Article

A New Process for the Recovery of Ammonia from Ammoniated High-Salinity Brine

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Abstract: This paper describes a new method for the recovery of high-concentration ammonia from water in the form of ammonium chloride, ammonium hydroxide and ammonium carbonate. The method was applied to the Solvay process, in which sodium bicarbonate is produced through the reaction of ammoniated brine and CO_2 gas. The Solvay effluent contains ammonia in the form of soluble ammonium chloride. The proposed method is based on the recovery of ammonia using a high-alkalinity reactant, calcium oxide (CaO), in a closed electrocoagulation cell operating at a specific current density. The recovered ammonia is collected as a gas within a closed cell containing deionized (DI) water at room temperature. Afterwards, the collected solution (DI water–NH_3 gas) is concentrated through a separate process, and is then reused in the Solvay process and other applications. The electrocoagulation process is applied to the treatment cell using aluminum electrodes and a current density of 5–15 mA/cm^2. After 7 h of treatment using the electrocoagulation cell, a high reduction of the ammonia concentration—99%—was realized after ~9 h of the electrochemical treatment. The initial ammonia concentration in a Solvay effluent of 13,700 mg/L N was decreased to 190 mg/L N. Furthermore, an ammonia recovery of 77.1% in the form of ammonium hydroxide was achieved. Generally, this process, which starts at room temperature, can result in an energy reduction of 80%—from 7.8 to 2.3 kWh/kg NH_3—compared to conventional processes, which entail heating the Solvay effluents to 160 °C. The proposed system and method were found to be suitable for the recovery of ammonia from ammoniated water, and can be utilized for the treatment of landfill leachate, and municipal and industrial wastewater.

Keywords: ammonia recovery; ammonium chloride; brine; calcium oxide; electrocoagulation cell; solvay process

1. Introduction

The ammonia content in effluents is typically not recovered, and is instead converted to nitrogen, which is a loss of valuable fixed nitrogen. Recovering ammonia from different water effluents using conventional treatment techniques, such heating the solution in the presence of CaO up to 160 °C, only to release the ammonia back in the gaseous phase, requires extensive energy. The energy consumption of any ammonia-recovery method is very important for the estimation of whether the process is energy efficient and hence cost effective. An efficient recovery method is beneficial for the environment because it removes ammonia as a pollutant, decreasing the carbon footprint and reducing the use of raw materials or energy input. An important case is the Solvay process, where the development of inexpensive and sustainable methods for the recovery of the nitrogen content in high-salinity brine before and after the Solvay process has received considerable attention from researchers in the brine desalination and valorization sector. The Solvay process requires

excessive amounts of ammonium hydroxide to produce sodium bicarbonate or carbonate and to recover magnesium hydroxide from brine [1]. In this study, a new method is presented for the recovery of ammonia in a gaseous form from different initial forms (chloride, hydroxide and bicarbonate), taking the effluents generated in the Solvay process as a case.

In the literature, several methods are described for the removal of ammonia at different concentrations from different types of water, such as wastewater, groundwater, and municipal and industrial water [2–7]. However, less attention has been paid to finding more efficient and cost-effective ammonia-recovery methods. Conventional ammonium-removal and ammonia-recovery processes include ammonia distillation, stripping, biological denitrification, ion exchange, chemical precipitation and breakpoint chlorination. Furthermore, hybrid methods such as photocatalysis and electrochemical oxidation, and systems such as the osmotic membrane bioreactor exist [8]. Some common ammonia-recovery/removal methods, along with their strengths and weaknesses, are listed in Table 1. Among the mentioned methods, many limitations could restrict the applicability of these techniques, such as the limited ammonia removal efficiency, high energy input, the need of specific treatment conditions and the additional separation/purifications steps. It was reported that ammonia recovery based on the recovered nitrogen percentage reached up to ~53% N through crystallization at a pH level of 8.92 [9], 77% N through anaerobic treatment at a pH level of 9.2 [10], 75% N through air stripping and absorption at a H_2SO_4 concentration of 0.4 mol./l [11], 79% N through electrochemical cell extraction at a feed rate of 6 l/h [12], ~50% N through chemical precipitation at an airflow rate of 4–8 l/min [13], 55–81% N through gas-permeable tubing at a pH level of 8.6 [14], 48% N through ion exchange at a flow rate of 5.6 mL/min [15], and ~45% N through capacitive membrane stripping at a current density of 17.2 A/m^2 [16]. The air-stripping method is considered a slow process, and is only applicable to high ammonia concentrations; moreover, air pollution hazards are sometimes expected when this method is used. The economic efficiency of membrane contactors appears to be problematic because they require high maintenance costs [17,18]. Furthermore, the ion exchange approach may face resin fouling in some cases. However, the advantages of the process generally outweigh the resin fouling [19]. Osman et al. evaluated the use of electrocoagulation for the treatment of high-salinity brine with an initial ammonia concentration of 14,250 mg/L of NH^{4+} and an applied a current density of 0.2 A/cm^2, and reported 66.7% ammonia removal efficiency [20]. The following table lists the main methods for ammonia recovery and removal with their strengths and weaknesses. It can be concluded that most of the conventional methods face major limitations/disadvantages that could decrease their applicability for large-scale applications. These include high energy consumption in the vacuum distillation, limited ammonia recovery/ removal efficiency in the air-stripping, a high capital cost in the membrane contactors, and high operational cost in the membrane distillation method.

Table 1. Common ammonia-recovery/removal methods, with their strengths and weaknesses.

Method	Ammonia Recovery/Removal Percentage	Strength	Weakness
Ammonia air-stripping process, wherein caustic soda (lime) is used to obtain a high pH level [3].	45–75%	- Economical and simple method - Ammonium ions are converted into ammonia gas that leaves the solution with the air stream. - The most efficient apparatus is the packed stripping towers.	- Limited ammonia-removal efficiency.

Table 1. *Cont.*

Method	Ammonia Recovery/Removal Percentage	Strength	Weakness
Membrane contactors, wherein the gas-permeable hollow fiber membrane removes ~99% of ammonia. The dissolved ammonia diffuses from the gas-permeable membrane under vacuum pressure [4,5].	99–100%	- Excellent removal of ammonia - Fast separation process - Low energy input - Wide contact area - Pure ammonia concentrator - The ammonia concentration and flow rate do not affect ammonia removal efficiency.	- High capital cost.
Chemical precipitation, wherein ammonium ions are precipitated by forming magnesium ammonium phosphate solids [21,22].	95–98%	- A well-known chemical precipitation method applied for ammonium removal.	- Types and sources of treated water.
Ion exchange, wherein treated water is passed through a resin bed of zeolite and ammonium ions are exchanged with the resin's free ions [23,24].	-	- Applicable to high concentrations of ammonium ions and a wide temperature range.	- Ammonia removal efficiency is limited by the organic content in treated water samples.
Atmospheric and vacuum distillation, wherein ammonia from different concentrations of landfill leachates evaporates under both atmospheric and vacuum pressure conditions [25].	95–98%	- High ammonia-removal efficiencies at atmospheric pressure and temperature of 300 °C - High ability to recover ammonia from high-concentration leachates and industrial and agricultural wastewater.	- High energy input.
Membrane distillation, wherein the vapor volatility and pressure through the membrane is controlled to concentrate ammonia on the permeate side [26].	20–70%	- A promising approach to recover ammonia from sludge digestate. - Nanoporous honeycomb-structured Nafion membranes showed high ammonia-recovery performance and high mechanical strength. - High ammonia-recovery efficiency of 59.74% was recorded at a pH level of 12.	- High initial and operational cost.
Ammonia recovery by a bioelectrochemical system, wherein the organic content in the treated water is oxidized by the exoelectrogens growing on an anode electrode, the released electrons are freely flowing from anode to cathode [27–30].	70–80%	- Highly efficient transition of ammonium ions from anode to cathode.	- Ammonia recovery is limited by the organic content in the treated water.
Ammonium chloride leaching process, wherein ammonium chloride solutions are reacted with metal oxides such as zinc to form zinc ammine chloride [31,32].	84–95%	- A high concentration of ammonium chloride samples is treated. - Metal oxides such as cupric and cadmium oxides are efficient in the ammonium chloride leaching process.	- The need for further purification and separation process to obtain the final product.
Osmotic membrane bioreactor, wherein ammonium ions are recovered via struvite precipitation. Adding sodium hydroxide is required for increasing the pH level to ensure the struvite precipitation [33].	-	- Low energy input is required. - Low membrane fouling is recorded. - High-quality treated water is obtained.	- Ammonium ions and mineral salts accumulate inside the bioreactor, and further separation process is required.

In the Solvay process, sodium carbonate is produced by bubbling CO_2 gas through a solution of high-salinity water and ammonia [34]. Ammonia only buffers the solution, and is not consumed as a reactant. The required CO_2 is generated by limestone calcination at high temperatures (950–1100 °C), and calcium oxide (CaO) and CO_2 are produced [35]. The precipitated sodium bicarbonate is filtered out of the hot ammonium chloride solution, and is then used in many applications [36]. The ammonia recovery based on this method has a major limitation, which is the high energy consumption associated with the release of

ammonia in the gas form from the treated brine effluent gas from salt solutions [37]. On the other hand, it was reported that once the ammonia is added to high-salinity brine, most of the magnesium content in the brine is precipitated in the form of magnesium hydroxide, and an effluent solution containing ammonium hydroxide and ammonium carbonate is produced [1]. The recovery of ammonia from this effluent is also considered a challenge because of the limited recovery efficiency and high energy consumption associated with the release of ammonia gas from the treated solution.

This work aims to recover ammonia from brine effluents which contain ammonia in different forms, such as ammonium chloride, ammonium hydroxide or ammonium carbonate. The recovery method is based on the Solvay process by adding calcium oxide without the need of high energy input. Ammonia stripping from the highly ammoniated brine solution is combined with chemical dissociation using calcium oxide (CaO) and electrochemical treatment using a closed electrocoagulation cell at a moderate reaction temperature in the range of 23 °C to 43 °C. The outcomes of the proposed new method could have a significant impact on the recovery of the ammonia content not only from Solvay effluents but also from landfill leachates and different wastewater sources. This method also has economic benefits in the recovery of ammonia and the reduction of the energy requirement for such processes. In addition, the presence of ammonia in wastewater represents a major environmental challenge, as it can cause toxicity to living organisms in soil or water bodies, and can decrease the concentration of dissolved oxygen. Overall, this study proposes an alternative ammonia-recovery method using electrocoagulation and chemical dissociation in a single step.

2. Materials and Methods

2.1. Thermodynamic Evaluation for the Recovery of Ammonium Chloride

The common ammonium chloride recovery method involves the reaction of a hot solution with CaO at temperatures of 160°C–230°C [38]. CaO makes a strong basic solution, and the released ammonia gas is recycled and used again in the initial step of the Solvay process according to the chemical reaction given below:

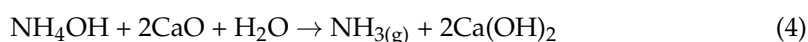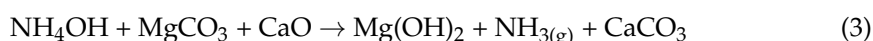$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_{3(g)} + 2H_2O + CaCl_2 \tag{1}$$
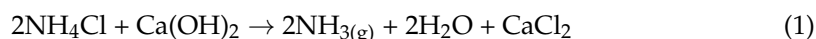
The thermal energy consumed in this chemical recovery process is high, and for each mole of recovered ammonia, 0.5 moles of CaO are required. In order to evaluate the Gibbs free energy (ΔG) and heat of reactions (ΔHs) for the previous reaction at different temperatures, a thermodynamic analysis was performed (Reaction 1) using a chemical reaction and equilibrium software package (HSC Chemistry).

2.2. Thermodynamic Evaluation for the Recovery of Ammonium Hydroxide/Carbonate

The ammonia solution (NH_4OH) which was added to the high-salinity brine reacted with magnesium carbonate ($MgCO_3$), which is a major component of the rejected brine. The magnesium reacted with the ammonia, yielding a mixture of ammonium bicarbonate and magnesium hydroxide [1], as given by the following reaction:

$$NH_3 + 2H_2O + MgCO_3 \rightarrow NH_4HCO_3 + Mg(OH)_2 \tag{2}$$

However, not all of the ammonia reacted because it was added in excess in order to maintain a high pH value to ensure high magnesium recovery. Ammonium hydroxide and bicarbonate were recovered by adding CaO to the mixture to release ammonia as a gas according to the following reactions:

$$NH_4OH + MgCO_3 + CaO \rightarrow Mg(OH)_2 + NH_{3(g)} + CaCO_3 \tag{3}$$

$$NH_4OH + 2CaO + H_2O \rightarrow NH_{3(g)} + 2Ca(OH)_2 \tag{4}$$

Reaction 3 represents the reacted ammonia, and Reaction 4 represents the free unreacted (excess) ammonia. In order to evaluate the ΔG and ΔHs for each reaction at different temperatures, a thermodynamic analysis of the previous Reactions (3 and 4) was performed using the HSC software package.

2.3. The Preparation of the Ammonium Hydroxide/Carbonate Effluent Solution Based on the Magnesium Recovery Process

In the evaluation of the ammonia recovery from ammoniated brine, real high-salinity reject brine samples (same source, three replicates) were collected from a real multi-stage distillation process. The reject brine samples had salinity and magnesium contents of $73{,}540 \pm 18$ mg/L and 2974 ± 9 mg/L, respectively. The brine sample was mixed with an excess amount (2.65 mol./l) of ammonium hydroxide solution (25% wt.). Then, a filtration process was performed to recover all of the solids in the form of magnesium hydroxide. For the determination of the feasibility of ammonia recovery from ammonium hydroxide/bicarbonate, CaO was added at 1–2 wt.% to the filtrate, which was then introduced to an electrocoagulation cell and treated for 4 h. The decrease in the ammonia concentration was measured using a HACH-Intellical™ ISENH3181 ammonia ion-selective electrode, Loveland, Colorado; as for the nitrogen (N) concentration, it could easily be referred to as the NH_4OH, NH_4Cl or NH_4HCO_3 concentration. Ammonia Ionic Strength Adjustor (ISA) Powder was used as a regent, which was added to the tested sample. Different concentrations of CaO were used. The electrocoagulation process was performed at room temperature and at different current densities.

A comparison between the common method to recover the ammonia based on Reaction 2 and Reaction 3 at different temperatures was conducted with the chemical dissociation inside the electrocoagulation cell in the presence of CaO in order to compare the ammonia efficiency for both process and the required time for the maximum removal efficiency.

### 2.4. The Preparation of the Ammonium Chloride Effluent Solution Based on the Solvay Process

The method described in this work was evaluated for ammonia recovery from ammonium chloride in a Solvay effluent, wherein a portion of the filtrate from the previous experimental step was reacted with carbon dioxide (CO_2) gas (10% vol. and balance air) in a bubble column reactor which was fabricated for previous studies [34,37,39–42]. The reaction was run for 24 h in order to ensure the formation of the maximum concentration of ammonium chloride. Then, a filtration step was performed to recover all of the sodium bicarbonate products. Afterwards, the Solvay effluent was mixed with CaO at 7.4 wt.%, which represents the stoichiometric molar ratio for the recovery of ammonia from ammonium chloride. The mixture was then introduced to the electrocoagulation cell and treated for 9 h. The reduction in the ammonia concentration was measured using the same ammonia-ion-selective electrode mentioned in the previous section. Different concentrations of CaO and current densities were tested at room temperature.

In addition, a comparison between the common method to recover the ammonia based on Reaction (1) at a high temperature of 160 °C and the chemical dissociation inside the electrocoagulation cell (at a temperature range of 23 °C to 43 °C) was conducted in order to evaluate the performance of each process.

2.5. Experimental Setup

The ammonia stripping in the presence of CaO inside the electrocoagulation cell involves passing an electric current through aluminum electrodes to initiate the following cathodic and anodic chemical reactions:
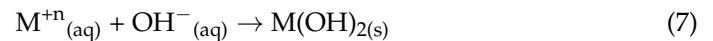
- The anode dissolution, which results in aluminum (metal) electrode ions $M^{+n}_{(aq)}$:

$$M_{(s)} \rightarrow M^{+n}_{(aq)} + ne^- \tag{5}$$
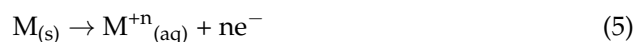
- Water electrolysis, which results in the generation of hydrogen gas and hydroxide ions:

$$2H_2O_{(aq)} + 2e^- \rightarrow H_{2(g)} + 2OH^- \tag{6}$$
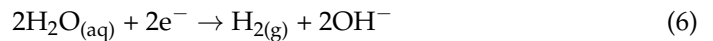
- The first step of the coagulant formation in its initial form:

$$M^{+n}_{(aq)} + OH^-_{(aq)} \rightarrow M(OH)_{2(s)} \tag{7}$$

During electrocoagulation EC, the reduction reactions at the cathode result in the formation of ammonia gas, as shown in Equation (8), and that is the main process for the removal of ammonium ions (NH^{4+}), which is the same equation found by Frank Jirsa for the electrolysis of aqueous solutions of ammonium iodide (1950) [43].

$$2NH^{4+} + 2e^- \rightarrow 2NH_{3(g)} + H_{2(g)} \tag{8}$$
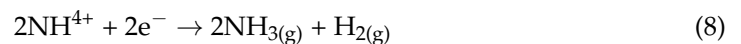
The closed electrocoagulation cell, shown in Figure 1, comprises two vertical Plexiglas cylinders with a total height of 135 mm, and an inner cylinder with an internal diameter of 145 mm. The mixture of the Solvay effluent and CaO is treated in the inner cylinder. The outer cylinder is considered a jacket for the inner cylinder, wherein water is circulated to control the reaction temperature. The total working volume of the inner cylinder is 1000 mL. In order to ensure a uniform liquid velocity distribution between the electrodes, an air jet with a flow rate of 100–300 mL/min was introduced through a tube extending to the bottom of the cell. In order to eliminate any bulk circulation, a magnetic stirrer trapped within the Plexiglas ring (ID: 50 mm, H: 10 mm) with a velocity of 120 rpm was placed at the center of the cell to enhance the mixing inside the reactor. Furthermore, rectangular aluminum plates with 55-mm width, 135-mm length, and 2.0-mm thickness were used as electrodes for the electrocoagulation reactor, and were inserted into the top base of the inner cylinder. The space between the two electrodes was 50 mm, and they were connected to a power supply to deliver the required voltage (1–4 V). In the center of the inner cylinder cover, two tubes were inserted, where one extended to the bottom of the reactor to provide the air jet, and the other extended to a level over the treated mixture to vent the accumulated gases out of the reactor, thus preventing the liquid mixture from leaving the reactor. The cover of the inner cylinder was tightly closed, and a silicone rap was used to prevent gas leakages from the edges. The electrocoagulation reaction starts at room temperature (22–25 °C), and then the temperature increases with time to reach 38–43 °C depending on the applied current density and calcium oxide concentration. Figure 1 presents a schematic of the closed electrocoagulation reactor. The effect of the temperature on ammonia removal was investigated using the electrocoagulation process for 1 h, and without the electrocoagulation process for 4 h.

In all of the experiments, the reactor was filled with a total volume of 250 mL of the treated mixture. The applied current and voltage were kept fixed for each experiment, and the temperature was controlled for each run at a specific value. After each run, the treated brine samples were collected and then filtered using a Buchner funnel filtering kit to separate the solid coagulants. A gas outlet tube (ammonia gas) was inserted into 50 mL deionized water at a controlled temperature and then analyzed at the end of each run for the recovered ammonia concentration. The following table (Table 2) shows the experimental design for the recovery of the ammonia from both ammonium chloride and ammonium hydroxide/bicarbonate solutions. The ranges of the selected current densities are in with agreement with a previous study reported by Osman et al. [20].
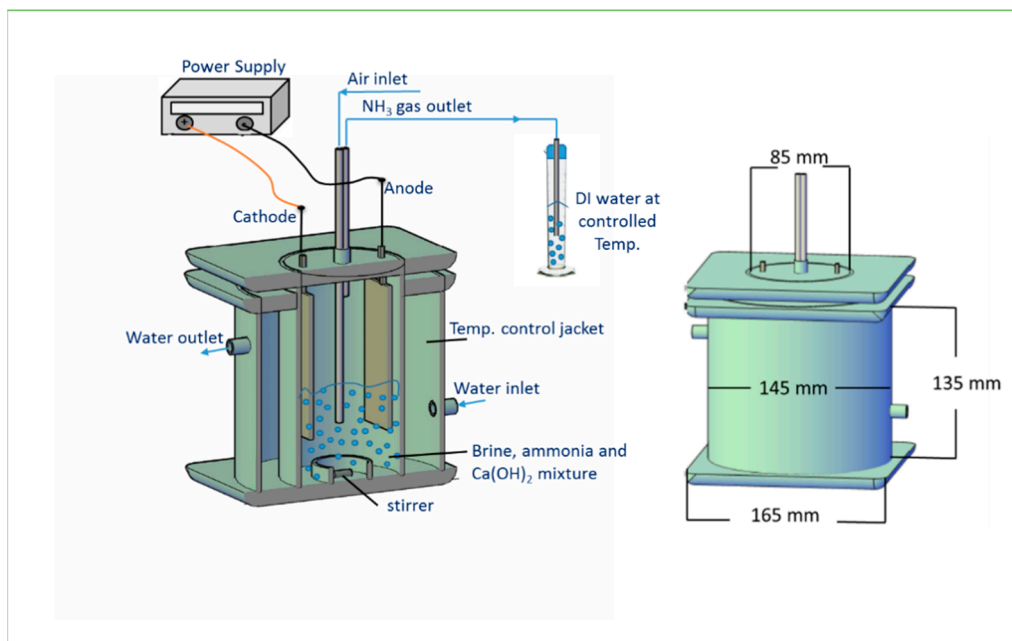
Figure 1. Schematic view of the closed electrocoagulation (EC) cell for ammonia recovery from ammonium chloride in the Solvay effluent.

Table 2. Experimental design for the ammonia recovery from the ammonium chloride and hydroxide/bicarbonate solutions.

# of EXP.	Applying EC	Run Time (h)	Temperature (°C)	Current Density mA/cm^2	Calcium Hydroxide CaOH g/l
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# of EXP.	Applying EC	Run Time (h)	Temperature (°C)	Current Density mA/cm^2	Calcium Hydroxide CaOH g/l
		Recovery the Ammonia from Ammonium Chloride Solution			
1	Yes	9	38–43	9.8	20
2	Yes	9	38–43	9.8	40
3	Yes	9	38–43	9.8	74
4	No	9	23–35	9.8	20
5	Yes	9	38–43	9.8	20
6	No	9	155–170	9.8	74
7	Yes	9	38–47	9.8	74
		Recovering the ammonia from ammonium hydroxide/bicarbonate			
8	Yes	4	37–40	1.9	0
9	Yes	4	37–40	4.9	0
10	Yes	4	37–40	9.8	0
11	Yes	4	37–40	14.7	0
12	Yes	4	37–40	19.6	0
13	Yes	4	37–40	1.9	20
14	Yes	4	37–40	4.9	20
15	Yes	4	37–40	9.8	20
16	Yes	4	37–40	14.7	20
17	Yes	4	37–40	19.6	20
18	Yes	1	37–40	9.8	20
19	Yes	1	40	9.8	20
20	Yes	1	60	9.8	20
21	Yes	1	80	9.8	20
22	No	4	37–40	9.8	20
23	No	4	40	9.8	20
24	No	4	60	9.8	20
25	No	4	80	9.8	20

3. Results and Discussion

3.1. Thermodynamic Analysis for the Recovery of Ammonium Chloride from Ammoniated Brine

The analysis for Reaction (1) is shown in Figure 2, which indicates that the reaction is endothermic with a positive ΔH value, and that it is spontaneous at temperatures >160°C, as indicated by the negative ΔG slope in Figure 2. Based on these findings, the electrochemical step using an electrocoagulation step was introduced to replace the heating parameter with the electrochemical striping of ammonia at moderate/room temperature.
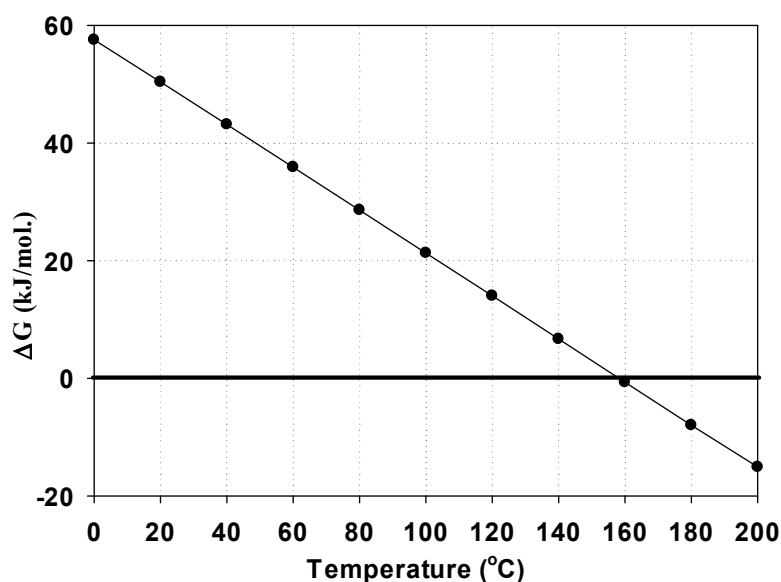

Figure 2. Calculated Gibbs free energy (ΔG) versus the temperature for Reaction (1) using the HSC software at atmospheric pressure and a stoichiometric ratio.

3.2. Thermodynamic Analysis for the Recovery of Ammonium Hydroxide/Carbonate

A thermodynamic analysis of Reactions 3 and 4 was performed, revealing that both reactions are spontaneous, as indicated by the negative ΔG values, and exothermic, as indicated by the negative ΔH values (Figures 3 and 4).

Figure 3. Calculated heat of the reaction (ΔH), Gibbs free energy (ΔG), and entropy (ΔS) versus the temperature of Reaction (3) using the HSC software, at atmospheric pressure and a stoichiometric ratio.
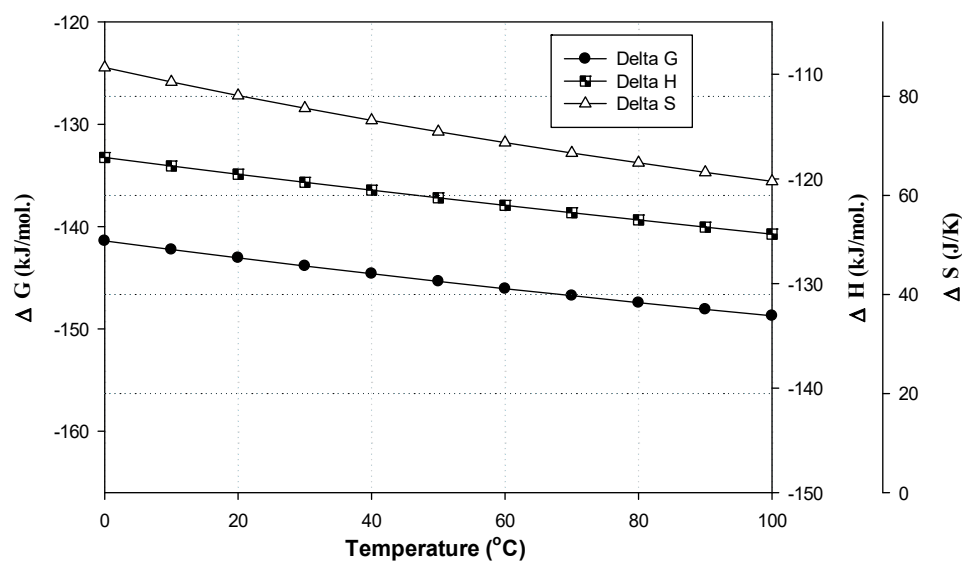
Figure 4. Calculated heat of the reaction (ΔH), Gibbs free energy (ΔG) and entropy (ΔS) versus the temperature of Reaction (4) using the HSC software, at atmospheric pressure and a stoichiometric ratio.
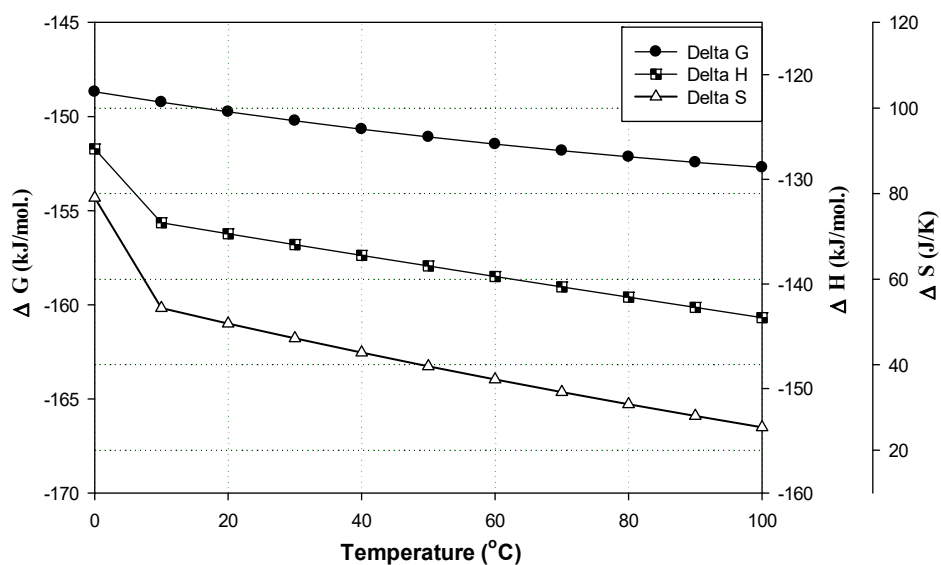
The thermodynamic analysis did not consider the presence of other components in the brine, such as sodium, calcium, potassium, or sulfate. Accordingly, several side reactions would decrease the efficiency of the desired process. However, the application of the electrocoagulation process at high pH values provides sufficient anodic potential, generating electrons that combine with ammonium ions at the cathode, thus generating ammonia gas. Accordingly, using the electrocoagulation process will even decrease the stoichiometric ratio of CaO as a reactant to reach the required ammonia recovery level, or to decrease the required energy (heating) to reach the dissociation point of ammonia gas, thus decreasing the operation cost of the process.

3.3. Ammonia Recovery from the Ammonium Chloride Solution

Figure 5 shows the effect of the CaO concentration on the ammonia removal percentage from the Solvay effluent with time. The results indicate that the concentration of CaO had a significant effect on the reaction time, while the high CaO concentrations increased the ammonia recovery rate.

The effect of electrocoagulation on the ammonia removal from the Solvay effluent was analyzed by comparing the removal of ammonia with the case of not using electrocoagulation at the same CaO concentration. The electrocoagulation process enhanced the removal percentage by ~80% in the same period, as shown in Figure 6.
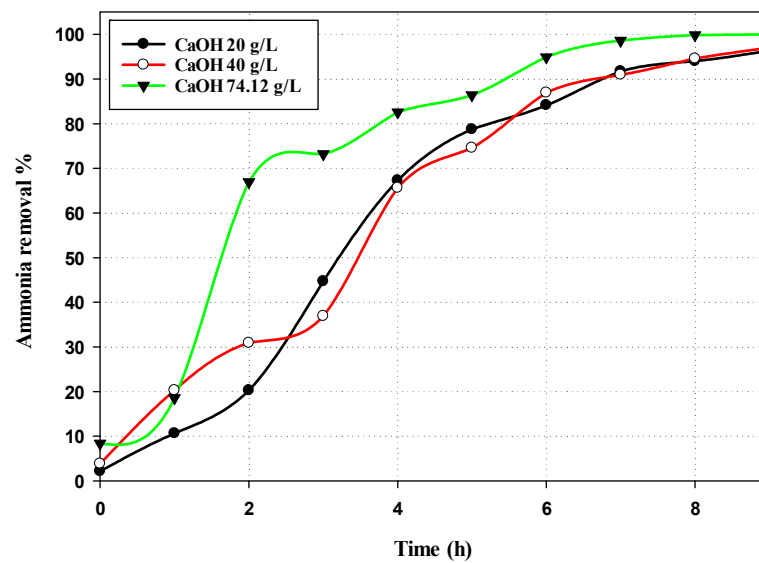
Figure 5. Ammonia removal percentage versus time for different CaO concentrations using the EC process at room temperature and a current density of 9.8 mA/cm^2.
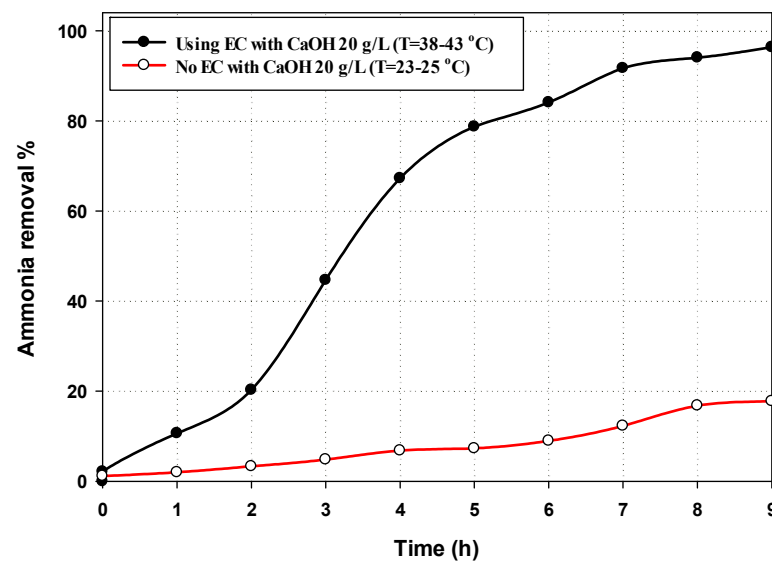

Figure 6. Ammonia removal percentage versus time with and without the EC process, at the same CaO concentration (20 g/l) and current density (9.8 mA/cm^2).

The decrease in the ammonia concentration in the Solvay effluent was tested using a common process that includes adding a stoichiometric quantity of CaO and increasing the solution temperature up to 160 °C. The results were compared with those of the proposed method by adding the same quantity of CaO and using electrocoagulation with a current density of 9.8 mA/cm^2 at room temperature. The results, shown in Figure 7, indicate that most of the ammonia was removed from the Solvay effluent after 4 h for the process without electrocoagulation, and after 7 h for the electrocoagulation process. Moreover, these results indicate a high potential for the use of the electrocoagulation process for ammonia recovery from ammonium chloride, and they encourage further method optimization.
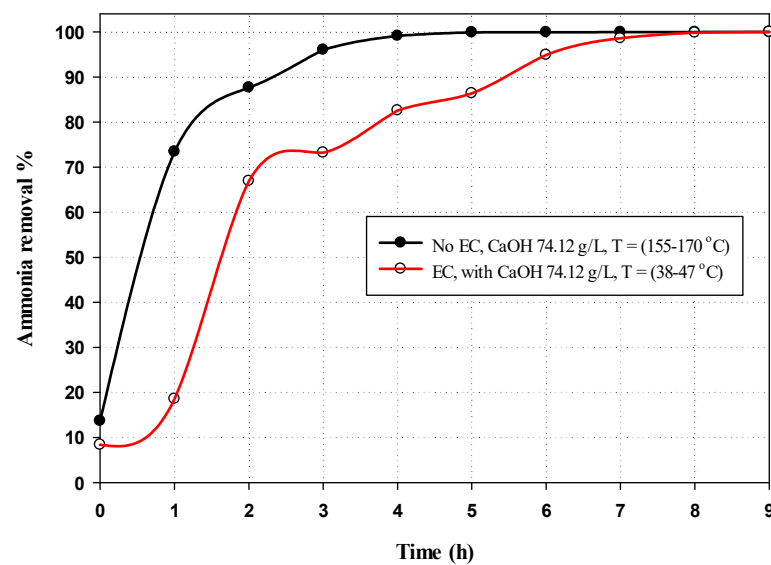
Figure 7. Ammonia removal percentage versus time without (heating up to a temperature of 160 °C) and with the EC process (at 38–47 °C), at a CaO concentration of 74 g and a current density of 9.8 mA/cm^2.

The concentration of ammonia in the recovery unit (deionized water) was measured and the recovery of the ammonia was calculated based on Equation (9).

$$\text{Ammonia recovery } = \frac{NH_3 \text{ mass in the deionized water}}{NH_3 \text{ mass in the feed solution}} \times 100\% \qquad (9)$$

It was observed that the electrocoagulation process could recover ~80% of the ammonia as ammonium hydroxide. In addition, the energy required for the electrocoagulation process in the mentioned conditions was found to be only 2.3 kWh/kg NH$_3$ based on the current density consumed within the specific electrochemical reaction time; thus, the proposed process saved ~80% of the consumed energy in the step of the ammonia disassociation from the Solvay effluent solution alone. Table 3 summarizes the main findings of the comparison study.

Table 3. Comparison between the traditional method of ammonia recovery from ammonium chloride and the proposed electrocoagulation process.

	Maximum Ammonium Chloride Removal (%)	Ammonia Recovery (%)	Energy Consumption	Time Required for 95% Ammonium Chloride Removal
EC	99.99	77.14	2.301 kWh/kg NH$_3$	6 h
Heating up to 160 °C	99.99	98.06	7.77 Wh/kg NH$_3$ *	3 h

* The amount of energy consumed was calculated using the HSC software package [44] based on the heat and material balance for the tested molar ratios of Reaction (1).

3.4. Ammonia Recovery from Ammonium Hydroxide/Bicarbonate

Figure 8 indicates the positive effect of CaO on the ammonia removal, which is related to the increase in the pH level of the treated solution, where the solution with no CaO has a pH of 10.5, while the treated solution—which contains CaO—has an initial pH of 12.4. The complete removal time was found to be ~4 h in the case of the use of a CaO concentration of 20 g/l, and the solution temperature was found to increase in the range of 37–40 °C for both cases.
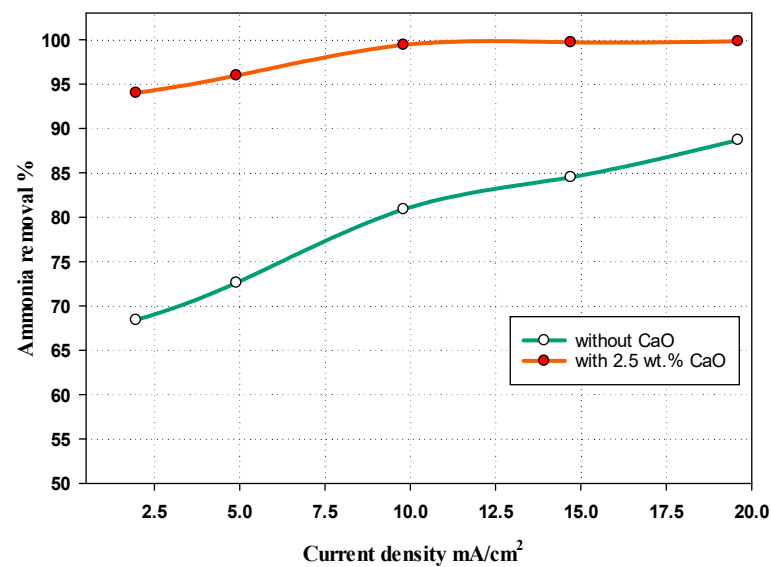
Figure 8. Ammonia removal versus current density after 4 h of electrocoagulation with and without CaO at room temperature.

The effect of the temperature on the ammonia removal showed the high ability of the electrocoagulation process, where >80% of the ammonia was removed after only 1 h at room temperature, compared with the case without the electrocoagulation process, where a high temperature (80 °C) was required to remove almost the same amount after 4 h (Figure 9).
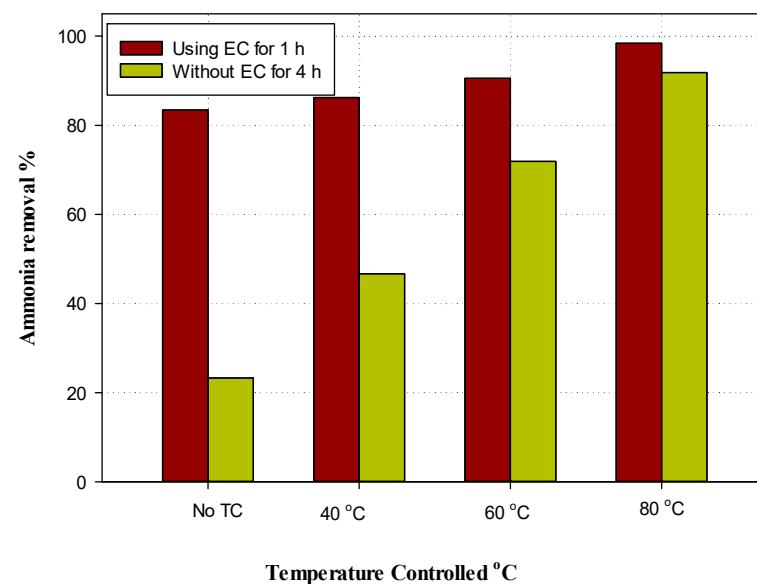

Figure 9. Ammonia removal percentage versus temperature after 1 h of EC and 4 h without EC, at a CaO concentration of 20 g/l and a current density of 9.8 mA/cm^2.

The ammonia concentration in the closed recovery unit (deionized water) for this process was measured, and the ammonia recovery percentage was calculated. The effect of the presence of CaO on the recovered ammonia percentage at different current densities was studied. It was found that the ammonia recovery from the ammonium hydroxide solution using the electrocoagulation process and a CaO concentration of 20 g/l reached up to 70.8% at a current density of 24.5 mA/cm^2 after 4 h. However, up to 46.7% ammonia recovery was reached at the same current density and treatment time without using CaO. Notably, the CaO concentration is considered to be a significant factor, and using higher

CaO concentrations can improve the process. However, further processes are required to recover the calcium content from the treated solution.

Based on these results, the proposed method is very promising for the removal and recovery of ammonia from any contaminated water body. The ammonia removal efficiency based on the proposed method competes very well with the traditional methods, such as ammonia air stripping and membrane distillation processes. In addition, the energy consumption is a significant factor that promotes the proposed method compared to the high energy consumption methods, such as atmospheric and vacuum distillation. The reasonable capital cost for the EC unit is also preferable compared with the high capital cost methods, such as membrane contactors processes.

4. Conclusions

In the present work, CaO was added to ammoniated brine, which uses a high concentration of ammonium chloride/hydroxide/carbonate, at 2.5–7.5 wt.%, to obtain a solution with high pH (~12). The mixture was then fed into a closed electrocoagulation cell, and a current was applied with a specific density to enhance the dissociation of ammonia from the solution at a much lower temperature compared with the conventional heating method. Moreover, air bubbling was applied through the mixture at a low gas flow rate of 100–300 mL/min to enhance the ammonia stripping from the mixture, where the treating cell has one air inlet and one ammonia gas outlet. The electrocoagulation process was applied to the treatment cell using aluminum electrodes and a current density of 5–15 mA/cm^2. In the case of ammonia recovery from ammonium chloride, 7 h of treatment was needed using the electrocoagulation cell to reach a high ammonia reduction compared to the initial concentration in a Solvay effluent of 13,700 to 190 mg/L N. Furthermore, after ~9 h, the removal efficiency of the ammonium chloride from the Solvay effluent reached up to 99%, with an ammonia recovery of 77.1% in the form of ammonium hydroxide. Generally, this process—conducted at moderate temperatures—can result in an energy reduction of 80%, from 7.8 to 2.3 kWh/kg NH$_3$, compared to conventional processes, which entail heating the Solvay effluents to 160°C.

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