Optimization of a Solvay-Based Approach for CO_2 Capture

Ameera F. Mohammad, Muftah H. El-Naas, Mabruk I. Suleiman, and Mohamed Al Musharfy

***Abstract*—The present work optimizes the CO_2 capture based on the Solvay process, where carbon dioxide is passed into ammoniated brine and reacts with sodium chloride to form a precipitate of sodium bicarbonate and a soluble ammonium chloride. The process has the dual benefit of decreasing sodium concentration in the reject brine and reducing carbon dioxide emissions to the atmosphere. Process parameters were studied in a semi-batch reactor to determine their effect on CO_2 capture efficiency and ions removal. The optimum conditions for maximum CO_2 capture efficiency and ions removal have been determined using response surface methodology. The optimum CO_2 capture efficiency and ions removal was found to be at temperature of about 19 ^oC, a gas flow rate of 1.54 L/min, and a molar ratio of 3.3NH_3:1NaCl. The CO_2 capture efficiency in 180 min was equal to 86% and the maximum sodium removal was 33%. These results indicated the technical feasibility of the Solvay approach for the capture of CO_2 through reactions with desalination reject brine.**

***Index Terms*—Desalination reject brine, CO_2 capture, sodium bicarbonate, sodium removal, Solvay process.**

I. Introduction

Carbon dioxide is the most widespread greenhouse gas that traps heat and raises the global temperature, contributing to climate change. Existing techniques to sequester carbon dioxide have numerous environmental concerns and usually require extensive amount of energy. Brine management is another environmental concern, as many desalination plants need to find suitable approaches for the treatment or disposal of the large amounts of concentrated brine, resulting from the desalination processes. Many conventional methods are used such as disposal through deep well injection, land disposal and evaporation ponds. However these methods still suffer from many drawbacks. An alternative approach is to further process the brine to extract all the salts through reactions with carbon dioxide. The chemical reaction of reject brine with carbon dioxide is believed to be a new effective, economic and environmental friendly approach [1]. The chemical reactions are carried out based on Solvay process to convert the reject brine into useful and reusable solid product (sodium bicarbonate). At the same time, the treated water can be used for irrigation and other industrial applications. Another advantage is capturing CO_2 gas from the industrial exhaust or flue gases. Solvay process is initially developed for the manufacture of sodium carbonate, where a concentrated brine solution is reacted with ammonia and carbon dioxide to form soluble ammonium bicarbonate, which reacts with the sodium chloride to form soluble ammonium chloride and a precipitate of sodium bicarbonate according to the following reactions [2]:

$$NaCl + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3 + NH_4Cl \quad (1)$$

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O \quad (2)$$

The resulting ammonium chloride can be reacted with calcium hydroxide to recover and recycle the ammonia according to the following reaction:

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O \quad (3)$$

The overall reaction can be written as:

$$2NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2 \quad (4)$$

The ammonia is not involved in the overall reaction of the Solvay process, but it plays an important role in the intermediate reactions; it buffers the solution at a basic pH and increase the precipitation of sodium bicarbonate from the first reaction. The sodium bicarbonate ($NaHCO_3$) is the most important intermediate product in the Solvay process, where its solubility plays an important role in the success of the process. To achieve high conversion, the solubility of $NaHCO_3$ must be as low as possible, so it is very important to optimize the factors that can limit or reduce its solubility [2].

II. Materials and Methodology

A. Experimental Apparatus

The main unit of the experimental set-up is the contact reactor, which is a stainless steel jacketed, bubble column reactor (SSR), with a total working volume of 1 liter. The temperature was controlled by water circulation through the jacket. The feed gas was bubbled through the reactor, while the liquid was fed at the top of the reactor and was controlled by a piston pump. The reactor had a port for liquid sampling and drainage at the bottom. The gas effluent from the top was passed through a moisture trap then to CO_2 gas analyzer (Model 600 series, NDIR analyzers). A SCADA station was installed to control and monitor the process parameters such as: temperature, pressure, liquid level, gas flow rate and liquid flow rate.

B. Brine Samples and Other Reactants

Reject brine samples were obtained from a local desalination plant utilizing MSF desalination process. The characteristics of the brine are presented in Table I. Ammonium hydroxide (25 wt. % NH_3) was purchased from scientific progress medical and scientific equipment, UAE. A

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gas mixture of (10% CO_2 and 90% Air) was obtained from Abu Dhabi Oxygen Company, UAE.

TABLE I: CHARACTERISTICS OF THE REJECT BRINE

pH	TDS	Salinity	COD	Na^+	Mg^{+2}	K^+	Ca^{+2}
9.16	73.8 g/L	71,700 ppm	1560 ppm	23,712 ppm	2,794 ppm	762 ppm	1,375 ppm

TABLE II: RANGE AND LEVEL OF INDEPENDENT VARIABLES FOR CENTRAL COMPOSITE DESIGN RUNS

		Level				
Factors	**Units**	**-α**	**-1**	**0**	**1**	**+α**
Temperature	℃	13.2	20	30	40	46.8
Flow rate	L/min	0.659	1	1.5	2	2.341
Molar ratio	-	1.7	2	2.5	3	3.3

C. Experimental Methods

A set of screening experiments were carried out to determine the direction of the optimal domain. One factor at a time was employed in the screening step to determine the significant factors affecting ions removal and CO_2 capture. One liter of the reject brine was mixed for five minutes with ammonium hydroxide in the molar ratio of $3NH_3$:1NaCl, and the mixture was then fed to the reactor, which was operated in a semi-batch mode (batch for liquid phase and continues for gas phase) at a controlled-temperature of 20 ℃. A gas mixture CO_2 containing 10 vol. % CO_2 in air was bubbled into the reactor at a flow rate of 1 L/min for 180 minutes. Brine samples (15 ml each) were collected every 60 minutes and tested for ions (Na, Ca, Mg and K) removal using ICP (Inductively Coupled Plasma spectrometry). Meanwhile, the effluent gas was continuously passed through a moisture trap then sent to the CO_2 gas analyzer to detect the CO_2 percentage; the variation of pH with time was also measured. Factors studied in the screening step were: ammonia to sodium chloride molar ratio NH_3: NaCl, temperature, gas flow rate and reaction time. The CO_2 capture and ions removal was optimized using RSM (Response surface Methodology) in Minitab 17.0 application. The design of runs was in accordance with central composite design (CCD). The reaction time was investigated in screening study and set to be three hours, since maximum ions removal was achieved at this time. The three major effect factors which affect both CO_2 capture efficiency and ions removal were gas flow rate, temperature and ammonia to sodium chloride molar ratio; these factors were operated in the range of 0.6 to 2.3 L/min, 13.18 to 46.82 ^oC and 1.66 to $3.3NH_3$:1NaCl, respectively. The experimental conditions for central composite design (CCD) runs are presented in Table II.

III. RESULTS AND DISCUSSION

The analysis of variance in Minitab 17.0 software was used for regression analysis for the obtained data to estimate the coefficient of the regression equation. The fitted polynomial equation was expressed as 3D surface in order to visualize the relationship between the responses and experimental levels of each factor and to infer the optimum conditions. A total of 20 runs for optimizing the three individual parameters in the central composite design (CCD) were undertaken.

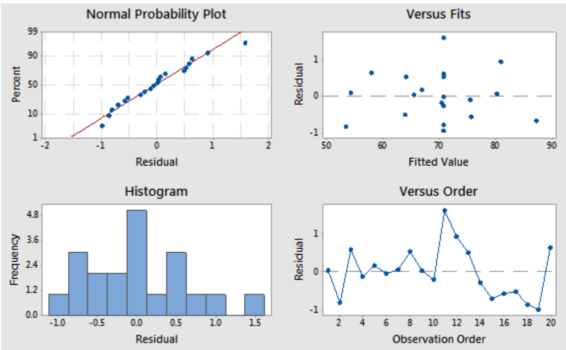
CCD results show that the CO_2 capture, Na, Mg, K and Ca removal varied in the range of 52.5 – 86.7 %, 12.0 – 33.5 %, 65.4 – 95.3 %, 11.6 – 54.8 % and 58.9 – 94.2 % respectively.

A. CO_2 Capture Efficiency and Sodium Removal

RSM was undertaken to obtain the process factors and response. The statistical significance was evaluated using the P-value, and the lack-of-fit value of the model. The goodness of fit of the polynomial model was expressed by the determination coefficient R^2, adjusted R^2, and predicted R^2. The results indicate that the model is significant (P-value < 0.05). The effect of temperature, gas flow rate and molar ratio are significant (P-value < 0.05). The P- value for the lack of fit (P-value > 0.05) implies that the fit is significant. The measures of R^2, adjusted R^2, and predicted R^2 are close to 1, which implies an adequate model. The residuals analysis shows that there was no evidence of outliers, as all the residuals fell within the range of -1 to + 1 and they are randomly distributed around zero, which indicates a high degree of correlation between the observed values and predicted values as shown in Fig. 1.The predicted model of CO_2 capture efficiency and sodium removal was obtained by a second-order polynomial functions as following.

$$CO_2 \text{ capture efficiency} = 97.9 + 1.36\, T - 49.3\, F - 10.5\, M - 0.0153\, T^2 - 8.65\, F^2 - 0.89\, M^2 + 0.127\, T\, F - 0.278\, T\, M + 21.47\, F\, M \quad (5)$$

$$\text{Na removal } \% = -22.0 + 1.254\, T + 18.76\, F + 1.93\, M - 0.00639\, T^2 - 4.49\, F^2 + 3.07\, M^2 - 0.1019\, T\, F - 0.4296\, T\, M + 1.41\, F\, M \quad (6)$$



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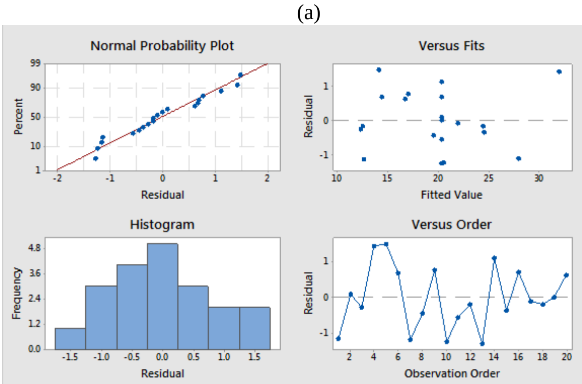

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Fig. 1. Residual plots for (a) CO_2 capture efficiency and (b) sodium removal %.

B. Models Validation

The model equations for predicting the optimum response values were tested using the selected conditions to confirm the RSM validity. Two confirmation experiments were applied with temperature, gas flow rate and NH_3: NaCl molar ratio chosen randomly from the ranges of Table II to validate the mathematical models. Table III shows the experimental values, predicted values and 95% Confidence Interval (95% CI) for CCD. Fig. 2 shows the actual and predicted values for CO_2 capture efficiency and sodium removal. The results demonstrate that the developed models can successfully predict the capture efficiency and ions removal using the Solvay method.

C. CO_2 Capture and Ions Removal Optimization

Process optimization was implemented to find the conditions under which maximum CO_2 capture efficiency and ions removal would be possible. The optimal values of the selected variables were obtained using response optimizer, and the optimum CO_2 capture efficiency and ions removal was found to be at a temperature of 19.3 ^{o}C, a gas flow rate of 1.544 L/min, and a molar ratio of 3.3NH_3:1NaCl as shown in Fig. 3. The optimum conditions have been tested experimentally and presented in Table IV.

TABLE III: VALIDITY RESULTS BY RSM FOR CCD

T °C	F L/min	M	Results	CO_2 capture efficiency %	Na removal %
15.0	0.800	3.0	Exp.	90.0	20.0
			Pred.	92.8	22.9
			95% CI	89.9-95.7	19.2-26.7
32.0	1.300	2.0	Exp.	65.9	15.0
			Pred.	65.1	16.0
			95% CI	64.1-66.0	14.8-17.3

TABLE IV: PREDICTED AND EXPERIMENTAL CO_2 CAPTURE AND IONS REMOVAL AT THE OPTIMUM CONDITIONS

T °C	F L/min	M	Results	CO_2 capture efficiency %	Na removal %
19	1.54	3.3	Exp.	86.2	33.0
			Pred.	86.6	35.2
			95% CI	84.5-88.8	32.5-38.0

D. Effect of Temperature

The effects of temperature on CO_2 capture and sodium removal and their interactions can be represented through 3D response surface plots. Fig. 4 represents the maximum CO_2 capture efficiency and sodium removal against temperature and flow rate while keeping the NH_3: NaCl molar ratio constant. An increase in the ions removal and CO_2 capture efficiency could be achieved when the value of temperature was decreased from 46.8 to 13.2 ^{o}C. The results indicated that increasing the temperature has a negative effect on the CO_2 capture and sodium removal. This can be explained by the reversibility of Solvay process reactions [3]. Previous studies suggested that the forward reactions are dominant at room temperature [4], while the backward reactions occur in the temperature range of 38–60 ^{o}C [5]. The CO_2 capture increased with decreasing the temperature since the solubility of CO_2 gas increases with decreasing the temperature [6]. It was reported by Zhu *et al.* That the lower the reaction temperature is, the less stripping of ammonia and more stable the reaction inside the reactor [7].

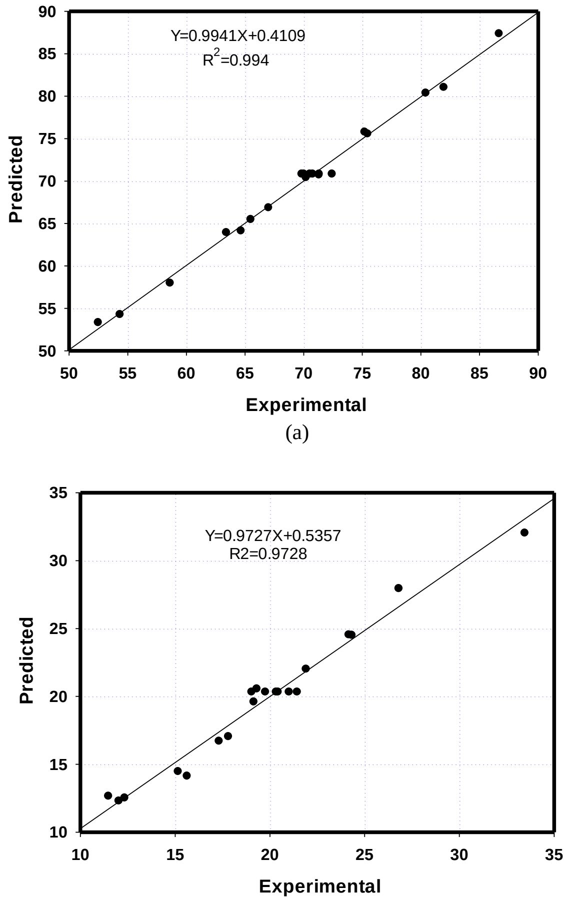

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Fig. 2. Experimental versus predicted values for (a) CO_2 capture efficiency and (b) Na removal %.

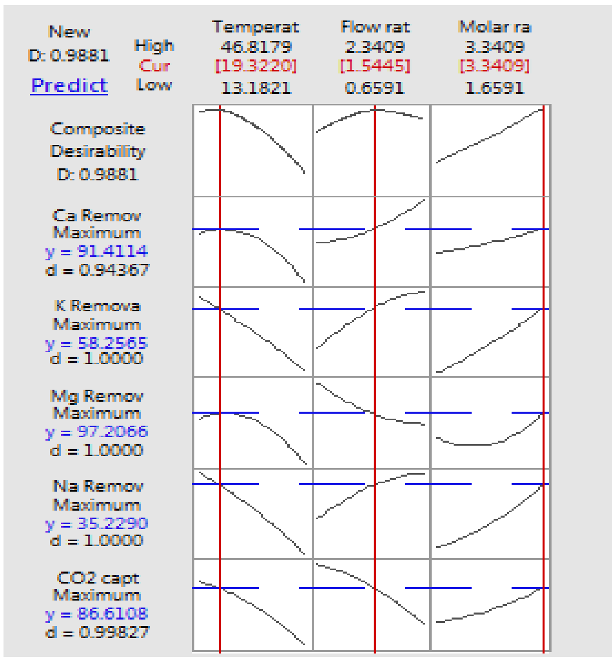
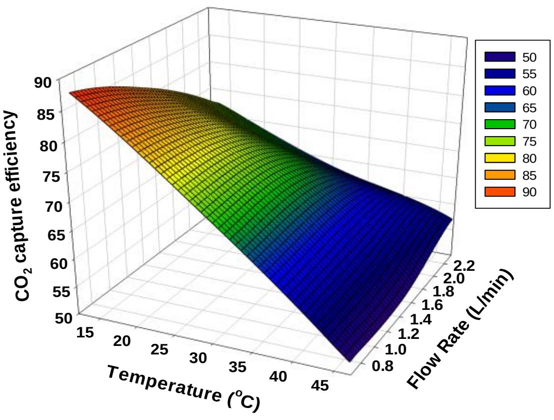


Fig. 3. The optimum temperature, flow rate and NH_3:NaCl molar ratio to have maximum CO_2 capture efficiency and ions removal.

E. Effect of Gas Flow Rate

Fig. 5 shows the maximum CO_2 capture efficiency and sodium removal against flow rate and NH_3:NaCl molar ratio, while keeping the temperature constant. A 6% to 10% increasing in ions removal could be achieved when the value of flow rate increased from 0.659 to 2.341 L/min, which can be explained by enhancing the reaction rate due to increasing the CO_2 loading and hence capture by the ammoniated brine. However the CO_2 capture efficiency decreased 10% with increasing the flow rate to 2.341 L/min and this is mainly due to reducing the gas residence time in the reactor and hence decreasing the reaction rate [7]. The CO_2 capture efficiency increased with decreasing the gas flow rate, which can be attributed to the residence time of the gas in the reactor. As expected, longer residence time results in higher reaction rate since the gas will have more contact time with the reactants in the reactor [7]. The lowest gas flow rate provided the highest capture efficiency of CO_2. Zhang et al reported that by increasing the gas flow rate, the absorption capacity by the ammoniated brine decreased [8].



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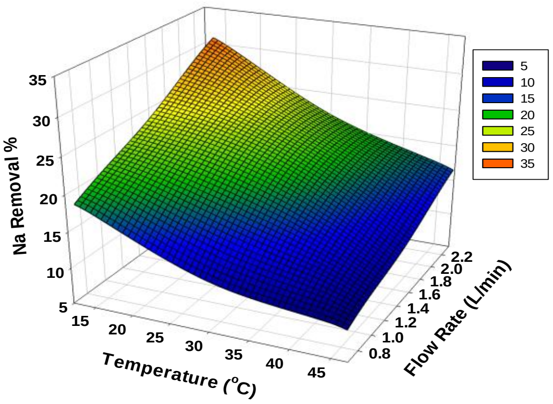

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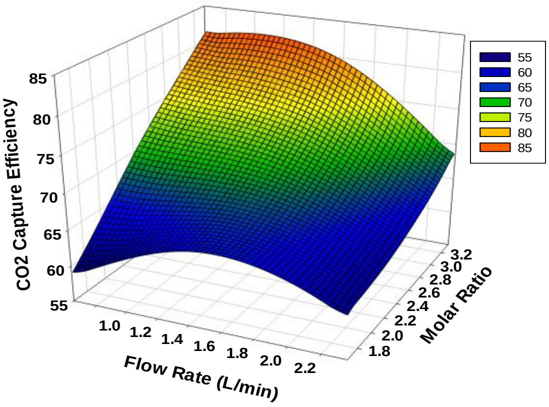
Fig. 4. (a) CO_2 capture efficiency and (b) Na removal% on 3-D graphics for response surface optimization versus temperature and gas flow rate.

F. Effect of NH_3: NaCl Molar Ratio

As can be seen from Fig. 5, a significant improvement in sodium removal and CO_2 capture efficiency could be achieved by increasing the molar ratio from 1.7 to 3.3NH_3:1NaCl. This can be explained by increasing the initial pH, which accordingly shifted the reaction towards bicarbonate formation [9]. As a whole, the increase of the molar ratio is favorable for brine desalination, but this will increase the energy requirement of the NH_3 recovery system [10]. With increasing ammonia to sodium chloride molar ratio, the initial pH of the solution will increase and, consequently the CO_2 capture efficiency will increase. For the chemical reaction, high molar ratio would enhance the mass transfer and push the reaction forward according to the classic two-film theory, leading to the increase of CO_2 capture percentage. However increasing the molar ratio more than 3NH_3:1NaCl does not seem to increase the CO_2 capture efficiency any further, indicating that the reaction is close to its limit; this is in agreement with previous studies [3].



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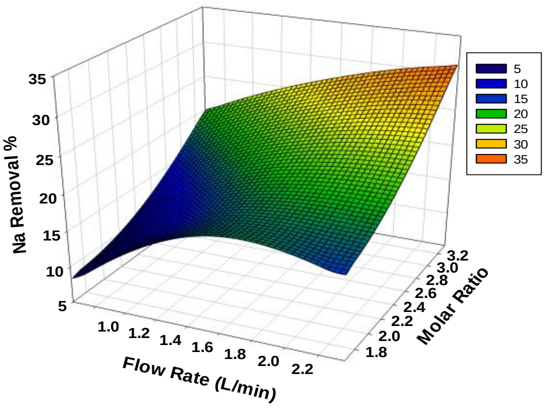

(b)

Fig. 5. (a) CO_2 capture efficiency and (b) Na removal % on 3-D graphics for response surface optimization versus gas flow rate and NH_3:NaCl molar ratio.

IV. Conclusions

Second order polynomial equations were adequate to predict the ions removal and CO_2 capture efficiency within three independent variables: ammonia to sodium chloride molar ratio, temperature and gas flow rate. All three variables indicated significant effect on the ions removal and CO_2 capture efficiency. The total CO_2 capture efficiency in 180 minutes was 86% and the maximum sodium removal was 33%.

Abbreviations

CCD	Central composite design
CI	Confidence interval
DoE	Design of experiments
Exp.	Experimental result value
F	Gas flow rate (L/min)

M	Ammonia to sodium chloride molar ratio
MSF	Multi-stage flash distillation
Pred.	Predicted result value
R^2	Determination coefficient
RS	Response surface methodology
SSR	Stainless steel reactor
T	Temperature (^oC)
w/*w*	Weight to weigh ratio

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