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TECHNICAL ARTICLE

Use of Electrocoagulation with Aluminum Electrodes to Reduce Hardness in Tunisian Phosphate Mining Process Water

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Abstract This study evaluated electrocoagulation using Al electrodes for removal of non-carbonate hardness in phosphate mining process water. Examination of process parameters identified optimal conditions for hardness removal at pH 7, a NaCl concentration of 4 g/L, a current density of 22.2 mA/cm^2, an inter-electrode distance of 2 cm, a stirring speed of 450 revolutions per minute, and a treatment time of 30 min. Production of primary coagulant during electrolysis improved removal of both calcite and magnesium hydroxide. The optimized hardness removal was highly efficient, with an overall removal rate of 83.8 % at 30 min of retention time.

Keywords Mine water treatment · Electrochemistry · Optimization of electrocoagulation parameters

Introduction

The Tunisian phosphate mining industry consumes 400 m^3/day of process water. Reusing more of this water could significantly reduce water consumption, but requires efficient hardness removal. The water used by the Tunisian Chemical Group (TCG) has elevated hardness and contains 0.7 g/L of Ca and 0.2 g/L of Mg. While the Ca and Mg poses no health risk, their reaction with fatty acids and other ions can produce thick scum and scale deposits that interfere significantly with water treatment and industrial processes. To a lesser degree, Fe, Mn, and strontium (Sr) also contribute to water hardness (HDR Engineering 2001; Yildiz et al. 2003).

All of the conventional methods for hardness removal has advantages and disadvantages. The most widely used methods are reverse osmosis, ion exchange, co-precipitation, complexation, electrochemical treatment, and adsorption (Gasco and Mendez 2005; Park et al. 2007), but reverse osmosis and electrodialysis are inefficient and have high maintenance costs (Kamaraj et al. 2014). An alternative approach, electrocoagulation (EC) is more conventionally used for: (1) removal of arsenic from water (Kumar et al. 2004); (2) defluoridation (Emamjomeh and Sivakumar 2006); and (3) removing suspended solids, oil, and fat (Chen et al. 2000). Chen et al. (2002) also suggested that EC could be an attractive alternative to conventional hardness removal processes.

The EC process forms coagulants by electrochemical dissolution of an Al anode. This is followed by the: (a) destabilization of suspended particles (colloids) through compression of the electrostatic double layer by the generated ions; (b) charge neutralization of Al species; and (c) formation of Al compounds that act as flocculants (Nouri et al. 2010). The two initial steps are followed by flocculation because of the hydrogen (H$^+$) released from the cathode and

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oxygen released from the anode (Mavrov et al. 2006). The Al^{3+} ions immediately undergo further spontaneous reactions to produce corresponding hydroxides and/or polyhydroxides over a wide pH range. The hydroxides/polyhydroxides/poly-hydroxy metallic compounds, such as $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$, and $Al_{13}(OH)_{34}^{5+}$, which ultimately transform into $Al(OH)_3$, have a strong affinity for dispersed and/or dissolved ions, resulting in coagulation/adsorption. The water we studied contains elevated hardness, nitrate (NO^{3-}), and fluoride (F^-).

This research optimized the electrochemical variables for EC treatment of wastewater to enhance Ca and Mg removal efficiency and thus reduce treatment costs. The effects of key parameters, such as initial pH, applied current density, state of the Al plates, conductivity, stirring speed, electrolyte doses, initial hardness, distance between electrodes, and energy consumption on Ca and Mg removal, were studied.

Materials and Methods

Reagents and Analytical Procedures

All chemicals used were of analytical grade. Conductivity was measured during the experiments using a Jenway 4510 conductivity meter (Ω Metrohm). A calibrated digital Cyber Scan 510 pH meter (WDW, Germany) was used to measure pH and the temperature of the solution. Hardness was determined using the titrimetric method (APHA/AWWA/WEF 1999).

Cell Construction

A schematic diagram of the electrochemical cell is shown in Fig. 1. The electrodes (anode and cathode) used in this work were two parallel rectangular Al plates (250 mm × 80 mm × 2 mm). Both sides of the electrode were active (85 mm × 80 mm), corresponding to 136 cm^2 of electrode surface area. The anode–cathode distance was varied experimentally from 1 to 4 cm.

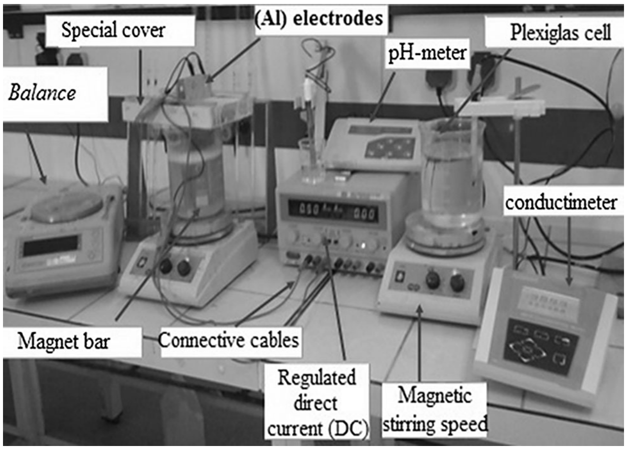

Fig. 1 Laboratory scale cell

Treatment Procedure

Prior to each treatment, and in order to avoid a passivation film, the Al anode and cathode were rubbed with sandpaper and then cleaned with NaOH (2 M) and HCl (2 M) aqueous solutions. If required, the electrolyte pH was adjusted with 0. 1 M HCl and NaOH solutions before each EC test. Water was agitated gently with a magnetic mixer during the coagulation process. Current intensity was maintained at 0–3 A, using a regulated direct current power supply (AFX 2930 SB DC), and the difference in electrostatic potential between the electrodes was continuously recorded. Wastewater was filtered and preserved immediately after onsite collection. Each EC test and measurement of hardness concentration was repeated three times to determine an average concentration and to assess reproducibility and repeatability. EC was carried out under the following initial conditions: Ca, Mg, and NaCl concentrations of 0.7 g/L, 0.2 g/L mol/L, and 3 g/L (respectively), 60 min duration, a pH of 7, a temperature of 18 °C, an electrode distance of 2 cm, a stirring speed of 200 revs/min, and a surface-to-volume ratio of 13.6 m^{-1}. Each parameter was then varied independently to determine its effects on removal efficiency. The parameters were optimized by studying Ca and Mg uptake, as follows: (1) initial pH values of 3, 5, 6, 7, 8, and 10; (2) an initial concentration ranging from: 0.5 g/L of Ca and 0.1 g/L of Mg to 1 g/L of Ca and 0.35 g/L of Mg); (3) a current density of 7.4–22.2 mA/cm^2 (corresponding to a current intensity of 1–3 A); (4) an NaCl dose of 0.5–4 g/L (corresponding to conductivities of 0.87–7.6 mS/cm); (5) an inter-electrode distance of 1–4 cm; and (6) stirring speeds of 0, 300, 450, 600, and 750 revs/min. The effect of pH, temperature, electrode consumption, initial and final hardness, and electrodes potential difference were studied using actual mining-influenced groundwater that was being used in a TCG industrial process. Prepared solutions with a fixed pH were injected into the reactor and samples were collected at select time steps throughout the 60 min of total electrolysis. After filtration (0.2 µm), the pH, total hardness, and Ca hardness of each sample were measured. Ca and Mg removal efficiency was calculated by Eq. (1).

$$\text{Ca and Mg removal efficiency}\ (\%) = \frac{C_i - C}{C_i} \times 100 \qquad (1)$$

where C_i and C were the initial and residual concentration (g/L), respectively, of the dissolved Ca and Mg.

Results and Discussion

Influence of Initial Solution pH

Determination of the Optimum pH

The effect of pH on Ca and Mg removal by EC is shown in Figs. 2, 3, and 4. Hardness removal (45.3 %) was best at a pH of 7 after 60 min of electrolysis. Based on the work of Bazrafshan et al. (2007) and Kumar et al. (2004), we infer that the amount of oxidized Al increased, supporting the formation of $Al(OH)_3$ flocs with high adsorption capacity, and increased efficiency. The effect of pH on coagulants depends on the Al speciation and its control on surface area under different conditions, as described in the following reactions and illustrated in Supplemental Fig. 1. At neutral pH (pH 7):

$$3Al^{3+}_{(aq)} + 14H_2O_{(aq)} \leftrightarrow 2\left(Al(OH)_2\right)^{+}_{(aq)} + Al(OH)_{3(s)} + 7H_3O^{+}_{(aq)} \tag{2}$$

Under acidic conditions (pH 2):

$$2Al^{3+}_{(aq)} + 8H_2O_{(aq)} \leftrightarrow 2\left(Al(OH)_2\right)^{+}_{(aq)} + 4H_3O^{+}_{(aq)} \tag{3}$$

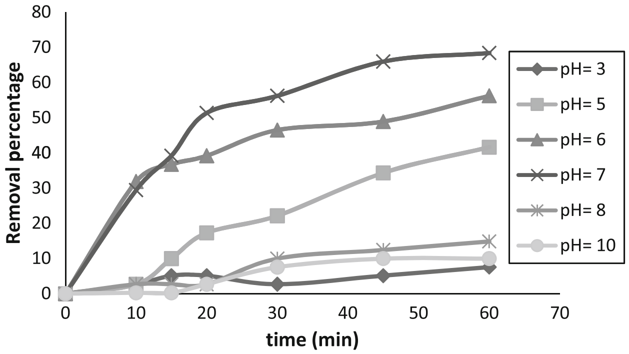

Fig. 2 Effect of initial pH on the removal of Ca and Mg as a function of EC time

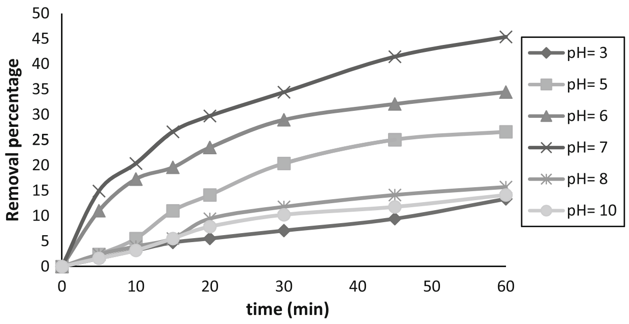

Fig. 3 Effect of initial pH on the removal of Ca as a function of EC time

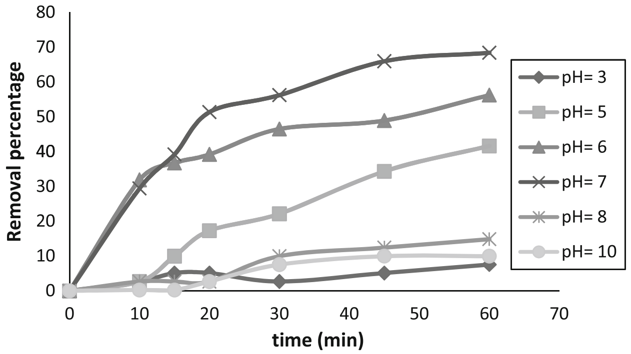

Fig. 4 Effect of initial pH on the removal of Mg as a function of EC time

Under alkaline conditions (pH 10):

$$2Al^{3+}_{(aq)} + 14H_2O_{(aq)} \leftrightarrow 2Al(OH)_{3(s)} + 2H_2O_{(aq)} + 6H_3O^{+}_{(aq)} \tag{4}$$

The $Al(OH)_3$ and $Al(OH)_2$ precipitated and settled, while the H_2 gas caused flotation. The activity-pH diagram of dissolved Al(III) species in equilibrium with amorphous $Al(OH)_3$ (Jiang et al. 2002), (Supplemental Fig. 1) illustrates the changing forms of $Al(OH)_3$ relative to pH and Al^{3+} concentration (Parsa et al. 2011). At high and low pH, $Al(OH)_3$ occurs in a charged form and is insoluble. Hence, $Al(OH)_3$ is not an efficient coagulant for EC at extremely high or low pH values. Under more neutral conditions, the hardness removal rate increases due to the formation of Ca, $MgCO_2$, and ($Mg(OH)_2$).

$$(HCO_3)^{-}_{(s)} + OH^{-}_{(aq)} \leftrightarrow CO^{2-}_{3(aq)} + H_2O \tag{5}$$

$$2CO^{2-}_{3(aq)} + Mg^{2+}_{(aq)} + Ca^{2+}_{(aq)} \leftrightarrow MgCO_{3(s)} + CaCO_{3(s)} \tag{6}$$

$$Mg^{2+}_{(aq)} + 2OH^{-}_{(aq)} \leftrightarrow Mg(OH)_{2(s)} \tag{7}$$

At alkaline pH (>8), the formation of $MgCO_{3(s)}$ and $CaCO_{3(s)}$ films on the active surface of the electrode is shown in Supplemental Fig. 2. This film reduced the active surface of the anode, which prevented the anodic dissolution of the Al plate. The optimal initial pH for the removal of hardness by EC was thus found to be ≈ 7.

pH Change During EC

As has been previously pointed out (Bayramoglu et al. 2007; Daneshvar et al. 2006), the use of soluble anodes changes a solution's pH during EC. Escobar et al. (2006) showed that the final pH depended not only on the concentration of metal ions but also the initial pH of the treated water. The pH increases when the initial pH is acidic and decreases when the initial pH is alkaline, meaning that the EC stabilizes the pH:

$$Al(OH)_3 + OH^{-} \leftrightarrow Al(OH)^{-}_{4} \tag{8}$$

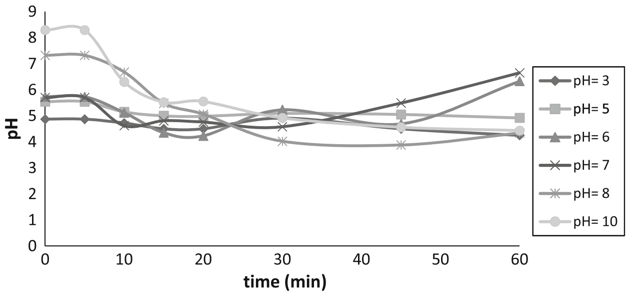

Fig. 5 Effect of EC time on the pH of the solution

following OH^- ion production at the cathode:

$$H_2O + 1e^- \leftrightarrow 1/2H_{2(g)} + OH^- \tag{9}$$

The final pH, although affected by initial pH and buffering ($Al(OH)_3/Al(OH)_4^-$) capacity (Eq. 8), is due to OH^- ion production and consumption during EC (Eq. 9) (Chen 2004). The initial and final pH of the solutions were measured for each test. The final pH value was usually acidic, except for the initial pH values of 6 and 7 (Fig. 5). For initial pHs of 3, 5, 8, and 10, the pH of the solution decreased in the first 20 min of electrolysis and stabilized below 5. At high and low pHs, $Al(OH)_3$ occurred in its charged form and was insoluble in water, rendering EC less effective in hardness removal. At initial pH values of 6 and 7, however, the pH decreased during the first 20 min of electrolysis to <5, but then increased to 6 after 60 min of electrolysis. It was found that the pH of the treated solution deceased during hardness removal, which contrasts with results reported in several studies that have tracked pH changes during EC and found that pH increases as electrolysis time progresses due to OH^- ion production (Brahmi et al. 2014, 2015; Hu et al. 2005; Kobya et al. 2006). The observed pH decrease could be due to OH^- ion consumption due to the formation of $CaCO_3$, $CaOH_2$, $MgOH_2$, and $MgCO_3$ (Pathak et al. 2012).

Effect of Initial Ca and Mg Concentration

Several experiments were performed using mixtures of Ca and Mg to study the adsorption capacity of EC flocculants; Ca and Mg removal efficiency was low at high concentrations (Fig. 6). The removal efficiency was 37 % after 60 min for the mixture of 1 g/L of Ca and 0.35 g/L of Mg. But at lower concentrations (0.5 g/L of Ca and 0.1 g/L of Mg), the removal efficiency reached 69 % after 60 min. Thus, hardness removal efficiency decreased with increased initial hardness. This can be explained by an increased adsorption capacity of the flocs due to an increased probability of contact between Ca and Mg ions and flocculants. Additionally, intermediate products that formed would have competed with hardness for active sites on the electrode, resulting in diminished solubility of $Al(OH)_3$, as well as decreased hardness removal (Ghosh et al. 2008; Mollah et al. 2001).

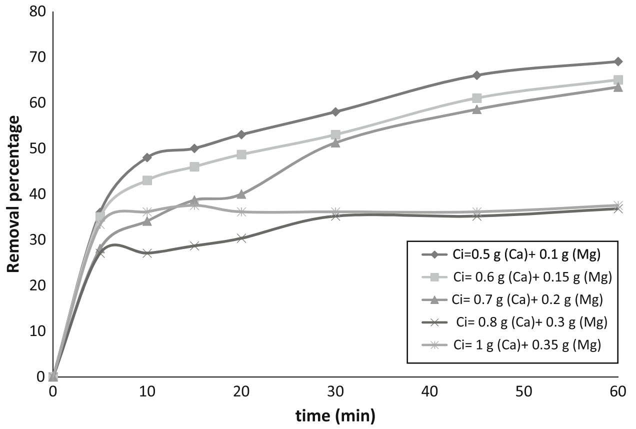

Fig. 6 Effect of initial concentrations on the removal of Ca and Mg as a function of EC time

Effect of Retention Time

Increased EC retention time at constant current density and a fixed pH increased hardness removal due to floc precipitation. The mixing rate also affected efficiency, since mixing promotes floc growth and decreases retention time (Kim et al. 2002). To investigate the effect of electrolysis time on hardness removal, a series of EC experiments were conducted (Supplemental Fig. 3). Most of the hardness was removed in the first 30 min, as found by Kumar et al. (2004) in their study of arsenic removal efficiency and Bazrafshan et al. (2008) in their study on chromium $(Cr)^{+6}$ removal by EC. These results suggest that 30 min of electrolysis is sufficient to obtain efficient removal.

Effect of Current Density

Current density is one of the most powerful parameters influencing hardness removal efficiency by EC, as the process requires optimization of the electrical current to reduce energy loss. The electrical current determines the coagulant dosage rate, the bubble production rate and size, and floc growth (Xiong et al. 2001). In order to further enhance this effect, a high salt concentration of 3 g/L, corresponding to an initial conductivity $\sigma_i = 5.86$ mS/cm, was used. Figure 7 displays the effect of current density on Ca and Mg removal.

Ca and Mg removal increased during the first stage of the process (Fig. 7), yet the EC time required for better Ca and Mg removal decreased as current density was increased. The Ca and Mg removal exceeded 15 % after 60 min at all of the applied current densities. At an applied current density of

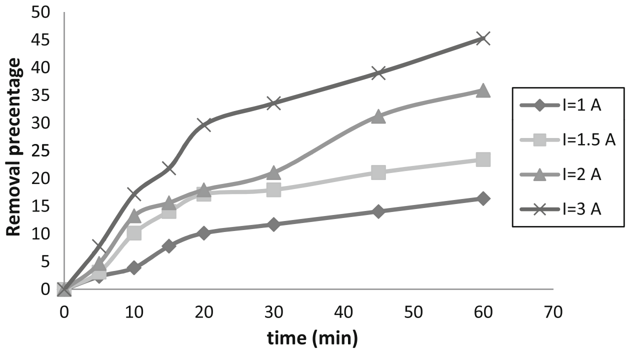

Fig. 7 Effect of current intensity (A) on the removal of Ca and Mg as a function of EC time

7.4 mA/cm^2, Ca and Mg removal exceeded 16.4 % after the first 60 min. A higher current density of 22.2 mA/cm^2 resulted in 45.3 % after 60 min. Thus, as the current density increased, processing time decreased, due to strong dissolution of the electrodes. This resulted in further removal of Ca^{2+} and Mg^{2+} as well as an increase in the hydrogen bubble production rate, whose size decreased as the current density increased (Mollah et al. 2004).

The higher current density of 22.2 mA/cm^2 yielded better hardness removal, but a darkening that could be removed only by mechanical polishing appeared at the cathode due to its chemical corrosion. A lower current density of 7.4 mA/cm^2 did not achieve the desired hardness removal due to a white gelatinous film that formed on the anode, which reduced the active surface of the anode and prevented its dissolution. A current density between these two avoided these problems and achieved a high hardness removal percentage. In order to determine the effect of the current density on energy consumption, the difference in potential between the electrodes was recorded for all EC tests as a function of time (Table 1).

Increased current density reduced cathode passivation and increased the potential between the two electrodes, which increased energy consumption. Higher energy consumption was also caused by the Joule effect. Thus, it would be most efficient to work at low current densities (Holt et al. 2002). The electric energy consumption W (kWh/m^3) is a very important EC parameter and can be calculated using Faraday's law:

$$W = \frac{U \cdot I \cdot t}{V} \tag{10}$$

Energy consumption is proportional to the voltage applied between the electrodes. These results were confirmed by tracking the potential difference between the two electrodes at a constant NaCl dose of 3 g/L (Table 1), and agree well with those reported in previous studies (Garcia-Soto and Camacho 2005; Lin and Chang 2000).

Supplemental Figure 4 shows that energy consumption (W) varied linearly with EC time and that the increase in the current density resulted in a fairly rapid increase in W. Thus, to choose the current density and the EC duration, it was necessary to compromise between economically suitable energy input and removal efficiency. A current density of 14.8 mA/cm^2 was sufficiently effective to remove over 35.9 % of the hardness in 60 min.

Effect of Conductivity

A conductive electrolyte is required for the proper function of the EC process using Al electrodes (Huang et al. 2007; Mameri et al. 1998). Comparison between salts such as Na_2SO_4 and NaCl has shown that NaCl is the most efficient supporting electrolyte for EC (Huang et al. 2007). Chloride ions significantly reduce the adverse effects of other ions such as HCO^{3-} and $SO_4{}^{2-}$, which can form an insulating layer at the electrode surface and increase the resistance of the electrochemical cell (Lin and Chang 2000).

Figure 8 shows that increasing the NaCl dose and the conductivity of the solution improved hardness removal efficiency by virtue of what we infer to be better chemical dissolution. Increasing the dose of NaCl from 0.5 to 4 g/L improved the removal efficiency from 32.8 to 39.8 % after 30 min. Table 2 shows the effect of NaCl concentration on electrolysis voltage, as a measure of energy consumption.

NaCl was used to increase effluent conductivity in the EC process, which reduced the voltage between the electrodes at a constant current density. The chloride ions avoided passivation via deposition on the surface of the electrodes. Supplemental Figure 5 shows that the energy consumption (W) varied linearly as EC time progressed and that a higher NaCl dose resulted in a fairly rapid decrease in W. There was an associated overconsumption

Table 1 Record of the potential difference between the electrodes over the electrolysis time for different applied current intensities (A)

Current intensity (A)	Time (min)							
	0	5	10	15	20	30	45	60
I = 1.0	5.8	5.4	5.2	5.1	5.1	5.0	5.0	4.9
I = 1.5	7.5	7.1	7.0	7.0	7.0	7.0	6.9	6.9
I = 2.0	7.6	7.3	7.1	6.9	6.8	6.9	6.8	6.8
I = 3.0	11.9	11.6	11.3	11.0	10.6	10.4	10.2	10.2

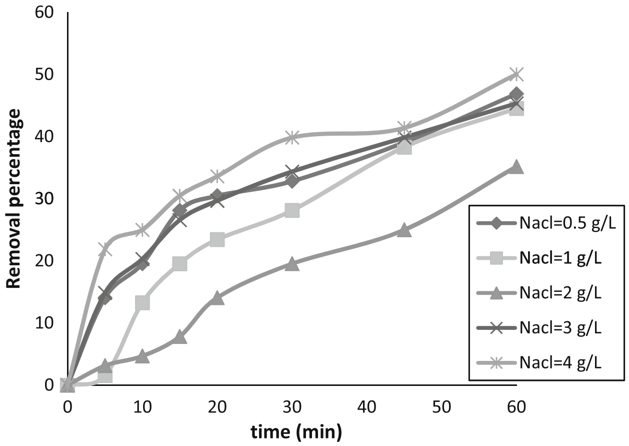

Fig. 8 Effect of initial NaCl concentration on the removal of Ca and Mg as a function of EC time

of Al electrodes due to corrosion attack at low NaCl concentration (Un et al. 2013). For this reason, a dose of NaCl of 4 g/L appeared to be optimal in terms of energy consumption as well as removal efficiency to prevent rapid electrode dissolution. The corresponding elimination of hardness reached 50 % in 60 min of electrolysis.

Effect of Stirring Speed

As shown in Fig. 9, hardness removal was much faster at higher agitation speeds. Without agitation, the amount of removal did not exceed 29.7 % after 60 min. At an agitation speed of 450 revs/min, the elimination percentage reached 51.5 %. However, there was a decrease in removal efficiency at 750 revs/min, and the elimination percentage declined to 37.5 % after 60 min. This could be explained by the breaking of coagulant EC under the effect of strong agitation. It is important to note that the amount of sludge decanted increased with the stirring speed. With a higher agitation speed, a greater amount of flocculants was formed in the EC cell reactor and the treated solution grew turbid. At a stirring speed of zero, the solution appeared homogeneous and not clear. The flocs were very stable at the top of the reactor and the hardness residual concentration decreased gradually as EC time progressed.

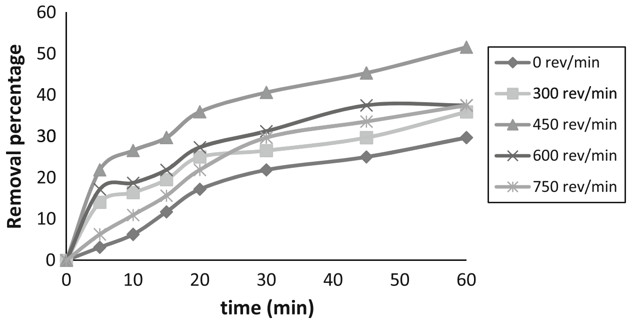

Fig. 9 Effect of agitation speed on the removal of Ca and Mg as a function of EC time

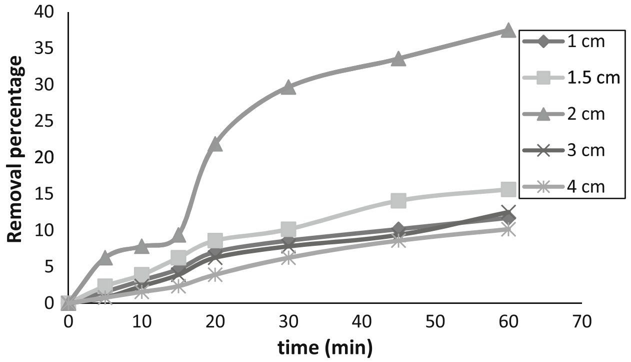

Fig. 10 Effect of inter-electrode distance on the removal of Ca and Mg as a function of electrocoagulation time

Effect of Inter-electrode Distance

Hardness removal is shown as a function of time for different inter-electrode (cathode–anode) distances (Fig. 10). The percentage of hardness removal decreased at smaller inter-electrode distances. Greater hardness removal was obtained for an intermediate inter-electrode distance of 2 cm, exceeding 37.5 % after 60 min. Anodic oxidation starts with the application of the potential to electrodes (Ghosh et al. 2008; Ramesh et al. 2007). As electrolysis progresses, a fine gelatinous film, which increases electrode resistance, forms on the anode's active surface, and increases with inter-electrode distance. As the resistance to mass transfer increases, the kinetics of charge transfer and

Table 2 Effect of the NaCl concentration on the difference in potential between the electrodes U (V)

Initial [NaCl] (g/L)	Time (min)							
	0	5	10	15	20	30	45	60
0.5	15.8	15.7	15.1	14.7	14.4	13.9	13.5	13.1
1.0	14.5	14.1	13.1	12.8	12.4	12.1	11.9	11.7
2.0	10.5	10.3	10.3	10.1	10.1	9.9	9.8	9.8
3.0	10.2	10.2	10.0	9.9	9.7	9.5	9.4	9.5
4.0	8.5	8.4	8.4	8.4	8.4	8.3	8.2	8.2

Table 3 Characteristics of the industrial wastewater before and after the treatment by EC

	pH	Conductivity (mS/cm)	T (°C)	MS %	[Ca^{2+}] (mol/L)	[Mg^{2+}] (mol/L)	[K^+] %	[Na^+] %
Before treatment	8.12	3.20	14.50	0.015	0.018	0.008	0.024	0.570
After treatment	6.65	17.16	37.10	0.004	0.002	0.000	0.000	0.130

Table 4 Record of the temperature, energy consumption, and difference in potential between the two electrodes as a function of time for the treatment of the wastewater at an initial pH of 7

Time (min)	U (V)	pH	T (C°)	[Ca + Mg] (mol/L)	W (KWh/m^3)
0	11.9	7.00	14.5	0.0256	0.00
5	11.6	5.73	1789	0.0203	2.90
10	11.3	5.12	19.2	0.0142	5.65
15	11.0	4.81	21.5	0.0099	8.25
20	10.6	4.76	23.4	0.0076	10.60
30	10.4	4.58	27.6	0.0043	15.60
45	10.2	5.49	32.7	0.0021	22.95
60	10.2	6.65	37.1	0.0017	30.60

the rate of Al oxidation slows; consequently, removal efficiency is less at greater inter-electrode distances. Hence, this experiment showed the benefit of an intermediate inter-electrode distance of ≈ 2 cm, which minimizes energy consumption while enhancing hardness removal efficiency.

Investigating the Effect of Optimized Parameters on Hardness Removal

In order to examine the performance of the optimized EC technique on removal of hardness from the water being treated by TCG, tests were conducted after adjusting the pH of the water from 8.1 to 7. The mining-influenced groundwater sample contained initial Ca and Mg concentrations of 0.7 and 0.2 g/L, respectively, and had a conductivity of 3.2 mS/cm. The physico-chemical characteristics of the industrial wastewater before and after treatment are shown in Table 3. The pH, temperature, energy consumption, and the difference in potential between the two electrodes were measured for each sample (Table 4). The Al electrodes were extremely effective, removing with up to 83.8 % of the hardness at a retention time of 30 min. Based on Eq. 10, the energy consumption was 10.4 kWh m^{-3}, which led to a significant increase in temperature (27.6 °C). Table 4 shows that the conductivity increased (due to the amount of dissolved Al and OH^- ions) as electrolysis progressed. In addition to removing Ca and Mg, the EC simultaneously efficiently removed other contaminants in this water (Table 3). This affirms that the EC process is highly efficient in removing various pollutants simultaneously.

Conclusion

The main objective of this study was to identify optimal conditions for hardness removal using the EC process with Al electrodes. Based on an examination of the individual EC parameters for initial Ca and Mg concentrations of 0.7 and 0.2 g/L, respectively, the operating conditions resulting in the highest hardness removal efficiency were: (1) a current density of 22.2 mA/cm^2, (2) an initial pH adjusted to 7, (3) a NaCl concentration of 4 g/L, (4) a distance between electrodes of 2 cm, (5) a stirring speed of 450 revs/min, and (6) an electrolysis duration of 30 min. These operating conditions achieved efficient removal in a relatively short operating time, while minimizing energy consumption. The pH generally decreased as electrolysis time progressed. The treatment of TCG process water using the optimized EC process showed a hardness removal efficiency of 83.8 %, after 30 min of electrolysis. The EC method concurrently removed Ca and Mg as well as other pollutants. This study proved that EC is a highly efficient method for hardness removal to support water reuse and the treatment of mining-affected water.

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