Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.24473

163 (2019) 325–335
September

Electrocoagulation treatment of reject brine effluent from Solvay process

Miada A. Osman[a], Muftah El-Naas[b], Sulaiman Al-Zuhair[a,*]

[a]*Chemical Engineering Department, UAE University, 15551 Al-Ain, UAE, Tel. +971-3-3713 5319; emails: s.alzuhair@uaeu.ac.ae (S. Al-Zuhair), 200734767@uaeu.ac.ae (M.A. Osman)*
[b]*Gas Processing Center, College of Engineering, Qatar University, 2713 Doha, Qatar, email: muftah@qu.edu.qa*

Received 15 January 2019; Accepted 26 May 2019

ABSTRACT

Solvay process is an efficient treatment technique for reject brine from desalination, where salinity is reduced by removing Na^+ by adding NH_3. However, in this process large amounts of NH_3 are consumed and Cl^- ions are not affected. Electrocoagulation has been tested for removing Cl^- and NH_3 regeneration. When no current was applied, removal of the ions was insignificant. Applying a current density of 0.1167 A/cm^2 increased the removal percentages of NH^{4+} and Cl^- by 71.6% and 26.9%, respectively, which proved that the removal was due to electrocoagulation. It was found that the removal percentages and rates increased with increasing the current density and temperature but decreased as the initial ion concentration increased. Three-experiment design levels and response surface methodologies were used to model the system. A second-order polynomial model was developed and used to predict the optimum conditions, which were found to be at a 0.2 A/cm^2 current density, 36.8°C temperature, and initial Cl^- concentration of 7.4×10^3 mg/L. The accuracy of the model was verified against an independent run, not used in the development of the model, and the error did not exceed 10% for both ions.

Keywords: Electrocoagulation; Reject brine; Solvay process; Desalination; Chloride; Ammonium

---

1. Introduction

Natural fresh water resources, including rivers, lakes, and underground aquifers are under stress due to excessive withdrawal and pollution [1]. In dry climates, such as that in the Middle East, water scarcity is already a very serious problem [2]. Desalination of seawater has become an important method to secure a freshwater supply for many countries, including the Gulf States [3]. This is a process that separates saline water into two streams: desalinate, which is the fresh low-salt concentration, and reject brine, which is the high-salt concentration stream [4]. Desalination can be achieved either using physical filtration (membrane separation) processes such as reverse osmosis (RO) or using thermal desalination, such as multi-stage flash (MSF) and multiple-effect distillation.

In spite of the development of new and highly efficient desalination processes, little improvements have been reported for handling and managing reject brine, the waste by-product. For every 1 m^3 of desalinated water, it is estimated that an equal amount of the reject brine is generated [4]. The main environmental challenges to most desalination plants are the management or the disposal of the concentrated brine. The cost of brine disposal ranges between 5% and 33% of the total cost of the desalination process [5]. There are limited options for the treatments which include: discharge to wastewater treatment plants; deep well injection; land disposal and evaporation ponds [4]. A common process to deal with this product is to discharge it back into the sea, which as a result will affect the aquatic life and the quality of the sea water in the long run [6]. For the disposal of industrial, municipal and liquid hazardous wastes, deep well injection

---

* Corresponding author.

1944-3994/1944-3986

is often considered [5]. This method is usually more expensive compared with the discharge to surface water; because in the latter method long brine transport pipelines are not required. Another common method for brine disposal from inland desalination plants is the evaporation ponds. There are some advantages of using this process, such as low maintenance and operation cost, easy to construct and no mechanical equipment requirements [7]. On the other hand, there are many drawbacks of using evaporation ponds, such as contaminations because of the dissipation of the reject brine into the soil and groundwater and also the need of large area. In addition, the evaporation rate strongly depends on weather conditions [5].

A much better option to treat the reject brine is the Solvay process, in which concentrated brine interacts with ammonia and carbon dioxide to form soluble ammonium bicarbonate, which further reacts with sodium chloride to form soluble ammonium chloride and a sodium bicarbonate precipitate, as described in Eq. (1) [6]:

$$Na^+ Cl^- + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3 + NH_4^+ Cl^- \quad (1)$$

The added ammonia plays an important role in the reaction of the Solvay process, by which it buffers the solution at a basic pH and increases the precipitation of sodium bicarbonate. In industrial application, the first step is passing the ammonia gas through the concentrated brine to have the ammoniated brine, and then the carbon dioxide is bubbled through the ammoniated brine to form ammonium chloride [6]. While the Solvay process is efficient in removing the Na^+ ions, it leaves the Cl^- ions intact, and consumes large amounts of NH_3.

In this study, electrocoagulation (EC) was selected to remove Cl^- ions from the effluent of the Solvay process, and regenerate NH_3. Iron and aluminum electrodes are the most common types preferable in the EC [8–11]. In this work Fe electrodes were used, which could dissolve into divalent Fe^{2+} and trivalent Fe^{3+} forms, whereas there is only one form for aluminum dissociation, which is the trivalent form Al^{3+} [8]. The anodic equations illustrate the oxidation of the iron electrodes according to Eq. (2), which further react with OH^- to form $Fe(OH)_n$ according to Eq. (3):

$$Fe_{(s)} \rightarrow Fe^{n+}_{(aq)} + n\, e^{-1} \quad (2)$$

$$Fe^{n+}_{(aq)} + n\, OH^- \rightarrow Fe(OH)_{n(s)} \qquad \text{where } n = 2 \text{ or } 3 \quad (3)$$

The divalent form of the iron goes through further oxidation to form $Fe(OH)_3$, as shown in Eq. (4) [8]:

$$4\, Fe^{2+}_{(aq)} + 10\, H_2O + O_{2(aq)} \rightarrow 4\, Fe(OH)_{3(s)} + 8\, H^+ \quad (4)$$

When an ammonium chloride solution, such as the Solvay effluent, is subjected to electrolysis, chlorine, ammonia and hydrogen are the expected products provided that sodium chloride is present in the solution [12]. Chlorine gas is produced according to Eq. (5), and that is the main process for the removal of chloride.

$$2\, Cl^- \rightarrow Cl_2 + 2\, e^- \quad (5)$$

At alkaline pH and sufficient anodic potential, evolution of oxygen at the anode might also take a place as the following equation [8]:

$$2\, H_2O \rightarrow O_2 + 4\, H^+ + 4\, e^- \quad (6)$$

Both ammonia and hydrogen gases are generated at the cathode according to Eqs. (7) and (8), respectively, and that is the main process for the removal of ammonium ions [13].

$$2\, NH_4^+ + 2\, e^- \rightarrow 2\, NH_{3(g)} + H_{2(g)} \quad (7)$$

$$2\, H^+_{(aq)} + 2\, e^- \rightarrow H_{2(g)} \quad (8)$$

Other electrochemical reactions that could take place in EC are the formation of hydroxides at the cathode according to Eqs. (9) and (10):

$$2\, H_2O + 2\, e^- \rightarrow H_{2(g)} + 2\, OH^-_{(aq)} \quad (9)$$

$$O_2 + 2\, H_2O + 4\, e^- \rightarrow 4\, (OH)^- \quad (10)$$

Although there are a few side reactions involving the liberated chlorine, which are expected during the electrolysis of ammonium chloride solutions, such as the formation of hypochlorite, these reactions depend heavily on the concentration of chloride in the solution. It has been reported that the formation of hypochlorite and the solubility of Cl_2 in the solution can be controlled by the concentration of chloride ions in the solution [14]. Having high concentration of chloride ions reduces the chances of the side reactions and limits the solubility of chlorine gas in the solution. Since the concentration of chloride ions in the Solvay effluent is more than twice that of the ammonium ions, hypochlorite is less likely to be formed.

Owing to the many advantages of EC, which include high efficiency compared with chemical coagulation [8], concurrent flotation by the formed bubbled gasses and small equipment size [9], it has been selected to simultaneously remove Cl^- ions and regenerate NH_3. The process has been successfully used to remove NH_4^+ from simulated wastewaters using an activated carbon-air cathode and a sacrificial aluminum anode [15], and for the extraction of corrosive chloride from concrete [16] and wastewater [17]. Despite being used separately for the treatment of Cl^- and NH_4^+ ions, EC has never been tested for treating the Solvay effluent, containing both ions. In this study, the simultaneous removal of Cl^- ions and regeneration of NH_3 using EC are optimized, which would have a great effect on the enhancement of the Solvay process and the reject brine treatment.

2. Materials and methodology

2.1. Chemical reagents

Ammonium hydroxide aqueous solution (25 wt.% NH_3) and ammonium bicarbonate (99.9% purity) were obtained from Sigma-Aldrich (USA). A gas mixture (10% CO_2 in air) was purchased from Abu Dhabi Oxygen Company, UAE. Nitrogen-ammonia Reagent Set, Nessler, was purchased from Concorde Trading Co. L.L.C., UAE. Reject brine samples with salinity ranging between 65,000 and 75,000 ppm were obtained from a local desalination plant utilizing an MSF desalination process. The average values of the pH and concentrations of the main ions in the reject brine are presented in Table 1.

The reject brine was treated using the Solvay process, operated at optimum conditions [18]. Briefly, 1 L of the reject brine was mixed for 5 min with ammonium hydroxide in a 3:1 molar ratio relative to the initial Na^+ concentration. The mixture was then fed into a stainless steel jacketed bubble column reactor at a 20°C controlled-temperature. A gas mixture containing 10% vol CO_2 in air was bubbled through the reactor at a flow rate of 1 L/min for 6 h. The composition of the solution at the end of the process is shown in Table 1. As shown in the table, although the Solvay process reduced the concentrations of Na^+, Mg^{2+}, K^+, and Ca^{2+}, the drop in Cl^- concentration was negligible and the NH_4^+ concentration increased significantly.

2.2. Experimental setup

The EC experiments were conducted in a plexiglass jacketed reactor with an internal diameter of 14.5 cm and a physical height of 14.5 cm. The volume of the effluent solution from the Solvay process used in all experiments was 500 mL. The electrodes were connected to a strip hanging on the edges of the reactor, which left the reactor uncovered allowing the generated gasses to escape. Two rectangular 13.5 cm × 6 cm Fe electrodes were used, and the contact area of the electrodes immersed in the solution was 15 cm^2. As mentioned earlier, iron and aluminum electrodes are most commonly used in EC. It has been reported though that Fe electrodes showed better energy savings and were much less affected by initial pH when EC was used for decolorizing of solutions containing Orange II, a highly soluble dye, as compared with Al electrodes [19]. Therefore, Fe electrodes were selected in this work. The electrodes were placed 8.5 cm apart and were connected to a DC power supply (PE-23005, 2X0-30V/5A-5V/3A). A mechanical stirrer (RW10R, Janke and Kukel, IKA-WERK, Germany) was immersed between the electrodes and used to agitate the solution. The distance between the electrodes was selected to allow the insertion of the mechanical mixer in between. The temperature inside the reactor was controlled by circulating water from a temperature-controlled water bath (Julabo F34, Germany) through the surrounding jacket. A schematic diagram of the batch reactor is shown in Fig. 1.

2.3. Experimental design

A central composite design (CCD) technique was used to design the three experiment levels, using the Minitab 17.0 software to randomize the experimental runs, as shown in Table 2.

The preliminary study performed to determine the time needed to achieve the maximum removal of ions using the EC process showed that most of the removal took place within the first 6 h. Therefore, the duration of the experiments was set to that time. The three major factors affecting the removal of ions were selected to be temperature, current density, and initial concentration of Cl^- ions prepared by diluting the effluent Solvay solution. The tested ranges of the three factors are shown in Table 3. The pH is another important factor, but it is interconnected with the initial ions concentration. In other words, changing one affects the other, and it is not possible to assess the effect of pH without changing the ions concentration in the solution. Above that, a significant amount of ions, with added acid, were required to be added in order to cause a considerable change in the pH, especially with the undiluted samples. Therefore, in this work the initial concentration was selected as the independent parameter, because is more likely to change in reject brine, after the Solvay process.

The maximum concentration used was that obtained in the effluent from the Solvay process without any dilution. Several dilutions of that was then used to test the effect of the concentration. The maximum current density used was the highest value the instrument could reach for all concentrations, which was determined to be 0.2 A/cm^2. Several fractions of that value was used to test the effect of the current density. The temperature range was above and below –room temperature. The current density and the temperature were monitored throughout the experiment. The latter was measured using an immersed probe inside the reactor, and was found to remain constant with a maximum variation of ±1°C. Samples were collected every 60 min and analyzed

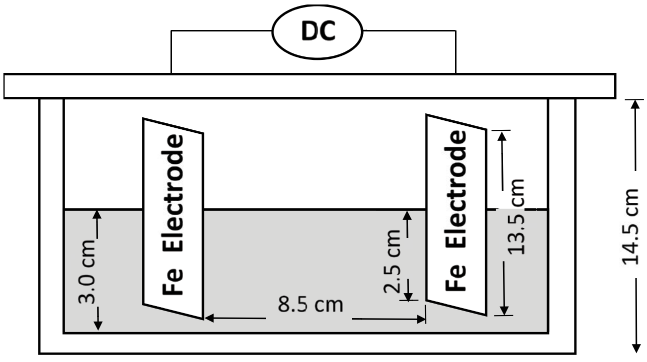

Fig. 1. Schematic diagram of the EC reactor.

Table 1
Characteristics of the reject brine and effluent from the Solvay process

Sample	pH	Concentration (mg/L)					
		Na^+	Mg^{2+}	K^+	Ca^{2+}	Cl^-	NH_4^+
Reject brine	9.16 ± 0.01	23.712×10^3	2.795×10^3	7.620×10^2	1.375×10^3	33.225×10^3	0
Solvay effluent	9.77 ± 0.01	$15.887 \times 10^3 \pm 12$	55.9 ± 8.7	$3.322 \times 10^2 \pm 4.6$	$1.416 \times 10^2 \pm 3.1$	$32.600 \times 10^3 \pm 27$	$17.875 \times 10^3 \pm 18$

for Cl^- and NH_4^+ concentrations using ion chromatography (IC) (Dionex ICS-1100, USA) and UV-Vis spectrophotometry (Hach DR 5000, USA), respectively.

2.4. Analysis

The concentration of Cl^- ions was determined using IC, as described in the 2012 edition of the Dionex ICS-1100 Ion Chromatography System Operator's Manual. The IC was connected to the Degas and Chromeleon software and equipped with a suppressor (AERS [2 mm]), a column (Dionex IonPac AS23, 2 × 250 mm), and a column guard (Dionex IonPac AG23, 2 × 50 mm). The eluents: 4.5 mM Na_2CO_3 and 0.8 mM $NaHCO_3$ were streamed at a 0.25 mL/min rate. The current and oven temperatures were kept at 7 mA and 30°C, respectively. The instrument was calibrated using standard Cl^- solutions of different dilutions, in the 5–40 ppm range. Each sample was diluted and its concentration was brought into this range prior to measuring.

Table 2
Randomization of factors in experimental runs and the removal percentages

Factor			Removal (%)	
I	T	IC	Cl^-	NH_4^+
0	0	0	25.87 ± 0.68	45.96 ± 0.38
0	0	−α	30.29 ± 1.008	56.94 ± 5.89
+1	+1	−1	28.78 ± 0.115	80.05 ± 0.376
+1	−1	+1	22.15 ± 0.540	44.76 ± 1.71
+1	+1	+1	22.47 ± 0.759	66.61 ± 0.258
0	+α	0	29.81 ± 0.376	72.37 ± 1.86
0	0	0	25.87 ± 0.68	45.96 ± 0.38
−α	0	0	22.80 ± 0.177	45.34 ± 0.597
+α	0	0	28.38 ± 0.820	66.67 ± 2.62
−1	−1	+1	11.00 ± 5.17	35.65 ± 1.23
0	−α	0	21.82 ± 0.983	42.93 ± 3.84
0	0	0	25.87 ± 0.68	45.96 ± 0.38
−1	−1	−1	23.92 ± 0.824	58.52 ± 2.41
0	0	+α	25.60 ± 1.07	45.28 ± 0.247
−1	+1	+1	15.44 ± 3.20	65.45 ± 0.575
0	0	0	25.87 ± 0.68	45.96 ± 0.38
−1	+1	−1	24.83 ± 0.142	69.26 ± 0.478
+1	−1	−1	28.51 ± 0.0718	61.54 ± 0
0	0	0	25.87 ± 0.68	45.96 ± 0.38
0	0	0	25.87 ± 0.68	45.96 ± 0.38

The concentration of ammonium ions was determined using a UV spectrophotometer (Hach DR 5000, USA), as described by the Hach Company manual [20]. Three drops of mineral stabilizer, three drops of polyvinyl alcohol dispersing agent, and 1.0 mL of Nessler's reagent, were added in a sequential manner to a 25 mL sample. The sample was thoroughly mixed before a new reagent was added, and the mixtures were allowed to react for 1 min before measurements. The instrument was zeroed using a blank prepared using the same procedure, substituting the sample with 25 mL of deionized water. The ammonium concentration was then measured at a 425 nm wavelength. A calibration curve was prepared using the same procedure described above using standard NH_4^+ solutions of different dilutions in the 0.1–2.0 mg/L range.

3. Results and discussion

3.1. Applied current effect

The percentage removals of NH_4^+ and Cl^- were measured at different EC times, at 30°C, 0.167 A/cm^2 current density, and initial concentrations of 15.6×10^3 and 27.5×10^3 mg/L, respectively. The results in Fig. 2 show that the removal percentages of NH_4^+ and Cl^- reached 70% and 23%, respectively, within 6 h. After that, each curve reached a plateau, and the removal did not increase much. Therefore, the equilibrium is assumed to be reached after 6 h, and all subsequent experiments were carried out up to this time.

The effect of the current density, in the 0–0.2 A/cm^2 range, on NH_4^+ and Cl^- removal percentages and rates are shown in Figs. 3a and b, respectively. The temperature during the test was 20°C and the initial concentrations of NH_4^+ and Cl^- were 14.2×10^3 and 20.0×10^3 mg/L, respectively, which represent the middle values of the two effects (i.e., X_2 and $X_3 = 0$). As shown in Fig. 3, when no current was applied, the recorded removal percentages: 12.5% and 3.55%, and removal rates: 2.08 and 0.59 h^{-1}, for NH_4^+ and Cl^-, respectively, were very small. Increasing the current density to 0.033 A/cm^2 resulted in a significant increase in the removal of both ions, with removal percentages increasing to 45.33% (p-value = 0.00024) and 22.8% (p-value = 0.00037) and removal rates increasing to 12.1 h^{-1} (p-value = 0.0049) and 4.66 h^{-1} (p-value 0.02), for NH_4^+ and Cl^-, respectively. This proves that the removal of the ions was mainly due to the EC, and any other effect, such as evaporation, was minimal. To further confirm that all factors, other than EC, had minimum effects, the experiment without current was repeated at a higher temperature of 30°C, that is, $X_2 = 1$. Very small removal percentages of 12.7% and 4.8% were still

Table 3
Ranges and levels of independent variables for CCD runs

Factors	Tag	Symbol	Units	Levels				
				−α	−1	0	1	+α
Current density	I	x_1	A/cm^2	0.033	0.067	0.117	0.167	0.2
Temperature	T	x_2	°C	3.2	10	20	30	36.8
Initial Cl^- concentration	IC	x_3	mg/L	7,400	12,500	20,000	27,500	32,600

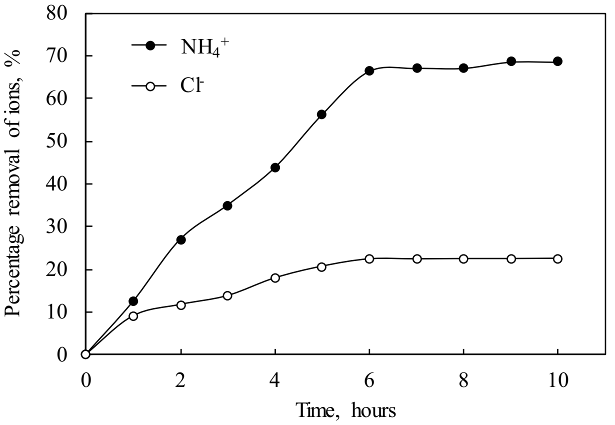

Fig. 2. Removal percentage of NH_4^+ and Cl^- as a function of time at 30°C, 0.167 A/cm² current density and initial concentrations of 15,594 and 27,500 mg/L, respectively.

recorded for NH_4^+ and Cl^-, respectively. Increasing the temperature from 20°C to 30°C did not show a significant effect on the removal percentages of either ion, with p-values of 0.637 and 0.359 for NH_4^+ and Cl^-, respectively.

By increasing the current density by 0.083 to 0.1167 A/cm², the removal percentages increased to 45.96% (p-value = 0.336) and 25.8% (p-value = 0.0255), and the removal rates to 13.7 h^{-1} (p-value = 0.259) and 4.97 h^{-1} (p-value = 0.735), for NH_4^+ and Cl^-, respectively. Further increasing the current density by another 0.083 to 0.2 A/cm² resulted in a significant increase in the removal percentage of NH_4^+ to 66.66% (p-value = 0.008), but was less significant for Cl^- with the removal increasing to 28.37% (p-value = 0.0805). A similar trend was observed for the removal rates as they increased to 18.5 h^{-1} (p-value = 0.056) and 5.88 h^{-1} (p-value = 0.464), for NH_4^+ and Cl^-, respectively.

The results in this study agree with those obtained using EC for the removal of hexavalent chromium from wastewater [21]. However, the initial Cr^{6+} concentrations tested were in the 40–200 mg/L range, much lower than those tested in this study. In addition, the current density tested ranged from 0.0005 to 0.002 A/cm², which was also lower than the range used in this study. The results in this study also agree with those found using EC for the removal of ammonia in synthetic wastewater with different sodium chloride concentrations [22]. The current density tested was 0.005–0.05 A/cm², which was also lower than the one tested in this study.

3.2. Initial concentration effect

For an initial Cl^- concentration of 32.6 × 10³ mg/L, the effects of initial concentration, in the 0–77.3% dilution range on the removal percentages and rates of NH_4^+ and Cl^- are shown in Figs. 4a and b, respectively. The tested current density and temperature were 0.1167 A/cm² and 20°C respectively, which represent the middle values of the two effects (i.e., X_1 and X_2 = 0). The results show that the removal percentages and rates for both ions, NH_4^+ and Cl^-, decreased with decrease in dilution. By decreasing the dilution percentage from 77.3% to 38.65%, the removal percentages decreased from 56.9% to 45.9% (p-value = 0.119) and from 30.2% to 25.8% (p-value = 0.036), and the removal rates from 22.2 to 14.4 h^{-1} (p-value = 0.108) and from 6.5 to 4.9 h^{-1} (p-value = 0.191), for NH_4^+ and Cl^-, respectively. Further decrease in dilution from 38.65% to 0 resulted in decreasing the removal percentages from 45.9% to 45.2% (p-value = 0.826) and 25.8% to 25.5% (p-value = 0.787), and the removal rates from 14.4 to 13.28 h^{-1} (p-value = 0.225) and from 4.9 to 4.2 h^{-1} (p-value = 0.328), for NH_4^+ and Cl^-, respectively.

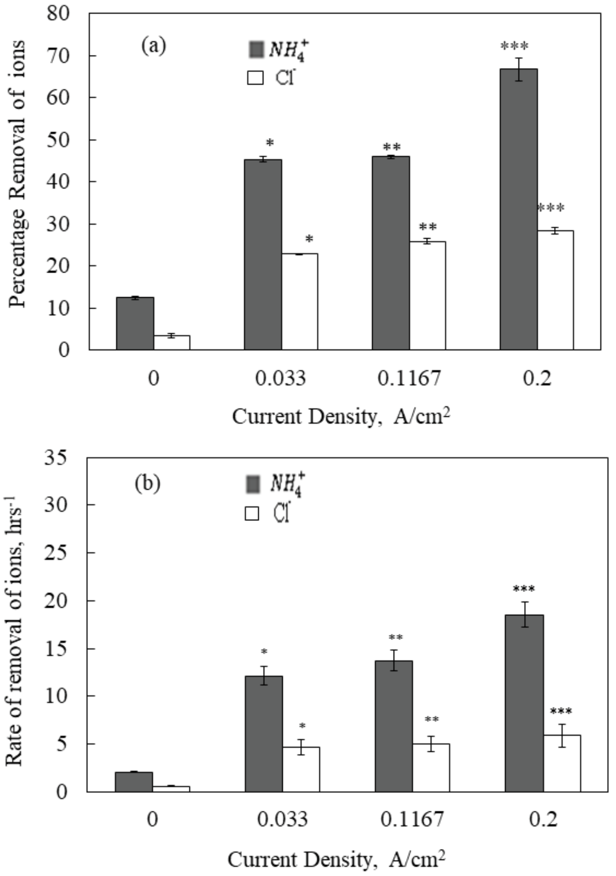

Fig. 3. Effect of current density on (a) removal percentages and (b) removal rates of NH_4^+ and Cl^- ions after 6 h at 20°C and initial concentrations of 14,250 and 20,000 mg/L, respectively.
*indicates comparison between removal percentages and rates at 0 and 0.033 A/cm² (removal percentage p-values = 0.00024 and 0.00037 and removal rate p-values = 0.0049 and 0.02 for NH_4^+ and Cl^-, respectively).
** indicates comparison between removal percentages and rates at 0.033 and 0.1167 A/cm² (removal percentage p-values = 0.336 and 0.0255 and removal rate p-values = 0.259 and 0.735 for NH_4^+ and Cl^-, respectively).
*** indicates comparison between removal percentages and rates at 0.1167 and 0.2 A/cm² (removal percentage p-values = 0.008 and 0.0805 and removal rate p-values = 0.056 and 0.464 for NH_4^+ and Cl^-, respectively).

Our results are in agreement with those obtained using EC for removing ammonium and phosphorous from wastewater [15]. At a 0.0008 A/cm² current density, it was found that increasing the initial concentration resulted in decreasing the removal percentages for ammonium and phosphorous

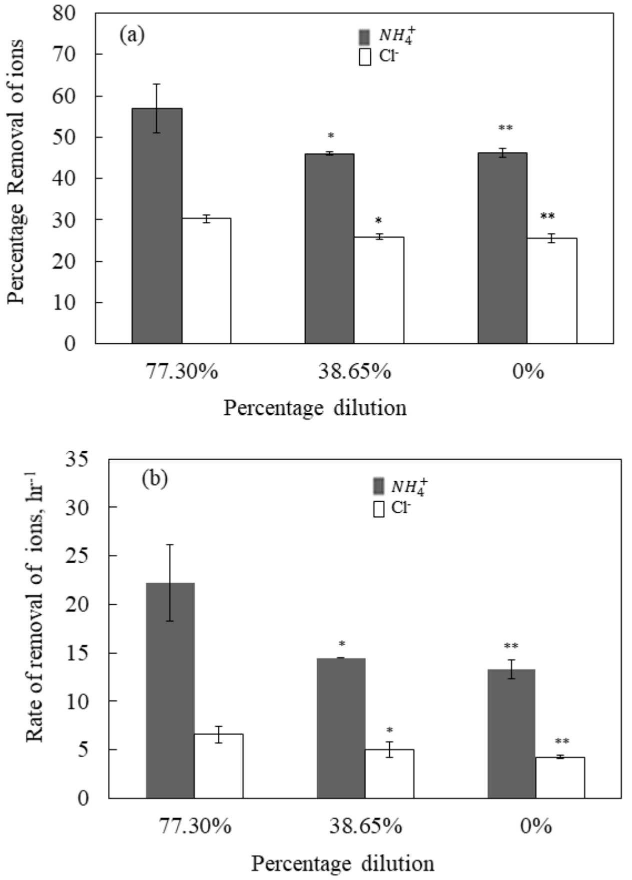

Fig. 4. Effect of initial concentration of NH_4^+ and Cl^- on (a) removal percentage and (b) removal rate after 6 h at 20°C and 0.1167 A/cm^2. The dilution is considered with respect to the maximum concentration of 17,875 and 32,600 mg/L for NH_4^+ and Cl^-, respectively.

* indicates comparison between removal percentage and rate at the 77.3% and 38.65% percentage dilutions (removal percentage p-values = 0.119 and 0.036 and removal rate p-values = 0.108 and 0.191 for NH_4^+ and Cl^-, respectively).

** indicates comparison between removal percentage and rate at the 38.65% and 0 percentage dilutions (removal percentage p-values = 0.826 and 0.787 and removal rate p-values = 0.225 and 0.328 for NH_4^+ and Cl^-, respectively).

from 93% to 75% and from 76% to 45%, respectively. A similar trend was also observed when EC was tested for arsenic removal from drinking water at a 0.54 mA/cm^2 current density and an initial concentration in the 10–100 mg/L range. Using EC for methylene blue removal with a similar initial concentration range and a larger current density of 8 mA/cm^2, also resulted in similar trends [23].

The reason for the drop in removal effectiveness with the increase in ion concentration can be summarized as follows: for the same current density, the same amount of electrode metal ions passes through the solution for all concentrations. As a result, the amount of released metal ions would become insufficient at higher concentrations [22]. Moreover, at higher ion concentrations, the amount of the formed metal hydroxide flocs may not be enough to settle the huge amount of pollutant molecules [24].

3.3. Temperature effect

The effect of temperature, in the 3.2°C–36.8°C range, on the removal percentages and rates of NH_4^+ and Cl^- is shown in Figs. 5a and b, respectively. The tested current density and initial concentration were 0.1167 A/cm^2 and 14.2 × 10^3 and 20.0 × 10^3 mg/L for NH_4^+, and Cl^-, respectively, which represent the middle values of the two effects (i.e., X_1 and $X_3 = 0$).

The results show that the removal percentages and rates of both ions, NH_4^+ and Cl^-, increased with the increase in temperature. The increase in temperature from 3.2°C to 20°C increased the removal percentages from 42.9% to 45.9% (p-value = 0.38) and from 21.8% to 25.8% (p-value = 0.04) for NH_4^+ and Cl^-, respectively and the removal rates from 11.9 to 13.7 h^{-1} (p-value = 0.163) and from 3.5 to 4.9 h^{-1} (p-value = 0.131) for NH_4^+ and Cl^-, respectively. Within this temperature range, the temperature effect was generally insignificant. However, increasing the temperature from 20°C to 36.8°C resulted in a

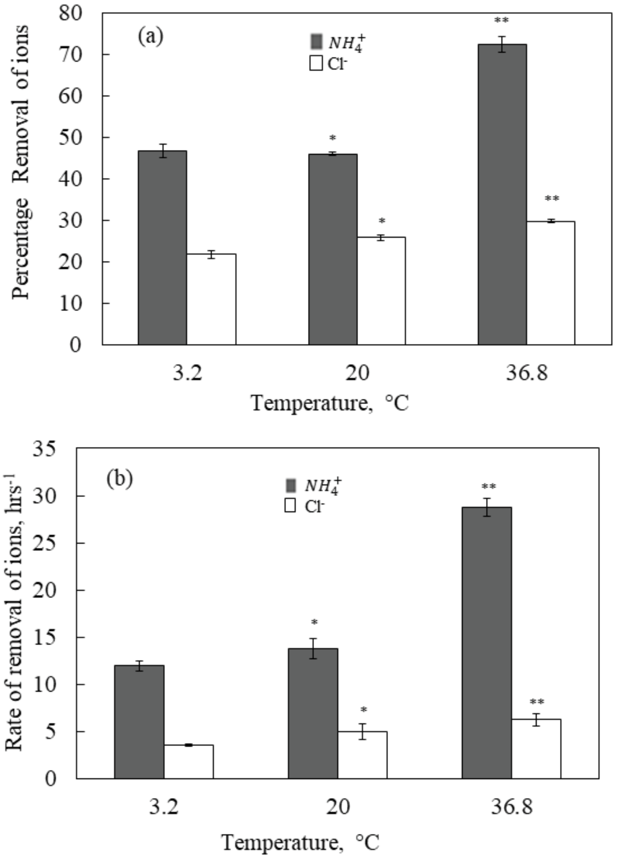

Fig. 5. Effect of temperature on (a) removal percentage and (b) removal rate of NH_4^+ and Cl^- ions after 6 h at 0.1167 A/cm^2 and 14,250 and 20,000 mg/L initial concentrations of NH_4^+ and Cl^- ions, respectively.

*indicates comparison between removal percentages and rates at 3.2 and 20°C (removal percentage p-values = 0.561 and 0.0409 and removal rate p-values = 0.163 and 0.131 for NH_4^+ and Cl^-, respectively).

**indicates comparison between removal percentages and rates at 20 and 36.8°C (removal percentage p-values = 0.00257 and 0.0192 and removal rate p-values = 0.00438 and 0.213 for NH_4^+ and Cl−, respectively).

significant increase in the removal percentages of both ions from 45.9% to 72.3% (*p*-value = 0.002) and from 25.8% to 29.8% (*p*-value = 0.019) for NH_4^+ and Cl^-, respectively, and in the removal rate of NH_4^+ from 13.7 to 28.7 h^{-1} (*p*-value = 0.004). However, the change in removal rate for Cl^- was insignificant from 4.9 to 6.2 h^{-1} (*p*-value = 0.213).

The increase in the removal percentages and rates with temperature is due to the enhanced rate of diffusion of the ions and the kinetic collisions of particles [25]. In addition, the increase in temperature enhances the formation of hydrogen bubbles which enhances the flotation speed [24]. Similar temperature effects were observed using EC for the ammonia removal from synthetic wastewater in the 25°C–40°C temperature range [25], indium ion removal in the 15°C–45°C range [26], and boron removal in the 19.85°C–59.85°C range. In an investigation of the effect of the temperature on the percentage of phenol removal using a fixed bed aluminum electrode, an increase from 88% to 95% was observed when the temperature increased from 25°C to 45°C [24].

3.4. Combined effects

To evaluate the combined influence of temperature and initial concentration on the significance of the effect of current density on the percentage removal of the ions, the experiment was repeated at different temperatures (10°C and 30°C) and different initial concentrations: 10.4 × 10^3 and 15.6 × 10^3 mg/L for NH_4^+, and 12.5 × 10^3 and 27.5 × 10^3 mg/L for Cl^-. The results are shown in Figs. 6a and b. It is obvious that the increase in initial concentration reduced the overall removal but increased the significance of the current density. In addition, at the lower initial concentrations, increasing the temperature from 10°C to 30°C increased the removal percentages and the significance of the current density effect for both ions. At 10°C, as the current density increased from 0.067 to 0.167 A/cm^2, the removal increased from 58.5% to 61.5% (*p*-value = 0.218) and from 23.9% to 28.5% (*p*-value = 0. 0.015) for NH_4^+ and Cl^-, respectively, while at 30°C, the removal increased from 69.2% to 80.05% (*p*-value = 0.0015) and from 24.8% to 28.7% (*p*-value = 0.001) for NH_4^+ and Cl^-, respectively. At the higher initial concentration, increasing the temperature from 10°C to 30°C increased the removal percentages; however, it lowered the significance of the current density effect for NH_4^+ and Cl^-. While at 10°C the removal increased from 35.6% to 44.7% (*p*-value = 0.025) and from 10.9% to 22.1% (*p*-value = 0.093), at 30°C the removal increased from 65.4% to 66.6% (*p*-value = 0.121) and from 15.4% to 22.4% (*p*-value = 0.094) for NH_4^+ and Cl^-, respectively.

Furthermore, the increase in temperature increased the significance of the initial concentration. At the lower temperature, increasing the initial concentration from 10.4 × 10^3 to 15.6 × 10^3 mg/L, resulted in a decrease in the removal percentages of NH_4^+ from 58.5% to 35.65% (*p*-value = 0.006) and from 61.5% to 44.7% (*p*-value = 0.0051), at current densities of 0.067 and 0.167 A/cm^2, respectively. Similarly, increasing the initial concentration of Cl^- from 12.5 × 10^3 to 27.5 × 10^3 mg/L resulted in a decrease in the removal percentages from 23.9% to 10.9% (*p*-value = 0.073) and from 28.5% to 22.1% (*p*-value = 0.0036). At the higher temperature, increasing the initial concentration from 10.4 × 10^3 to 15.6 × 10^3 mg/L, resulted in a decrease in the removal percentage of NH_4^+ from 69.25% to 65.04% (*p*-value = 0.006) and from 80.3% to 66.6% (*p*-value = 0.0016), at current densities of 0.067 and 0.167 A/cm^2, respectively. Similarly, increasing the initial concentration of Cl^- from 12.5 × 10^3 to 27.5 × 10^3 mg/L, resulted in decreasing the removal percentages from 24.8% to 15.4% (*p*-value = 0.05) and from 28.7% to 22.4% (*p*-value = 0.007), respectively.

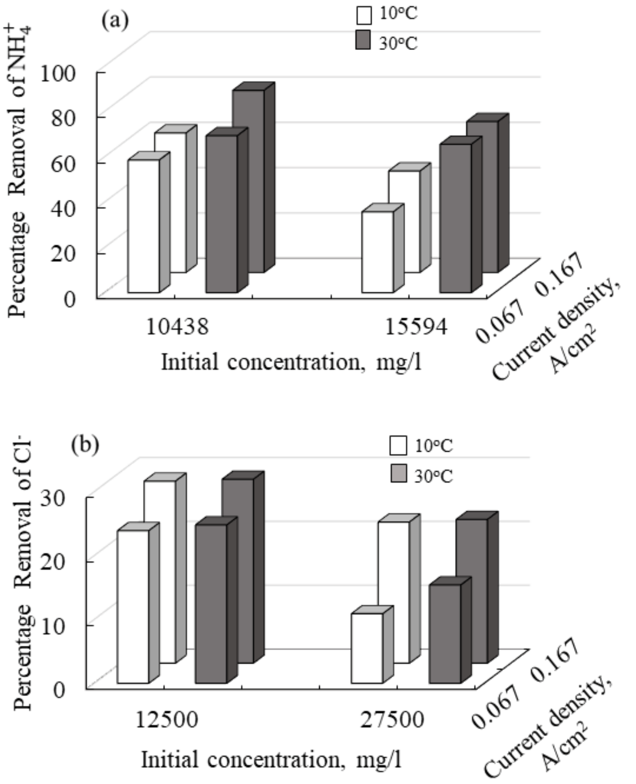

Fig. 6. Effect of current density and initial concentration on removal percentage of (a) NH_4^+ and (b) Cl^- ions after 6 h at 10 and 30°C.

At the lower current density, and initial concentrations of 10.4 × 10^3 and 12.5 × 10^3 mg/L for NH_4^+ and Cl^-, respectively, increasing the temperature from 10°C to 30°C resulted in an increase in the removal percentages from 58.5% to 69.2% (*p*-value = 0.25) and from 23.9% to 24.8% (*p*-value = 0.26), respectively. Increasing the initial concentration to 15.6 × 10^3 and 27.5 × 10^3 mg/L for NH_4^+ and Cl^-, respectively, caused an increase in the removal percentages from 35.6% to 65.4% (*p*-value = 0.001) and from 10.9% to 15.44% (*p*-value = 0.41), respectively. At the initial concentrations of 10.4 × 10^3 and 12.5 × 10^3 mg/L for NH_4^+ and Cl^-, respectively, increasing the temperature from 10°C to 30°C lead to an increase in the removal percentages from 61.5% to 80% (*p*-value = 0.0002) and from 28.5% to 28.7% (*p*-value = 0.104), respectively. A high initial concentration and current density, led to a decrease in the significance of the removal of NH_4^+ and Cl^-. At the higher current density, and at initial concentrations of 15.6 × 10^3 and 27.5 × 10^3 mg/L for NH_4^+ and Cl^-, respectively, a high initial concentration and current density caused an increase in the removal percentage from 22.1% to 22.4% (*p*-value = 0.003) for NH_4^+.

It was interesting to compare the removal percentages of the Cl^- ions based on the initial ammonium chloride concentration generated in the Solvay process, which was considered equal to the initial concentration of NH_4^+. At a 0.1167 A/cm^2 current density, a 30°C temperature, and initial concentrations of 14.2×10^3 and 20.0×10^3 mg/L for NH_4^+ and Cl^-, respectively, the removal percentage of Cl^- based on the initial ammonium chloride concentration was found to be 37.7%, compared with 26.88% based on the initial Cl^- concentration.

3.5. Statistical analysis

Minitab 17.0 software was used to perform regression analysis of the experimental data and to determine the coefficients of the regression equation. Twenty runs were carried out; each run was repeated twice, and the relationship between the experimental levels of each factor and the responses was expressed using a fitted polynomial, as shown in Table 4. The significance of the factors was evaluated using the *p*-value, while the lack-of-fit value of the model was determined from the analysis of the variance. It was shown that the effects of current density, temperature, and initial concentration were all significant for NH_4^+, whereas for Cl^-, the effect of the initial concentration was found insignificant. For both ions, the lack-of-fit implied that the fit was significant.

After removing the insignificant factor, having *p*-values larger than 0.05 as provided by Minitab, the predicted polynomial models for NH_4^+ and Cl^-, namely Y_1 and Y_2, as functions of the significant factors and their combinations, were developed, as shown in Eqs. (11) and (12):

$$Y_1 = 77.3 - 324\,X_1 - 1.018\,X_2 - 0.000748\,X_3 + 1764\,X_1^2 + 0.0493\,X_2^2 \tag{11}$$

$$Y_2 = 26.90 + 52.9\,X_1 - 0.000419\,X_3 \tag{12}$$

where X_1, X_2, and X_3 are the current density, temperature, and initial concentration, respectively. To validate the model, an independent experiment was performed at 0.1167 A/cm^2, 30°C, and initial concentrations of 14.2×10^3 and 20.0×10^3 mg/L for NH_4^+ and Cl^-, respectively. For these conditions, the removals of NH_4^+ and Cl^-, were found to be 71.6% and 26.9%, respectively. At the same conditions, the model predictions were 66.7% and 24.7%, respectively. The difference between the experimental results and the model predictions were 7.3% and 8.8%, respectively.

An optimization process was carried out using response optimizer in Minitab. The results in Fig. 7 show that increasing the current density increased the removal of chloride linearly as the first order variable was the significant effect, wheareas the removal of ammonium was parabolic, due to the significant second order terms. No effect of temperature was observed on the percentage of removal of chloride, as suggested by Eq. (11), whereas, the percentage removal of ammonium increased parabolically with temperature, owing again to the significant second order term. The initial concentration had a similar effect on the percentage removals of ammonium and chloride ions. The optimum removal for both ammonium and chloride ions was determined to be at a 0.2 A/cm^2 current density, 36.8°C temperature, and initial Cl^- concentration of 7.4×10^3 mg/L.

The developed polynomial (Eq. (10)) was used to determine the simultaneous effects of two factors on the percentage removal of NH_4^+ in 3-D surface response graphs as shown in Figs. 8a–c. Two factors were changed while keeping the third at the central value, that is, $X_i = 0$. The results clearly show the parabolic effect of the current density and temperature, as a result of the significant effect of

Table 4
Anova results for the modeling of (a) ammonium and (b) chloride, removals

Response surface regression: ammonium removal vs. x_1, x_2, x_3
Analysis of variance

Source	DF	Adj SS	Adj MS	*F*-Value	*p*-Value
Model	9	2,676.13	297.35	15.62	0.000
Linear	3	1,937.15	645.72	33.92	0.000
x_1	1	263.19	263.19	13.83	0.004
x_2	1	1,245.33	1,245.33	65.42	0.000
x_3	1	428.63	428.63	22.52	0.001
Square	3	674.69	224.90	11.81	0.003
x_1*x_1	1	299.26	299.26	15.72	0.001
x_2*x_2	1	380.52	380.52	19.99	0.008
x_3*x^3	1	115.11	115.11	6.05	0.073
2-Way interaction	3	64.29	21.43	1.13	0.385
x_1*x_1	1	0.00	0.00	0.00	0.989
x_2*x_2	1	1.57	1.57	0.08	0.780
x_3*x_3	1	62.72	62.72	3.29	0.100
Error	10	190.35	19.04		
Lack-of-fit	5	190.35	38.07		
Pure error	5	0.00	0.00		
Total	**19**	**2,866.48**			

Removal of chloride

Source	DF	Adj SS	Adj MS	*F*-Value	*p*-Value
Model	9	298.613	33.179	3.03	0.049
Linear	3	257.501	85.834	7.84	0.006
x_1	1	95.449	95.449	8.72	0.014
x_2	1	27.495	27.495	2.51	0.144
x_3	1	134.557	134.557	12.29	0.006
Square	3	25.062	8.354	0.76	0.540
x_1*x_1	1	14.890	14.890	1.36	0.271
x_2*x_2	1	12.650	12.650	1.16	0.308
x_3*x_3	1	0.487	0.487	0.04	0.837
2-Way interaction	3	16.050	5.350	0.49	0.698
x_1*x_1	1	2.832	2.832	0.26	0.622
x_2*x_2	1	11.616	11.616	1.06	0.327
x_3*x_3	1	1.602	1.602	0.15	0.710
Error	10	109.474	10.947		
Lack-of-fit	5	109.474	21.895		
Pure error	5	0.000	0.000		
Total	**19**	**408.087**			

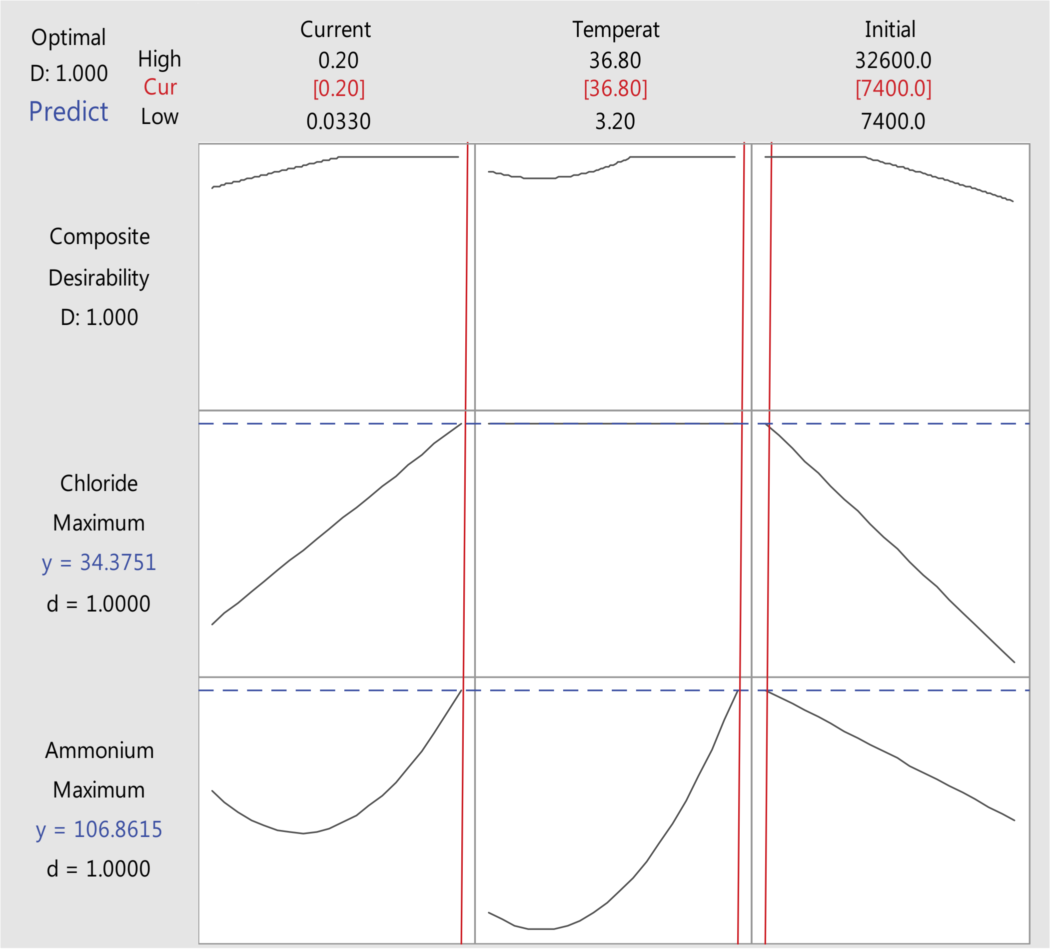

Fig. 7. Optimization results of the effects of current density, temperature and initial concentration for maximum chloride and ammonium removals.

the second order terms; whereas, the effect of the initial concentration was linear.

The other polynomial equation (Eq. (11)) was also used to determine the simultaneous effects of the current density and initial Cl^- concentration, at a constant temperature of 20°C, on the percentage removal of Cl^- in a 3-D surface response graph. The other combinations that included the temperature were not shown, because its effect was found to be insignificant, as shown in Eq. (11). The results in Fig. 9 show the linear effects of both factors: current density and concentration, with the former having a positive and the latter a negative effect.

4. Conclusion

The performance of EC for the removal of NH_4^+ and Cl^- from the effluent of the Solvay process was evaluated. Increasing the current density from 0 to 0.2 A/cm^2 resulted in increasing the removal percentage of Cl^- from only 3.55% to 28.4%, which proves that the removal was mainly due to the EC effect. The effects of temperature in the 3.2°C–36.8°C range, the initial Cl^- concentration in the 7.4×10^3–32.6×10^3 mg/L range, and the 0.033–0.2 A/cm^2 current density range were assessed in a batch EC cell. Increasing the temperature and current density resulted in increasing the removal percentage and rate. Whereas, increasing the initial concentration resulted in decreasing the removal. The effect of current density was more significant at low initial concentrations and high temperatures, whereas the effect of temperature was found to be insignificant. The effect of the initial concentration was more significant at high current densities. The experimental results were used to develop statistical models to predict the removals of NH_4^+ and Cl^- ions. The models were subsequently validated against an independent experimental point not used in the development of the models. The results of this study are essential for optimizing the design of EC units for the simultaneous removal of Cl^- ions and regeneration of NH_3, which would have a significant effect on the enhancement of the Solvay process and the reject brine treatment.

References

[1] L. Yu, I. Yıldızf, 1.24 Energy and Water Pollution, Comprehensive Energy Systems, 1 (2018) 950–979.
[2] J. Le Dirach, S. Nisan, C. Poletiko, Extraction of strategic materials from the concentrated brine rejected by integrated nuclear desalination systems, Desalination, 182 (2005) 449–460.

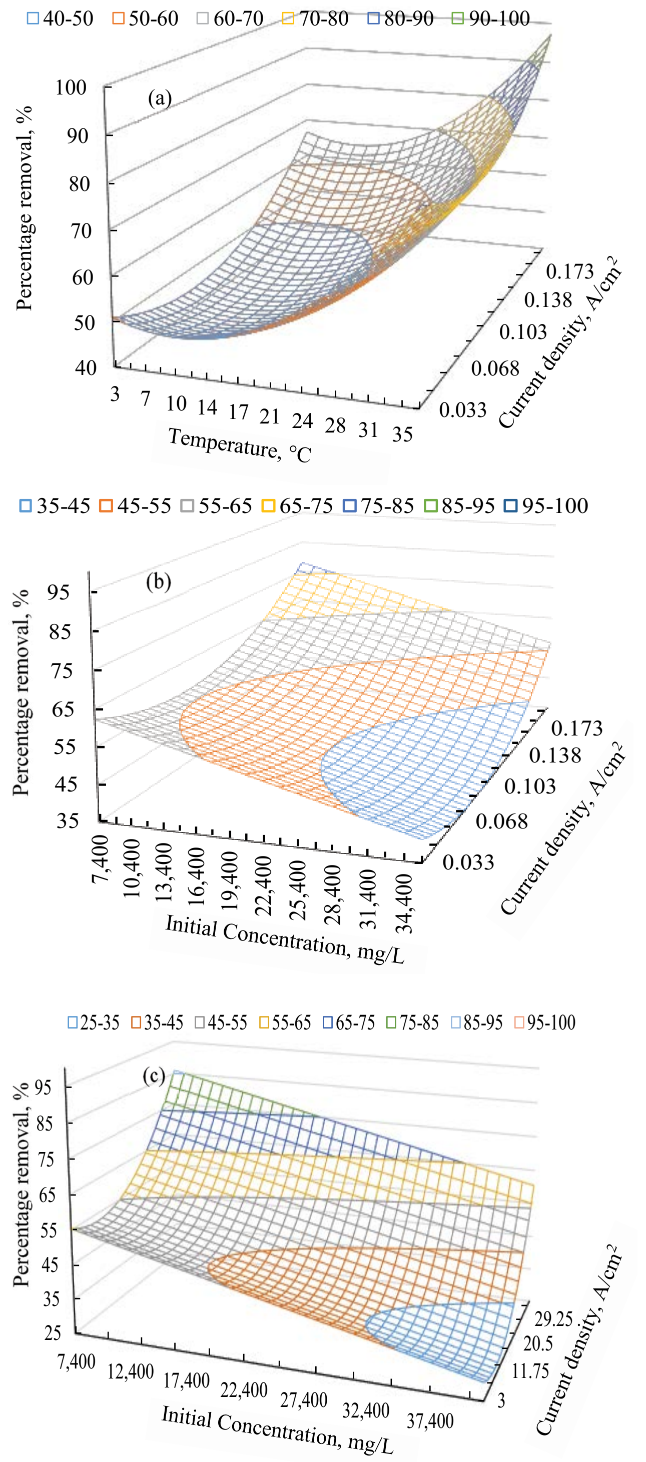

Fig. 8. 3-D plot of the removal percentage of NH_4^+ as a function of the combined effects of (a) current density and temperature at a constant initial Cl^- concentration of 20,000 mg/L, (b) current density and initial concentration at 20°C, and (c) temperature and initial concentration at a 0.117 A/cm² current density.

[3] M.A. Dawoud, The role of desalination in augmentation of water supply in GCC countries, Desalination, 186 (2005) 187–198.
[4] M.H. El-Naas, Teaching water desalination through active learning, Educ. Chem. Eng., 6 (2011) 97–102.

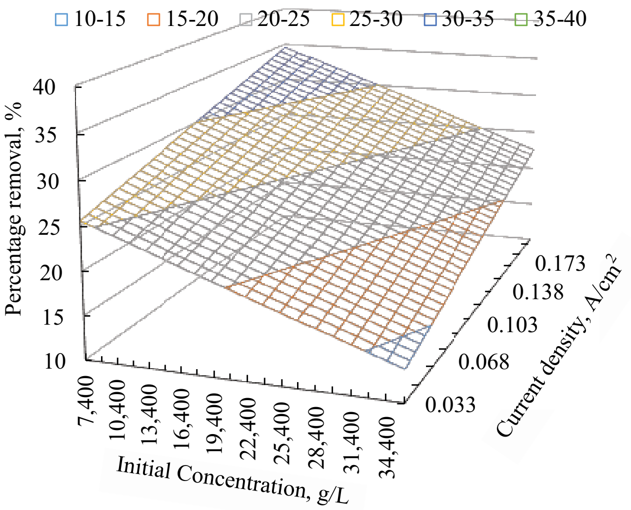

Fig. 9. 3-D plot of the removal percentage of Cl^- as a function of the combined effects of current density and temperature at a constant initial 20,000 mg/L Cl^- concentration.

[5] A. Pérez-González, A.M. Urtiaga, R. Ibáñez, I. Ortiz, State of the art and review on the treatment technologies of water reverse osmosis concentrates, Water Res., 46 (2012) 267–283.
[6] M.H. El-Naas, A.H. Al-Marzouqi, O. Chaalal, A combined approach for the management of desalination reject brine and capture of CO_2, Desalination, 251 (2010) 70–74.
[7] N. Ahmad, R.E. Baddour, A review of sources, effects, disposal methods, and regulations of brine into marine environments, Ocean Coastal Manage., 87 (2014) 1–7.
[8] D.T. Moussa, M.H. El-Naas, M. Nasser, M.J. Al-Marri, A comprehensive review of electrocoagulation for water treatment: Potentials and challenges, J. Environ. Manage., 186 (2016) 24–41.
[9] T.R. Devlin, M.S. Kowalski, E. Pagaduan, X. Zhang, V. Wei, J.A. Oleszkiewicz, Electrocoagulation of wastewater using aluminum, iron, and magnesium electrodes, J. Hazard. Mater., 368 (2019) 862–868.
[10] M. Reilly, A.P. Cooley, D. Tito, S.A. Tassou, M.K. Theodorou, Electrocoagulation treatment of dairy processing and slaughterhouse wastewaters, Energy Procedia, 161 (2019) 343–351.
[11] N.S. Graça, A.M. Ribeiro, A.E. Rodrigues, Modeling the electrocoagulation process for the treatment of contaminated water, Chem. Eng. Sci., 197 (2019) 379–385.
[12] Y. Ito, T. Ohmori, S. Nakamatsu, S. Yoshizawa, A molten salt electrolytic process for recovering chlorine and ammonia from ammonium chloride, J. Appl. Electrochem., 10 (1980) 419–425.
[13] T. Picard, G. Cathalifaud-Feullade, M. Mazet, C. Vandensteendam, Cathodic dissolution in the electrocoagulation process using aluminium electrodes, J. Environ. Monit., 2 (2000) 77–80.
[14] C.B.F. Young, E.G. Lundstrom, The Electrolytic Decomposition of Aqueous Ammonium Chloride Solutions, the 81st General Meeting, held at Nashville, Tennessee, April 17, 1942.
[15] Y. Tian, W. He, X. Zhu, W. Yang, N. Ren, B.E. Logan, Energy efficient electrocoagulation using an air-breathing cathode to remove nutrients from wastewater, Chem. Eng. J., 292 (2016) 308–314.
[16] L. Kumar, S.K. Singh, Removal of chloride from ground water by Bio adsorption, Int. J. Adv. Res., 3 (2015) 140–154.
[17] T. Ueda, K. Wakitani, A. Nanasawa, Influence of electrolyte temperature on efficiency of electrochemical chloride removal from concrete, Electrochim. Acta., 86 (2012) 23–27.
[18] A.F.M. Mohammad, Optimization of a Combined Approach for the Treatment of Desalination Reject Brine and Capture of CO_2, Master's Thesis, UAE University, UAE, 2015.
[19] M. Chafi, B. Gourich, A.H. Essadki, C. Vial, A. Fabregat, Comparison of electrocoagulation using iron and aluminium

electrodes with chemical coagulation for the removal of a highly soluble acid dye, Desalination, 281 (2011) 285–292.

[20] Colorimeter: Procedure Manual, Hach Company, USA, 2013.

[21] Y.A. El-Taweel, E.M. Nassef, I. Elkheriany, D. Sayed, Removal of Cr(VI) ions from waste water by electrocoagulation using iron electrode, Egypt. J. Pet., 24 (2015) 183–192.

[22] B.Z. Can, R. Boncukcuoglu, A.E. Yilma, B.A. Fil, Effect of some operational parameters on the arsenic removal by electrocoagulation using iron electrodes, J. Environ. Health Sci. Eng., 12 (2014) 1–10.

[23] M.S. Mahmoud, J.Y. Farah, T.E. Farrag, Enhanced removal of Methylene Blue by electrocoagulation using iron electrodes, Egypt. J. Pet., 22 (2013) 211–216.

[24] A.S. Naje, S. Chelliapan, Z. Zakaria, M.A. Ajeel, P.A. Alaba, A review of electrocoagulation technology for the treatment of textile wastewater, Rev. Chem. Eng., 33 (2016) 263–292.

[25] Y. Wang, X. Guo, J. Li, Y. Yang, Z. Lei, Z. Zhang, Efficient electrochemical removal of ammonia with various cathodes and Ti/RuO_2-Pt anode, Open J. Appl. Sci., 2 (2012) 241–247.

[26] W.-L. Chou, Y.-H. Huang, Electrochemical removal of indium ions from aqueous solution using iron electrodes, J. Hazard. Mater., 172 (2009) 46–53.