

Intensification of CO₂ absorption using nanofluids in a structured packed column

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The current advances in science and technology revolve around sustainable development. A lot of efforts has been made to reduce carbon dioxide emission which accounts for climatic change. Among them, the carbon dioxide capture by chemical absorption is close to commercialization. This paper presents a comparative study of a conventional solvent, aqueous ammonia, with a next generation working fluid, graphene oxide nanofluid. Aqueous ammonia is used as the solvent which has good thermal and oxidative stabilities with lower regeneration energy. It is reported that nanofluids increase mass transport compared to base fluids. Instead of traditional random packing, structured packing is used which increases the efficiency of the absorption. Several other parameters are taken into consideration such as solvent flow rate, gas flow rate, temperature of the process, concentration of the solvent and gas, etc., for calculating the efficiency and mass transfer characteristics. The nanofluids are prepared by ultrasonic treatment and show good dispersion stability. This accounts for an increase in the absorption efficiency of the solvent by 82 %.

Keywords: Absorption, Nanoparticles, Mass Transfer, Carbon dioxide, Ammonia

INTRODUCTION

The recent changes in the climatic conditions of the Earth are due to the emission of greenhouse gases into the atmosphere. Usually, the carbon dioxide present in the atmosphere is utilized by green plants. Research has found that the increase in carbon dioxide content raises global warming [1]. At higher temperatures, there is a decrease in the absorption of carbon dioxide by the plants. Global Carbon Project has found that there is an increase in carbon dioxide emission of 2 % in 2018 and about 2.6 % in 2019. The scientists claim that there will be an increase in carbon dioxide emission by 45% than the preindustrial levels [2, 3]. A special report from the Intergovernmental Panel on Climate Change reported that carbon emission should fall to 50% by 2030 in order to keep the global temperatures within ± 1.5 °C [4, 5]. An increase in coal consumption by 7.1% in India and 4.5% in China causes increased release of carbon dioxide into the atmosphere than normal. The shift in the trend line from an increase in carbon dioxide emission can be done by two methods. One is to support the emission reduction and the other is to restrict the emission growth of the nations that increase the emission of carbon dioxide. The increase in the growth of renewable and low carbon technologies accounts to strengthen emission reduction. Recent technologies developed should outpace the climatic impacts and drive the emission to zero by 2050 [6-8].

The main contributing factor in the chemical absorption is attributed to the packing materials. These materials provide a large area of contact

between the solvent and the acidic gas phase. There are mainly two types of packing materials: dumped or random packing and regular or structured packing. In general, random packing is made of cheap inert materials such as clay, porcelain or a variety of plastics. Different packing materials have different surface area and void space between the packing which accounts for packing performance.

Table 1. Physical properties of the CO₂/NH₃ system.

Liquid density (kg/m ³)	0.86
Liquid viscosity (cp)	0.276
Gas density (kg/m ³)	1.977
Gas viscosity (kg/ms)	1.8×10^{-5}
Temperature (K)	303
Pressure (atm)	1

Most of the carbon dioxide emission comes from the power plants and chemical industries. Hence, advancement should be made to the present carbon dioxide capture technology to reduce the emission. One such technique is the Carbon Capture Sequestration (CCS). Among these techniques, the absorption of carbon dioxide by chemical solvents can be commercialized. Research has found that the amine solutions account for the increased absorption rate of carbon dioxide. Recent literature studies prove that ammonia is a promising solvent. The major advantage of ammonia over other amine solutions is that it does not degrade easily, has low energy input and no corrosion problem [9, 10]. The use of structured packing increases the efficiency and good mixing of carbon dioxide and ammonia solvent. The recent working fluid that is a nanofluid attracts the attention of the

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recent researchers. It is found that the nanofluid increases the absorption of carbon dioxide into the solvent by several possible mechanisms. Among them, grazing or shuttle mechanism and Brownian mechanism account for mass transport [11]. During grazing mechanism, at the gas-liquid interface nanoparticles adsorb the carbon dioxide in the film layer and after some time desorb them in the solvent, which increases the rate of absorption. In the Brownian mechanism, the nanoparticles disturb the flow and enhance the mixing of the liquid leading to an increase in residence time and good gas-liquid contact within the absorption column [12]. This accounts for an increase in the rate of absorption. The aim of the present work is to examine the outcome of nanoparticles in carbon dioxide absorption by studying the effects of nanofluid concentration, liquid flow rate and its concentration.

MATERIALS AND METHODS

Synthesis of graphene oxide

Graphene is an allotrope of carbon and graphene oxide was prepared using modified Hummer's technique [13]. Graphite fine powder (0.5 g), 0.5 g of sodium nitrate and 23 ml of sulphuric acid were added in a conical flask surrounded by an ice bath with constant stirring. After 4 hours, 3 g of potassium permanganate was added and the reaction was continued for about 2 hours at 35 °C. Then, 46 ml of distilled water were added, and the mixture was kept at 98 °C for 2 hours without boiling and then the contents were let to cool to ambient temperature. After that 100 ml of distilled water were added and stirred constantly for 1 hour. Ten ml of hydrogen peroxide was added and stirred constantly for another hour. The resultant solution containing graphene oxide nanoparticles was washed, filtered and the sample was kept in an ultrasonicator to maintain the stability of the graphene nanofluid. Then the graphene nanofluid was dried and submitted to particle size analysis.

Nanofluid characterization

Particle size analysis. Graphene oxide nanoparticles, that were prepared using the modified Hummer's method, were analyzed for particle size using a particle size analyzer. Three different samples of the synthesized particles were produced. Their frequency and diameter of the particles were interpreted from the analyzer report. The readings of the three different samples were collected and an average of the three readings was made. A graph was plotted against the average diameter of the particles and their average

frequency as shown in Figure 1. It was inferred that the average size of the particle ranges from 100–530 nm [14].

Table 2. Experimental conditions of the structured packed column.

S. No	Parameter	Conditions
1	Absorption solvent	Aqueous ammonia solution
2	Gas flow rate (L min ⁻¹)	9, 12, 14, 17, 19, 21, 23
3	CO ₂ : Air ratio	4:1
4	Liquid flow rate (L h ⁻¹)	10, 12, 15, 18, 20, 22
5	Ammonia concentration (% v/v)	2, 4, 6, 8, 10, 12
6	Temperature (°C)	28

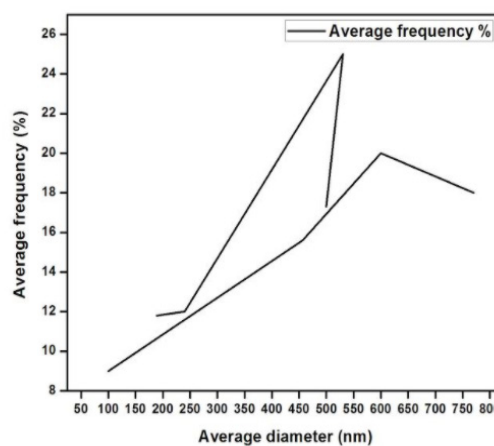


Fig. 1. Average frequency vs average diameter.

Experimentation for CO₂ absorption with nanofluids

The experimental setup for the packed absorption column is shown in Figure 2 and Table 1. The column was made of glass by 0.6 m height with 0.05 m ID. The absorption column was packed with laboratory BX-DX structured packing material with 0.045 m OD and 0.05 m height. Porosity of the packing material was 90 % with specific surface area of 250-750 m²/m³ (Tables 2 and 3). Both the gas and solvent flow rates were controlled by flow meters. CO₂ gas and compressed air was sent at the bottom of the column. When blend gas attained steady-state, aqueous ammonia was sent to the top of the column. After that the reacted sample was collected in the reservoir. The collected reacted sample was titrated against 0.1N HCl because, during the reaction of the gas mixture with aqueous ammonia, ammonium carbonate was formed which is a weak base and should be titrated against strong acid. The nanoparticles were taken at concentrations of 0.0001, 0.001 and 0.0015 %

(w/v). For stability of nanoparticles in the base liquid, it was kept in the ultrasonicator for 3 hours. The prepared nanoparticles were immediately sent to the container and used in the CO₂ capture to prevent the deposition of the nanoparticles [15].

Experimentation for enhancement of CO₂ absorption by inducing magnetic field

To generate a homogeneous magnetic field, a coil of 1.1 mm thick copper wire with windings was wrapped around the external surface of the absorption column. The coil of 0.5 m height was placed in the middle part of the column and a maximum electrical current of 2 A was applied.

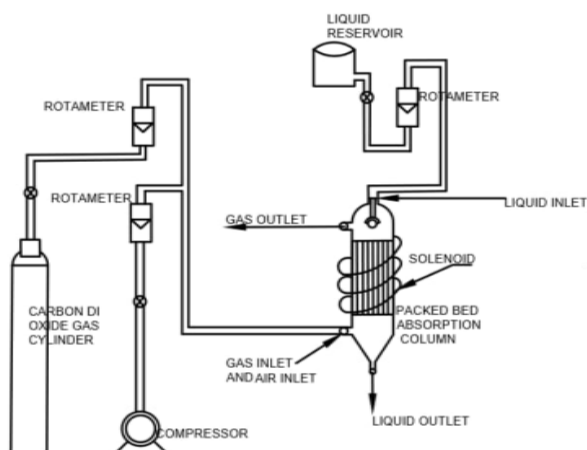


Fig. 2. Schematic diagram of the experimental setup.

Table 3. Equipment used in the study.

S.No	Component	Specification
1	Gas flow rate	1-25 lpm
2	Solvent flow rate	1-25 lph
3	CO ₂ cylinder	100 % pure
4	Compressor	ELGI air compressor (0-8 kg/cm ²)
5	Pump	¼ HP fractional pump (Tullu water pump)



Fig. 3. Packed absorption column with external magnetic field.

RESULTS AND DISCUSSION

CO₂ absorption with structured packing employing graphene oxide nanofluid with solvent

Graphene oxide nanoparticles were dissolved in the 12 % (v/v) ammonia solvent at various concentrations ranging from 0.0001 to 0.0015 % (w/v). An enhancement of mass transfer coefficient, removal efficiency and absorption rate with the introduction of graphene oxide nanofluid was found. This enhancement was due to both Brownian motion and grazing effect. The nanoparticles increased the interfacial area, which simultaneously increased the rate of absorption. This is because nanoparticles break the gas bubbles into smaller ones and thereby the liquid ammonia molecules stick around these nanoparticles, which enhances the CO₂ absorption. Figures 4–6 & 8 infer that the % CO₂ removal, NTU, rate of absorption, and mass transfer coefficient increase with solvent flow rate and concentration. In Figure 7, HTU decreases with an enhancement of liquid flow rate along with concentration. Similar results have been reported in [17] for absorption studies of CO₂ with different nanofluids in packed and wetted-wall columns.

Effect of liquid flow rate on % CO₂ removal

The effect of liquid flow rate on % CO₂ removal for structured packing material with 12 % (v/v) solvent concentration for different graphene oxide nanofluid concentrations (varying from 0.0001 to 0.0015 % (w/v) is shown in Figure 4.

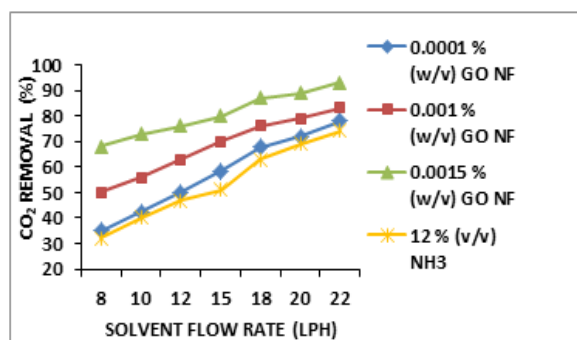


Fig. 4. Effect of solvent flow rate on % CO₂ removal by employing graphene oxide nanofluid.

It is seen that the % CO₂ removal increases with the increase in the concentration of graphene oxide. This is due to the increase in surface area of the nanoparticles which results in the enhancement of Brownian movement and the grazing effect of the nanofluid leading to a higher percentage of CO₂ removal. The gas-liquid flow rates showed a

positive effect on mass transfer. Here the liquid phase of the gas-liquid system was dominant. CO₂ absorption increased at higher solvent flow rates due to the turbulence effect. For graphene nanofluid of 0.0001 % (w/v), the % CO₂ removal efficiency was 78 %; for 0.001 % (w/v) it was 83 % and for 0.0015 % (w/v) - 93 %. Without a nanofluid, the % CO₂ removal was 74 %. Similar results have been reported in a previous study in a packed column with nanofluid [16].

Effect of solvent flow rate on rate of absorption

The effect of solvent flow rate on mass transfer rate per unit volume for a structured packing material with 12 % (v/v) solvent concentration for the different graphene oxide nanofluid concentrations (varying from 0.0001 to 0.0015 % (w/v) is shown in Figure 5.

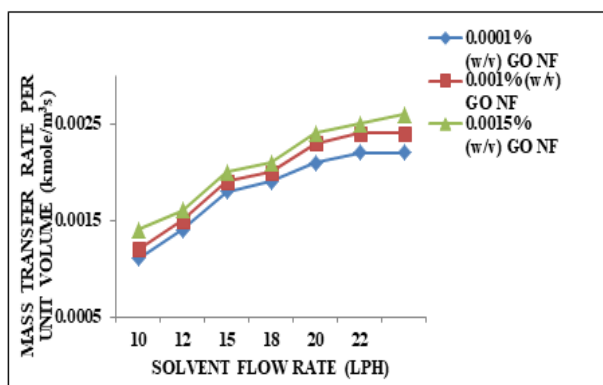


Fig. 5. Effect of solvent flow rate on the rate of absorption by employing graphene oxide nanofluid.

It is seen from this graph that the mass transfer rate increases with an increase in the concentration of nanoparticles and the maximum enhancement in the mass transfer rate was obtained at 0.0015 % (w/v) graphene oxide nanofluid. Besides, on increasing the mass fraction of nanoparticles from 0.0001 % (w/v) to 0.0015 % (w/v), the higher amount of nanoparticles supplies more energy to the solvent and thereby decreases the gas bubble size. With the Brownian movement and grazing effect, gas molecules adsorbed on the nanoparticles and moved to the liquid phase where desorption took place. The rate of absorption for 0.0001 % (w/v) graphene oxide nanofluid was 0.0022 kmol/m³s, for 0.001 % (w/v) graphene oxide nanofluid it was 0.0024 kmol/m³s and for 0.0015 % (w/v) graphene oxide nanofluid - 0.0026 kmol/m³s. As the concentration of the nanofluid increased from 0.0001 to 0.0015 % (w/v), the greater surface area of the particles led to a higher absorption rate of CO₂. Similar results have been reported in a

previous study [18] in a packed column with nanofluid.

Effect of liquid flow rate on the number of transfer units

The effect of solvent flow rate on the number of transfer units (NTU) for a structured packing material with 12 % (v/v) solvent concentration for the different graphene oxide nanofluid concentrations (varying from 0.0001 to 0.0015 % (w/v) is shown in Figure 6. The NTU is given by:

$$NTU = \ln\left(\frac{y_1}{y_2}\right)$$

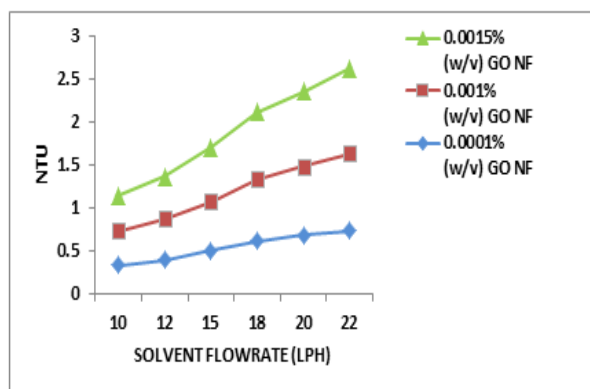


Fig. 6. Effect of solvent flow rate on NTU by employing graphene oxide nanofluid.

It is seen that the NTU value is 2.5 for 0.0015 % (w/v) graphene oxide nanofluid. For 0.001% (w/v) graphene oxide nanofluid the NTU value is 1 and for 0.0001 % (w/v) graphene oxide nanofluid the NTU is 0.5. The higher the number of transfer units, the higher will be the purity of the separation of the CO₂ gas. Hence, the NTU increased for a structured packing material with 12 % (v/v) ammonia concentration. This may be due to an increase in the number of smaller gas bubbles in the graphene oxide nanofluid. Similar results have been reported in a previous study [19] in a packed column with nanofluid.

Effect of solvent flow rate on the height of transfer unit (HTU)

The effect of solvent flow rate on HTU for a structured packing material with 12 % (v/v) solvent concentration for the different graphene oxide nanofluid concentrations (varying from 0.0001 to 0.0015 % (w/v) is shown in Figure 7. The graph illustrates the effect of HTU on the liquid flow rate for the different nanofluid concentrations. Bubble coalescence of two gas bubbles was achieved by both grazing and hydrodynamic effects when the

graphene oxide nanoparticles were present in the solvent and hence reduced the HTU value.

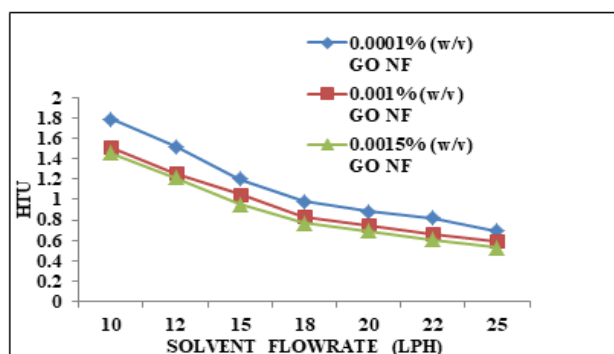


Fig. 7. Effect of solvent flow rate on HTU by employing graphene oxide nanofluid.

The HTU value is 1.8 for 0.0001 % (w/v) graphene oxide nanofluid. For both the 0.001 % (w/v) and 0.0015 % (w/v) graphene oxide nanofluids the HTU value is almost 1.5. Hence, the lower the HTU value, the higher is the separation purity of the gas thereby increasing the mass transfer coefficient. Similar results have been reported in a previous study [20] in a packed column with nanofluid.

Effect of solvent flow rate on the volumetric mass transfer coefficient

The effect of solvent flow rate on the mass transfer coefficient for a structured packing material with 12 % (v/v) solvent concentration for the different graphene oxide nanofluid concentrations (varying from 0.0001 to 0.0015 % (w/v) is shown in Figure 8. The overall mass transfer coefficient $K_G a$ in kmol/hm³ is determined by:

$$K_G a = \frac{N_A}{Z A_c P_T \Delta y}$$

where a is the interfacial area in m²/m³, A_c is the area of the column in m², P_T is the total pressure in atm and Δy is the difference in the mole fraction.

The overall absorption rate can be described as:

$$\dot{Q} = K_G a_v P_{CO_2}$$

Due to the hydrodynamic effect, the nanoparticles surrounding the gas molecules break the gas-liquid interfacial boundary layer into a thin layer and the gas diffusion into the liquid phase increases with the presence of graphene oxide nanoparticles near the interfacial layer which creates turbulence and increases the volumetric mass transfer coefficient. It is seen from the graph that $K_G a$ is 8 kmol/hm³ for 0.0001 % (w/v)

grapheme nanofluid. For 0.001 % (w/v) and 0.0015 % (w/v) the mass transfer coefficient is 13 and 14 kmol/hm³, respectively. This is mainly due to the introduction of a nanofluid along with the absorbent. Similar results have been reported in a previous study [17] in a packed column with nanofluid.

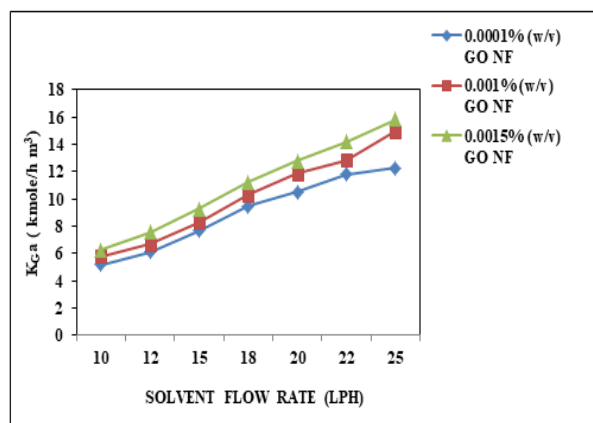


Fig. 8. Effect of solvent flow rate on the volumetric overall mass transfer coefficient by employing graphene oxide nanofluid.

CONCLUSIONS

From this study, the following conclusions are made for the absorption of CO₂ in a structured packed column using aqueous ammonia solvent, and graphene oxide nanoparticles with external magnetic field:

- i. The mass transfer coefficient increased with the addition of graphene oxide nanoparticles.
- ii. The increase in solvent flow rate and the increase in solvent concentration up to 12% increased the removal efficiency.
- iii. Nanoparticles in the magnetic field yielded the best results compared to those without the addition of nanoparticles in a normal column.
- iv. The removal efficiency in the presence of a magnetic field is 82% which is higher than former results. The 0.0015% concentration of graphene nanoparticles showed better results.

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