Clarification of Industrial Mining Wastewater Using Electrocoagulation

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The treatment of industrial mining wastewater (IMWW) by electrocoagulation (EC) using aluminum electrodes has been conducted with real wastewater taken from a mining industry. For reuse this water, several experiments were carried out in order to optimize the conditions of technique’s applicability. The results showed that turbidity (560 NTU) was removed reaches 99% at current density 10 mA/cm², free pH 7.2 and temperature of wastewater ~ 20 °C. The clarification of IMWW is very quick (EC time < 10 min) and adequately described by pseudo-second-order kinetics model. Moreover under optimal conditions, all parameters of pollution measured after EC are below the standard norms of industrial discharges. The EC process can be applied 10 times without loss of efficiency, it led to a minimal volume of sludge (65-75 cm³/L), and a low cost treated effluent ~ 6 $/m³.

Keywords: Electrocoagulation, mining, operating cost, turbidity, Wastewater treatment.

1. INTRODUCTION

Water scarcity caused by climate change and population growth creates an unbalance between supply and demand. The reuse of wastewater has become an absolute necessity. Thus, management and treatment wastewater has become a major concern for agriculture and industry who consume a lot of water. For example, water is the first and indispensable resource in all mining projects [1]. It can be used in all production levels; in the cooling of certain equipment, waste separation of valuable minerals, reduce dust etc. However, large volumes of water produced present a variety of environmental risks; because of leachate and sludge produced [2]. The quality of the mine water varies largely from mine to mine, depending upon the local conditions. However, from the available data [3], the following general characteristics can be identified: high suspended solids (turbidity), hardness as
CaCO\textsubscript{3} and conductivity, low BOD and COD. Moderate concentrations of minerals (K, Ca, P\textsubscript{2}O\textsubscript{5} etc.) and heavy metals can be recovered in the leachate. This wastewater has to be properly treated and managed, in order to prevent any water or soil pollution. Various techniques of treatment can be applied for mining effluents, such as: coagulation-flocculation, sedimentation, exchange of ions and the membrane treatment, which produces a better quality of treated water [4]. However, the choice of a technique relates to several criteria: economic, facility and rapidity [5]. The EC proposed in this study, is another alternative treatment that has not been used for the type of selected effluent. At this point, the process has attracted a great deal of attention in treating various wastewaters, because of its versatility and environmental compatibility. Researchers have achieved successful results in treatment of these wastewaters such as: landfill leachate [6], humic acid [7], food and protein [8], textile [9], oil [10] and domestic wastewater [11]. Advantages of EC are simple low cost equipments, ease of operation, a shorter retention time, high sedimentation velocities and reduced amount of sludge [12]. This study is focused on the evaluation of the efficiency clarification of the EC process, using aluminum electrodes, applied to the treatment of IMWW. Turbidity removal was monitored during the experiments, because it is a good indicator parameter of clarification wastewater. Effect of operating parameters, as: the density of current, initial pH and EC time on turbidity removal efficiency, were investigated. Also, operating cost (energy and electrode consumption) of the EC process was calculated. The efficiency of the treatment with regular samples was followed by the measurement of turbidity. The abatement of other parameters, such as: BOD\textsubscript{5}, COD, phosphorus etc. was controlled punctually, before and after EC treatment.

2. MATERIALS AND METHODS

2.1. Wastewater source

The IMWW used in this study has been provided from the complex of Djebel-Onk, which is located, at the eastern end of the country to the north Algerian-Tunisian border. The mine is one of the most important iron and phosphate production units throughout the Algerian territory. The water supply to the site is about 4459 m\textsuperscript{3}/day. This volume of water is consumed completely; it is still insufficient for the growing needs of production and development, cleaning and dusting apparatus etc. The majority of wastewater is collected in a 6500 m\textsuperscript{3} capacity sedimentation tank. The muddy part (decanted water), is released into the environment near the production unit.

2.2. Sampling, characterization of wastewater and analytical procedures

A volume (50L) of wastewater is collected from the sedimentation tank in full and low activity of production, every month during August-December 2014 and January-March 2015. In order to confirm the repeatability of measurements before and after EC treatment, other point samples from 50L, were taken during this sampling campaign. Sampling techniques, conservation and measurement, were respected [13,14]. The measurements of the different parameters such as: COD, BOD\textsubscript{5}, pH,
suspended solids matters (SSM), turbidity, sulphate, phosphorus and all heavy metals, were led according to protocols "AFNOR T90" [13].

**Table 1.** General characteristics of IMWW.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Average value</th>
<th>*Standard norms in Algeria</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (at 21°C)</td>
<td>7.7</td>
<td>5.5 at 8.5</td>
</tr>
<tr>
<td>Conductivity at 21°C (mS.cm⁻¹)</td>
<td>1.5</td>
<td>-</td>
</tr>
<tr>
<td>BOD₅ (mg/L)</td>
<td>85</td>
<td>40</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>4.6</td>
<td>120</td>
</tr>
<tr>
<td>SSM (mg/L)</td>
<td>250</td>
<td>30</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>560</td>
<td>-</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>1300</td>
<td>1000</td>
</tr>
<tr>
<td>PO₄³⁻ (mg/L)</td>
<td>5.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Al (mg/L)</td>
<td>0.001</td>
<td>-</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>3.5</td>
<td>-</td>
</tr>
<tr>
<td>As (mg/L)</td>
<td>0.55</td>
<td>-</td>
</tr>
<tr>
<td>Cu (mg/L)</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>Zn (mg/L)</td>
<td>1.30</td>
<td>-</td>
</tr>
<tr>
<td>Pb (mg/L)</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>Cd (mg/L)</td>
<td>0.07</td>
<td>-</td>
</tr>
</tbody>
</table>


The characteristics of the wastewater used in this study, are given in Table 1. In order to evaluate the efficiency of clarification wastewater treatment of IMWW by EC, the turbidity was monitored continuously, while other parameters; BOD₅, COD, phosphorus, etc., were checked punctually before and after the EC to satisfactory operating conditions. The relative error of measurement of turbidity is weak and around 5%. The rate of abatement of the pollution of a parameter given X (COD, turbidity…), is expressed according to Eq.(1):

\[
TX (%) = \left[ \left( C_i X - C_f X \right) / C_i X \right] \times 100 \quad (1)
\]

Where, \(C_i X\) and \(C_f X\) are, respectively, the concentrations of a given parameter before and after EC treatment. The operating parameters of the treatment are: current density (from 5 to 25 mA/cm²), the initial pH (from 2 to 11), the temperature (from 5 to 40°C) and the initial turbidity (from 100 to 560 NTU). All the chemicals compounds are of recognized purity (Sigma®-Aldrich, the U.K), and the water of preparation of the solutions with a resistivity of 18 cm MQ. In order to avoid any salt deposit,
the aluminum electrodes, are cleaned with the hydrochloric acid (0.01 M), then, frequently rinsed with the distilled water after each test of EC. The adjustment of the initial pH was made with 1 M solution of HNO₃ or NaOH respectively.

2.3. Principles of EC and experimental setup

EC rests on three principal processes: electrolytic reaction at electrode surfaces, production of coagulants in the aqueous phase, adsorption of soluble or colloidal pollutants on coagulants and removal by sedimentation or floatation [15]. Generally, electrode materials for EC are aluminum and iron. In this study, both electrodes are of aluminum.

The mechanism of EC gathers these various components of coagulation, adsorption, precipitation and the floatation, which have for the origin of the formation of insoluble aluminum hydroxides [16].

The tests were carried out in a cylindrical reactor of 1L. The temperature was controlled using a water bath (Julabo). Two parallel plate electrodes of aluminum (99.3% purity) which were identical with 15cm length and 2cm width, both electrodes, were placed vertically inside the vessel, the depth of their immersion was 13cm in the IMWW solution, constituting a surface of 26 cm². The electrodes gap was fixed to 1cm, in order to limit the ohmic voltage drop. The current density applied to the electrodes was fixed using a potentiostat (Metrix – AX – 502). The current was fixed through the potentiostat and controlled with an Ampere-meter (SKY-Sronic-600-527) connected in series. The solution was stirred at 100 rpm (Selecta) to reduce the mass transport over potential of the EC reactor. pH and conductivity were continuously measured in the reactor. At the end of each test of EC, the treated water sample is sedimented for 30 min to allow the optimal decantation of flocs formed. The centrifuging and the filtration had not been realized. All experiments were repeated three times, and the experimental error was around 2%. Fig. 1 illustrates the experimental set-up.

Figure 1. Device of electrocoagulation cell.
3. RESULTS AND DISCUSSION

3.1. Effect of current density and EC time reaction on the turbidity removal

The current density is an important parameter in removal efficiencies. At higher current density, the quantity of metal oxidized augmented, resulting in a higher amount of hydroxide flocs for the elimination of essentially colloidal materials. Furthermore, the bubbles density increased and their size reduced with the increasing of cell current, resulting in a faster removal of materials [17]. The influence of current density was investigated using 5, 10, 15, 20 and 25 mA/cm² at free pH 7.2, initial turbidity 560 NTU, conductivity 1.5 mS.cm⁻¹ and temperature of wastewater ~ 20°C. The removal efficiency of turbidity increased rapidly with increase of current density, as seen in Fig. 2. The turbidity removal efficiencies of 95 to 99 % were obtained between 5 and 25 mA/cm² respectively. Maximum turbidity was reduced for all current density unless 10 min of retention time as we can be seen in Fig. 2. The EC reaction time is another important parameter affecting the EC process. The weak reaction time as that obtained generally would reduce the formation of sludge, the aluminum and energy consumption hence the operational cost. This reaction time is closely linked to the evolution of the current density. These findings are often reported by authors [18,19]. From these results, the optimal current density and reaction time for treatment of the IMWW are considered to be 10 mA/cm² and 10 min, respectively. Of these optimal values will be set for subsequent experiments.

![Figure 2. Effect of current density on the turbidity removal.](image)

3.2. Effect of initial pH on the turbidity removal

pH is an important operating factor that influence the performance of the EC process. It is well known that pH of wastewater can either have a positive or negative influence on the treatment quality, as it would affect the stability of various hydroxide species formed [20]. Moreover, the change of pH can modify the surface charge of particles and greatly influence the removal of colloidal dispersed organics from solution [21]. In this fact, the effect of pH was studied by varying the pH from 2 to 11 keeping the other variable constant (current density 10 mA/cm², reaction time 10 min, initial turbidity
560 NTU, conductivity 1.5 mS.cm\(^{-1}\) and temperature of wastewater \(\sim\) 20°C). Fig. 3 shows the removal efficiencies of turbidity, as a function of initial pH and pH evolution in the reactor during the treatment of EC. For the reduction of turbidity, two branches of curves were obtained. The first portion corresponds to formation hydroxides of aluminum, while the second one, the destabilization of flocs formed with an increasing turbidity. In optimum, it can be noticed that the turbidity removal is most effective (\(\sim\) 99%) at initial pH 8. According to the solubility diagram of aluminum, this corresponds to the maximum formation of insoluble aluminum hydroxide flocs (clarification). After the optimum, the final pH is constantly increasing independently of the initial value of pH. The basic pH observed is attributed to the hydrogen generated at the cathode during EC [15]. This pH, facilitates the formation of monomeric species soluble such as anion Al(OH)\(_4^-\) Eq. (2), thereby reducing the form of aluminum hydroxide. Therefore, the rate of reduction of turbidity is affected (descending part of curves Fig. 3). In the end, the initial pH of IMWW does not require pH adjustment for treatment.

\[
2Al + 6H_2O + 2OH^- \rightarrow 2Al(OH)_4^- + 3H_2 
\] (2)

![Figure 3](image_url)

**Figure 3.** Effect of initial pH on the turbidity removal and pH values during EC.

3.3. Effect of initial turbidity on treatment efficiency and kinetic

Fig. 4 shows the efficiency of the treatment clarification in relation to various initial turbidity and EC time. For this, a series of experiments were carried out under the following conditions: current density of 10 mA/cm\(^2\), free pH 7.2, conductivity 1.5 mS.cm\(^{-1}\), temperature of wastewater \(\sim\) 20°C and initial turbidity of 100 to 560 NTU. We observe a rapid reduction of turbidity around 99% in the first 10 minutes of EC and then a gradual stabilization between 10 and 30 min. In this study, pseudo-second-order Eqs. (3,4) kinetic model was tested and compared with experimental data. The equations can be simplified by assuming the generation of aluminum/aluminum hydroxide constant for a given current density.
\[ \frac{dT}{dt} = -K_{ap}T^n \quad (3) \]

\[ \frac{1}{T} - \frac{1}{T_0} = K_{ap} t \quad (4) \]

Where, \( T_0 \), \( T \) are the influent and effluent Turbidity respectively (NTU), \( t \) is the reaction time EC (min), and \( K_{ap} \) is the pseudo-second-order reaction rate constant (min\(^{-1}\)), which can be estimated from the plot \( \frac{1}{T} \) versus reaction EC time.

**Figure 4.** Effect of initial turbidity on treatment efficiency.

**Figure 5.** The pseudo-second-order rate linear fitting constants.
The results exploited in the exponentials parts of curves Fig. 5 show, that the kinetics modeling fitted very well with all experiments (R² > 0.99), demonstrating that the EC clarification of IMWW is adequately described by pseudo-second-order kinetics model. Moreover, it can be observed that \( K_{ap} \) of turbidity removal decreased gradually with increase of \( T_0 \) from 100 NTU to 560 NTU.

### 3.4. Effect of temperature on the turbidity removal

The influence of the temperature on EC was infrequently investigated. In this study, EC has been used to remove turbidity of IMWW at temperatures between 5 and 40 °C, keeping the other variable constant (\( T_0 \) 560 NTU, current density 10mA/cm², reaction time 10 min and conductivity 1.5 mS.cm⁻¹). The temperature range chosen covers a wide field of application even under extreme conditions of temperature. The results Fig. 6 show that the reduction of water turbidity increases up to its optimum at 25 °C; above this temperature, the clarification rate decreases. The reasons are complex; they can be due to increase in mobility, opportunity to aggregate and produce metallic hydroxide flocs and variation of the solubility of precipitates. These phenomena were evoked by some authors differently [22,23].

![Figure 6](image)

**Figure 6.** Effect of temperature on the efficiency of turbidity removal.

### 3.5. Effect of different salts on conductivity and turbidity removal

The purpose of this section is to investigate the influence of the presence of different salts for example; \( \text{Na}_2\text{SO}_4 \), \( \text{CaCl}_2 \), \( \text{Na}_2\text{CO}_3 \), \( \text{KCl} \) and \( \text{NaCl} \) on the treatment of IMWW by EC. In this case, the key parameter is the conductivity of the solution that will play an important role in treatment efficiency. For each electrolyte, the experiments were carried out at \( T_0 \) 560 NTU, current density 10 mA/cm², reaction time 10 min and temperature of wastewater ~ 20 °C. The conductivity of the water was adjusted to ~ 3 mS.cm⁻¹ by adding an appropriate amount of electrolyte salt, as
recommended by various authors [23,24]. This conductivity is required in EC. It helps to maintain a sufficient ionic strength to the flow of current in the reactor. The increase of the conductivity by the addition of salts is known to reduce the cell voltage at constant current density, due to the decrease of the ohmic resistance of wastewater [25]. From Fig. 7, except NaCl, all electrolytes exhibit a good efficiency of the wastewater clarification. Their reduction rates of turbidity are not significantly different. The comparison of these results with those of the wastewater of initial conductivity 1.5 mS.cm\(^{-1}\) (without salt), implies that, water to be treated by EC does not need to increase its conductivity for good yields of treatment. This was reported by different authors [26,27]. The EC of IMWW without the addition of salt presents the advantage of forming fewer of sludge ~ 65 cm\(^3\)/L of treated effluent. On the other hand for NaCl, it is observed a decrease in the efficiency of the treatment, observed by some authors [28,29]. The presence of chlorine and chloride in solution may form organochloride. Chloride anions can also be oxidized and give active chlorine forms, such as: hypochlorite anions that can oxidize colloidal materials [30].

![Figure 7. Effect of the presence and absence of salt on turbidity removal.](image.png)

### 3.6. Efficiency of the treatment

The comparison of analytical results before and after EC treatment of IMWW Table. 2 shows that all parameters examined in the optimum on processing conditions; present at the end of treatment, a significant reduction. Whether for organic or mineral substances, the values obtained after treatment are inferior that the standards of industrial discharges. In addition, the aluminum concentration, even if it increases after clarification, it remains below the standards of industrial discharges. Reducing pollution of IMWW can be explained by conventional mechanisms widely studied, which are adsorption, neutralization/destabilization of charges and complexation/precipitation [31]. Aluminum positively charged species may under certain operating conditions, neutralizing the colloidal particles causing a destabilization of all the particles in solution. Thus, a close relationship is found between colloidal particles, dissolved aluminum and turbidity of the solution. The excess aluminum can adsorb or trap airborne particles in the flocs formed previously. Furthermore, the solution of aluminum
species can be complexed with the negatively charged functional groups forming a Me-MO precipitate, which may be removed by filtration.

The experiments of repeatability at the optimal conditions (current density, EC free time, pH etc.) kept constant, shows Fig. 8 than on 10 trials without change of electrodes, the treatment efficiency is maintained satisfactorily 98-99%. The sludge volumes formed, are substantially constant and weak (65-75 cm³/L) compared to some works on the wastewater, where greater volumes are obtained: 150-200 cm³/L of treated effluent [15,18]. The mass losses of aluminum in the sacrificial anode are negligible (maximum of 30 mg for each test). The electrodes might be used several times without being changed.

Table 2. Evaluation of EC in the optimal conditions of treatment

<table>
<thead>
<tr>
<th>Parameter</th>
<th>wastewater</th>
<th>Clarified water</th>
<th>Reduction rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (at 21°C)</td>
<td>7.7</td>
<td>7.8</td>
<td>-</td>
</tr>
<tr>
<td>Conductivity at 21°C (mS.cm⁻¹)</td>
<td>1.5</td>
<td>1.90</td>
<td>89.0</td>
</tr>
<tr>
<td>BOD₅ (mg/L)</td>
<td>85</td>
<td>9.3</td>
<td>99.3</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>4.6</td>
<td>1.1</td>
<td>76.0</td>
</tr>
<tr>
<td>SSM (mg/L)</td>
<td>250</td>
<td>1.75</td>
<td>99.3</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>560</td>
<td>5.0</td>
<td>99.1</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/L)</td>
<td>1300</td>
<td>253</td>
<td>80.5</td>
</tr>
<tr>
<td>PO₄³⁻ (mg/L)</td>
<td>5.1</td>
<td>0.9</td>
<td>82.3</td>
</tr>
<tr>
<td>Al (mg/L)</td>
<td>0.001</td>
<td>0.19</td>
<td>-</td>
</tr>
<tr>
<td>Fe (mg/L)</td>
<td>3.5</td>
<td>1.18</td>
<td>66.2</td>
</tr>
<tr>
<td>As (mg/L)</td>
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<td>Cu (mg/L)</td>
<td>0.01</td>
<td>1.9x10⁻³</td>
<td>81.0</td>
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<td>Zn (mg/L)</td>
<td>1.30</td>
<td>0.27</td>
<td>79.2</td>
</tr>
<tr>
<td>Pb (mg/L)</td>
<td>0.01</td>
<td>0.9 x 10⁻³</td>
<td>91.0</td>
</tr>
<tr>
<td>Cd (mg/L)</td>
<td>0.07</td>
<td>9.8 x 10⁻³</td>
<td>86.0</td>
</tr>
</tbody>
</table>

Figure 8. Repeatability tests and treatment efficacy.
3.7. Energy and aluminum consumption and cost

Operating cost is one of the most important parameters in the EC process, because it justifies the application of the method of wastewater treatment. The knowledge of energy and aluminum consumed in optimal working conditions, allows the calculation of this operational cost. It is formulated by Eq. 5 employed by different authors [17,32].

\[
\text{Operational cost} = a \ C_{\text{energy}} + b \ C_{Al^{3+}(\text{electrode})} \quad (5)
\]

Where, \((a)\) and \((b)\) are ratios for the price calculation of the international market on energy and chemicals for the year 2011, they are successively \(0.05\) US $/kWh, and \(3.08\) $/kg of aluminum.

![Figure 9. Effect of current density on the energy and electrode consumption.](image-url)

![Figure 10. Effect of EC time on the energy and electrode consumption.](image-url)

The theoretical concentration of dissolved aluminum by unit of treated wastewater volume (KgAl/m³) is given by Faraday law expressed by Eq. 6:

\[
C_{Al^{3+}(\text{electrode})} = \frac{I \cdot t \cdot M}{Z \cdot F \cdot V} \quad (6)
\]
Where, $M$ the aluminum molecular weight (27 g/mol), $I$ the current intensity applied (A), $t$ the mean residence time in the reactor, $Z$ the number of electrons involved in reaction of dissolution ($Z = 3$ for aluminum), $F$ the constant of Faraday (96500 C/mol) and $V$ the volume of the reactor (1L).

The consumed energy by unit of treated wastewater volume (KWh/m$^3$), is given by Eq. 7:

$$C_{\text{energy}} = U \cdot I \cdot t / V \quad (7)$$

Where, $U$ is the applied tension during the treatment (Volt).

Applied current density and EC time directly affect process performance and operating costs [18,19]. Therefore, they were studied separately.

![Figure 11. Effect of current density and EC time on the operating cost.](image)

The results Fig. (9,10) show that the energetic and aluminum consumption increases with increasing current density or EC time. This ascension affects negatively the results of the operational cost Fig. 11. In the optimum conditions of current density (10 mA/cm$^2$) and EC time (10 min), the cost is satisfactory around 6 $/m^3$ of treated effluent. Presently, calculations of cost realized on IMWW are nonexistent; nevertheless, much work [32,33] show that in wastewater, in general, costs are comparable to those found in this study.

4. CONCLUSION

Under optimal conditions of current density 10 mA/cm$^2$, free pH 7.2, initial turbidity 560 NTU, conductivity 1.5 mS.cm$^{-1}$and temperature of wastewater ~ 20°C, the EC was found to be an effective
method for the treatment of IMWW. The rate of clarification or reduction of turbidity is significant (~ 99%) and very quick (< 10 min). The EC clarification is adequately described by pseudo-second-order kinetics model. The others characterization parameters COD, BOD$_3$ and metals have also been reduced. According to the standard norms of Algerian industrial discharges, the clarified water obtained is of good industrial quality. The volume of sludge formed is low, 65 to75 cm$^3$/L. However, the sludge formed by this type of treatment, requires physico-chemical and bacteriological analysis, before its eventual utilization in agriculture, energy recovery or other.

Finally, the operational cost of 6 $/m^3$ of treated effluent and the possibility of using the electrodes more than 10 times, without loss of efficiency, encourage the use of the EC process for economically treat IMWW.

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References

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