrocoagulation treatment is a pH depended process and acidic pH favours its performance. The increase in nitrate concentration during the electrooxidation with inert Ti-coated and carbon electrodes revealed adsorption as the main removal mechanism of nitrate. The increase in concentration was most probably due to the reduction of ammonia ions presented in treated mining waters.

In addition to nitrate removal, the decrease in chloride content was observed. The initial chloride concentration was 150 mg/L, the applied current was equal to 3 A, at initial pH 3 using C/Ti , Fe/Al and C/C electrodes pairs the removal of chloride was as high as 79%, 74% and 63%, at pH 7 85%, 70% and 85%, at pH 11 0%, 75% and 85% respectively. No chloride removal was observed when other combinations of electrodes were tested.

The influence of current densities and

***Table 1** Removal of sulfate by electrocoagulation using batch and continuous operation*

Operation mode	Water source	Operational conditions	Studied compounds	Achieved results
Batch	Synthetic	3A, pH 4 and 10, Fe electrodes	sulfate, Zn, Cu, Ni, nitrate	50% removal of sulfate, 99% removal of Zn, Ni, Cu, nitrate
		3A, pH 3, 7 and 11, Fe anode, Al cathode	sulfate, nitrate, chlorine	95% removal of sulfate, 99% removal of nitrate, 75% removal of chlorine
	Real	2A, pH 7, Fe electrodes	sulfate, Zn, Cu, Ni, nitrate	30% removal of sulfate, 90% removal of nitrate, 99% removal of Zn, Ni, Cu
Continuous	Synthetic	6.25A, pH 2, Fe electrodes	sulfate, Zn, Cu, Ni, nitrate	70% removal of sulfate, 99% removal of Zn, Ni, Cu, nitrate

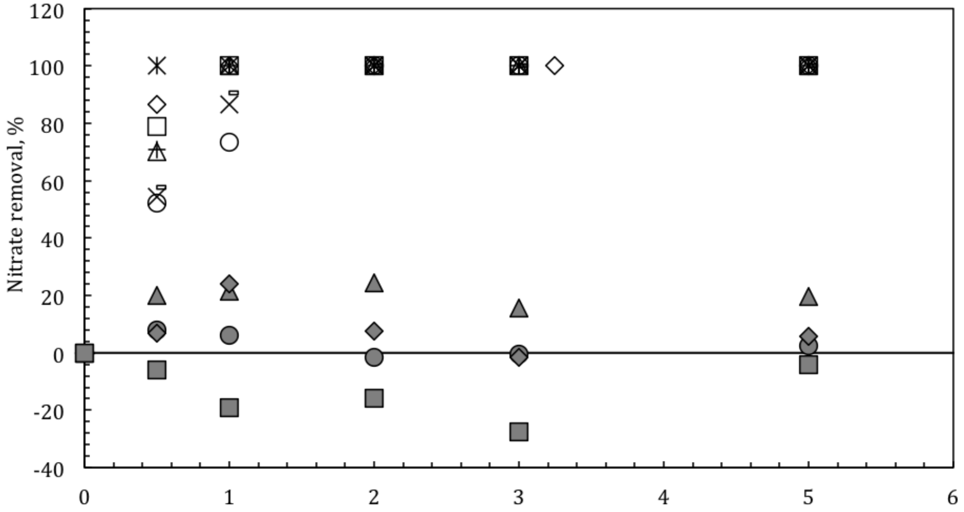

Figure 1 *Nitrate removal profiles during batch electrochemical treatment of mining waters, pH 3*

electrodes materials was studied in regards of cyanide removal. The tests were only performed at pH 11 due to the safety reasons and due to possible formation of HCN gas when operating at lower pH values. It should be noticed that the application of carbon electrodes was limited by the pH decreasing up to 6 that did not allow safe handling of cyanide solutions. Thus, the results obtained only using Al, Fe and Ti-coated electrodes were presented with an exception of Fe/C pair when the pH was maintained at around 11. The summary of the result on cyanide removal is given in Fig. 2. The concentration less then 1 mg/L of cyanide was achieved using Fe as anode regardless the applied current. However, the same cyanide removal was observed using Ti/Al pair. Application of inert electrode as anode resulted in very small amount of solids added to the system, solids were mainly formed due to the insignicant dissolution of Al cathodes. The shortest treatment time of 5 minutes was obtained at applied current 3A using Fe/Fe, Fe/C and Fe/Ti pairs. At current of 0.3A and 1A almost complete removal of cyanide was observed after 30 minutes.

Conclusion

Treatment of mining waters by electrochemical methods at the laboratory scale enabled the removal of harmful contaminants. Moreover, this study provides further understanding about the phenomenon occurring during the process. Thus, the highest sulfate

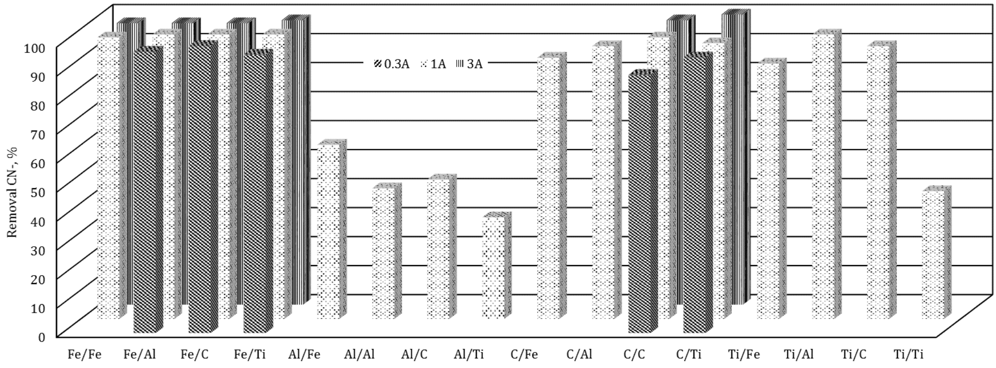

Figure 2 *Cyanide removal during batch electrochemical treatment of mining waters, pH 11*

removal using continuous electrocoagulation is possible by the neutralization of the particle charge. Nitrate is removed by electrocoagulation while electrooxidation was found to be inefficient. Cyanide was removed due to both adsorption and oxidation. The knowledge about the removal mechanisms of the anionic contaminants from mining waters and operational parameters tested favor the possible development of electrochemical treatment technologies and scale-up of the existing units.

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