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CO_2 SOLUBILIZATION IN ALKALINE SOLVENTS

SOUMAYAT ALI IBRAHIM MZE[1], AZLIN SUHAIDA AZMI[1*], NOOR ILLI MOHAMAD PUAD[1], FARAH AHMAD[1], FIRDAUS ABD WAHAB[1], SYARIFAH NOR FAIZAH SY ABD RAHMAN[2]

[1]Department of Chemical Engineering and Sustainability,
Kulliyyah of Engineering,International Islamic University. Malaysia,
Jalan Gombak, 53100 Kuala Lumpur, Malaysia.
[2]Petronas Research Sdn. Bhd. Lot 3288 & 3299, off Jalan Ayar Itam,
Kawasan Institusi Bangi, 43000 Kajang, Selangor Darul Ehsan, Malaysia.

**Corresponding author: azlinsu76@iium.edu.my*

ABSTRACT: CO_2 removal by chemical reaction of sodium carbonate (Na_2CO_3), and aqueous ammonia (NH_3) shows promising absorption quality for CO_2 removal and sequestration. Nevertheless, the solubility of CO_2 by those alkaline solutions has been reported to be highly dependent on the temperature and the pH drop. This study focuses on screening the different solvents used for maximum CO_2 solubility using pure CO_2 based on 2 sets of experiments: First identifying the optimum temperature for distilled water which is considered as control under 3 different temperatures (20, 30 and 40°C). The Second was to identify the maximum CO_2 capture from the solvents under two factors: the type of solvent used (Na_2CO_3, NH_3), and their concentration (1-5%). The solubility behaviours of the CO_2 in the solvents will be analysed according to pH change, CO_2 capture rate, and CO_2 capture efficiency using the water displacement method. The experimental results show that the control condition provided higher solubility than the proposed solvents; the CO_2 removal using water value at 99.49% at 30°C while at the same condition, the highest removal efficiency for Na_2CO_3 value at a concentration of 3% 99.12% and NH_3 at a concentration of 5%, 98.54% respectively.

KEYWORDS: *carbon dioxide (CO_2) capture, sodium carbonate, aqueous ammonia*

1. INTRODUCTION

Reducing the emission of greenhouse gases, particularly carbon dioxide (CO_2), is crucial in addressing global warming and achieving carbon neutrality by 2050[1]. Much research has been performed on CO_2 capture from various industrial gas streams in order to reduce the contribution of CO_2 to global warming. Among those methods, chemical absorption through amine reaction has proven to be the most employed method nowadays. Nonetheless, the chemical absorption process based on amines such as monoethanolamine (MEA) is still too expensive to apply for large CO_2 sources like power plants [2,3]. The amine process is commonly associated with drawbacks such as absorbent degradation due to acidic compounds and oxygen in the gas stream, high energy usage, and equipment corrosion[1]. Alternatively, an alkaline solution such as aqueous ammonia (NH_3) and sodium carbonate (Na_2CO_3) seems to provide good CO_2 removal efficiency and less toxicity[1–3]. Recent research has proven that the aqueous NH_3 and Na_2CO_3 have a larger capacity of CO_2 compared to the amine solution, low regeneration energy required, low material cost, and potential ability to capture acidic gases in flue gas[1–3].

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Yeh and Bai[4]'s experiments using ammonia and MEA to capture CO_2 in a bubble reactor proved that NH_3 is a superior absorbent to MEA in removing CO_2 from flue gas systems. With a CO_2 removal efficiency of up to 99% under optimal conditions and an absorption capacity of over 1.0 kg CO_2 kg NH_3, NH_3 outperformed MEA, which had a maximum CO_2 removal efficiency of 94% and an absorption capacity of 0.4 kg CO_2 kg. These findings indicate that NH_3 is more efficient option for CO_2 capture in industrial settings[1,5,6]. Similar results were obtained with Na_2CO_3. Barzagli et al.[3] studied the removal efficiency of CO_2 by Na_2CO_3 at different concentrations (5.43% to 13.81%), and it was found that 8.12% could provide a CO_2 removal of 80%. Additionally, due to their low toxicity, and capability to react at moderate conditions, both solvents can be used to turn CO_2 into chemicals with an economic value and a commercial scale utilization such as calcium carbonate, and ammonium carbonate as sources for fertilisers[7,8]. It is also allowed to be coupled with biological absorption to provide sustainable CO_2 fixation and valorisation of biomass[7,9].

In view of all those advantages this paper studied the removal of CO_2 by aqueous ammonia and Na_2CO_3 solutions were carried out in a laboratory-scale reactor by comparing them to the CO_2 absorption profile of water (control solution). The effects of several operating parameters such as absorbent temperature, and absorbent concentration, on the CO_2 removal efficiency were studied as it seems that the solubility of CO_2 by those alkaline solutions has been reported to be highly dependent on the temperature and the pH drop.

2. MATERIALS AND METHODS

2.1. Materials

The chemical reagents used in this project are ammonia solution (25%) A.R from R&M chemicals and sodium carbonate anhydrous (Na_2CO_3) from HmBG chemicals. The compressed gas was measured using the GM CO2 flow meter Regulator.

2.2. CO_2 capture experimental set-up.

An airlift photobioreactor with a 2L working volume was used as the absorption reactor of this project. All inlets of the bioreactor were covered except for the gas inlet and vented gas outlet. To adjust the reaction temperatures, a circulating water bath was connected to the jacketed reactor. Both solvents, aqueous NH_3 and Na_2CO_3, were introduced to the reactor at three different concentrations (1%, 3%, and 5%). CO_2 gas was injected at a flow rate of 1ml/min from the pure CO_2 cylinder for 2 min at room temperature and pressure.

A simple water displacement method was used to measure the vented CO_2 from the process as illustrated in Figure 1. The method consists of measuring the displacement of water inside an inverted graduated measuring cylinder inside a water bath every 30 seconds in order to identify the flow rate of the outlet gas.

2.2. Experimental design

The study consisted of two sets of experiments. The first set consisted of determining the optimum temperature for CO_2 dissolution in distilled water (control solution) based on 3 different temperatures (20°C-40°C) using pure CO_2 at a flow rate of 1 Lpm. The second set was based on two factors which are the solvent used (Na_2CO_3 and NH_3) and the concentration of the solution (1%-5%) at the optimum temperature found previously. Table 1 presents the design summary of the experiments. The effect of those variables was tested through the records of the change in pH, and CO_2 removal efficiency.

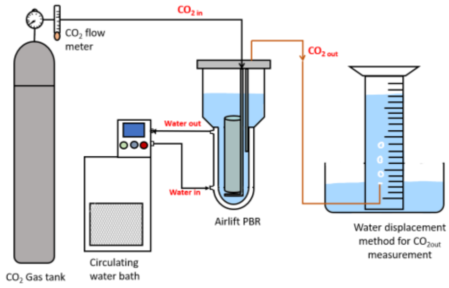

Fig. 1. Experimental set up of the experiment

The pH, which is considered an indication of the dissolution of CO_2 gas, was measured at the beginning and end of the experiment, after 60 min of run. The percentage of absorption was calculated according to the capture efficiency, as it varies with temperature, solvent concentration and reaction time, by the relation indicated in Equation 1.

$$\eta = \frac{V_{in} - V_{out}}{V_{in}} \times 100 \quad (1)$$

Where η is the dissolution efficiency V_{in} is the inlet gas flow rate (1 Lpm), and V_{out} is the outlet gas flow rate.V_{in} which was obtained from the standard curve of the water displacement method.

Table 1. The design of the experiments

No	Fixed variables	Manupilated variables	Responses
1	Solvent: Water Flow rate: 1L/min or 16.67mL/s Duration of CO_2 supply: 2min Duration of the experiment: 60 min	Temperature: 20, 30 and 40 °C	pH change CO2 out (mL/s) Solubility efficiency (%)
2	Solvent: Sodium carbonate (Na_2CO_3) Temperature: 30°C Flow rate: 1L/min or 16.67mL/s Duration of CO_2 supply: 2min Duration of the experiment: 60 min	Solvents concentrations: 1%, 3% and 5%	pH change CO2 out (mL/s) Solubility efficiency (%)
3	Solvent: aqueous ammonia (NH_3) Temperature: 30 °C Flow rate: 1L/min or 16.67mL/s Duration of CO_2 supply: 2min Duration of the experiment: 60 min	Solvents concentrations: 1%, 3% and 5%	pH change CO2 out (mL/s) Solubility efficiency (%)

3. RESULTS AND DISCUSSION

3.1. Effect of temperature on the CO_2 dissolution by water

Table 2 shows the CO_2 dissolution efficiency profile of water under different temperatures (20°C,30°C,40 °C) of the experiment. The temperature of the solution affects the reaction rate of CO_2 and water ultimately reducing the removal efficiency of CO_2 in water at 30°C provided higher removal efficiency with 99.49 % compared to 20°C and 40°C with 90.22% and 97.98 % respectively. These findings opposed the results obtained previously as they concluded that higher temperatures decrease the reaction of CO_2 [8,10,11]. Research conducted by Duan and Sun[10] shows that as temperature increases from 0°C to 90°C, the solubility of CO_2 in water decreases from 0.0693 mol/kg to 0.036 mol/kg. Wolfbeis[11] conducted a separate study using pure CO_2 and found that at temperatures ranging from 5°C to 35°C, the solubility decreased from 2982 to 1173 ppm. While our findings differ from other studies, it is important to note

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that CO_2 solubility can increase under high pressure and with increasing temperature. Additional research by Erfan Muhammadian et al, [12] indicates that at higher pressures (1-400 atm), CO_2 solubility increases with temperature (0-2.25 mol/kg). Nevertheless, all research shows a very low solubility of CO_2 in water, (CO_2< 30%), opposing the results obtained in this research. This could be due to the use of the water displacement method to measure the CO_2 leaving the system. The water used for the water displacement method was from regular tap water which pH was towards alkaline value[13]. Thus, when passing through the measuring cylinder, more CO_2 was absorbed leading to the low volume of CO_2 gas released in the measuring cylinder.

Related to the pH change in the system, it showed that all solutions turned to acidic validating the CO_2 capture data obtained. Water becomes acidic since a part of the water will react to become carbonic acid (H_2CO_3). Its hydrogen ions make the water acidic. Equation (2) presents the reaction taking place between water and CO_2 [14].

$$CO_2(g) + H_2O(l) \leftrightarrow H_2CO_3(\,aq) \quad (2)$$

The difference observed between the trend of the pH value and CO_2 capture is due to in the initial pH of the water in the experiment. Indeed, all solutions have different initial pH values. When the initial pH of water is higher, the CO_2 solubility is more favourable due to the forward reaction (2) is faster. However, after reaching equilibrium, the reverse equation will take place, and more CO_2 will be released instead of absorbed. Thus, by having a high initial pH (pH>7,8), CO_2 was easily absorbed and reached equilibrium faster. It became highly acidic and started releasing CO_2 which in turn increase the pH of the solution. Nonetheless, because of the highest removal efficiency at 30°C temperature, the comparison of the aqueous NH_3 and Na_2CO_2 was performed at 30°C.

Table 2. Comparison of the CO_2 capture efficiency based on the temperature in water.

Temperature (°C)	pH initial	pH final	pH change	CO_2 in (mL/s)	CO_2 out (mL/s)	Dissolve CO_2 (mL/s)	Efficiency (%)
20	7.82	5.78	2.04	16.67	1.63	15.04	90.22
30	7.23	5	2.23	16.67	0.0845	16.58	99.49
40	7.84	4.62	3.22	16.67	0.3357	16.33	97.98

3.2. Effect of the concentration of the solvent on the CO_2 dissolution by Na_2CO_3 and NH_3

The influence of the concentration of the absorbent solution on the removal efficiency of CO_2 was investigated. Figure 2 and Table 3 show that Na_2CO_3 has the highest CO_2 capture at a concentration of 3% (99.12% capture efficiency) followed by aqueous ammonia at 5% (98.54% efficiency). The ammonia results followed the results obtained by other studies since its removal profile increases as the concentration increases[1,4–6]. Nonetheless, Table 3 clearly indicates that both solvents have a lower CO_2 capture rate than water (99.49%). However, this directly contradicts previous research. Barzagli et al[3] studied the effect of concentration of the solvent (5.43 wt%-13.81 wt%) on the CO_2 capture by Na_2CO_3. It was found that with 15% CO_2, the higher the sodium carbonate concentration, the higher the CO_2 capture (with a capture rate > 80%), however, to reduce the excess use of solvent 8.12 wt% of Na_2CO_3 was considered as the optimum concentration. Similar results were observed with CO_2 dissolution by aqueous ammonia (5% to 15%) at room temperature. Liu et al,[14] reported that the higher the ammonia concentration, the higher the CO_2 capture (with a capture rate > 90%)., However, to avoid

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volatilization of the ammonia, a concentration below 10% should be able to achieve similar results. It is possible that the variance observed in our results could be attributed to the analytical approach chosen for scrutinizing the CO_2 emitted from the system. The experiment employed a displacement method that did not differentiate between the various gases collected, which may have impacted the obtained measurement. Additionally, the water used for the displacement method was ordinary tap water that was not degassed and potentially contained unidentified gases, resulting in an overestimation of the gas emitted from the system. Besides that, the temperature was monitored from the circulating water instead of the direct measurement of the temperature of the solution. However, Barzagli [3] reported that the reaction between CO_2 and aqueous NH_3 and Na_2CO_3 is exothermic. This could have resulted in the release of NH_3 gases if the temperature increased above 35°C leading to an increase in the volume of gas vented to the measuring cylinder for the 3% NH_3.

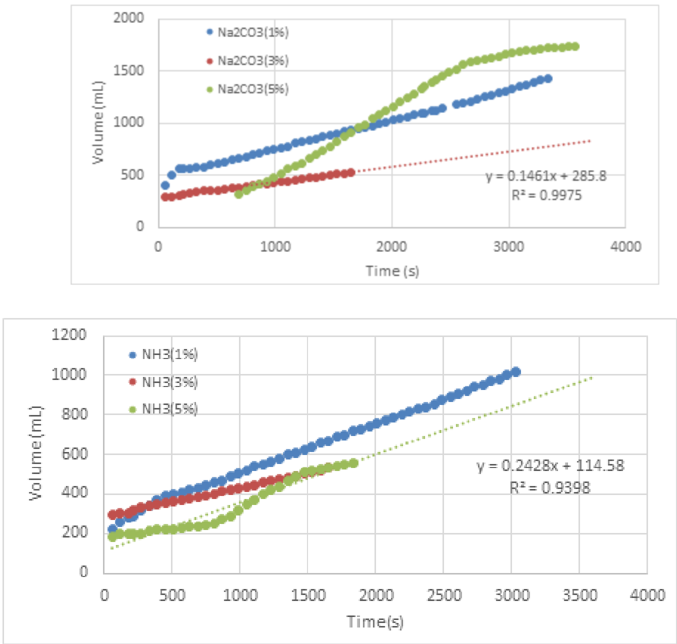

Fig. 2. Release CO_2 based on Na_2CO_3 and NH_3 concentration.

Table 3. Comparison of the CO_2 capture efficiency based on the solvents used.

Experimental condition	pH initial	pH final	pH change	CO_2 in (mL/s)	CO_2 out (mL/s)	Efficiency (%)
water (30°C)	7.23	5	2.23	16.67	0.08	99.49
Na_2CO_3 (1%)	10.3	9.28	1.02	16.67	0.28	98.32
Na_2CO_3 (3%)	10.21	9.73	0.48	16.67	0.15	99.12
Na_2CO_3 (5%)	10.19	9.81	0.38	16.67	0.49	97.07
NH_3(1%)	10.93	9.24	1.69	16.67	0.25	98.49
NH_3(3%)	11.28	10	1.28	16.67	0.54	96.75
NH_3(5%)	11.44	9.68	1.76	16.67	0.24	98.54

4. CONCLUSION

The results of the experiment at current setup and condition revealed that a temperature of 30°C and distilled water to be the best conditions for CO_2 dissolution. Distilled water provided higher CO_2 dissolution than chemical absorption by alkaline solvent, with almost 99.94% of CO_2 being removed. For the alkaline solvent, Na_2CO_3 had the highest CO_2 capture at a concentration of 3%, amounting to 99.12% removal efficiency, followed by aqueous ammonia at concentration of 5%, with 98.54% removal efficiency. These findings do not align with previous research in this field, which could be due to differences in CO_2 gas outlet measurement. Further research is necessary to provide conclusive reasons for the high CO_2 dissolution in water when using pure CO_2 gas. To enhance the study of CO_2 capture, it is highly recommended to select a fast and effective CO_2 capture analysis that specifically targets CO_2 gases.

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