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Research paper

The effect of electro-activation and eggshell powder on the neutralization of acid mine drainage



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ARTICLE INFO

Article history:

Received 3 July 2017

Received in revised form

11 September 2017

Accepted 13 September 2017

Available online 18 September 2017

Keywords:

Acid mine drainage

Electro-activation

Neutralization

Effectiveness

ABSTRACT

Acid mine drainage (AMD) production by sulfide mine tailing (SMT) is a major environmental preoccupation because it can degrade water surface quality on account of its strong acidity and advanced content of sulfide, iron (Fe) and other metals and metalloids. Acid neutralization and the precipitation of metals present in AMD were carried out by electro-activation with ion-exchange membranes, which is based on the self-generation of necessary conditions for acid neutralization and metal precipitation. The treatment of SMT was carried out by using an electro-activation cell generated alkaline solution in the cathode compartment. After 60 min of electro-activation, a $\text{pH}_{\text{catholyte}}$ of 7.9–9.6, depending on the experimental conditions, was obtained. The absence of Fe and other trace metal ions in the catholyte provide evidence that the electro-activation of SMT promotes the precipitation of insoluble trace metals in the cathode compartment. This approach can be applied to real conditions in combination with a pretreatment of SMT neutralization, in which biological calcareous amendments are available. Finally, the electro-activation technology of acid mine drainage may be a feasible, cost-effective approach for SMT neutralization because it focuses on sustainable development.

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1. Introduction

Acid mine drainage (AMD) is a result of sulfur-bearing mineral oxidation in the presence of water. This process can be considerably accelerated by bacterial activity, such as from *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*. AMD contains high concentrations of heavy metals such as iron (Fe), lead (Pb), nickel (Ni) and chromium (Cr). It is a serious hazard to humans and nature. However, this drainage is also a promising source of dissolved metals. Among the different approaches that could solve the negative influence of AMD, electrochemical treatment has become increasingly useful. The broad experience of electrochemical application in the restoration of various industrial wastewaters and polluted soils could be very useful in the case of AMD. As discussed in the work of Walsh and Reade (1994), the electrochemical technique is not capable of providing a single solution of metal containing solution treatment because of some adverse factors such as: (a) the strong dependence on the composition and temperature of treated solutions, (b) joule heating problems due to increased resistance,

(c) a small electrode area (material economy) and (d) the limited chemical and mechanical stability of cell materials and components (electrode, membrane). At present, economic (high prices of recovered materials) and ecological factors combined with new engineering decisions are leading to the rise of electrochemical applications despite these problems (Kurniawan, Chan, Lo, & Babel, 2006).

Electrolysis is a process that uses a direct electric current to drive different chemical reactions. The basis of electrolysis is oxidation-reduction reactions near the electrodes' surfaces. In some cases, the electrodes can be separated by neutral membranes (filtration, porous) or ion exchange membranes, which leads to the establishment of specific conditions in the controlled sections. Thus, heavy metal ions can be derived from polluted water in the form of metal deposition on the cathode (Britto-Costa & Ruotolo, 2014; Leahy & Schwarz, 2014; Mokmeli, Dreisinger, & Wassink, 2015) or slightly soluble substances in the bulk solution (Bunce, Chartrand, & Keech, 2001; Chartrand & Bunce, 2003). Indeed, metal deposition (plating) of the target element extracted from the solution on the cathode is a very popular practice (Britto-Costa, Pereira-Filho, & Ruotolo, 2014; Haghghi, Moradkhani, Sedaghat, Najafabadi, & Ali, 2013; Leahy & Schwarz, 2014; Luptakova, Ubal-dini, Macingova, Fornari, & Giuliano, 2012). For example, the

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proportion of world copper production represented by electro-winning was nearly 15% in the mid-1980s (Cooper, 1985) and several pieces of research were devoted to this process. Some of them proposed using an Fe sacrificial anode (Shelp, Chesworth, & Spiers, 1996). Shelp et al. (1996) evaluated the effectiveness of an electro-winning technique to eliminate the negative impact of AMD. The authors used a massive sulfide-graphite rock from the Sherman open pit iron mine (Temagami, Ontario, Canada) as the cathode, scrap iron as a sacrificial anode and collected acidic leachate as the electrolyte. The experiments were carried out by increasing the pH from 3.0 to 5.6 and significantly decreasing the redox potential from $> +650$ down to $< +300$ mV. Iron was precipitated in the form of sulfate with a concomitant decrease of solution concentration for Cd, Al, Co, Cu and Ni. A Canadian research group (Bunce et al., 2001; Chartrand & Bunce, 2003) investigated the electrochemical remediation of AMD (synthetic AMD solution) by means of electrolysis with ion exchange membranes. In their work, Bunce et al. (2001) and Chartrand and Bunce (2003) described the electrolytic reduction of solutions of synthetic AMD, comprising $\text{FeSO}_4/\text{H}_2\text{SO}_4$ and $\text{CuSO}_4/\text{H}_2\text{SO}_4$, in flow-through cells whose anode and cathode compartments were separated using either cation or anion exchange membranes. The effluent pH increased in steps by increasing the applied electric current. Cathodic reduction lowered the acidity of the synthetic AMD and pH values of >7 were readily achieved. Different heavy metals such as iron, copper and nickel were precipitated in hydroxide forms in the cathode compartment owing to elevated OH^- ion concentration under the alkaline conditions produced in the hydroxide forms. The effectiveness of iron and copper ion removal reached 100%. In the case of Ni and Cu, hydroxide precipitation dominated electrodeposition. Re-electrolysis or chemical precipitation was recommended for nickel. Sparging of electrolyzed catholyte was applied to remove the precipitate outside the electrolyzer. Removal of metal was achieved by sparging air or gas into the catholyte effluent, thereby precipitating metal outside the electrochemical cell. The experiments with copper, graphite and carbon cathodes showed similar results (for iron precipitation) (Chartrand & Bunce, 2003). It was also found that the efficiency of the process (the increase of pH and metal precipitation) was higher with an anion exchange membrane rather than with a cation exchange membrane used as a diaphragm to separate the anodic compartment from the cathodic. Cell design, optimization of mass transfer and application of new materials were assigned by authors as necessities in the development of AMD electro-remediation (Bunce et al., 2001; Chartrand & Bunce, 2003).

Electrochemical based processes are also applicable in wastewater treatment because of the selective separation of charged dissolved components by ion exchange membranes under an electric current. This method has an efficiency of over 97% in the purification of recovering water from acid mine drainage (Buzzi, Viegas, Rodrigues, Bernardes, & Tenório, 2013). Such processes have one significant limitation in AMD treatment, as the precipitate formation at the surface of the cation exchange membrane leads to the blocking of ion migration and to the increase of cell electric resistance (Buzzi et al., 2013; Martí-Calatayud et al., 2014). Hansen, Ribeiro, Mateus, and Ottosen (2007) showed that when a three-sectional electro-dialysis cell is used, it is possible to mobilize heavy metals from the polluted soils and different mining tailings placed in the central section. The greatest amount of copper was extracted from mine tailing with low pH. Moreover, it has been shown that H_2O was more efficient as an extracting solution compared with NH_4Cl and H_2SO_4 (Hansen et al., 2007).

Another type of possible electrochemical treatment of AMD can be realized through electro-activated water technology, as with regard to electro-winning, electro-activation is based on the

electrolysis of activated water (Tanaka, Hirakata, Kaku, Yashida, & Takemura, 1996). The distinctive features of this technology are a water splitting reaction at the electrode surfaces and extremely active oxidative (for anolyte) and reductive (for catholyte) meta-stable compounds of the electro-activated solution. The dominance of the water splitting reaction (generation of H^+ and OH^-) in aggregate with ion flow correction (control) by an electro-activator with ion exchange membranes could be more effective under the specific operating conditions that are necessary for AMD neutralization (high pH) and metal extraction.

The main objectives of this study was to evaluate the effectiveness of the electro-activation process for the extraction of Fe from FeSO_4 -rich water using an electro-activation reactor.

2. Materials and methods

2.1. Mine tailing and eggshells

The sulfide mine tailing (SMT) used in this study originated from the Solbec-Cupra site at Thetford-Mines (Quebec, Canada). Applied chicken eggshells (CES) were taken from the market, washed, dried in an oven and then finely ground (<2 mm). All chemicals used were of analytical grade. Ferrous sulfate solution was prepared by dissolving $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in double-distilled water. The commercial CEM and AEM (MK-40 and MA-40, respectively) were subjected to pretesting treatment to eliminate organic contaminants that provoke unstable conditions in the target processes.

2.2. Analyses

At the end of each experiment, the pH of the solutions (anolyte and central solution) was measured using a digital pH-meter (Omega PHB-62, OMEGA Technologies Co., Stamford, CT, USA) and an Orion double-junction electrode (Orion, ThermoScientific, Beverly, MA, USA). The concentrations of Fe(II) and Fe(III) (after the reduction of Fe(III) with hydroxylamine chlorhydrate) were determined by the *o*-phenanthroline colorimetric method (Tamura, Goto, Yotsuyanagi, & Nagayama, 1974), using Spectronic 20D (Milton Roy Company, Rochester, NY, USA) and a molar absorption coefficient for the Fe(II)–phenanthroline complex of $1.100 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 510 nm. The total Fe in the anolyte and central solutions was also determined by atomic absorption spectroscopy (AAAnalyst 200, Perkin Elmer, Shelton, CT, USA). X-ray diffraction (XRD) and elemental analysis using SEM-EDX (scanning electron microscopy-energy-dispersive X-ray spectroscopy) were used to detect any precipitate that could form on the membrane surfaces. This analysis was performed using a JEOL scanning electron microscope (Japan Electro Optic Laboratory, model JSM840A, Peabody, MA, USA) equipped with an energy-dispersive spectrometer (EDS) (Princeton Gamma Tech., Princeton, NJ, USA). The experimental conditions for the EDS were 15 kV accelerating voltage and a 13-mm working distance. The membrane samples were dried and coated with a thin film of gold/palladium to impart them with electrical conductivity and ameliorate the photograph quality of the microscopy. The membrane sample preparation was the same for SEM and XRD (Ait Aissa & Aïder, 2014; Cifuentes-Araya, Pourcelly, & Bazinet, 2011).

2.3. Ion exchange and nanofiltration membranes

A commercial cation-exchange membrane (MK-40), anion-exchange membrane (MA-40) and nanofiltration membrane (N30F) were used as separating membranes in the electro-activation process. The MK-40 and MA-40 membranes were manufactured by Shchekinoazot Ltd. (Shchekino, Russia). The

membranes were first treated with ethanol for 6 h to extract the monomer residues and surfactant inclusions that are usually present in the material after synthesis. The membranes were then treated with solutions of NaCl (saturated solution, 100 g/L and 30 g/L) (Saldadze, Pashkov, & Titov, 1960) for 24 h. Finally, the membranes were conditioned in distilled water for 48 h. The commercial flat sheet nanofiltration membrane, NADIR® N30F, was purchased from NADIR Filtration GmbH (Wiesbaden, Germany).

2.4. Removal of Fe(II) from the aqueous FeSO_4 solution by the electro-activation process

Ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was used as a source of iron in the form of Fe(II) to simulate acidic Fe-rich mine water because iron occurs in most coal mine drainage waters predominantly as the soluble Fe^{2+} ion (Stauffer & Lovell, 1968). The experimental electro-activator (Fig. 1) was composed of cathode and

anode compartments separated by a central compartment. The purpose of using three-compartment cell units is to remove most of the total Fe from the anodic compartment and to recover it in the central compartment. This method is attractive because the removal of Fe from the anolyte to the central compartment can be accomplished without the need for chemical extractant, and the acidic anolyte can be neutralized, leaving no secondary pollution. The electrode material used for both the anode and cathode was made of titanium coated with a ruthenium-iridium layer (Qixin Titanium Co., Ltd., Baoji, China). The central compartment was separated from the anode compartment by cation-exchange membrane (CEM) MK-40 which has an active area of 30 cm^2 , and from the cathode compartment by anion-exchange membrane (AEM) MA-40 with the same active area as MK-40. This type of membrane configuration enables the selective transfer of metal cations from the anode compartment to the central one, where further migration will be blocked by the AEM because of its specific

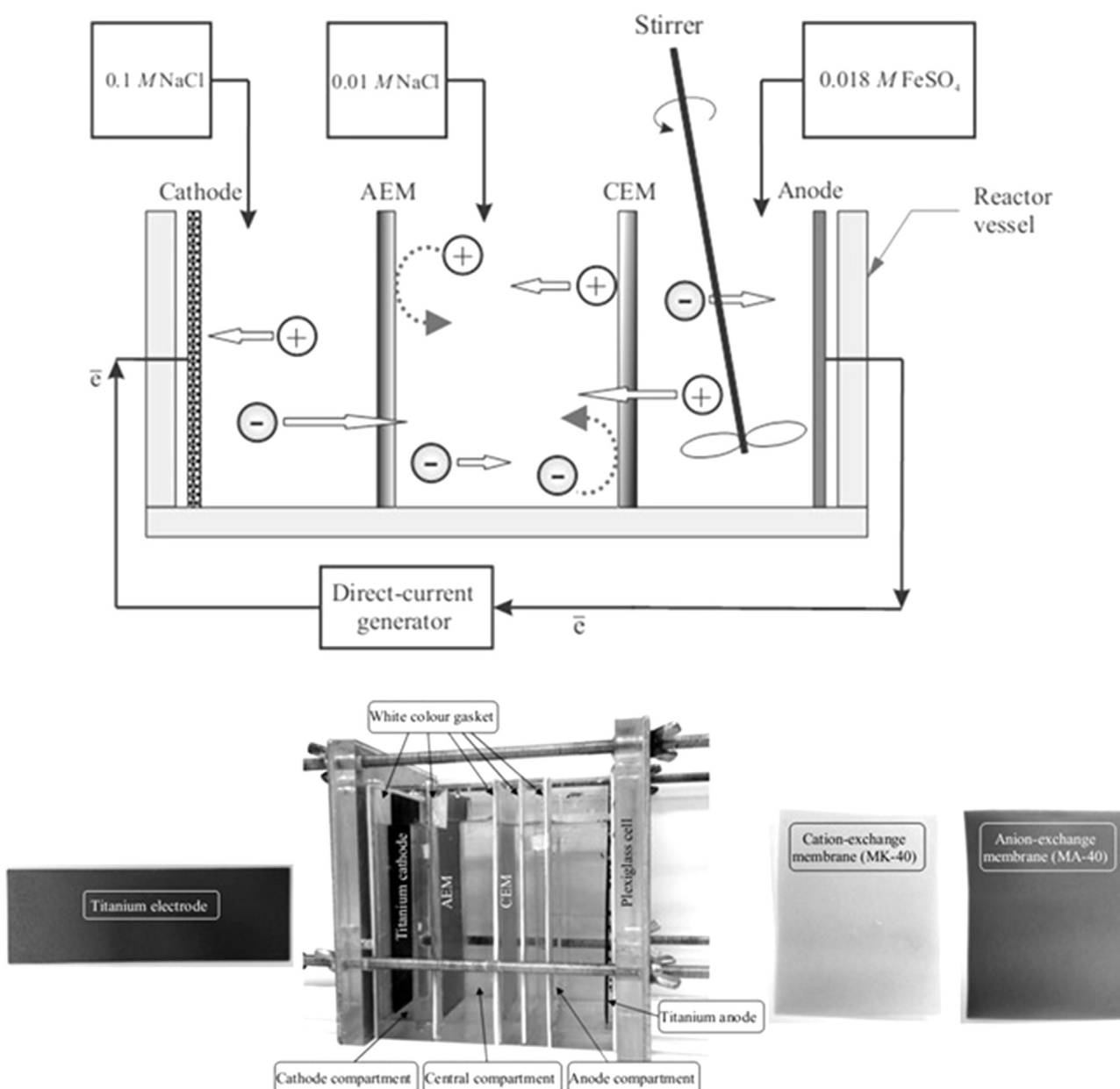


Fig. 1. Schematic representation of the electro-activation reactor and neutralization process.

permeability for the negatively charged ions. The CEM was placed between the anode and AEM to prevent anions such as hydroxyl (OH^-), generated initially in the cathode compartment, and chloride (Cl^-), present in the central compartment, from migrating towards the anode compartment, and to allow the total Fe (Fe^{3+} generated by oxidation of Fe^{2+} and remaining Fe^{2+}) present in the anolyte to pass through the membrane, resulting in the accumulation of soluble Fe ions in the central compartment. The anode compartment is filled with aqueous FeSO_4 solution (200 mL) containing 1000 mg/L of Fe^{2+} , and the supporting electrolyte solution (120 mL of 0.1 and 0.01 M NaCl) was placed in the cathode and central compartments. The concentration of Fe(II) was selected to represent moderate Fe concentration in AMD. The length of both the central and cathode compartments was kept constant at 3 cm. The two electrodes were connected externally using a conductive copper wire. The current intensities (I) applied were 50, 100, 150, 200 and 250 mA. The electro-activation times (t) were set at 30, 60, 75, 90, 105 and 120 min.

2.5. Neutralization of acid aqueous sulfide mine tailing and precipitation of toxic metals by electro-activation

The aim of this experiment was to determine the effect of the quantity of the SMT to be treated (R), current intensity (I), mixing speed (ω) and electro-activation time (t) on the effectiveness of the electro-neutralization of aqueous acid SMT. Electro-activation with anion-exchange membrane (AEM) was used to increase the pH of the aqueous suspensions of SMT to a range of 9.0–10.0. At this pH range, most toxic metals become insoluble and precipitate. The investigation was carried out in electro-activation cell units divided by AEM and equipped with titanium electrodes. The anode compartment was fed with a solution containing 90 mL of 0.005 M K_2SO_4 . The cathode compartment was filled with 150 mL of distilled water containing a different quantity of SMT. By setting the distance between the cathode and AEM to 5 cm, the volume of distilled water in the cathode compartment remained constant, regardless of the quantity of SMT to be treated in the cathode compartment. At each time interval, samples were taken from the catholyte to determine the concentrations of Al, Ca, Cu, Fe, Mn, Mg and Zn by atomic absorption spectroscopy (AAAnalyst 200, Perkin Elmer, Shelton, CT, USA).

2.6. Combination of electro-activation and chicken eggshell powder (CES) for acid aqueous sulfide mine tailing neutralization

The ratio of SMT/Distilled water in the cathode compartment was set at 0.2/1 (w/v). The anode compartment was fed with a solution containing 90 mL of 0.005 M K_2SO_4 . The electro-activation cell was operated at 50 mA for 60 min. After a given interval of time, the pH values of the solution in the cathode compartment were measured potentiometrically, and samples were taken from the catholyte to determine the concentrations of Al, Ca, Cu, Fe, Mn, Mg and Zn by atomic absorption spectroscopy (AAAnalyst 200, Perkin Elmer, Shelton, CT) and S by ICP. Moreover, the effect of different concentrations and geometric parameters of the electro-activation reactor were investigated. The effectiveness of the electro-neutralization of aqueous acid SMT previously treated with 4% CES and trace metal precipitation was studied as a function of voltage, cathode materials, three types of ion-exchange membrane and electro-activation time. The distance between the membranes and the cathode was kept at 4 cm.

2.7. Statistical analysis

Statistical analysis was performed using a complete randomized

factorial design with repeated measurements. Each treatment was carried out in triplicate, and mean values \pm std were used. The statistical analysis (ANOVA) of the data was performed using the SAS software application (V9.3, SAS Institute Inc., Cary, NC, USA).

3. Results and discussion

3.1. The removal of Fe(II) from aqueous FeSO_4 solution by the electro-activation process

As expected, the electro-activation reactions of aqueous FeSO_4 generated acidic solutions in the anode and central compartments, an alkaline solution in the cathode compartment and the recovery of Fe in a soluble form in the anodic compartment. It is known that electrolysis-based reactions create acidic solutions near the anode and alkaline solutions near the cathode (Flores et al., 2012). Different studies addressed the recovery of metallic iron or an iron-rich alloy, oxygen and sulfuric acid from iron-rich metal sulfate wastes using electrochemical processes. In general, electrolyzing the iron-rich metal sulfate solution in an electrochemical cell using a separator allowing anion passage causes iron to be electro-deposited at the cathode, nascent oxygen gas to evolve at the anode, sulfuric acid to accumulate in the anodic compartment and an iron-depleted solution to be produced (Cardarelli, 2011).

3.2. Evolution of the pH of the used solutions

All electro-activation conditions significantly influenced the pH of the anolyte (anode compartment) and electrolyte solution in the central compartment ($p < 0.001$). As shown in Fig. 2, the pH values of the FeSO_4 solution in the anode compartment (anolyte) and those of the solution filed in the central compartment decreased with increasing I , D_A and time (t). There is an inverse relationship between the current I and the pH values of anolyte and central solution. In general, at each electro-activation time, the pH values decreased in the following order: I_5 (250 mA) $<$ I_4 $<$ I_3 $<$ I_2 $<$ I_1 (50 mA). This finding indicates that the electric current gradually reduces the pH with increasing electro-activation time, confirming that the electro-activation of FeSO_4 generates acidity at the anode and in the central compartments. These results can be explained by the oxidation of water on the anode surface. As the electrolysis progressed, oxidation of water occurs at the anode/solution interface. Moreover, the reaction is more intense with a higher electric current. The pH values of the solution in the central compartment of the electro-activation reactor are lower (i.e. more acidic) than those of the anolyte, regardless of D_A values. This result could be attributable to three possible causes, including (i) the continual generation of H^+ ions at the anode, (ii) the high electro-mobility of many H^+ ions from the anode to the central compartment through the CEM and (iii) the characteristics of the CEM, which contains 65% cation-exchange resin and 35% polyethylene.

It is recognized that some H^+ ions produced at the anodic compartment during the electro-activation migrate to the central compartment through the CEM, where they are blocked by the AEM and consequently do not reach the cathode compartment. Thus, the presence of protons (H_3O^+) in the central compartment at high concentrations contributes to the considerable reduction of the pH of the solution. However, H^+ ions have great mobility in the electrolyte solutions and in cation-exchange resins and Zundel (1969) explained this phenomenon by the presence of proton conduction in both cation-exchange resin and electrolyte solution. Moreover, water is a good conductor of protons because of the effect of H-bonded networks between water molecules. Thus, proton conduction is carried out through the proton transfer from one water molecule to another. This process is due to a high polarization of

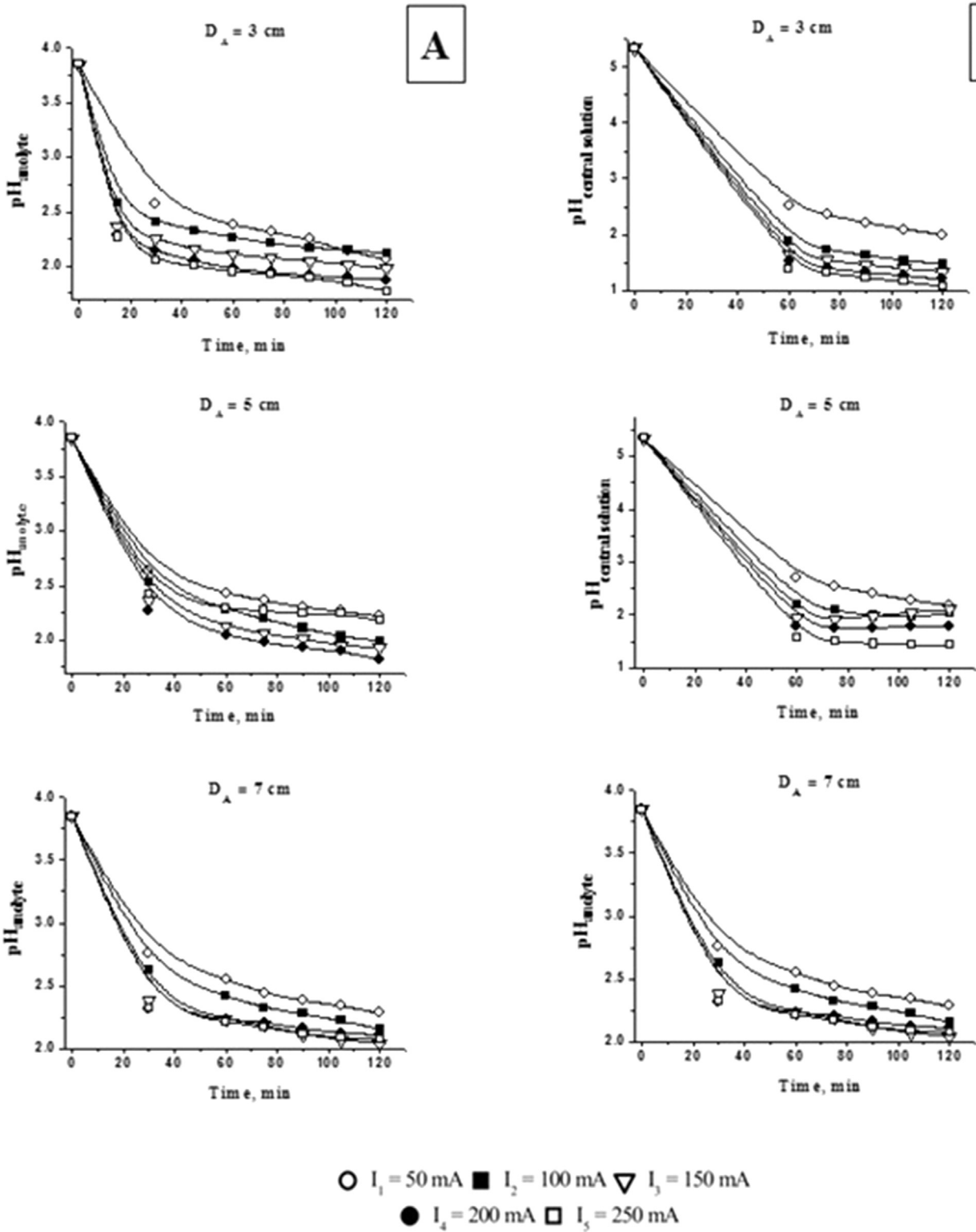


Fig. 2. Evolution of pH of solution in the anode (A) and central (B) compartments as a function of electro-activation time and current intensity.

hydrogen bonds in the H_5O_2^+ group and a proton tunnel junction from one bond to another (Zundel, 1969).

3.3. Concentration of Fe in the anolyte and central solution

Analysis of the variance (ANOVA) revealed the highly significant

effect ($P < 0.001$) of I and D_A on the concentration of Fe as a function of electro-activation time. Changes in total Fe and Fe^{2+} ion concentrations in the anode and central compartments are illustrated in Fig. 3A and B. The concentration of Fe in anolyte decreased gradually with time for all I and D_A values (Fig. 3A). Meanwhile, the concentration of Fe(II) in the electrolyte solution of the central

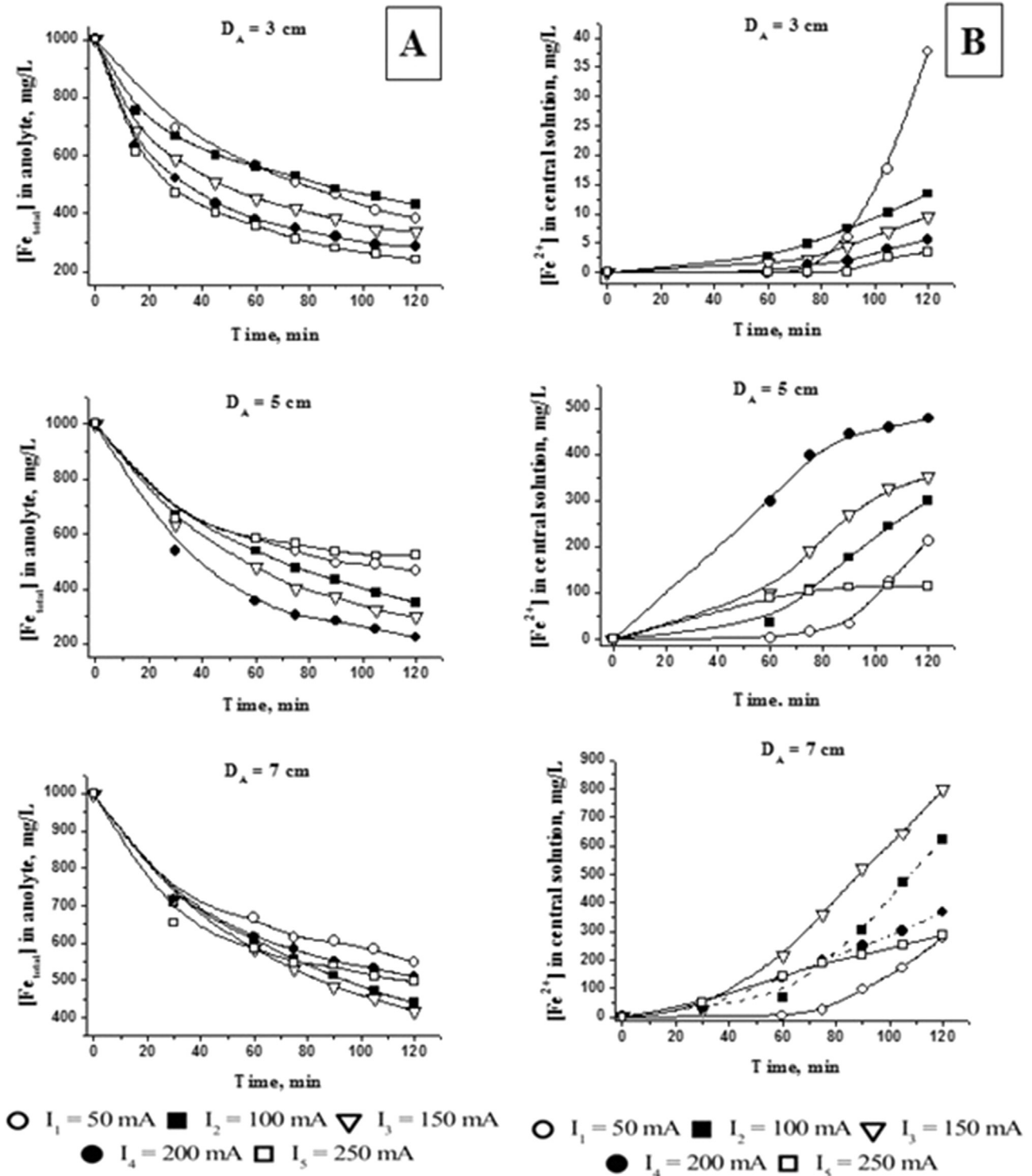


Fig. 3. (A) Evolution of Fe_{total} concentration in the anolyte as a function of electro-activation time. (B) Evolution of Fe^{2+} concentration in the central solution as a function of electro-activation time.

compartment increased gradually with t , I and D_A (Fig. 3B). This result would be attributable to two processes: (i) depletion of Fe^{2+} in the anode compartment due to the oxidation of Fe^{2+} to Fe^{3+} and (ii) the migration of Fe^{2+} ion through the CEM to the central compartment. Iron concentration curves differed considerably among I treatments throughout the entire range of electro-activation times. As shown in Fig. 3B, Fe^{2+} recovery was highest

under the highest electric current (I). The recovery was also significantly different among D_A throughout the entire range of electro-activation times. Fe^{2+} recovery was highest under the highest D value. The effect of I on Fe recovery was linear until $t = 60$ min and curvilinear up to $t = 120$ min. The lowest Fe^{2+} concentration (478 mg/L) in the central solution was recorded with the following conditions: $t = 120$ min; $I = 200$ mA; anode-CEM

distance = 5 cm; pH = 1.8. The highest Fe concentration (800 mg/L) in the central solution was recorded with the following conditions: $t = 120$ min; $I = 150$ mA; anode-CEM distance = 7 cm; pH = 1.5. Moreover, it is advisable to mention that part of soluble Fe could precipitate at the CEM/anolyte interface in the anode compartment as $\text{Fe}(\text{OH})_3$, therefore blocking the transfer of Fe^{2+} from the anode to the central compartment. The qualitative composition of the precipitate was examined by energy-dispersive X-ray spectroscopy and the Fe peak is identified as adsorbed Fe^{2+} ions. The analysis of the obtained crystals shows predominance and pronounced Fe and O peaks, demonstrating the presence of iron hydroxide. The formation of $\text{Fe}(\text{OH})_3$ is based on the duality of I and D_A . High voltage or very high current intensity promotes the precipitation of Fe in a short period of time. Indeed, precipitates were observed at I values > 50 mA and $D_A = 3$ cm. However, at higher D_A value (5 or 7 cm), precipitate was observed at $I > 200$ mA. The precipitate was highest under the highest D_A value. In a preliminary test, it has been observed that when a very high voltage (126 V) was applied, the values of I increased from 700 mA to approximately 2600 mA after 6 min of the electro-activation process, and the surface of the CEM (anode side) became black-brown as a result of the precipitation of the total amount of Fe (1000 mg/L) and its deposition on the membrane (data not shown). In summary, the current intensity and electro-activation time induce a decrease in the pH of solutions in the anode and central compartments, and the recovery of Fe in the central compartment increased with increasing I , t and D . The highest Fe concentration (800 mg/L) in the central solution was recorded with the following conditions: $t = 120$ min; $I = 150$ mA, anode-CEM distance = 7 cm; pH = 1.5. The close distance between the anode and CEM ($D = 3$ cm) along with the high value of I promoted the precipitation of some of the Fe.

3.4. Electro-neutralization of acid aqueous sulfide mine tailing treated with chicken eggshell (CES) powder

The evolution of the pH values of aqueous SMT (pH = 3.2), SMT + 4% CES (pH = 4.3) and SMT + 10% CES (pH = 5.4) in catholyte ($\text{pH}_{\text{catholyte}}$) were examined as a function of (i) the cathode distance from the AEM (D_C) and (ii) the membrane active surface area (AS). Among all of the treatments, the CES content of SMT and D_C were the most important factors influencing $\text{pH}_{\text{catholyte}}$. The positive effect of the CES rate on the rise of $\text{pH}_{\text{catholyte}}$ over electro-activation time was linear for AS values (25%, 50% and 100%) in combination with D_C values (3, 4 and 5 cm) (Fig. 4A–C). At $t = 60$ min, higher $\text{pH}_{\text{catholyte}}$ values (pH 9.5) were obtained under the following conditions: SMT + 10% CES, $D_C = 3$ cm and either 50% AS (pH 9.6) or 100% AS. This result indicates that the electro-activation of CES-amended mine tailing generated alkalinity and achieved a pH range of 9.0–10.0. As seen in Fig. 4A–C, $\text{pH}_{\text{catholyte}}$ increased with increasing the membrane of the active surface area. For instance, the pH values were 4.96 and 9.05 at the lowest and highest points of trials with 25% AS, and they became 6.05 and 9.63 for the trials with 100% AS. This means that decreasing AS is conducive to the quantitative reduction of active ion-exchange centers needed for ion transport. In this condition, the electric current through the unit of the membrane area will increase and in turn will generate additional H^+ ions in the cathode compartment, as mentioned previously. This supports increasing voltage values. All voltage values obtained with 25% AS over a 50-min electro-activation period were higher than those obtained with 50% and 100% AS. A sharp increase in V was recorded for $D_C = 3$ cm and AS = 50% and 100%. This can be explained by the intensive desalination process in the cathode compartment that results in the increased electric resistance of the catholyte.

The effect of D_C on $\text{pH}_{\text{catholyte}}$ over the electro-activation time

was linear for each AS value (25%, 50% and 100%) in combination with the CES rate in SMT (0, 4 and 10%). For example, 4% CES and 50% AS generated $\text{pH}_{\text{catholyte}}$ values of 7.29, 8.59 and 9.49 for $D_C = 5$, 4 and 3 cm, respectively. This finding could be attributable to the amount of OH^- generated at the cathode surface. The amount of OH^- ions produced by the water splitting reaction is a function of the electric current density, and the qualitative and quantitative composition of the initial solution (Tanaka, 2010). In this trial, only the ion quantity is a variable parameter. Because of the constant initial concentration and different volume of the solution, the overall number of ions is lower in the compartment with the smallest geometric parameters. This means that fewer initial ions will reach the cathode surface to be reduced and more OH^- will be produced to support the electric current without changing. More OH^- ions will be present in the small volume of the electro-activation cell unit.

As mentioned previously, the changes in pH depend on the electrolyte concentration. The SO_4^{2-} ions make a major contribution to this process owing to their electro-migration from the cathode section, resulting in pH increase. The degree of S desalination increased as the cathode-AEM distance decreased and as AS increased (Fig. 5). Maximum S desalination (elimination from the catholyte) from 384 to 46 ppm was recorded with CES = 10%, $D_C = 3$ cm and AS = 100%. An absence of S desalination was observed in the case of CES = 4%, $D_C = 5$ cm and AS = 25%. This result was due to the competition in the ion transport through the anion-exchange membrane between carbonate, sulfate and hydroxyl ions. The carbonate ions from CES could accelerate this reaction — a fact that is confirmed by the increase in S concentration from 257 to 385 mg/L with an increase in CES from 0 to 10%, respectively. The lowest (73 mg/L) and highest (302 ppm) Ca concentrations for CES = 10% were recorded with the following conditions: $D_C = 3$ cm and AS = 100% and $D_C = 5$ cm and AS = 25%, respectively. The initial Ca content increased from 87 mg/L for the solution with CES = 0% to 232 ppm with CES = 10%. This finding indicates that the electro-activation of CES-amended SMT could extract Ca from the tailing (see Fig. 6).

In summary, the treatments significantly influenced the $\text{pH}_{\text{catholyte}}$. At each level of CES, $\text{pH}_{\text{catholyte}}$ increased D_C decreased and AS increased. For each D_C value, $\text{pH}_{\text{catholyte}}$ increased with an increasing CES rate. Higher $\text{pH}_{\text{catholyte}}$ values were obtained under the following conditions: SMT + 10% CES, $D_C = 3$ cm and either 50% AS (pH 9.6) or 100% AS (pH 9.5). The absence of Fe and other trace metal ions in the catholyte provide evidence that the electro-activation of SMT under the studied parameter conditions promotes precipitation of insoluble trace metals in the cathode compartment. A combination of pretreatment SMT applications, where biological calcareous amendments are available, followed by electro-activation of effluent may be a feasible, cost-effective approach for SMT neutralization. For all combinations of the studied parameters, after 1 h of electro-activation, $\text{pH}_{\text{catholyte}}$ values using CEM varied from 4.1 (before the electro-activation process) to a range of 4.6–5.1. The slow generation of alkalinity in the cathode compartment under the selected conditions could be due to the transfer of H^+ from the anode to cathode compartments through the CEM and neutralization of OH^- produced at the cathode compartment.

The electro-neutralization of the CES (4%)-amended SMT pattern was similar for electro-activation conditions using a nanofiltration membrane, regardless of the type of electrode material (e.g. stainless steel, titanium, copper). The obtained data showed that $\text{pH}_{\text{catholyte}}$ increased as electro-activation time increased and achieved an alkaline pH range of 8.9–9.1 when using a nanofiltration membrane as a separator and stainless steel, copper or titanium as the cathode material. The increase in $\text{pH}_{\text{catholyte}}$

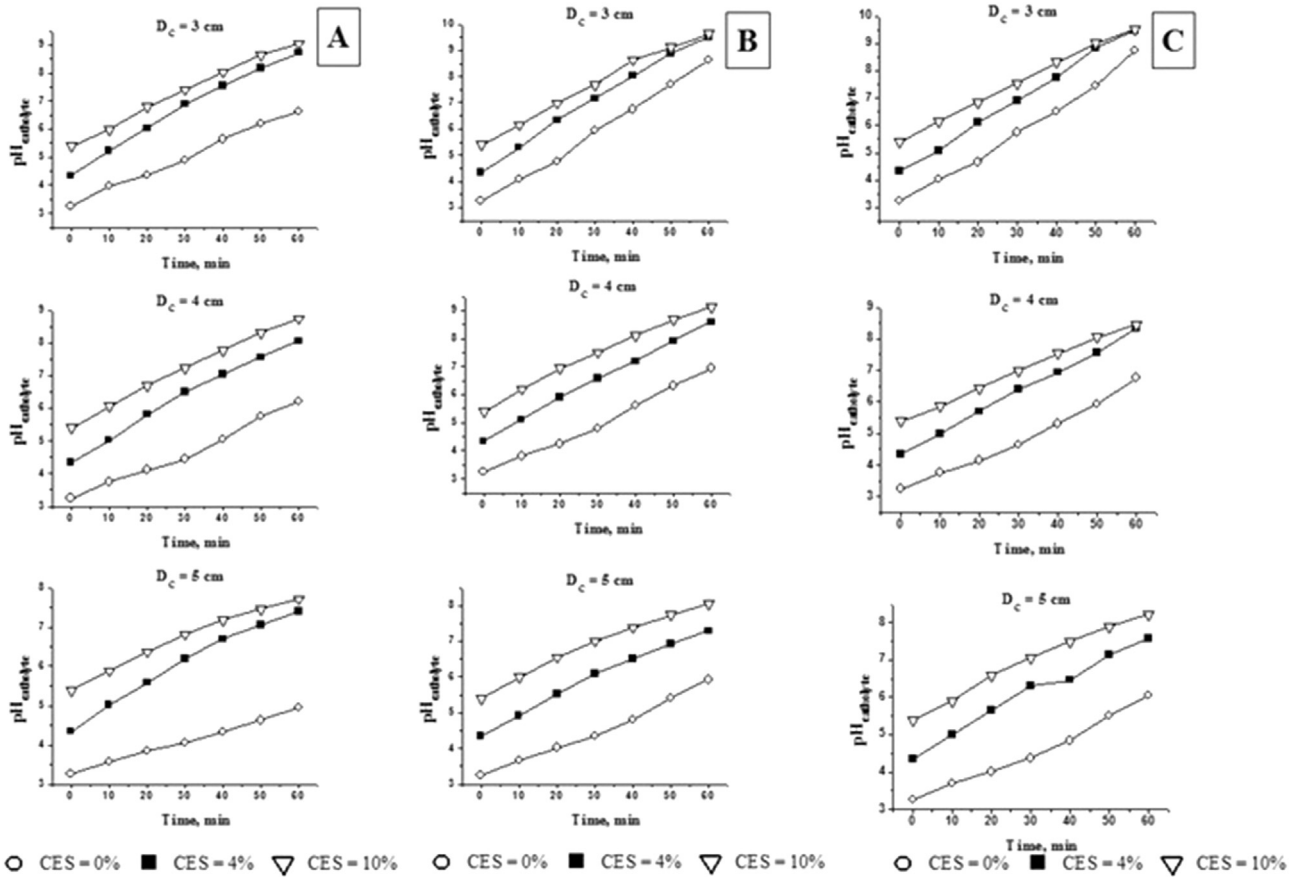


Fig. 4. (A) Effect of the current intensity on $pH_{catholyte}$ values as a function of electro-activation time. $R = 0.1:1, 0.2:1$ and $0.3:1$ and (B) Effect of the amount of SMT in the cathode compartment on $pH_{catholyte}$ as a function of electro-activation time. $I = 50$ mA, 100 mA and 150 mA.

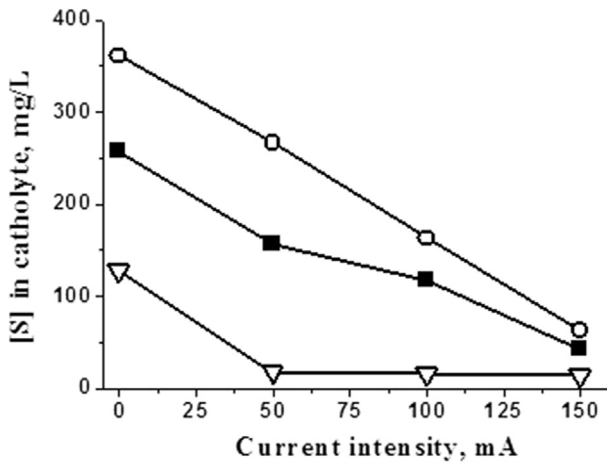


Fig. 5. Evolution of sulfur concentration in the cathode compartment of the electro-activation reactor.

was lowest with 15 V and highest with 60 V. When compared to the current intensity at 60 V, the current intensity produced from 15 V and 30 V was more stable. According to Pokonova (2007), the nanofiltration membranes are more useful for the separation of multi-charged ions from mono-charged ions in a solution, and their separation efficiency decreases with increasing ion concentration. In the absence of ionogenic groups in the structure of a nanofiltration membrane (NFM), the transfer of ions can be realized in

both ways: cathode and anode. Thus, the OH^- and H^+ ion flows generated on the anode and cathode surfaces will migrate through the membrane more easily than other ions. The overall possible ion flows in the cathode compartment result in increased OH^- concentration with increased electro-activation time and voltage. Changes in pH were different when using different voltages and electrode materials throughout the entire range of electro-activation times. The $pH_{catholyte}$ values after 60 min were higher with 60 V in combination with electrode materials (e.g. N7, N8 and N9). When considering all the treatments related to the nanofiltration membrane, the values of $pH_{catholyte}$ varied from 4.1 (initial pH of aqueous CES(4%)-amended SMT) to a range of 5.6–6.0, 6.3–7.0 and 9.0–9.1 for 15 V (N1, N2 and N3), 30 V (N4, N5 and N6) and 60 V (N7, N8 and N9), respectively. The lowest $pH_{catholyte}$ value (pH 5.6) was recorded in 15 V + copper electrode treatment. The $pH_{catholyte}$ was greatest (pH > 8) for N7, N8 and N9. Among all the treatments with the nanofiltration membrane, the voltage of the electro-activation system (V) was the most important factor influencing $pH_{catholyte}$. In general, V had a significant positive linear effect on pH. The electro-activation of acid mine tailing previously treated with CES contributes not only to neutralizing their acidity but also to increasing the concentration of Ca and S in the solution. However, the electro-activation process using a higher voltage (e.g. 60 V) maintains a lower concentration of these elements than when using lower voltage or initial solution. The concentration of both S and Ca in catholyte increases in the following order: $V_{15V} > V_{30V} >$ initial solution (without V). Higher Ca concentrations (331–337 mg/L) were recorded in the following conditions: nanofiltration membrane + 15 V + copper or stainless steel electrode

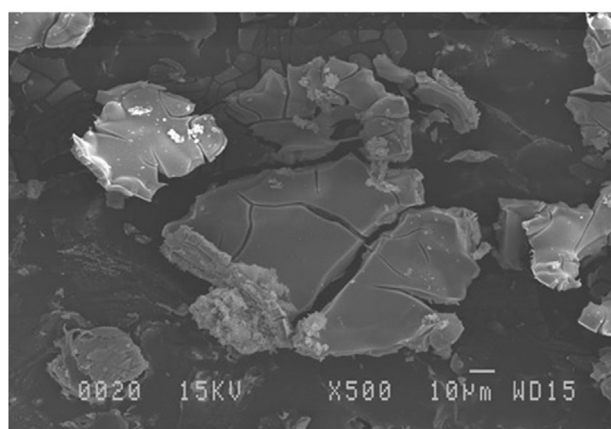
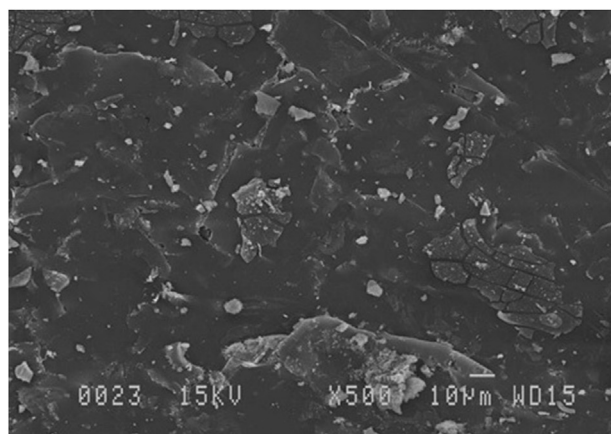


Fig. 6. Scanning electron microscope image of the membrane in the cathodic compartment showing $(\text{Fe}(\text{OH})_3)$ as light crystals.

material. This finding indicates that it is possible to extract Ca from mine tailings treated with chicken eggshell residue by the current electro-activation process using a nanofiltration membrane as a separator. The absence of Fe and other trace metal ions in the catholyte provides evidence that the electro-activation of SMT under the studied parameter conditions promotes the precipitation of insoluble trace metals in the cathode compartment. These results are consistent with those obtained in the previous section.

The electro-neutralization of the CES(4%)-amended SMT pattern was similar for electro-activation conditions using AEM, regardless of the type of electrode material (e.g. stainless steel, titanium, copper). The $\text{pH}_{\text{catholyte}}$ increased with increased electro-activation time and achieved an alkaline pH range of 7.9–10.1 when using AEM as a separator and stainless steel, copper or titanium as the cathode material. Similar findings have been reported by (Bunce et al., 2001; Chartrand & Bunce, 2003), who found that the increase in pH was dependent on current intensity. When electricity is applied to the solution, OH^- ions in anolyte will move toward the cathode compartment. As a consequence, the catholyte becomes alkaline. These $\text{pH}_{\text{catholyte}}$ values are higher than those obtained with a nanofiltration membrane. The increase in $\text{pH}_{\text{catholyte}}$ was lowest at 15 V and highest at 60 V. Compared to 60 V and 30 V, the increase in current intensity produced at 15 V was stable. The overall possible ion flows in the cathode compartment result in increased OH^- concentration with increased electro-activation time and voltage. Changes in pH were different among voltages and electrode materials throughout the entire range of electro-activation times. The $\text{pH}_{\text{catholyte}}$ values after 60 min were higher when using 60 V in combination with electrode materials. When

considering all the treatments with AEM, the values of the $\text{pH}_{\text{catholyte}}$ varied from 4.1 (initial pH of aqueous CES(4%)-amended SMT) to a range of: 7.9–8.3, 9.2–9.9 and 9.8–10.1 for 15, 30 V and 60 V, respectively. The lowest $\text{pH}_{\text{catholyte}}$ value (pH 7.9) was recorded for 15 V + stainless steel electrode treatment (A1). The $\text{pH}_{\text{catholyte}}$ was greatest (pH > 9.9) in A7, A8 and A9. These values are much higher than those obtained with a nanofiltration membrane and a cation-exchange membrane under the same electro-activation conditions. It is possible that a part of the OH^- generated did not participate in water splitting and was not transferred across the AEM. As a result, the remaining OH^- ions have made the catholyte more alkaline. In a laboratory experiment, Iurash, Nikonenko, Pismenskaya, Zabolotsky, and Volodina (1999) studied the desalination channel of an electro-dialyzer stack with an ion-exchange bed formed by a smooth anion-exchange membrane MA-40 and cation-exchange membrane MK-40 positioned at a distance of $h = 0.8$ mm. They found that the anion-exchange membrane may cause a misbalance of cations and anions, resulting in the pH growth of the desalted solution. Among all the treatments with AEM, the voltage of the electro-activation system (V) was the most important factor influencing the $\text{pH}_{\text{catholyte}}$. In general, V had a significant positive linear effect on pH. These results are consistent with those obtained in the previous section.

In summary, the anion-exchange membrane, nanofiltration membrane and voltage of the electro-activation system (V), regardless of cathode material, are the most important factors that contribute to efficiently neutralizing acidity and achieving the target alkaline pH range. Higher $\text{pH}_{\text{catholyte}}$ values (pH \geq 7.9) were obtained in the following conditions: nanofiltration membrane + 60 V + stainless steel, titanium or copper electrode (pH 8.9–9.1); and AEM + 15 V, 30 V or 60 V + stainless steel, titanium or copper electrode (pH 7.9–10.1).

4. Conclusions

This study shows that electro-activation technology can increase the alkalinity of acid mine tailing suspensions up to pH > 8. Several geometrical, electric, qualitative and quantitative parameters could promote the electro-activated neutralization of CES-amended SMT. The selective permeability of ion-exchange membranes and water splitting reaction on the anode surface in the electro-activation technology yielded results confirming that a three-sectional electro-activation reactor could be applied under some conditions for iron ion ($\text{Fe}(\text{II})$) extraction from the treated solution. The hydrogen ion produced in the water splitting reaction at the anode surface played an important role in the process that created favorable conditions to avoid the precipitation of $\text{Fe}(\text{OH})_3$ on the membrane surface or dissolution of the slightly soluble compounds of target elements. The electro-activation method showed positive results in selective $\text{Fe}(\text{II})$ extraction from the modelled FeSO_4 solution. The maximum concentration of $\text{Fe}(\text{II})$ (800 ppm) recovered in the central section was obtained under the following experimental conditions: $t = 120$ min, $D_A = 7$ cm and $I = 150$ mA.

Finally, the results of this work may have practical implications in tailing management for the reduction of acid generation and trace metal mobility in sulfide mine drainage system and of water contamination risk.

Acknowledgements

The authors would like to thank Mr. Daniel Marcotte for his technical support with the atomic absorption analyses.

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