Sulfate (SO$_4^{2-}$) removal by electrocoagulation process under combined electrical connection of electrodes

A A Al-Raad$^{1,2}$ and M M Hanafiah$^{1,3}$*

$^1$Department of Earth Sciences and Environment, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, Bangi 43600, Selangor, Malaysia
$^2$Ababil School, Al-Muthanna Education Directorate, Samawa 66001, Iraq
$^3$Centre for Tropical Climate Change System, Institute of Climate Change, Universiti Kebangsaan Malaysia, Bangi 43600, Selangor, Malaysia

*Corresponding E-mail: mhmarlia@ukm.edu.my

Abstract. Inorganic compounds in water can have detrimental effects on human health and the environment due to the high toxicity level of these ionic contaminants. This study assessed the efficiency of electrocoagulation process for removing sulfate (SO$_4^{2-}$). The technology of electrocoagulation depends mainly on electrical applied that produce coagulant species in a certain position via electro-dissolution of sacrificial anodes which are often made of iron or aluminum. EC process illustrated great potential as a vital method in eliminating numerous types of contaminants including inorganic contaminants at a lesser cost, and ecologically friendly technique. In the present study, aluminum materials were utilized in both cathode and anode electrodes. Water samples were obtained from Sawa Lake, Al-Muthanna Province located in Iraq. Electrocoagulation formations with static electrodes were used under mutual electrical connection. The effects of the different variables such as pH, current density, inter electrode distance, reaction time and stirring speed were scrutinized to obtain a higher removal of SO$_4^{2-}$. Preliminary outcomes exhibited the following optimal and functional conditions; pH = 8, current density = 0.8A, reaction time (RT) = 80 min, IED = 1 cm, temperature = 27 °C and agitation speed = 500 rpm. The maximum removal efficiency of SO$_4^{2-}$ is 88 %. The present statistical rates proved the effectiveness of EC method in terms of removing salts from lake water.

Keywords: Electrocoagulation, Cathode and anode electrodes, Desalination, Water purification, Salt water

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1. Introduction
Climate change and rapid population growth which led to water paucity have a disastrous effect on the ecosystem and human health [1]. It was proved in the literature that the desalination process had a fundamental effect to yield sufficient water that may sustain large population in dry areas. In fact, seawater desalination via reverse osmosis (RO) has been established to be an effective method in removing high concentrations of salts such as sulfate (SO$_4^{2-}$), and other salinities [2]. In the recent years,
the technology of RO was considered as the most prevalent system for desalination [2]. Nevertheless, numerous operations in the system of desalination influence the performance of reverse osmosis membranes in treatment plant by destroying the membrane system. The differential pressure in RO can be noticed through abrasion processes such as degeneracy due to time or cleanings, oxidation processes, fouling or backpressure. These impacts are associated with a reduction in the salt rejection and an upsurge in the flow rate which in turn cause to growing operation budgets [3, 4]. The electrocoagulation (EC) method is also considered as one of the utilized alternative methods to treat wastewater. This method was effectively utilized in the wastewater plants and yielded promising outcomes in terms of eliminating salts, pollutants and various types of contaminants [5].

Recently, the EC process has attracted the attention of many academics. In the real situation, they could apply this process to remove different kinds of salts from wastewater. The high capacity of this technology has paved the way for numerous authors to apply this process to remove various ions, such as, heavy metals [6], bromide (Br⁻) [7], chloride ion (Cl⁻) [8], fluoride [9], and some elements namely lead and copper [10]. The core-mechanism of EC process depends on generating the coagulants in situ via dissolution of the electrodes-substances. The application of various electric currents on the sacrificial (anodes and cathodes) metal electrodes involves immersing them in polluted water in an EC reactor to dissolve metallic substance and induce coagulants in situ. More accurately, EC technique is utilized in delivering metallic hydroxide to water via coagulants by electro-dissolution of applied substances [5]. During EC method, particularly when electrodes have been used, the Al electrode dissolved and acted as a coagulate aid which leads to induce hydrogen gas at the cathode (denoted in Equations (1 and 2)). Various aquatic aluminum species are produced, during the dissolution of Al at the anode. These kinds of Al serve as the coagulants by merging with pollutants to generate insoluble-hydroxides, which can be removed from the solution [6], as presented in Equations (1 and 2) below:

\[
\text{Al}_{(s)} \rightarrow \text{Al}^{3+}_{(aq)} + 3e^- \quad \text{anode} \tag{1}
\]

\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-_{(aq)} \quad \text{cathode} \tag{2}
\]

When Al ions produced at the anode are solvable and will thereafter react with the hydroxide ions (OH⁻) induced at the cathode, subsequently the Al hydroxides Al(OH)₃ are formed as presented in Equation (3) below:

\[
\text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3 \tag{3}
\]

The eco-friendly trend of the EC made it highly demanded technology since it generates a low level of waste which can simply being eradicated via purification with the aid of produced bubbles, no chemicals needed, low operating costs, as well as can be utilized with an amalgamation of renewable energies from wind or solar powers [6]. The main substances that were applied in this technique comprise iron and aluminum [11]. The purpose of the present study is to assess the effectiveness of EC technique in terms of removing the high concentration of SO₄²⁻ from saline water. The study also determines the optimal parameters for elimination of sulphate (SO₄²⁻) using EC configurations with static electrodes under combined electrical connections.

2. Materials and Method

2.1 Saline water samples

The samples of brackish water were collected from Sawa Lake, located in Al-Muthanna province in Southern Iraq between 31° 18’ N (latitude) and 45° 00’ E (longitude) [12]. The concentrations of SO₄²⁻ was measured using ion-chromatography (IC, ICS-2100, Dionex, Sunnyvale, CA, USA). The SO₄²⁻ concentrations was analysed using the procedures described in the standard-method [13].
2.2 Experimental design

Figure 1 illustrates the experimental setups of electrocoagulation procedure utilized in the present study. The experimental design comprises of a batch reactor made of glass. The volume of treatment water was 1 L for each run. Two aluminium plates were linked in the monopolar electrodes arrangement (MP-P) with the main power supply. Both of the electrodes were at plates configuration with equal dimensions 4x10 cm² (length and width) and 0.1cm thickness. The two cells of anode and cathode electrodes were connected to the positive and negative terminal with DC power supply. A magnetic field was applied to control the stirring speed. The voltage was adjusted to 6 V to each run.

Figure 1. Experimental setup of the EC method.

Six electrical densities (0.5, 1, 1.5, 2, 2.5 and 3 mA/cm²) were examined to gauge the effectiveness of each ratio on the coagulant method. The ammeter (Aswar DT830D, China) was employed to assess the applied current. The volt-meter was utilized to count the applied voltage by correlation of the voltmeter in parallel with the cell, and maintained at 6 V as a fixed rate for each run.

Numerous velocities (250, 350, 500, 650 and 750 rpm) were tested at baseline temperature (25-27 °C). The operating times (20, 40, 60, 80 and 100 minutes) were tested. Inter-space between cathode and the anode was fixed at three spaces 10, 15 and 20 millimeters. The experiments were also carried out at different pH values ranged from 5 to 11, with the initial pH value was 8.20. In fact, pH was steadily adjusted by adding sodium hydroxide (NaOH) and hydrochloric acid (HCl) during the experiment. Water circulation (WiseCircu ModelWCR-P6) was employed to fix the temperature between 25-45 °C during the electrocoagulation experiment. A 1-liter amount of brackish water was utilized in every process. Distilled water with a 5 % hydrochloric acid solution for a period of 10 minutes was added for internal cleaning of the reactor and electrodes. The concentrations of SO₄²⁻ was scrutinized for pre- and post-experiment. After the completion of the experiments, the best operation conditions were repeated three-times for validity and to ensure that the electrocoagulation method works competently for the treatment of brackish water. The following equation was used to compute removal efficiencies (RE %) for each of SO₄²⁻ :

\[
\text{RE} \, (\%) = \frac{C_0 - C}{C_0} \times 100
\]  

(4)
Where \( C_0 \) represents salts concentration in pre-treatment and \( C \) represents salts concentration in post-treatment.

3. Results and Discussion

3.1 Effect of current density and reaction time

The essential parameters that influence the performance of the EC and electrodes lifetime are current density and reaction time, thus the overall operating cost is influenced as well [5, 14]. It is worthy to mention here that the most vital parameters influencing the operating costs in the EC method are the electrode substances utilized and wasted electrical energy. The variation in removal efficiency of \( \text{SO}_4^{2-} \) was gauged over a fixed time (80 min) at numerous current densities (\( I = 0.5, 1.0, 1.5, 2.5, 2.5 \) and 3).

Figure 2 shows the outcomes of the tests of the applied current density (mA/cm\(^2\)). During the 80 min of reaction time, it was found that an upsurge in current density from 0.5 to 2.0 mA/cm\(^2\) caused to an increase in the elimination efficiency of \( \text{SO}_4^{2-} \) from 52 % to 83 %. On the other hand, the low efficiency elimination rate was gained via the upsurge in current density from 2.0 to 3.0 mA/cm\(^2\) during the same reaction time. It was noticeable that the increase of the current density to 2.5 and 3.0 mA/cm\(^2\) (above the optimum current value of 2.0 mA/cm\(^2\)) resulted in producing a high number of hydroxyl radicles, which led to an increase in the pH of the solution. It is called that the coagulant breaks down in high pH, which then results in a reduction in the performance of the EC method. In this study, experiments were carried out over different reaction times ranged from 20 to 100 minutes. The samples were taken at intervals every 20 minutes. The increases of time from 20 to 80 minutes resulted in the enhancement of the elimination percentage of \( \text{SO}_4^{2-} \) from 63 % to 83 %.

![Figure 2](image_url)

**Figure 2.** Effect of reaction time and current density on removal of \( \text{SO}_4^{2-} \).

Figure 2 shown, there is a minor increase in the removal process when the reaction time is increased from 80 min to 100 minutes. Further, that increase in reaction time led to an increase in costs of electrical consumption and electrode materials. Therefore, 80 min was selected to reduce power consumption and lower operational costs. Additionally, the elimination rate was noticeably decreased when the reaction time becomes more than 100 minutes. The main cause of this decline in the efficiency is the release increase of metal ions in the solution [15]. Thus, 2.0 mA/cm\(^2\) and 80 min were designated as the optimal
operational components to decrease power consumption and lower operational costs. These results are accordance with the outcomes of that obtained in previous literatures [13, 16].

3.2 Effect of pH

The chemistry of the aqueous medium and conductivity are considered as vein of the EC mechanism. On the other hand, the impact of pH solution on electrocoagulation process has been examined in previous studies [6, 9]. In the context of the present study, the pH solution impact on SO$_4^{2-}$ removal was examined by regulating the initial pH from 5 to 11 with the best conditions: current density = 2.0 mA/cm$^2$ and a RT of 80 minutes. The elimination outcomes exhibited the performance of EC method was improved as a consequence of raised pH from 6 to 8 as shown in Figure 3 with the removal efficiency of SO$_4^{2-}$ from 84 % to 86 %. The raises observed in the pH levels may lead to water electrolysis, which resulted in generating of hydrogen and (OH) ions.

It was noticeable also that the upsurge in the value of pH solution to more than 8.5 leads to decreasing the elimination efficiencies. The indices of higher efficiency of EC technique are influenced by the optimal pH range of 6.5 to 8.4, which is close to the optimal pH for Al(OH)$_3(s)$ formation. Flocs of Al(OH)$_3(s)$ can facilitate the absorption process of soluble organic molecules and trapping colloidal particles rapidly since they have large surface areas. It was proved that at low pH, ranging from 5 to 6, cationic soluble species Al$^{3+}$ and Al(OH)$_2^{+}$ are predominant [17]. When the pH is between 7 and 9, different aluminum-based polymeric and monomeric species are generated, which are finally transformed into unsolvable shapeless Al(OH)$_3(s)$ through complex polymerization/precipitation kinetics. When the pH is higher than 10, the soluble Al(OH)$_4^{-}$ anion concentration rises at the expense of Al(OH)$_3(s)$ [6].

![Figure 3](image-url)  
**Figure 3.** Impact of pH on SO$_4^{2-}$ removal at the best conditions (I = 2.0 mA/cm$^2$, reaction time = 80 minutes).

3.3 Effect of inter electrode space

Many previous studies revealed the impact of the inter-electrodes space in electrocoagulation [5, 15]. The resistance between the electrodes can be increased through increasing the distance between the two electrodes. The resistance between the electrodes can be improved by increasing the distance between the two electrodes. However, this resistance requires a higher potential to be conquered and thus causing
an upsurge in the treatment costs. From the theoretical perspective, the upsurge in distance between the electrodes resulting in a minimal interplay between the hydroxide polymers and ions [18].

In the current context of this study, the impact of inter space between electrodes were tested utilizing 10, 15 and 20 millimeters via employing optimal conditions of current density = 2.0 mA/cm$^2$, TR = 80 minutes, and pH = 8. Figure 4 indicates the optimal performance through using 1 millimeter. On the other hand, the treatment removal rate was declined via the expansion of the distance from 15 to 20 millimeters, with a drop of 86 % to 84 % for SO$_4^{2-}$. These outcomes are compatible with previous studies studeis [9, 19].

![Figure 4](image.png)

**Figure 4.** Influence of inter-electrode gap under best conditions (current density = 2.0 mA/cm$^2$, reaction time = 80 min, pH = 8).

### 3.4 Effect of agitation speed

As an important parameter, agitation speed plays a vital role in the electrocoagulation method [20, 21]. The upsurge in the agitation rate leads to increase mixing of the solution, subsequently conglomerating the pollutants and the precipitation as well as easier mass transfer. However, the opposite can occur particularly when the agitation rate is raised more than required. Whereas, pollutants are formed within the reactor getting degenerated inducing tiny flocks that are hard to separate from the solution. This leads to reducing the treatment efficiency [16, 20].

To scrutinize the impact of the agitation speed on SO$_4^{2-}$ elimination efficiency in this study, agitation speed of 250, 350, 500, 650, and 750 rpm were done utilizing the optimal conditions of current density= 2.0 mA/cm$^2$, $RT$ = 80 minutes, pH = 8, and inter electrode space = 1 millimeter. The highest elimination capacity was gained when the speed was set to 500 rpm as presented in Figure 5. The outcomes exhibit the SO$_4^{2-}$ elimination augmented SO$_4^{2-}$ from 83 % to 89 % for an increase in agitation speed of 250 rpm to 500 rpm. On the other hand, when the rate of agitation speed was augmented from 500 rpm to 750 rpm, the lower elimination efficiency was attained, where the SO$_4^{2-}$ elimination reduced to 78 %. These finding were discussed in the previous literatures [16, 20].
4. Conclusions
The present study assessed the feasibility of EC method in removing \( \text{SO}_4^{2-} \) from salt water utilizing aluminum electrodes. Furthermore, the effects of reaction time (minutes), current density (mA/cm\(^2\)), pH, stirrer speed (rpm), as well as the gap between the anode and cathode (millimeter) on removal of \( \text{SO}_4^{2-} \) were scrutinized. The best conditions were: \( I = 2.0 \text{ mA/cm}^2 \), \( RT = 80 \text{ min} \), \( \text{pH} = 8 \), \( \text{IED} = 1 \text{ millimeter} \) and agitation speed = 500. The EC method under the combined electrical linking of Al electrodes, was proved to be very effective for removing salts from brackish water. Utilizing optimal circumstances of the EC process, the removal efficiency was obtained at 89\% for \( \text{SO}_4^{2-} \). The outcomes of the present study show the technical viability of electrocoagulation as a reliable method for the removal of \( \text{SO}_4^{2-} \).

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