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Valorization of CO_2 in flue gas through alkalinity production: Parametric optimization for application in anaerobic digesters

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Abstract

The main aim of this work was to investigate the production of alkalinity by CO_2 absorption in sodium hydroxide (NaOH) solution and optimizing the CO_2 absorption efficiency (*E*) using statistically designed experiments. Based on the Box-Behnken's experimental design, fifteen experiments were conducted in a lab-scale batch reactor (80 mm × 1000 mm). The effect of three process parameters, i.e. NaOH solution concentration, X_1 (0.5~1.5% *w/w*), influent gas (10% CO_2 and 90% N_2) flow rate, X_2 (300~700 ml/min) and initial solution temperature, X_3 (20~60 °C) on the CO_2 absorption efficiency were investigated and statistically analyzed. A maximum CO_2 absorption efficiency of 74.3% was obtained at the following optimal conditions: X_1 - 1.5% (*w/w)*, X_2 - 300 ml/min and X_3 - 60°C. It was also observed that the hydroxide alkalinity shifts to carbonate and bicarbonate alkalnity at the end of reaction, which implied that the CO_2 can be recovered and the alkaline solution could then be utilized as a valuable carbonate and bicarbonate alkalinity resource. The results obtained from this research is intended to be utilized for economic bicarbonate neutralization in biological anaerobic digestion systems.

Keywords: Alkalinity production; CO_2 absorption; Anaerobic digester; Statistical optimization; Industrial symbiosis

Introduction

Global warming is one of the alarming issues because industrial and automobile emissions continues to emit heat-trapping greenhouse gases to the atmosphere and CO_2 is one of the primary contributor to this problem (Vavrus et al., 2008). The CO_2 concentration in atmosphere has increased significantly from 280 ppm in 1750 (pre-industrial era) to ~410 ppm, causing global temperature to increase and glaciers to melt (Solomon et al., 2009; NASA, 2019). Different approaches have been employed to mitigate global warming, e.g. improved resource efficiency (Heinz et al., 2016), energy conservation, use of renewable energy (Rahman et al., 2017) and CO_2 capture and sequestration (Younas et al., 2016; Chu, 2009).

Chemical absorption is one of the promising and industrially applied methods to capture CO_2. Solvents such as amines, hydroxides, carbonates and ammonia have been extensively used for CO_2 capture (Gondal et al., 2014; Wang et al., 2015, Bernhardsen et al., 2017)). Among all these absorbents, amines (e.g. monoethanolamine, MEA) are employed at the industrial scale for CO_2 capture in post-combustion processes (Dutcher et al., 2015). However, the degradation of amines, their corrosive property, and high cost of solution regeneration are the major disadvantages attributed to the use of amines (Rafat et al., 2016)). Compared to MEA, NaOH is a relatively cheap and easily available absorbent. However, the regeneration cost of NaOH is very high and therefore it is not likely to be commercially viable (Abdeen et al., 2016). In the case of power plants, the CO_2 concentration is relatively low, i.e., 10-17%, so it is known to be difficult to recover it economically (Lee et al., 2000; Na et al., 2001). However, power plant is the major source of the CO_2 emission, and an alternative to the regeneration of NaOH solution after CO_2 absorption could be to utilize it as an economically valuable resource. Emission of CO_2 from an industry or power plant is always a concern which could become an opportunity for another industry if a valuable product can be derived, thanks to the concept of industrial symbiosis (Martin et al., 2015).

In this context, CO_2 absorption by NaOH solution should to be explored and utilization of the generated alkalinity as a neutralizing agent in wastewater treatment and bioreactors can be thought of as a great solution in such systems. This concept has emerged in the recent past, for example, CO_2 in flue gas of a zinc smelter is transferred to a paper mill where it reacts with CaO to produce $CaCO_3$ and ultimately used as a filler material for paper production (Kim et al., 2018). In a recent study, the absorption of CO_2 in NaOH solution for the production of sodium carbonate was investigated (Salmón et al., 2018). The authors tested the effect of concentration of the alkaline sorbent (NaOH, NaOH/Na_2CO_3) and flue gas (containing 10-15% of CO_2) flow rate on the performance of a column reactor and a membrane contactor. According to the results, it was concluded that when the hydroxides were exhausted, a secondary reaction between the carbonates and the contaminant produced bicarbonates.

In this context, to the best of our knowledge, the alkalinity produced during CO_2 absorption in NaOH solution has not been investigated so far. For an anaerobic digester to be properly operated, a pH in the range of 6.8 -7.2 is optimal (Hilkiah et al., 2008; Hagos et al., 2017). The pH of anaerobic system is significantly affected by the CO_2 content in the biogas. The pH variations can be adjusted by the alkalinity produced from different sources such as $CaCO_3$, $NaHCO_3$, waste egg shells and lime from paper making, among others (Chen et al., 2015). However, there is no report on the utilization of alkalinity produced from CO_2 absorption in NaOH for the stability of anaerobic digestion. Keeping in mind the CO_2 capture as well as its utilization, this work is mainly focused on absorbing CO_2 in NaOH solution for the production of alkalinity which is to be used for pH adjustment in anaerobic digesters. However, in order to obtain the desired alkalinity, it is required to have high amounts of CO_2 absorbed into the NaOH solution. Regarding CO_2 absorption by NaOH solution, effects of different operational parameters on CO_2 absorption efficiency (E) have been invitigated and reported in literature. For example the effects of rotor speed, gas flow rate, liquid flow rate, and NaOH concentration on the CO_2 removal was investigated in a cross-flow rotating packed bed (Lin and Chen, 2011). The results from that study showed that increasing the gas flow rate decreases the CO_2 absorption efficiency, while the liquid flow rate, rotor speed and NaOH concentration had a positive effect on the CO_2 removal. In a study carried out in spray dryer, it has been demonstrated that increasing NaOH concentration and operational temperature enhances the CO_2 removal efficiency (Tavan et al., 2017). An optimum CO_2 removal efficiency of 66% was obtained for the highest concentrated NaOH solution (3M) in a study mainly focused on upgrading biogas (Maile et al., 2017). In a recent study, increasing gas flow rate and CO_2 concentration were found to have negative effect on CO_2 removal efficiency air-blast atomizing column (Li et al., 2019)

In most of these previous research works, the authors have focused on adopting a ''one-factor-at-a-time'' strategy to investigate the effects of various independent parameters on the response variable. The main disadvantage of this experimental approach is that it does not consider the interactive effects among the selected parameters. Besides, this technique requires a large number of experiments, i.e. material costs and time. Multivariate statistical techniques such as response surface methodology (RSM) can be used to overcome the limitations of one-factor optimization technique (Mertler and Reinhart, 2016; Bezerra et al., 2008). In the present study, RSM was employed to optimize and determine the effect of three process parameters, namely NaOH solution concentration (X_1), influent gas flow rate (X_2) and initial solution temperature (X_3), on the CO_2 absorption efficiency (E). Subsequently, carbonate and bicarbonate alkalinities were determined after CO_2 absorption for economic pH neutralization in biological anaerobic digestion systems as a climate countermeasure to minimize carbon emission.

Materials and methods

Materials

Sodium hydroxide (NaOH) with 98% purity was purchased from OCI Ltd, South Korea. All solutions were prepared at room temperature in de-ionized water. Nitrogen and CO_2 gases having purities of 99.99% each were purchased from Deokyang Company limited, South Korea. As this study is intended to be applied for CO_2 recovery from flue gas and for the production of alkalinity, the concentration of CO_2 was kept constant at 10% (*v/v*) in all the experiments, similar to the CO_2 concentration expected in flue gas from a coal-fired power-plant (Aouini et al., 2014).

Experimental design and response surface methodology

RSM combines statistical and mathematical techniques to explore the relationships among dependent and independent variables and give an optimized response (Bezerra et al., 2008). In this study, Box Behnken design (BBD) was used to design the experiments at three levels of the process variables. In BBD, the number of experiments to be performed was determined according to Eq. (1):

$$N = 2K\ (K - 1) + CP \tag{1}$$

Where, CP is the number of center points and K is the number of factors in the experimental design.

The range of process parameters were set as follows: NaOH solution concentration, X_1 (0.5~1.5% *w/w*), influent gas (10% CO_2 and 90% N_2) flow rate, X_2 (300~700 ml/min) and initial solution temperature, X_3 (20~60 °C). In total, fifteen experiments were conducted for three factors

(K=3) and three center points (CP=3). Center point ('0' level) experiments were performed as a measure of the precision property and for statistical analysis (Ravikumar et al., 2007). The optimal values of the experimental conditions were obtained by solving the regression equation and by analyzing the response surface contour plots. Coding of the variables was done according to Eq. (2):

$$X_i = \frac{x_i - x_o}{\Delta x} \tag{2}$$

Where, X_i is the coded value of variable i, x_i is the dimensionless un-coded (actual) value of X_i, x_o is the value of X_i at the center point, and Δx is the step change between levels -1 and 0, respectively. The following second order polynomial model equation was used to explain the behavior of the CO_2 absorption efficiency (Eq. 3):

$$Y = \beta_o + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_i X_j \tag{3}$$

where, Y is the predicted response, β_o the offset term, β_i the coefficient of linear effect, β_{ii} the coefficient of squared effect, X_j is the coded value of variable j and β_{ij} the coefficient of interaction effect.

In this study, the effects of NaOH solution concentration (X_1), influent gas flow rate (X_2) and solution initial temperature (X_3) were investigated for achieving maximum CO_2 absorption efficiency (Table 1). Statistical analysis was carried out using the software Minitab (versions 6.0.8) at the 95% confidence level.

Table 1. Independent variables for CO_2 adsorption experiments

Variables	**Levels**		
Solution concentration, X_1 (% *w/w*)	0.5	1	1.5
Gas flow rate, X_2 (ml/min)	300	500	700
Solution temperature, X_3 (°C)	20	40	60

NaOH solution preparation

For the individual experiments, solutions with different NaOH concentration (*w/w*) were prepared at room temperature in de-ionized water. For this purpose, a known amount of NaOH was dissolved in de-ionized water to obtain the desired concentration (Eq. 4):

$$C_{NaOH}(w/w\%) = \frac{m_{NaOH}}{m_{NaOH} + m_{H_2O}} \times 100\% \qquad (4)$$

where C_{NaOH} is the concentration of NaOH solution, m_{NaOH} is the mass of NaOH and m_{H_2O} is mass of water. Solution with NaOH concentration of 0.5,1 and 1.5% *w/w* were prepared for the different experiments performed in this study.

Experimental setup

The experimental setup (Fig. 1) used in this study consists of a batch pyrex glass reactor having an internal diameter (ID) of 80 mm and a height of 1000 mm. All the experiments were carried out at atmospheric pressure. 500 ml of the NaOH solution, at the desired concentration, was transferred into the reactor as per the experimental design. The absorbent solution was heated in the reactor using a heating plate (HS15-06P). A thermocouple was used to measure the temperature of the solution. A magnetic stirrer provided mixing of the solution at a constant rate. Before experimentation, the reactor and its accessories including pipes, fittings and space of the reactor were purged with N_2 for an hour. The gas flow rate was controlled using a mass flow controller (GMC-1200, ATOVAC M3030V, South Korea). Nitrogen gas was used to dilute CO_2 gas in order to obtain a constant CO_2 gas concentration of 10% (*v/v*) for all the experimental runs. A gas sparger placed at the bottom of the reactor allowed homogenous distribution of gas in the reactor and it facilitated good interaction between the gas molecules and the NaOH solution. The concentration of CO_2 at the reactors inlet and outlet was measured using an infrared CO_2 analyzer (Alpha Omega Instruments, Series 9610).

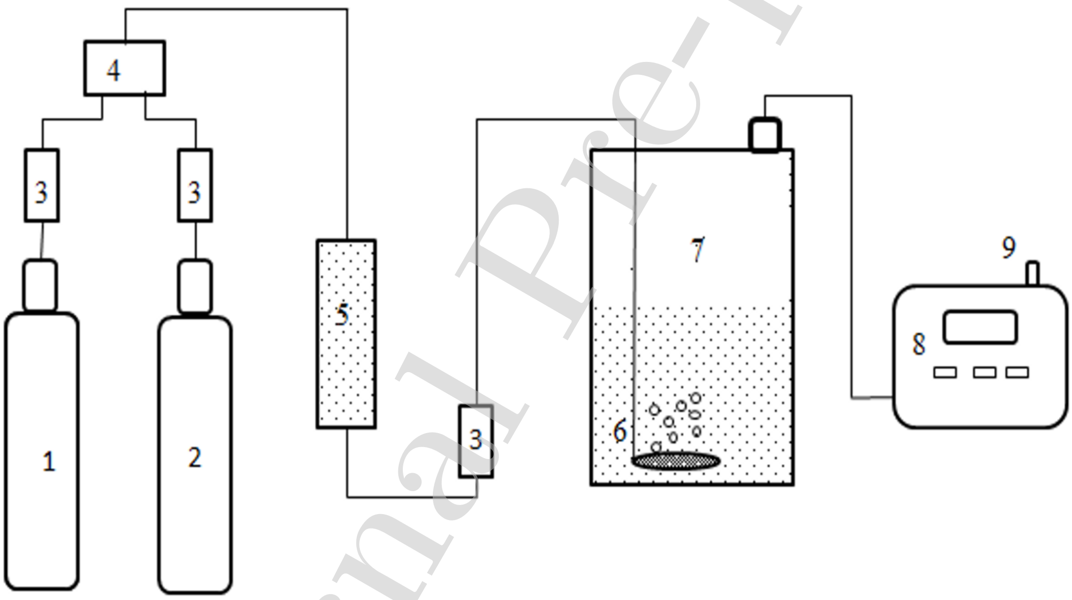

Figure 1. Schematic of the batch reactor used for CO_2 absorption in NaOH solution: (1) CO_2 cylinder, (2) N_2 cylinder, (3) mass flow controller, (4) flow controller, (5) gas mixer, (6) gas sparger, (7) reactor, (8) CO_2 analyzer and (9) vent.

The completion of the reaction was determined based on the point at which the outlet CO_2 concentration was recovered to 70% of the inlet CO_2 concentration. After each experimental run, the reactor and its accessories were purged with N_2 gas for one hour in order to use it for the next run. The CO_2 absorption efficiency (E) was calculated by using Eq. (5):

$$E(\%) = \frac{Total\ \mathrm{CO_2}\ absorbed}{Theoretical\ \mathrm{CO_2}\ absorption} \times 100 \quad (5)$$

The theoretical CO_2 absorption value was calculated using the stoichiometric chemical reaction between NaOH and CO_2 (Eq. 6):

$$\mathrm{NaOH} + CO_2 \rightarrow NaHCO_3 \quad (6)$$

The total mass (m_{tot}, g) of CO_2 fed to the reactor during each experimental run was estimated using Eq. (7):

$$\mathrm{m_{tot}} = \mathrm{q} \times \mathrm{t_{70}} \times \rho_{\mathrm{CO_2}} \quad (7)$$

Where, q is the volumetric flow rate of CO_2 (ml/min), t_{70} represents the time in minutes at which 70% of the inlet CO_2 concentration was observed at the outlet of the reactor and ρ_{CO2} is the density of CO_2 gas. The amount of CO_2 absorbed was calculated according to Eq. (8):

$$\mathrm{m_A} = \frac{\mathrm{A_t}}{\mathrm{A_{tot}}} \times \mathrm{m_{tot}} \quad (8)$$

Where, m_A is the mass absorbed at time t, A_{tot} is the total area and A_t is the area above the curve at time t. In the graph of normalized CO_2 concentration vs. time, the area above the curve represents the amount of CO_2 absorbed in the solution, while the area below the curve represents the amount of CO_2 that was not absorbed. A_t was determined according to Eqs. (9) and (10):

$$A_t = C_{inf} \times t \quad (9)$$

$$\mathrm{A} = \int_0^t (C_{inf} - C)dt \quad (10)$$

Where, C_{inf} is the influent CO_2 concentration and C is the concentration of CO_2 at any given time t.

Alkalinity measurements

In this study, alkalinity measurements were done before and after CO_2 absorption by the NaOH solution. The total alkalinity or methyl orange alkalinity was measured by titration of a known volume of the sample to a pH value of 4.5 using methyl orange as the indicator. Phenolphthalein alkalinity ($OH^- + \frac{1}{2}\ 2CO_3^{2-}$) was measured by titration of a known volume of sample to a pH value of 8.3. The difference between the total and phenolphthalein alkalinity, i.e.($\frac{1}{2}\ CO_3^{2-} + HCO_3^-$) was estimated (Yincheng et al., 2011). Alkalinity was measured according to the procedure outlined in Standard Methods (Eq. 11):

$$\text{Alkalinity}\left(\text{mg}\frac{\text{CaCO}_3}{\text{L}}\right) = \frac{\text{A}\times\text{N}\times 50{,}000}{\text{vol.of sample(ml)}} \tag{11}$$

Where, A is the volume of sulfuric acid (ml) and N is the normality of acid (0.1 N).

Results and discussion

Effect of individual parameters on CO_2 absorption

The absorption of CO_2 in NaOH solution is a two-step process (Krauβ and Rzehak, 2017):

Step 1: Sodium hydroxide reacts with CO_2 to produce sodium carbonate (Eq. 12):

$$2\text{NaOH} + CO_2 \leftrightarrow Na_2CO_3 + H_2O \tag{12}$$

Accordingly, 0.55 g of CO_2 is absorbed by 1 g of pure sodium hydroxide in the first step.

Step 2: Sodium carbonate reacts with the available CO_2 and water to produce sodium bicarbonate (Eq. 13):

$$CO_2 + Na_2CO_3 + H_2O \leftrightarrow 2\text{NaHCO}_3 \tag{13}$$

Thus, 0.55 g of CO_2 reacts with Na_2CO_3 to form 2.1 g of $NaHCO_3$ (Eq. 14):

$$0.55\text{g}\ CO_2 + 1.325\text{g}\ Na_2CO_3 + 0.225\text{g}\ H_2O \leftrightarrow 2.1\text{g NaHCO}_3 \tag{14}$$

In total, 1 g of sodium hydroxide is required to absorb 1.1 g of CO_2. Half of this amount is absorbed in the first step and the remaining is absorbed in the second step. Eqs. (12) and (13) can be combined as follows:

$$\mathrm{NaOH} + CO_2 \rightarrow NaHCO_3 \tag{15}$$

It is noteworthy to mention that, all chemical reactions are reversible in open carbonate systems. Hence, the reaction direction is affected by the availability of CO_2 and NaOH. For example, Eq. (13) is reversible in a way that the available NaOH can react with $NaHCO_3$ to form sodium carbonate (Na_2CO_3). Under neutral pH condition, the total alkalinity is the sum of same equivalent of carbonate alkalinity and bicarbonate alkalinity. Therefore, the overall reaction can be written as (Eq. 16):

$$2\mathrm{NaOH} + \frac{3}{2} CO_2 \rightarrow \frac{1}{2}\ Na_2CO_3 + NaHCO_3 + \frac{1}{2}\ H_2O \tag{16}$$

In addition to the experiments performed according to BBD, three additional experiments were performed to investigate the individual effects of parameters (solution concentration, gas flow rate and solution initial temperature) on *E*. Figures 2 (a, b and c) represents the breakthrough curves for normalized outlet CO_2 concentration as a function of time, at different NaOH solution concentration, initial solution temperature and inlet gas flow rate.

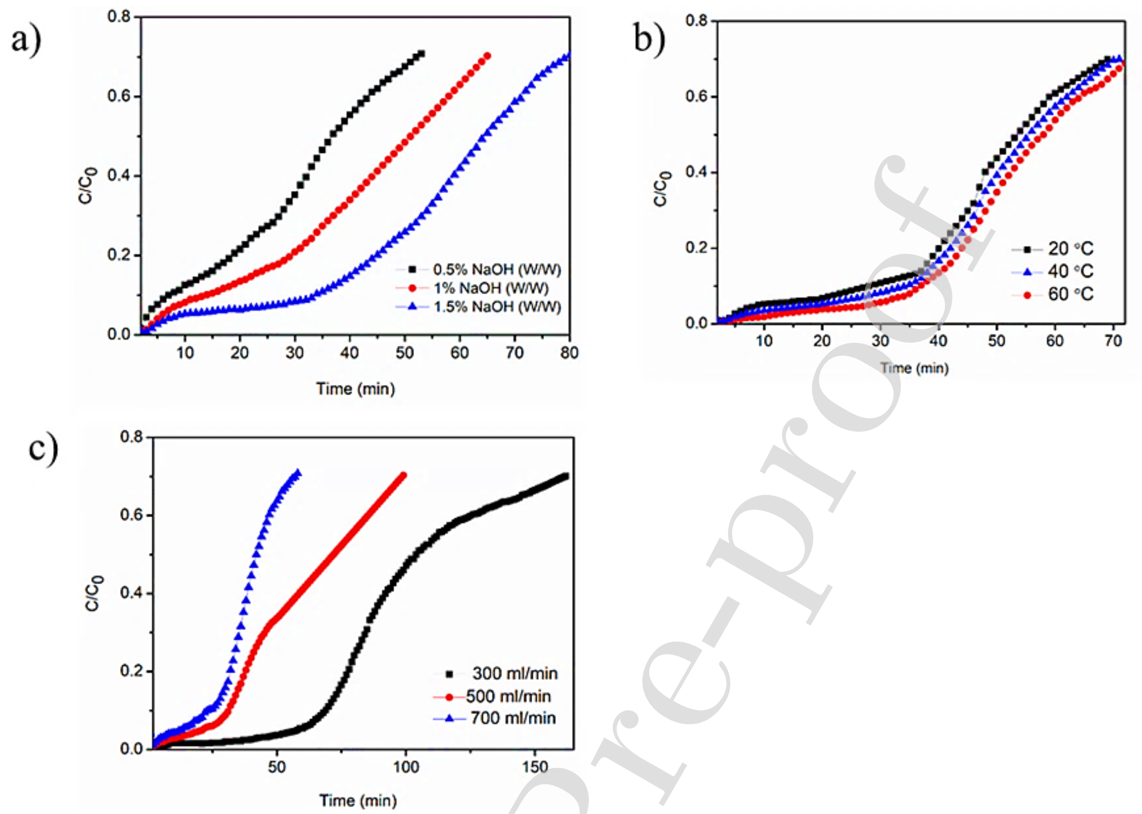

Figure 2. Variation of normalized outlet CO_2 concentration as a function of time at different (a) NaOH concentration (constant gas flow rate of 500 ml/min and solution initial temperature 20 ^{o}C); (b) solution initial temperature (gas flow rate of 500 ml/min and solution concentration 1.5% *w/w*); and (c) gas flow rate (solution initial temperature 60 $^{\circ}$C and solution concentration 1.5 % *w/w*).

Molar ratios (moles of CO_2/moles of NaOH) in the range of 0.58 ~ 0.76 were observed for the different experimental conditions. The highest molar ratio of 0.76 moles of CO_2/mole of NaOH was noted at high temperature, low gas flow rate and high solution concentration among the considered parameters. According to overall reaction (Eq. 16), one mole of NaOH can absorb one mole of CO_2 by considering the balanced stoichiometry. The experimentally determined values were less than the theoretical value. This is expected since the absorption process was terminated before the complete saturation of absorbent solution, i.e. when the outlet CO_2

concentration was 70% of the inlet concentration. The other reason for the deviation in experimental values is the production of lower trona as investigated in a previous report (Miran et al., 2013).

When the initial temperature (20 ºC) and gas flow rate (500 ml/min) were maintained at constant values, the CO_2 absorption efficiency was found to increase with an increase in the NaOH concentration (Data set No. 1 in Table 2 and Fig. 2a). The highest CO_2 absorption efficiency was observed at a NaOH solution concentration of 1.5% (*w/w*). Increasing NaOH concentrations provides more OH^- ions to react with CO_2 gas which results in higher CO_2 absorption efficiency. A same trend of NaOH concentration was also reported for different reactor configurations (Tavan et al., 2017; Maile et al., 2017). A small increase in the CO_2 absorption efficiency (from 64.6% to 67%) was observed when the solution temperature was increased from 20 °C to 60 °C, at constant values of NaOH solution concentration (1.5% *w/w*) and gas flow rate (500 ml/min) (Data Set No. 2 in Table 2 and Fig. 2b). This increase in CO_2 absorption efficiency with temperature can be ascribed to the high reaction rate at higher temperature which results in the enhancement of efficiency. In contrast, CO_2 absorption efficiency decreased from 76.5% to 58.1% with an increase in the influent gas flow rate from its low (300 ml/min) to high levels (700 ml/min), at constant value of NaOH concentration (1.5% *w/w*) and solution temperature (60 ºC) (Data Set No. 3 in Table 2 and Fig. 2c). This antagonistic effect can be explained by the fact that, with increasing gas flow rates, the reaction between CO_2 and NaOH is not complete due to less contact time. A similar negative effect was also reported for CO_2 absorption by NaOH solution in other reactor configurations (Li et al., 2019; Niu et al., 2009; Tippayawong and Thanompongchart, 2010).

Table 2. CO_2 absorption efficiency (E) at different conditions

NaOH Concentration (%)	Moles of NaOH	CO_2 absorbed (g)	Moles of CO_2 absorbed	Molar ratio (moles of CO_2/moles of NaOH)	Absorption efficiency E (%)
Data set No.1[a] NaOH conc. (%)					
0.5	0.062	1.606	0.036	0.5798	57.9
1.0	0.125	3.395	0.077	0.617	61.7
1.5	0.187	5.363	0.121	0.6501	65.0
Data set No. 2[b] Solution temperature (ºC)					
20	0.187	5.283	0.120	0.6404	64.0
40	0.187	5.363	0.121	0.6501	65.0
60	0.187	5.608	0.127	0.6798	67.9
Data set No. 3[c] Gas flow rate (ml/min)					
300	0.187	6.318	0.143	0.7659	76.5
500	0.187	5.566	0.126	0.6746	67.4
700	0.187	4.793	0.108	0.5810	58.1

Note: [a] At constant solution temperature and gas flow rate, [b] At constant NaOH concentration and gas flow rate, [c] At constant solution temperature and NaOH concentration.

Development of the regression model and interaction effects

The results from analysis of variance (ANOVA) is shown in Table 3. The analysis was done by means of the Fisher's 'F' test and the praobability ''P'' values. Generally, the 'F' value with la ow 'P' value indicates high significance of the regression model (Mertler and Reinhart, 2016; Rehman et al., 2018). From the ANOVA table, the model was found to be significant (P<0.1). The smaller value of 'P' and a high 'F' value for the linear effects (F = 30.09 and P = 0.001) suggests that the sum of the main effects were more significant than the interaction (F = 12.23 and P = 0.010) and quadratic effects (F = 0.56 and P = 0.663). This implies very poor antagonistic and synergistic relationships among the process parameters.

Besides, the correlation between the experimental and the model fitted data was found to be high as evident from the R^2 value of 0.962. This indicates that 3.8 % of the total variation in CO_2 absorption efficiency was not explained by the model equation (Eq. 17). This unexplained value of response is presented in terms of the residual error in Table 3. Generally, R^2 value greater than 0.75 is considered for the acceptance of any data driven model (Chauhan et al., 2004). Furthermore, the relation between the experimental and predicted values as shown in Table 4 are in close agreement which suggests the good fit of the model.

$$\mathrm{E}\ (\%) = +63.49 + 3.69\mathrm{X}_1 - 3.42\mathrm{X}_2 + 0.59\mathrm{X}_3 - 0.98.15\mathrm{X}_1^2 - 0.318\mathrm{X}_2^2 - 0.16\mathrm{X}_3^2 - 4.56\mathrm{X}_1\mathrm{X}_2 + 0.28\mathrm{X}_1\mathrm{X}_3 + 0.22\mathrm{X}_2\mathrm{X}_3 \quad (17)$$

Table 3. ANOVA for the response surface model

Source	*DF*	*Seq SS*	*Adj SS*	*Adj MS*	*F* value	*P* value
Regression	9	293.513	293.513	32.6126	14.29	0.005
Linear	3	205.972	205.972	68.6572	30.09	0.001
Square	3	3.850	3.850	1.2835	0.56	0.663
Interaction	3	83.691	83.691	27.8971	12.23	0.010
Residual error	5	11.409	11.409	2.2818		
Lack-of-fit	3	11.377	11.377	3.7922	235.04	0.004
Pure Error	2	0.032	0.032	0.0161		
Total	14	304.922				

Note: *DF*: degree of freedom; *F*: Fischer's variance ratio; *P*: probability value; *SS*: sum of squares; *MS*: mean squares

Furthermore, the student's '*t*' test (Table 5) was used in this study to determine the significance of the regression coefficients at the 95% confidence level. Generally, the corresponding coefficient term will be high for the smaller value of '*P*' and larger magnitude of '*t*' (Bezerra et al., 2008). Among the linear effects, the gas flow rate was found to have the largest negative linear effect (t = -6.416 and P = 0.001). Therefore, an increase of gas flow rate from its low to high level decreases E significantly. NaOH solution concentration was found to have the largest linear positive effect (t = 6.918 and P = 0.001) which indicates that increasing NaOH solution concentration from low to high value increases the E. Concerning the interaction terms, $X_1 \times X_2$ and $X_1 \times X_3$ showed antagonistic effects, while $X_2 \times X_3$ showed a synergistic effect on the CO_2 absorption efficiency.

Table 4. Box-Behnken experimental design

Run	X_1 (*w/w*), %	X_2 (ml/min)	X_3 (°C)	CO_2 absorption efficiency (%)		Residual
				Actual	Predicted	
1	0.5	500	20	67.32	66.58	0.73
2	0.5	300	40	61.17	60.09	1.07
3	1.0	700	20	60.27	58.66	1.61
4	0.5	700	40	65.31	66.38	-1.07
5	1.0	300	20	57.53	59.34	-1.80
6	1.0	300	60	63.57	63.47	0.10
7	1.0	500	40	63.27	63.47	-0.20
8	1.0	500	40	62.30	60.49	1.80
9	1.5	500	20	64.83	64.63	0.19
10	1.5	700	40	57.53	58.26	-0.73
11	0.5	500	60	66.53	68.1	1.610
12	1.5	500	60	59.30	59.49	-0.19
13	1.0	700	60	58.53	59.40	-0.87
14	1.5	300	40	74.90	74.02	0.87
15	1.0	500	40	63.57	63.47	0.10

Table 5. Regression coefficients and corresponding '*t*' and '*p*' values of the model

Factors	**Coefficient estimates**	***SE* Coefficient**	**'*t*' value**	**'*P*' value**
Constant	63.4977	0.8721	72.808	0.000
X_1	3.6946	0.5341	6.918	0.001
X_2	-3.4268	0.5341	-6.416	0.001
X_3	0.5946	0.5341	1.113	0.316
X_1*X_1	-0.9895	0.7861	-1.259	0.264
X_2*X_2	-0.3182	0.7861	-0.405	0.702
X_3*X_3	-0.1625	0.7861	-0.207	0.844
X_1*X_2	-4.5600	0.7553	-6.038	0.002
X_2*X_3	0.2807	0.7553	0.372	0.725
X_1*X_3	0.2245	0.7553	0.297	0.778

Note: R^2 = 96.2%, *Adj* R^2 = 89.52 %

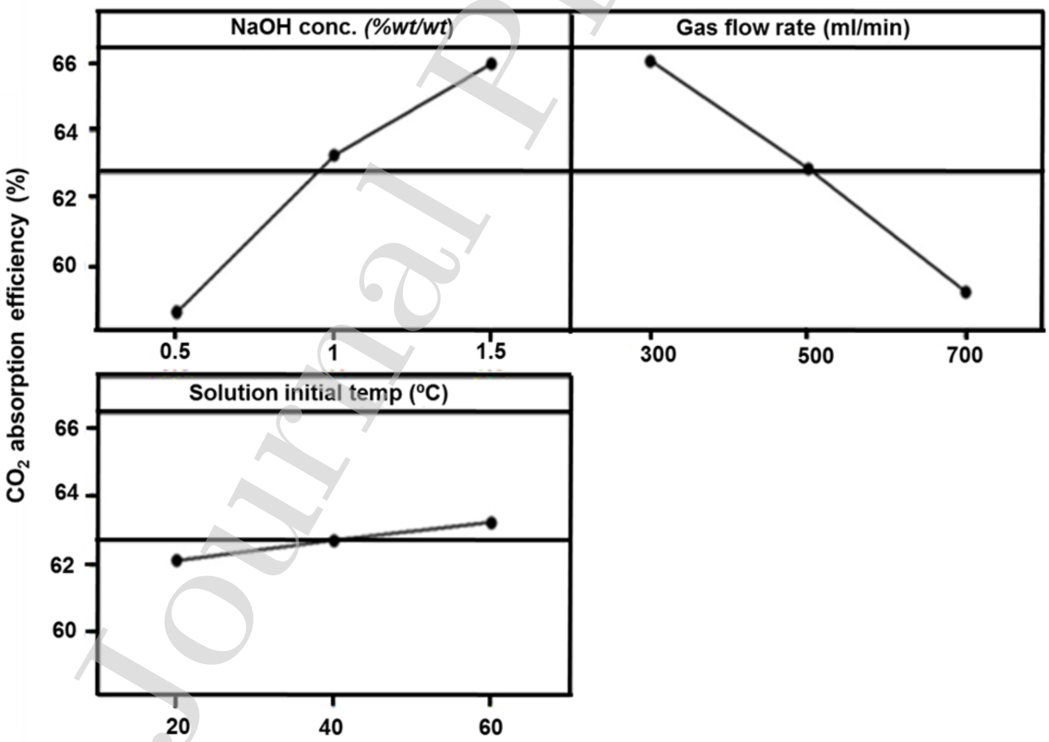

Figure 3. Main effects of NaOH concentration, initial temperature and gas flow rate on the CO_2 absorption efficiency (*E*).

Interaction effects are evident when change of response due to one factor is dependent on the level of a second factor. This is usually evident from the nature of cross-interactions between the lines of the interaction plot (Ravikumar et al., 2007). In this study, among the interaction effects, NaOH solution concentration × gas flow rate was found to have the highest effect on the CO_2 absorption efficiency (Fig. 4). In the range of NaOH concentration tested (0.5 % to 1.5% *w/w*), the highest CO_2 absorption efficiency was observed at the lowest gas flow rate of 300 ml/min.

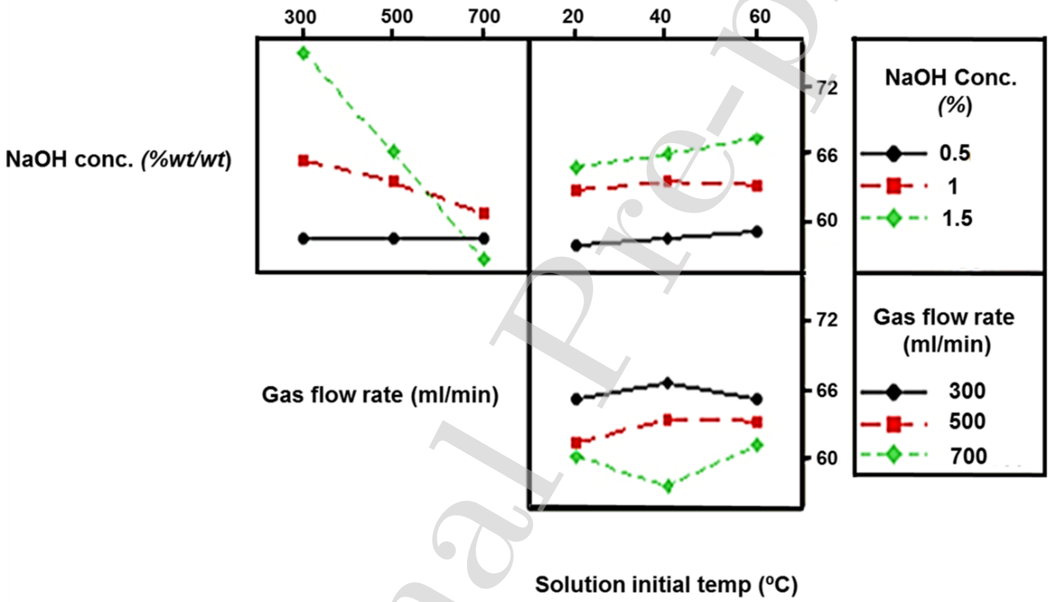

Figure 4. Interaction effects of NaOH solution concentration, solution initial temperature and gas flow rate on the CO_2 absorption efficiency.

The cumulative effects of different factors on CO_2 absorption efficiency, shown in the form of 3D surface plots, indicates that the maximum response is achieved at high solution concentrations, high initial temperature and low gas flow rate. It was observed that the CO_2 absorption efficiency values increases until a NaOH concentration of ~ 1.0 % (*w/w*) and a gas flow rate of 450 ml/min. The gas flow rate was shown to have a slightly positive effect initially, however, it showed a negative effect when the flow rate was increased beyond a certain value. Besides, when the reactor was saturated, the NaOH solution did not absorb more CO_2 and therefore the CO_2 absorption efficiency values started to decrease with increasing gas flow rate. NaOH concentration had a synergistic effect on the absorption of CO_2 at concentration less than 1.0 % (*w/w*). Similarly, it was evident that increasing the initial temperature at a constant NaOH concentration had a synergistic effect on the CO_2 absorption efficiency. This implies the fact that the rate of absorption increased with increasing temperature and saturation conditions were achieved faster. Although NaOH concentration showed a positive effect on the CO_2 absorption efficiency in majority of the experimental runs, its combined effect with temperature increased the CO_2 absorption efficiency up to a maximum of 74.3 %. The optimum process conditions achieved in this study were as follows: NaOH solution concentration - 1.5% (*w/w*), gas flow rate - 300 ml/min and solution initial temperature - 60 °C. To further verify these optimum conditions and check the reproducibility of the statistically significant experiments, a confirmation experiment was separately carried out. Under the optimum conditions, the experimental results obtained for CO_2 absorption efficiency was found to be 73.9±1.2 %.

Effect of CO_2 on the alkalinity of the absorbent solution

The results showed that, before CO_2 absorption, the pH of the NaOH solution was 13.56 and there was no bicarbonate and carbonate alkalinity present in the absorbent solution. The alkalinity was mainly due to the presence of hydroxides before CO_2 absorption. When CO_2 was passed through the concentrated NaOH solution, the alkalinity shifted to carbonate and bicarbonate alkalinity. When NaOH solution was saturated with CO_2, the solution was adjusted to neutral pH. At neutral pH, the total alkalinity is approximately equal to $HCO_3^- + 1/2CO_3^{2-}$. Thus, bicarbonate and carbonate alkalinities were present in the reactor after CO_2 absorption by the NaOH solution. The carbonate alkalinity found in the CO_2-absorbed solution was found to be 5483.5 mg/L (as $CaCO_3$), while the bicarbonate alkalinity was 11191.5 mg/L (as $CaCO_3$). The alkalinity distribution was also measured for the less concentrated solution (1%, *w/w*) and it was observed that a less concentrated solution results in less carbonate and bicarbonate alkalinity (Table 6). Hence, it can be concluded that if the concentration of NaOH is higher, high alkalinity can be produced which can then be used as a useful product. By employing this strategy, CO_2 can be absorbed in NaOH solution and the bicarbonate alkalinity obtained from the reaction can be utilized for pH and alkalinity adjustment of the anaerobic digester, thus limiting the utilization of fresh hydroxide or other alkaline solutions.

Table 6. Alkalinity before and after CO_2 absorption

Solution concentration (%, *w/w*)	Initial pH of solution	Volume of acid used for titration (ml)	Initial alkalinity (mg $CaCO_3$/L) - hydroxide only	Final alkalinity (mg $CaCO_3$/L) - carbonate and bicarbonate	Carbonate alkalinity (mg $CaCO_3$/L)	Bicarbonate alkalinity (mg $CaCO_3$/L)
1	13.45	43.5	10750	10750	3571.2	7178.8
1.5	13.56	66.7	16675	16675	5483.5	11191.5

Practical implications of this work

The results from this study showed the effects of three important process parameters on the CO_2 absorption efficiency which is very important for pilot- or semi-industrial scale facilities. The chemical conversion of CO_2 into valuable products is an emerging approach to mitigate global warming and conserve natural resources by employing the principle of industrial ecology. These win-win benefits can be better achieved by involving the industrial symbiosis (IS) strategy. In IS, a collective approach is adopted for the individual/participating industries to physically exchange energy, material, water and by-product among them to get overall economic and environmental benefits (Chertow, 2007).

Biogas from digester contains 30% to 60% CO_2 along with methane and other trace gases depending on the origin of the feedstock (Rasi and Veijanen, 2007). A new, the high partial pressure of CO_2 in the digester lowers the pH of an anaerobic digester which causes souring, resulting in deterioration of methane production (Andreottola and Cannes, 1992). Keeping in mind the practicality and importance of following an IS or eco-industrial park (EIP) approach, CO_2 can be captured in NaOH solution from coal fired power plants and the recovered alkaline solution having carbonate and bicarbonate alkalinity can be re-used as a neutralizing agent for maintaining the pH in anaerobic digesters. From an IS viewpoint, networks can be established between an incinerator and a biological waste treatment system as a climate change countermeasure to reuse CO_2 in the industry thereby minimizing carbon emission to the atmosphere.

Conclusions

The combined effects of three process parameters, i.e. NaOH solution concentration, influent gas flow rate, and initial solution temperature on the CO_2 absorption efficiency was investigated in this study. NaOH concentration and initial solution temperature showed positive effects while influent gas flow rate had a negative effect on the CO_2 absorption efficiency. Moreover, the results from ANOVA shows that the main effects of process parameters were more significant than the interaction and quadratic effects. From a chemical reaction and mechanism view point, during CO_2 adsorption in NaOH solution, the hydroxide alkalinity shifts to carbonate and bicarbonate alkalnity at the end of reaction. Practically, the alkaline solution could be utilized as a valuable carbonate and bicarbonate alkalinity resource for pH adjustments in an anaerobic digester.

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Research highlights

- Alkalinity production by CO_2 absorption for application in anaerobic digesters
- Process parameters were optimized for CO_2 absorption efficiency (74.3%)
- Optimum condition: NaOH conc.-1.5% (w/w), gas flow - 300 ml/min, solution temp.-60°C
- Resulting alkaline solution to be utilized as carbonate and bicarbonate alkalinity source

Declaration of interests

✓ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: