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DUAL ALKALI APPROACHES FOR THE CAPTURE AND SEPARATION OF CO₂

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Abstract

The Solvay process utilizes two alkalis in sequential order to convert CO₂ to sodium carbonate for commercial use. The ability to transform CO₂ into sodium carbonate cost-effectively would be a breakthrough in CO₂ sequestration by providing benign long-term storage of CO₂. However, the Solvay process was not designed for CO₂ sequestration and is not practical for use in the sequestration of CO₂ from fossil fuel power plants. This paper investigates methods to modify the process in order to make it effective for the control of power plant CO₂ emissions. The new modified process, called the Dual Alkali Approach, attempts to replace either or both bases, ammonia and lime, in the Solvay process with other compounds to make CO₂ capture and separation efficient. Ammonia was replaced with different amines in aqueous solutions of salts and it was found that bicarbonate precipitation did occur. A method to regenerate the amine in the second step has not been implemented. However, the second step in Solvay Process has been implemented without using lime, namely, ammonia has been regenerated from an ammonium chloride solution using activated carbon. The HCl adsorbed in the activated carbon was removed by water to regenerate the activated carbon.

Introduction

Existing techniques to sequester CO₂ from stationary power plants involve two steps. The first step uses an amine, as an alkali, to capture CO₂ from flue gas. The captured CO₂ is then stripped by steam at high temperatures. In the second step, the concentrated CO₂ gas is pressurized to supercritical CO₂ liquid and disposed of in geologic formations and/or the deep ocean. Although the pressurization of CO₂ is energy intensive, the first step accounts for two thirds to three fourths of the entire cost. In addition to the energy required for both steps, when large amounts of SO₂ and NO_x are present in the flue gas reagent loss also occurs. The reagent loss arises due to the formation of heat stable salts such as amine sulfates and nitrates. As well as the extensive energy required to implement existing CO₂ sequestration techniques, there are also ecological concerns regarding the consequences of storing CO₂ in the ocean and in geological formations.

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An alternative approach is the conversion of CO₂ to carbonate salts that can be safely returned to the environment. Weathering of alkaline rocks is a natural method of CO₂ sequestration. To enhance the rate of this natural process, Kojima et al.¹ suggested that alkaline minerals could be pulverized, dissolved, and reacted with power plant CO₂ to form magnesium and calcium carbonates. Lackner et al.² has extensively investigated the thermodynamics and processes of using chlorides to accelerate the carbonate formation from various minerals, including Serpentine and Peridotites. Rau et al.³ used a CO₂ reactor to enhance carbonate dissolution for disposal of CO₂ as a bicarbonate. Shibata et al.⁴ investigated an approach to convert CO₂ to bicarbonate by using water insoluble organic amines followed by an extraction step with aqueous organic solvents.

Expanding on previous research on the conversion of CO₂ to benign carbonate, this paper investigates methods to modify the Solvay process in order to make it effective for use in the utility industry to convert CO₂ to bicarbonate. The Solvay process, employing a dual alkali approach, uses ammonia as a catalyst to aid the reaction of CO₂ with sodium chloride for the production of sodium carbonate. The reaction was performed by first saturating brine with ammonia, and then with carbon dioxide.

Following the reaction, sodium bicarbonate, which is fairly insoluble, was separated by filtration. Sodium carbonate was subsequently obtained by heating sodium bicarbonate. The ammonia was recovered by reacting ammonium chloride with lime, Ca(OH)₂, where limestone serves as the source of lime.

However, this scheme poses several drawbacks when applied to power plants. Among others, the use of limestone for the regeneration of ammonia renders the process ineffective mainly because of the consumption of limestone, production of CO₂ and extensive energy requirement during calcination. In the Solvay process, for every two moles of CO₂ from power plants captured, one mole of CO₂ from calcination of limestone is released:

To circumvent the drawbacks of the Solvay process and develop a new dual alkali method for CO₂ sequestration, different alkalis must be tested for both steps of the dual alkali approach. Then the ideal combination can be found. Alkali used in the two steps of the approach have different purposes. The current research investigates whether the use of amines as a primary alkali can precipitate bicarbonate, the effect of salt on CO₂ absorption by amine solutions, the use of

activated carbon as a secondary alkali and activated carbon's ability to be regenerated.

Experimental Section

Materials. Methylaminoethanol (MAE, minimum 98%, Sigma Co.), Monoethanolamine (MEA, minimum 98%, Aldrich Co.), Sodium Chloride (NaCl, minimum 99.0%, Sigma Co.), CO₂ (10%, with N₂ as balance, Baygas Co.), Ammonium Chloride (minimum 99.5%, Sigma Co.), Hydrochloric Acid (36.5%, VWR Scientific Co.), Activated Carbon (F-300, Calgon Co.) with a Langmuir surface area of 800 m²/g (determined by Micromeritics ASAP 2010 analyzer).

Capacity of CO₂ Absorption. To determine the CO₂ absorption capacity, a CO₂ (10%) feed gas was passed through a bubbling absorption reactor (50 mm in diameter) with a sintered bottom at a flow rate of 230 ml/min at atmospheric pressure. In one of two different experiments the reactor contained a 200 ml amine solution and in the other experiment the reactor contained a 200 ml amine/salt mixtures. The temperature was controlled at 298 °K by a water bath thermostat. A cold trap was employed to eliminate moisture in the CO₂ gas stream coming out of the reactor. The change in the concentration of CO₂ with time was monitored by a FT-IR spectrometer (Model 1605, Perkin-Elmer Co.) with a 10-cm light pass gas cell. The amount of CO₂ absorbed was calculated using a concentration vs. time curve.

Rate of CO₂ Absorption. The experimental apparatus is the same as that given in Shi, Littlejohn, and Chang⁵. A CO₂ gas (10%) was saturated by bubbling the gas in deionized water at a rate of 1 L/min at atmospheric pressure. The gas then passed through a double stirred absorption reactor. The reactor had a diameter of 80mm and was equipped with four vertical baffles and two stirring blades. The baffles and stirring blades were independent of each other and driven by separate motors to agitate the gas and liquid phases at 900 rpm and 150 rpm, respectively. The temperature of the reactor was held constant at 298 °K with a water bath thermostat. Following the reactor, the gas was passed through a cold trap to eliminate moisture. The outlet concentration of CO₂ was measured by a FT-IR spectrometer. The absorption rates were then derived from the difference between the outlet and inlet concentrations of CO₂, the flow rate, and the area of the contact surface.

Regeneration of Ammonia from Ammonium Chloride by Activated Carbon. A peristaltic pump (Minipus 2, Gilson Co.) was utilized to pump an ammonium chloride solution through a water-jacketed chromatographic column (CHROMAFLEX, i.d.: 1 cm, length: 25 cm, Kontes Co.) at a flow rate of 1 ml/min. The column contained activated carbon (F-300, Calgon Co.) saturated by water. The temperature of the column was 298°K as controlled by a thermostat. Ten ml of eluent was then collected in a series of 10 ml volumetric flasks. A digital pH meter (Model 05669-20, Cole-Parmer Co.) with a combination probe was employed to measure the pH of the samples. The concentrations of ammonium and chloride in the samples were determined by Ion Chromatography (2020i, Dionex Co.). A cation separation column [CS-12 (10-32), Dionex Co.] and a

suppressor (CMMS-II, Dionex Co.) were used to determine ammonium concentrations. The eluent containing Na₂CO₃ (2mM) and NaOH (1mM), and H₂SO₄ (0.025M) was used as a regenerant. For the determination of chloride ion, an anion separation column (AS-5, Dionex Co.) and a suppressor (AMMS-II, Dionex Co.) were utilized with HCl (9mM) as an eluent and Tetrabutylammonium hydroxide (10mM) as a regenerant.

Adsorption of HCl from NH₄Cl and HCl solutions. Adsorption rates and equilibrium isotherms were obtained by using an Erlenmeyer flask with 100 ml of various concentrations of ammonium chloride ranging from 0.5 ~ 4 mM. Two grams of activated carbon were then added to the mixture and stirred constantly at 800 rpm by a magnetic stir bar at ambient temperature (298 °K). Aliquots were withdrawn at an interval of 5 min and were filtered by 0.2 µM Poly Pure Filters (Alltech Co.). The resulting liquid was then injected into an ion chromatography instrument to determine the chloride concentrations. The adsorption reaction was terminated after 3 hours. The concentration of hydrochloric acid adsorbed onto activated carbon was calculated by the difference between the concentration of ammonium, which remained unchanged during the reaction, and chloride. The adsorption rate of the reaction between activated carbon and ammonium chloride was estimated by the change in HCl concentration adsorbed on the activated carbon within the first 5 min. The amount of HCl adsorbed per gram of activated carbon, Q mmole/g, was calculated using the following equation:

$$Q = V \cdot \Delta C / W \quad (5)$$

where, V, ΔC, and W are the solution volume (L), the change in chloride concentration (mM), and the weight of adsorbent (g), respectively. The isotherm was then graphed by plotting Q vs. C_e where C_e is the equilibrium concentration of ammonium chloride, which is equal to the concentration of chloride in the solution at the final equilibrium of the reaction (Figure 6).

In addition to isotherms, adsorption enthalpies were measured using a 1.2-liter water-jacketed reactor with a reflux distillation tube, which prevented steam from being released into the atmosphere. The adsorption enthalpy of HCl by AC from ammonium chloride was determined by using a mixture of activated carbon (10g) and ammonium chloride solution (500mL at 2mM). The solution was mixed with a magnetic stir bar at 800 rpm and allowed to react at different temperatures (298, 313, 333, 353°K) until equilibrium was reached (~3 hours). Aliquots were withdrawn and the concentration of ammonium chloride was measured by Ion Chromatography.

Then the adsorption enthalpy of HCl by AC from an HCl solution was determined. The experimental setup was similar to those used for the adsorption enthalpy of HCl by AC from NH₄Cl solution. However, the solution was comprised of 500 mL of 2 mM HCl solution mixed with 10 g of AC. In addition, the temperature range studied increased by 20 °K, the highest temperature studied being 373 °K. The adsorption enthalpy, ΔH°, was then calculated by using the following equation⁶:

$$\ln(Q/C_e) = - \Delta H^\circ / (RT) + [(\Delta S^\circ / R) - \ln \psi] \quad (6)$$

Where ΔS° , ψ , R , T are standard entropy of adsorption (kcal/mole), solute activity coefficient, universal gas law constant ($\text{kcal}\cdot\text{g}\cdot\text{mole}^{-1}\cdot\text{K}^{-1}$), and absolute temperature ($^\circ\text{K}$), respectively. Assuming that ΔH° , ΔS° , and ψ are constant over the temperature range of study, ΔH° can then be calculated from the slope of the line given by plotting $\ln(Q/C_e)$ vs. $1/T$ (Figure 7).

Desorption of HCl from AC. To study the desorption of HCl from AC, 10 grams of activated carbon was added to 500 ml of 2 mM HCl solution. After the adsorption reached equilibrium, the activated carbon was filtered. The chloride concentration in the filtrate was determined by ion chromatography to obtain the amount of HCl adsorbed on activated carbon. The resultant activated carbon was mixed with either 500 ml of cold or boiling water and stirred constantly at 800 rpm with a magnetic stir bar. Aliquots were withdrawn at an interval of 30 min or longer and were filtered by 0.2 μ Poly Pure Filters (Alltech Co.). The resulting liquid was then injected into an ion chromatography instrument to determine the hydrogen chloride concentration in solution. The HCl concentration adsorbed on AC was calculated by the concentration of HCl originally adsorbed on AC minus that of HCl extracted by water. The kinetic curve was obtained by plotting HCl concentration adsorbed on AC vs. time (Figure 9).

Reusability of Activated Carbon. To demonstrate the capability of repeated use of activated carbon, 2 gram of AC was added to an Erlenmeyer flask with 100 ml of 1.3 mM HCl solution. The mixture was stirred constantly at 800 rpm. A reflux distillation tube was utilized to prevent the steam from being released into the atmosphere when the mixture was boiling. The first operation was run in cold water for 12 hours at ambient temperature for adsorption of HCl, 1 ml of aliquot was withdrawn and filtered and then injected into the ion chromatography instrument for the determination of chloride. The second operation was performed by boiling the remaining mixture to desorb the HCl adsorbed on activated carbon after reaction for 12 hours. One ml of the hot aliquot was withdrawn and filtered immediately, and analyzed by ion chromatography. The subsequent operations were run alternatively by adsorption in the same way as the first operation and by desorption in the same way as the second operation. The HCl concentration adsorbed onto activated carbon was calculated by the original HCl concentration (1.3 mM) minus the HCl concentration remaining in solution.

Results and Discussion

Absorption of CO_2 by Amine/Salt Mixtures. Although ammonia was used as a primary alkali in the Solvay process, it has been found that a sterically hindered amine, Methylaminoethanol (MAE), was also an effective primary alkali (Eq. 7).

A 10% CO₂ feed gas was reacted with MAE in the presence of sodium chloride at ambient temperatures resulting in the precipitation of bicarbonate. However, no bicarbonate precipitate was observed when MEA reacted with CO₂ in the presence of sodium chloride. In order to quantify the results, time dependence curves for CO₂ absorption by amines and amine/salt mixtures were recorded, as shown in Figure 1. The CO₂ absorption capacities of MEA, MEA/NaCl, MAE and MAE/NaCl were estimated to be 0.58, 0.58, 0.75 and 0.92 mole CO₂ per mole of amine.

Theoretically the maximum CO₂ absorption capacity of an amine is 0.5 if the reaction product is carbamate. On the other hand, it is 1 if the reaction product is bicarbonate. Therefore, the CO₂ absorption capacity of an amine increases with an increase of bicarbonate in the products. It has been established that the main reaction product of MEA with CO₂ is a carbamate, according to Eq. 8.

The capacity of MEA (0.58) being slightly greater than 0.5 suggests that besides the carbamate, a small portion of bicarbonate by product also exists. However, the concentration of bicarbonate in the solutions is too small to produce sodium bicarbonate precipitate when 3.4 M of sodium ions are present (the solubility product $K_{sp} = 1.25 \text{ M}^2$ at 20°C). Consequently, the addition of NaCl did not alter the amount of CO₂ absorbed by MAE solutions.

The CO₂ absorption capacity (0.75) of MAE was greater than that of MEA, indicating the presence of more bicarbonate and less carbamate in the MAE solutions than that in the MEA solutions. Further experimental results showed that an increase in MAE concentration led to a slight decrease in CO₂ absorption capacity in the absence of NaCl. Figure 2 shows that the absorption capacity peaked at 0.78 mole CO₂/mole MAE. These results can be described by an equilibrium between MAE and carbamate (Eq 9) and between carbamate and bicarbonate (Eq 10). Evidently, the increase in amine favors the production of carbamate, which results in a decrease in the CO₂ absorption capacity.

The CO₂ absorption capacity of MAE solutions when the MAE concentrations were less than 0.64 M remained unchanged with addition of 3.4 M (20%) NaCl to the solutions. This is due to the fact that the bicarbonate ions produced was not sufficient to form NaHCO₃ precipitate. As the concentration of MAE was increased to greater than 0.72 M, NaHCO₃ precipitate was observed and accompanied by an increase in CO₂ absorption. The higher the MAE concentrations, the more the CO₂ absorption capacity of MAE is (Figure 2). The CO₂ absorption capacity of a 1.2 M MAE solution increased from 0.75 to 0.92 (a 22.7% increase) with the addition of 3.4 M NaCl, while the absorption capacity of

a 0.72 M MAE solution increased from 0.76 to 0.81 (an 6.58% increase). The increase in CO₂ absorption by MAE in the presence of NaCl is attributed to the precipitation of NaHCO₃ (Eq. 11). The precipitation occurs when $[Na^+][HCO_3^-] \geq K_{sp}$. The precipitation of NaHCO₃ breaks the equilibrium between carbamate and bicarbonate in Eq. 10. As a result, the carbamate is converted to bicarbonate with a release of the free MAE. The free MAE leads to an increase in pH, which causes more CO₂ absorption. Increasing MAE concentration leads to more carbamate formation. The carbamate can subsequently decompose to produce more bicarbonate ions following the precipitation of NaHCO₃. This contributes to an increase in CO₂ absorption capacity.

Therefore, the increase of CO₂ absorption in the MAE/NaCl solutions can be attributed to the precipitation of NaHCO₃. The amount of NaHCO₃ precipitate was estimated to be 14.3 g per mole of MAE at a MAE and NaCl concentration of 1.2 M and 3.4 M, respectively. Meanwhile, the same percentage of the total MAE, measured as NaHCO₃ precipitate, is transformed into MAE chloride. It is expected that more NaHCO₃ precipitate will be produced with higher concentration of MAE and NaCl.

However, the presence of NaCl salt has an inhibitory effect on the reaction rate of MAE with CO₂. The higher the NaCl concentration, the more the inhibitory effect was observed (Figure 3). When the concentration of NaCl was increased from 0 to 3.4 M the absorption rate decreased by about 20% at a CO₂ concentration of 5%. This is probably due to the effect of the ionic strength. The increase in ionic strength of the solution decreased the diffusion rate and the solubility of CO₂ in the absorbent, thus decreasing the rate of the reaction.

In addition to NaCl, Na₂SO₄ and NaNO₃ are produced when SO_x and NO_x in flue gas interact with an alkaline solution containing sodium chloride. These salts also have inhibiting effects on the reaction rate of MAE with CO₂ (Figure 4). The CO₂ absorption rates decreased by about 12.5% with a CO₂ concentration of 5% when the MAE solutions contain either 0.91 M Na₂SO₄ (saturated) or 3 M NaNO₃. Thus, SO_x and NO_x in flue gas not only form heat-stable salts with amines but also decrease the absorption rate of CO₂ by MAE and MAE/sodium chloride mixtures.

The cost and supply of NaCl is critical to the present application since we are dealing with a large quantity of CO₂. The concentration⁷ of NaCl in seawater is approximately 0.46 M and is the most abundant salt available in the ocean. Brine (concentrated NaCl) can be obtained at cost of about \$5/ton based on Encyclopedia of Chemical Technology, Kirk-Othmer, Vol 21.⁸ Also, the benefit of NaCl is that only one mole is required to convert one mole of CO₂ into bicarbonate.

One possibility to avoid the inhibitory effects of NaCl on CO₂ absorption by MAE is the use of a two-step process. CO₂ absorption can be initially performed by 30% MAE in an absorber, then sodium chloride salt is added in a separate vessel to precipitate NaHCO₃.

Regeneration of Ammonia by Activated Carbon. The second step of the dual alkali approach involves a secondary alkali to regenerate the first alkali. Although a proper secondary alkali has not yet been identified to be able to regenerate MAE, it has been found that activated carbon (AC) can serve as a secondary alkaline to regenerate ammonia, the primary alkaline in the Solvay process, at ambient temperature (25°C). The purpose was to determine if activated carbon can decompose NH_4Cl and separate it into HCl and NH_3 . Experiments were performed by passing an aqueous solution of ammonium chloride ($\text{pH} = 4.7$) through a column of activated carbon and the resultant liquid was analyzed by ion chromatography. The results indicated that the liquid after the column contained more ammonium ions than chloride ions (Figure 5). The pH of the liquid also increased from 4.7 to as high as 9.5, indicating that ammonia was regenerated from the ammonium chloride solution (Eq. 12).

The basicity of the activated carbon was responsible for the adsorption of HCl molecules from NH_4Cl solution with the liberation of ammonia. The byproduct being HCl adsorbed on AC.

Further studies were done to determine the adsorption isotherm of HCl on carbon in NH_4Cl solution. The isotherm is shown in Figure 6. The amount of HCl adsorbed by AC was too small to determine by ion chromatography when the mother solution had a high concentration of ammonium chloride (3.60 mole/L).⁹ Thus, both the Freundlich and Langmuir equations were employed to predict the amount of HCl adsorbed on carbon. The parameters, K_F and n , of the Freundlich equation were determined and the equation can be expressed as $Q = 0.0399 C_e^{0.445}$, where Q and C_e refer to the adsorption capacity (mmole HCl/g AC) and chloride equilibrium concentration (mmole/L), respectively. On the other hand, by regressing $1/Q$ vs. $1/C_e$, the values for K and X_m were estimated to be 2.214 and 0.0637, respectively, and the Langmuir equation was derived to be $Q = 0.141 C_e / (1 + 2.214 C_e)$. The concentration of HCl was calculated to be 1.53 and 0.064 mmole per gram of activated carbon by the Freundlich equation and the Langmuir equation, respectively. A large discrepancy between the two results was found. Further experimentation is required to pin down this discrepancy.

The thermodynamic of the adsorption of HCl from NH_4Cl solutions by activated carbon was studied at 298, 313, 333, and 353K. The Van't Hoff plot (Figure 7) indicated that the adsorption is exothermic and releases -2.54 kcal/mole. Thus, low temperatures favor the regeneration of ammonia. Also, the kinetics of the decomposition of ammonium chloride and subsequent adsorption of hydrochloric acid by activated carbon were studied. It was observed that the adsorption reaction between NH_4Cl was rapid at the beginning, but slow down when approaching equilibrium. Final equilibrium was reached after approximately one hour. The reaction was 0.58 order with respect to the concentration of ammonium chloride (Figure 8).

Recycling of Activated Carbon. It is important to find a cost-effective method to remove the adsorbed HCl on carbon, so that the carbon can be recycled. We have studied the removal of the adsorbed HCl on carbon by water extraction.

The equilibrium between hydrochloric acid and activated carbon was studied at 298, 313, 333, 353, and 373 °K. The Van't Hoff plot revealed that the enthalpy of the adsorption of hydrochloric acid by activated carbon was -5.94 kcal/mole (Figure 7). Therefore, the enthalpy of desorption of HCl from the adsorbent is +5.94 kcal/mole, which is substantially less than that for the desorption of CO₂ from an MEA-carbamate (+17.22 kcal/mole CO₂)¹⁰. The desorption rate increased along with the increase of the temperature (Figure 9). The desorption efficiency of hydrochloric acid from activated carbon in boiling (~100 °C) and cold (20 °C) water after reaching equilibrium was found to be, respectively, 41.8% and 8.36% of the original concentrations of HCl adsorbed on the adsorbent. The desorption efficiency can be improved by about 5 folds with boiling water. The capability of a repeated use of carbon was performed. Several cycles of adsorption and desorption of HCl on carbon were demonstrated (Fig. 10), indicating carbon's regeneration capability.

Conclusion

The results obtained have demonstrated that: 1) It is feasible to capture CO₂ and directly transform it into a bicarbonate precipitate using an aqueous mixture of a steric hindered amine and a chloride, 2) It is possible to regenerate ammonia from an ammonium chloride solution using an activated carbon, and 3) The activated carbon can be regenerated by water extraction of the adsorbed HCl. An economic evaluation of the process will be performed after an optimal integrated system and condition is identified.

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References

- (1) Kojima, T.; Nagamine, A.; Ueno, N.; Uemiya, S. *Energy Convers. Mgnt.* **1997**, 38, S461-S466.
- (2) Rau, G. H.; Caldeira, K. *Energy Convers. Mgnt.* **1999**, 40, 1803-1813.
- (3) Lackner, K.S.; Wendt, C. H.; Butt, D. P.; Joyce, E. L.; Sharp, D. H. *Energy*, **1995**, 20, 1153-1170.
- (4) Shibata, J.; Mashimo, Y.; Sasamoto, N.; Matsumoto, S.; Yamamoto, H. *Chikyu Kankyo Tekio Kagaku Seisan Gijutsu Hokokusho(Janpan)*, **1996**, 3, 1-12.
- (5) Shi, Y.; Littlejohn, D.; Chang, S. G. *Ind. Eng. Chem. Res.* **1996**, 35, 1668-1672.
- (6) Dutta, M.; Baruah, R.; Dutta, N.N. *Separation and Purification Technology*, **1997**, 12, 99-108.
- (7) Demayo, A. *CRC Handbook of Chemistry and Physics*, 72th Edition; 1991-1992; Editor in Chief: Lide, D. R.; CRC Press, Inc.; 1991, pp14-10,.
- (8) Kirk-Othmer. *Encyclopedia of Chemical Technology, The Third Edition*, 1978, Vol.21, pp216.
- (9) Hou, T. P. *Manufacture of Soda with Special Reference to the Ammonia Process, A Practical Treatise*; Second Edition; American Chemical Society: Hafner Publishing Company, New York and London; 1969.
- (10) Chakma, A. *Energy Convers. Mgnt.* **1997**, 38, S51-S56.

Figure Captions

Figure 1. The effect of NaCl on the absorption capacity of MEA and MAE with and without the presence of 3.4 M NaCl.

Figure 2. The effect of MAE concentrations (0.64, 0.74, 0.89, 1.04, and 1.2 M) in the absence and presence of 3.4 M NaCl on CO₂ absorption capacity at 25°C. The CO₂ inlet concentration was 10% and flow rate was 230 ml/min, while the MAE was 200 ml.

Figure 3. The effect of NaCl on CO₂ absorption rate by MAE at 25°C. The absorbent contained 310 ml of MAE (2.50 M) with 0, 0.85, 1.7, 2.55 and 3.4 M NaCl. The CO₂ flow rate was 1 L/min and at various concentrations.

Figure 4. The effect of NaNO₃ (3 M) and Na₂SO₄ (0.91 M, saturated) on MAE's CO₂ absorption rate at 25°C. The absorbent was 310 ml of 3.75 M MAE with and without salt. The CO₂ flow rate was 1 L/min.

Figure 5. Regeneration of ammonia from ammonium chloride by the adsorption of hydrochloric acid onto activated carbon. 200 ml of a 10 mM NH₄Cl solution was passed thru a column containing 10g activated carbon at 25°C. The flow rate of the solution was 1 ml/min.

Figure 6. An isotherm of the adsorption of HCl by activated carbon from NH₄Cl at 25°C. The mixture was prepared by combining 2 g of AC and 100 ml of NH₄Cl solution at 0.5, 1, 2, 3, and 4 mM.

Figure 7. Van't Hoff plots for the adsorption of HCl from NH₄Cl and HCl solutions by activated carbon. One mixture contained 10 g of AC and 500 ml of 2 mM NH₄Cl solution. The temperatures studied were 293, 313, 333, and 353 °K. The other mixture was composed of 10 g of AC and 500 ml of 2 mM HCl solution, and the temperatures were 298, 313, 333, 353, and 373°K. The stirring speed was 800 rpm.

Figure 8. Reaction order for the adsorption of hydrochloric acid from ammonium chloride by activated carbon. The conditions are the same as those noted in Figure 6.

Figure 9. Kinetic curves for the desorption of HCl from AC in water at different temperatures. The mixture contained 10 g of a HCl adsorbed activated carbon and 500 ml deionized water. The stirring speed was 800 rpm.

Figure 10. The capability of repeated uses of an activated carbon for adsorption and desorption of HCl were demonstrated. The mixture contains 2 g activated carbon and 100 ml of 1.3 mM HCl.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 10