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Research Article

Enhanced CO_2 Capture Performance Using Methyl Diethanolamine-functionalized Silica Gels: Assessing CO_2 Capture Capacity

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Abstract

Carbon dioxide (CO_2) is a significant greenhouse gas. This causes harm to the environment and to humans. In 2023, atmospheric CO_2 levels rose to 420 ppm, marking a new record high. Therefore, technology for capturing CO_2 has been developed. At present, a wide variety of technologies have been proposed to capture CO_2. Adsorption technology is more affordable and requires less energy for regeneration. There are many potential solid adsorbents for CO_2 capture, such as zeolites, alumina, metal–organic frameworks (MOFs), and mesoporous silicas. Silica materials possess unique properties that make them promising candidates as solid sorbents for CO_2 capture. They provide several benefits, such as high adsorption capacity under dry conditions at ambient temperature, along with low energy requirements for regeneration. Amine-functionalized silica adsorbents are among the most promising methods for CO_2 capture, offering high efficiency and high uptake rates. In this study, silica gels were grafted and impregnated with amines via methyl diethanolamine (MDEA). The effects of water content and amine loading on CO_2 capture performance were investigated. The MDEAs grafted and impregnated on silica gel exhibited excellent CO_2 efficiencies of 0.36 and 0.38 mg CO_2 per gram sorbent, respectively, which are higher than the 15% efficiency of the unmodified adsorbent. The results showed that the modified silica gel had high CO_2 efficiency during the first three adsorption–regeneration cycles when the water content and amine loading increased. Moreover, the nitrogen content increased with increasing water content, leading to an increase in the adsorption capacity.

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Introduction

Today, carbon dioxide (CO_2) is a major greenhouse gas and a key factor in the global temperature rise crisis. From 1750-2023, atmospheric CO_2 levels rose from 277 to 420 parts per million (ppm) [1]. Considerable efforts have been made to capture CO_2 from major human-made sources, such as fossil fuel power plants, to reduce emissions. Recently, capturing CO_2 directly from ambient air, known as direct air capture (DAC), has gained attention [2].

DAC is an effective CO_2 removal method that can extract CO_2 directly from the atmosphere, irrespective of its emission source. One of the advantages of DAC technology is its flexibility in deployment, especially in areas with low energy costs or abundant renewable energy, positioning it as a promising solution for efficient CO_2 removal [3]. In DAC, both absorption and adsorption methods are commonly investigated. The adsorption process, which uses solid sorbents to capture CO_2 from stationary sources or ambient air, presents several benefits, including high CO_2 adsorption capacity, low energy consumption, and cost effectiveness [4].

The adsorptive capture of CO_2 with amine-functionalized porous adsorbents is a promising technology for managing CO_2 emissions. Ordered mesoporous silica materials, such as silica gel, feature a unique

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combination of high surface areas and large pore volumes [5]. However, silica gel has several disadvantages. For example, it tends to adsorb moisture at relatively high humidity levels, which can reduce its efficiency as a CO_2. Additionally, it has limited selectivity, meaning that it may not be as effective at adsorbing CO_2 compared with other adsorbents, such as zeolites, activated carbon, and metal–organic frameworks (MOFs) [6]. To solve this problem, amines are functionalized on a silica gel surface to increase the CO_2 adsorption efficiency. Amine materials, which contain nitrogen atoms, enhance the interaction between CO_2 and silica-based agents, facilitating CO_2 removal [7]. The reaction between an amine group and CO_2 results in the formation of a carbamate and is reversible [8]. The reaction for CO_2 capture using amines is shown in Eq.1 [9].

$$R_2NCH_3 + CO_2 + H_2O \leftrightarrow R_2NCH_4^+ + HCO_3^- \quad \text{(Eq. 1)}$$

The amine functionalization of these silica supports can be achieved in two ways: i) amine impregnation and ii) amine grafting [10]. Wet-impregnated adsorbents achieve high CO_2 capture capacity. However, they suffer from multicycle instability due to the leaching and degradation of amines [11]. In contrast, amine-grafted adsorbents are not affected by the issues mentioned earlier. Although this method produces stable amines that are more securely attached to the adsorbent, they do not achieve the high capacities observed in wet-impregnated adsorbents. This is primarily due to their lower nitrogen content than wet-impregnated adsorbents. To address this issue, water is introduced during the grafting process to hydrate the adsorbent surface [12]. Amine groups such as methyldiethanolamine (MDEA) are commonly used for functionalization because of their simple chemical structure and low price [13].

This study focused on improving silica gel by using MDEA to increase the CO_2 adsorption efficiency in a fluidized bed reactor. The objective of this study was to develop a solid sorbent by adding amines to silica gel. The amine solution is expected to be capable of optimizing the sorbent surface to capture CO_2 and adding surface modifications. In addition, improvements in functionalization methods, such as the water content in the grafting method and amine loading in the impregnation method, leading to more efficient CO_2 capture, were studied. Here, the modified solid sorbents were tested with 400 ppm CO_2 in simulated ambient air.

Methodology

1) Solid sorbent preparation

1.1) Grafting method

Five grams of silica gel (Thomas baker, India) was mixed with 90 mL of toluene (Qrec, New Zealand) and deionized water according to the amounts specified in Table 1. The mixture was stirred at room temperature for 2 hours, and 10 mL of MDEA (Hebei Guanlang Biotechnology, China) was added. The mixture was then refluxed and stirred at 85 °C for 6 hours. Finally, the solution was filtered and dehydrated in a hot air oven at 80 °C. To study the grafting method, the preparation parameters affecting the CO_2 capture capacity of the adsorbent were explored. The variable studied in the grafting method is the water content, which ranges from 0.0 to 2.0 mL in 0.5 mL increments [12].

1.2) Impregnation method

Five grams of silica gel was mixed with 1.0 mL of deionized water and toluene solution according to the amounts specified in Table 1. The mixture was stirred at room temperature for 2 hours. Next, MDEA was added according to the amount specified in Table 1. The mixture was subsequently stirred at room temperature for 24 hours. Finally, the mixture was filtered and dehydrated in an oven at 80 °C. To study the impregnation method, the preparation parameters affecting the CO_2 capture capacity of the adsorbent were explored. The variable studied in the impregnation method is the amine loading concentration, which ranges from 10% to 50% in 10% increments [14].

The prepared silica gel functionalized with MDEA was analyzed via Fourier transform infrared (FTIR) spectroscopy and elemental analysis (CHN) to identify the molecular functional groups and elemental composition of the solid sorbent functionalized with amines.

Table 1 Composition of sorbent preparation

Composition	Grafting					Impregnation				
Silica gel (g)	5	5	5	5	5	5	5	5	5	5
Toluene (mL)	90	90	90	90	90	90	80	70	60	50
H_2O (mL)	0.0	0.5	1.0	1.5	2.0	1.0	1.0	1.0	1.0	1.0
MDEA (mL)	10	10	10	10	10	10	20	30	40	50
%Volume of amine	10	10	10	10	10	10	20	30	40	50

2) CO_2 capture experiment

The experimental setup consists of three main components, as illustrated in Figure 1. The first component involves gas preparation, utilizing a CO_2 concentration of 400 ppm at a flow rate of 150 mL min^{-1}, which reflects the CO_2 levels found in ambient air. In the next stage, CO_2 was adsorbed in the adsorption column, which was operated at room temperature and humidity. The CO_2 used in the experiment was derived from ambient air, which typically contains 78% N_2, 21% O_2, and approximately 0.04% CO_2. The final component was a CO_2 analyzer, which measured the CO_2 capture capacity. The procedure began with the flow of N_2 (supplied by Thai Japan Company) into the column for air treatment. CO_2 was subsequently introduced into the column at a flow rate of 150 mL min^{-1}, and the CO_2 levels were monitored via an analyzer. The data were stopped when the outlet CO_2 level was equivalent to 400 ppm. The saturated sorbent was subsequently regenerated at 90 °C in a conventional heating furnace.

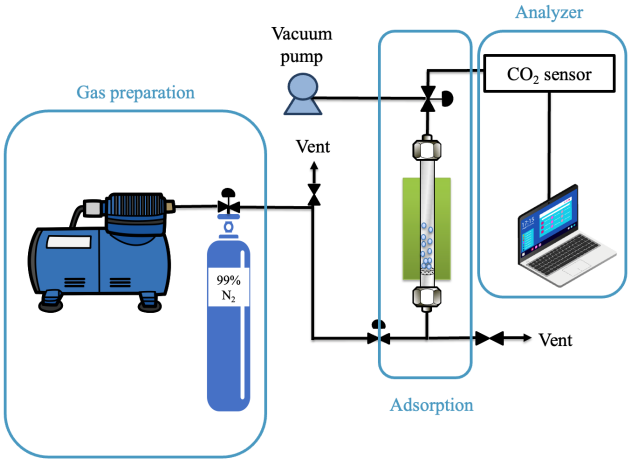

Figure 1 Schematic diagram of the CO_2 capture process.

During the process, the outlet CO_2 concentration data were logged until the CO_2 level reached equilibrium. The data collected from the CO_2 analyzer were used to calculate the CO_2 adsorption capacity [15], as shown in Eq.2.

$$q_e = \frac{1}{m}\int_0^t Q(C_{in} - C_{out})dt \quad \text{(Eq. 2)}$$

where q_e represents the amount of CO_2 adsorbed per unit mass of solid sorbent at equilibrium (mg CO_2 per gram sorbent), m represents the mass of solid sorbent (g), Q represents the mass flow rate of gas (mg min^{-1}), C_{in} represents the mass concentration of CO_2 in the inlet gas (%CO_2), C_{out} represents the mass concentration of CO_2 in the outlet gas (%CO_2), and t represents the adsorption time (min).

Results and discussion

1) Characterization of adsorbents

1.1) Surface area, porosity, and BET

Table 2 shows the comparison between the physical properties of pure silica gel in this study and those of silica gel in other works. The BET surface area, total pore volume and pore diameter were calculated via the Brunauer–Emmett–Teller (BET) method. The pure silica gel in this work presented the highest BET surface area of 414.8 m^2 per g compared with other methods. The high surface area of silica gel facilitates the adherence of a greater amount of amines to its surface, thereby enhancing the efficiency of CO_2 capture. However, the total pore volume and pore diameter are slightly smaller than those reported in other studies. Therefore, the silica gel used in this study has favorable properties for functionalization with amines.

1.2) Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of pure silica gel (red line), amine-impregnated silica gel (purple line) and amine-grafted silica gel (blue line) are presented in Figure 2. The characteristic peaks of Si-O-Si at approximately 1065 and 795 cm^{-1} are present in all the samples. Moreover, N–H bonds (approximately 1697, 1680, 1646, 1540 and 1507 cm^{-1}) and CH_2–N bonds (approximately 1488, 1472, 1456, 1417 and 1338 cm^{-1}) can be observed on the amine-impregnated and grafted silica gel sorbents [16]. These results suggest that the pore surface of the silica gel was effectively functionalized with amines.

Table 2 BET surface area and pore structure parameters of the adsorbents

Sample	BET surface area (m^2 per gram)	Total pore volume (cm^3 per gram)	Pore diameter (nm)	Reference
Silica gel 60A	338	0.84	8.15	[5]
Silica gel 150A	309	1.12	14.9	[5]
Pure silica gel	414.8	0.49	4.7	This study

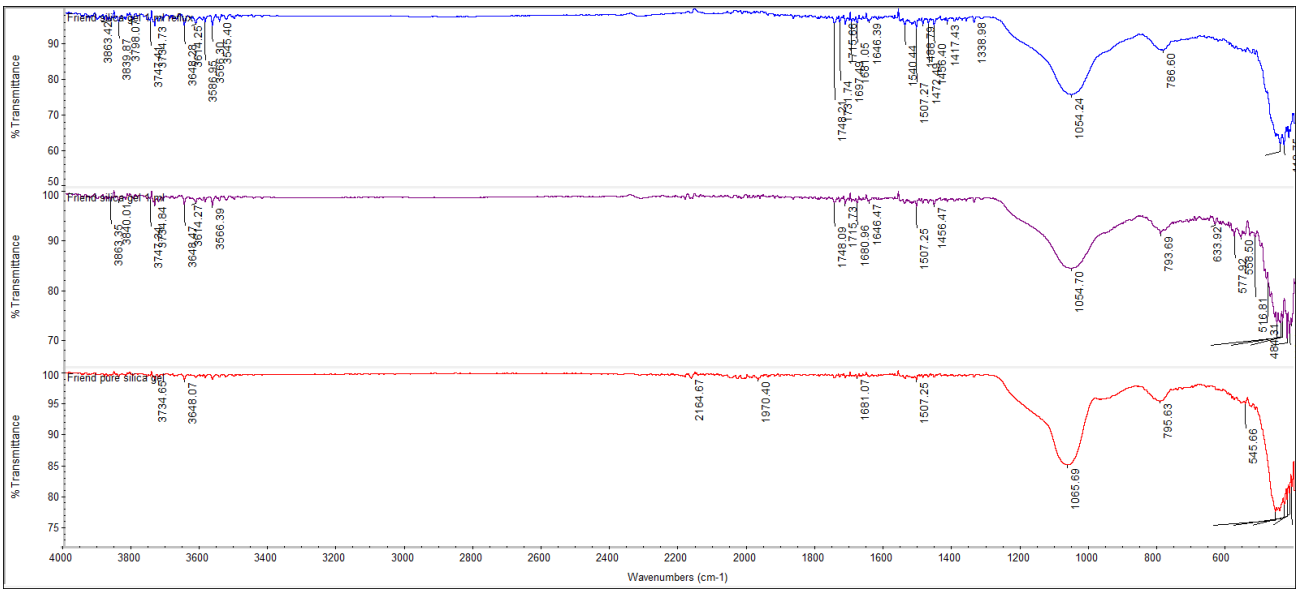

Figure 2 FTIR spectra of pure silica gel, amine-impregnated adsorbent and grafted adsorbent.

1.3) Elemental analysis

The CHN analysis measures the carbon (C), hydrogen (H), and nitrogen (N) contents in the adsorbent, making it the preferred method for assessing the amount of MDEA in the CO_2 adsorbent. This analysis provides the quantities of nitrogen deposited on the surface of silica gel that has been functionalized with MDEA, which were measured via CHN analysis. The nitrogen content obtained from the CHN analysis originates from the amino groups present in the structure of MDEA. When MDEA is used to functionalize silica gel, the analysis reflects the amount of nitrogen or amino groups of MDEA on the gel. Table 3 shows the nitrogen content of the MDEA-functionalized silica gel obtained via the grafting method with an amine loading of 10% and varying water content. Figure 3 shows that the nitrogen content increased with increasing water content up to 1.0 mL. Beyond this point, the nitrogen content decreases and then increases slightly, with the variation being less than 5%. Therefore, adding more than 1.0 mL of water results in a stable nitrogen content. This effect occurs because water is added during the grafting process to hydrate the adsorbent surface. This hydration enhances the density of the hydroxyl groups. This hydration increases the density of hydroxyl groups, which enhances the formation of strong covalent bonds between the silica surface and the amine groups. Therefore, adding 1.0 mL of water is sufficient to increase the nitrogen content.

Table 3 Nitrogen content of the amine-grafted adsorbent

Water content (mL)	Nitrogen content (%)	Nitrogen content (mmol N per gram sorbent)
0.0	2.21	1.58
0.5	2.46	1.75
1.0	3.84	2.74
1.5	3.75	2.68
2.0	3.94	2.81

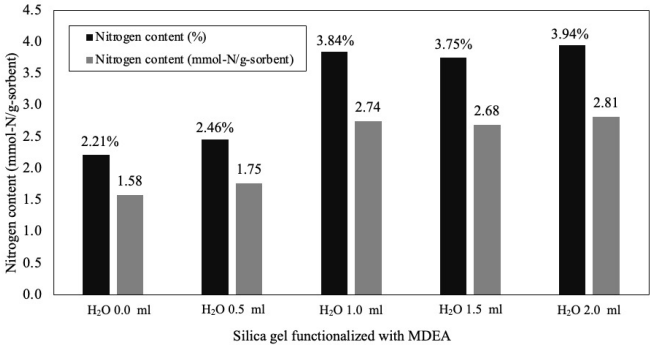

Figure 3 Nitrogen content of the amine-grafted adsorbent.

Table 4 shows the nitrogen content of MDEA-functionalized silica gel impregnated with varying amine loadings from 10% to 50%. Figure 4 shows that the nitrogen content is highest at 10% amine loading, where it reaches 3.98%. Beyond this point, the nitrogen content decreases and remains constant. This is because, with the same amount of water content, excessive amine loading may result in amine groups not binding as efficiently or being lost during subsequent processing.

Table 4 Nitrogen content of the amine impregnated adsorbent

Amine loading (%Vol)	Nitrogen content (%)	Nitrogen content (mmol N per gram sorbent)
10	3.98	2.84
20	3.23	2.30
30	3.53	2.52
40	3.44	2.45
50	3.28	2.34

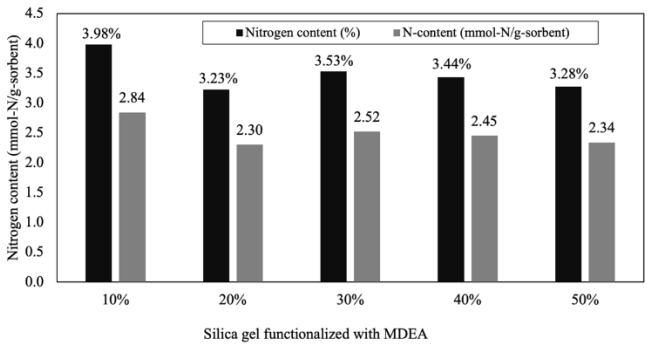

Figure 4 Nitrogen content of the amine impregnated adsorbent.

2) CO_2 capture capacity

2.1) Effect of water content

Figure 5 shows the CO_2 capture capacity of 10% MDEA grafted onto silica gel. From 0 mL of water to 2.0 mL, the CO_2 adsorption capacity increases with increasing water content, increases to 1.0 mL, and then remains constant. This trend is similar to that of the nitrogen content. The optimum water content was 1.0 mL. Moreover, 1 mL of water was added to the adsorbent, resulting in a capture capacity of 0.35 mg CO_2 per gram sorbent.

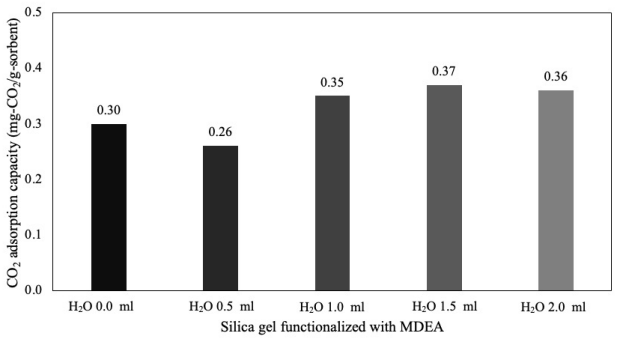

Figure 5 CO_2 capture capacity of the MDEA-grafted adsorbent.

2.2) Effect of amine loading

The CO_2 capture capacity was then studied by adjusting the amine loading, which was 10, 20, 30, 40 or 50% volume. Figure 6 shows that when the amine loading increases from 10% to 20%, the CO_2 adsorption capacity decreases slightly. When the amine loading increases to 30% and 40%, the CO_2 adsorption capacity increases, but it decreases again at 50%. These results align with the nitrogen content analysis in Figure 4. These variations do not significantly affect the CO_2 adsorption capacity. Moreover, the CO_2 adsorption capacity at amine loadings of 10%, 30%, and 40% is among the highest. In terms of cost-effectiveness, using the least amount of amine while achieving a high CO_2 adsorption capacity of 0.38 mg CO_2 per gram sorbent makes 10% amine loading the most suitable choice for silica gel functionalization. This demonstrates the cost-effectiveness of the adsorbent.

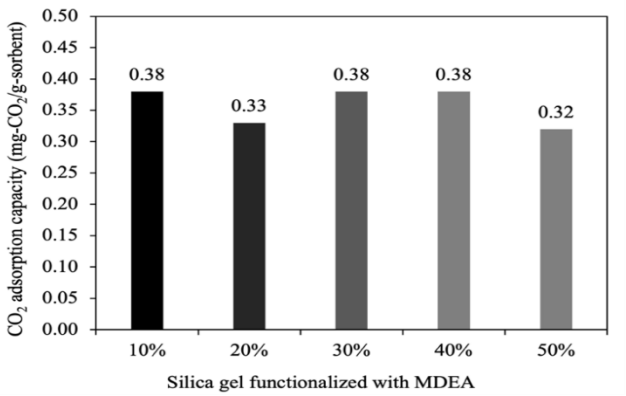

Figure 6 CO_2 capture capacity of the MDEA impregnated adsorbent.

2.3) Effect of the functionalization method

As shown in Figure 7, under the same conditions with 10% MDEA and 1.0 mL of water, both the grafted and impregnated adsorbents yielded similar results in terms of the CO_2 capture capacity and nitrogen content. The CO_2 capture capacities of the impregnated and grafted adsorbents are 0.38 and 0.35 mg CO_2 per gram sorbent, respectively. Therefore, the impregnation method was suitable for amine functionalization because of its simple preparation and suitability for large-scale production.

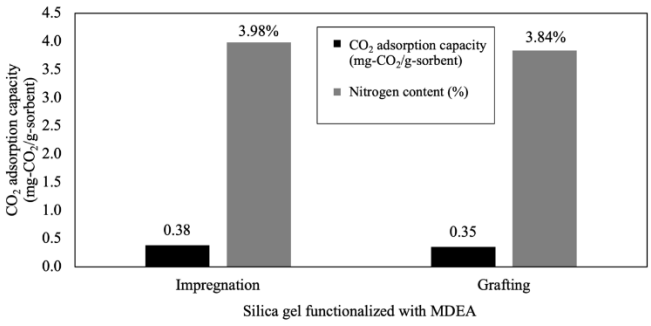

Figure 7 CO_2 capture capacity and nitrogen content of the MDEA-grafted and impregnated adsorbents.

Conclusion

This study aims to address the challenge of CO_2 emissions, a major contributor to greenhouse gases, by enhancing the CO_2 capture capacity of solid sorbents through amine functionalization. Silica gel was chosen as the base material, and its physical properties, including surface area and porosity, were characterized via BET analysis. The results indicated that the silica gel used in this study had a greater surface area than those used in previous studies did, making it well suited for amine functionalization.

Two functionalization methods were investigated, namely, grafting and impregnation, with MDEA as the amine agent. FTIR analysis confirmed the successful attachment of amines on the silica gel surface, as evidenced by absorption bands between 1400-1600 cm^{-1}, corresponding to N-H, CH_2-N, and CH_3-N bonds. CHN analysis was employed to quantify the nitrogen content and assess

the effectiveness of the functionalization. In the grafting method, the nitrogen content increased with increasing water addition, peaking at 1.0 mL before stabilizing, indicating that this was the optimal water content. For the impregnation method, the highest nitrogen content (3.98%) was observed at 10% amine loading.

CO_2 adsorption experiments revealed that the grafting method achieved a maximum adsorption capacity of 0.35 mg CO_2 per gram sorbent at a water content of 1.0 mL. In contrast, the impregnation method resulted in a slightly higher adsorption capacity of 0.38 mg CO_2 per gram sorbent at 10% amine loading. Among the tested loadings, 10%, 30%, and 40% produced the highest adsorption capacities. However, 10% amine loading has emerged as the most cost-effective choice, achieving optimal CO_2 adsorption performance while minimizing amine usage.

Overall, both methods demonstrated comparable results in terms of nitrogen content and CO_2 adsorption capacity. Nonetheless, the impregnation method was preferred because of its simpler preparation process and suitability for large-scale production.

Since silica gel has been modified with amines, several concerns have arisen. For example, the CO_2 capture capacity of silica gel, even after modification with amines, remains relatively low compared with that of other types of sorbents. Additionally, there is concern about the deterioration of amine-modified silica gel when it is used over an extended period.

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