Adsorptive removal of carbon dioxide using polyethyleneimine loaded glass fiber in a fixed bed

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Abstract

Low-cost glass fiber (GF) was modified by loading polyethyleneimine (PEI) using a physical impregnation method and applied as an adsorbent for CO₂ capture. The structure and morphology of the PEI-loaded GF were characterized by thermogravimetric analyzer (TGA), fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). The PEI-loaded GF possessed a core-shell structure. The CO₂ dynamic adsorption-desorption performances were investigated in a PEI-loaded GF fixed bed. The effects of PEI loading ratio, adsorption temperature, relative humidity (RH), flow rate and bed depth (H/D) ratio were examined, and the maximal dynamic CO₂ adsorption capacity was 60.04 mg·g⁻¹ with a PEI/GF ratio of 0.70 g·g⁻¹. In addition, the PEI-loaded GF was regenerated with only a slight decrease in the adsorption capacity after multiple regenerations using an optimum regeneration temperature of 100 °C. The results suggest that the PEI-loaded GF can be used as an economical adsorbent system for CO₂ capture.

Keywords: CO₂ capture; Glass fiber; Polyethyleneimine; Dynamic adsorption

1 Introduction

Anthropogenic CO₂ emission from the burning of fossil fuels is causing general public concern because it is speculated to be the primary contributor to global warming and climate change [1-3]. According to NOAA, the current atmospheric concentration of CO₂ has reached 400 ppm compared to a level of 300 ppm in the pre-industrial period. The CO₂ emissions related to the energy sector will further increase by 130% by 2050 due to increasing fossil fuel usage [4, 5]. Currently, chemical absorption [6-8], membrane [9, 10], ionic liquids [11, 12] and cryogenic techniques have been investigated for CO₂ capture. Among these technologies, aqueous amine chemical absorption systems including monoethanolamine and diethanolamine [13, 14] have been commercially utilized for CO₂ capture from power plant effluents. However, this system suffers from several drawbacks including severe equipment corrosion and amine degradation as well as the high-energy consumption for the regeneration of aqueous solutions during stripping CO₂ from the spent amine solution [15]. Therefore, advanced CO₂ capture and storage technologies that are energy efficient and environmentally friendly are important.

As a promising technology, solid-form amine adsorbents have attracted much attention due to

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its less energy intensive regeneration process. The solid supports are normally porous materials with a high surface area and large pore volume (e.g., porous silica [16, 17], activated carbon [18, 19], zeolites [20, 21], metal-organic frameworks (MOFs) [22, 23] and some other materials, such as bentonite [24] and activated alumina [25]).

As the substrate for the amine, porous carbon has relatively weak retention, which results in poorer selectivity to CO₂ in the range of 50-120 °C. Due to its hydrophilic surface characteristics, zeolite supported amines are extremely sensitive to moisture, and their performance is substantially reduced in high humidity environments during CO₂ adsorption. MOFs exhibit exceptional CO₂ adsorption capacity with pure CO₂ at high pressures but its performance was dramatically reduced when exposed to gas mixtures. Silica-supported amine materials suffer from slow kinetics due to poor transport of CO₂ molecules from the surface into the loaded amine bulk due to the compact entity formed by the loaded amine [26].

A glass fiber, which has a small diameter and is an inexpensive and mechanically and thermally stable substrate, has been successfully applied as a substrate for the synthesis of novel carbon fibers [27-29] and other functional materials [30, 31]. Polymeric-amine coatings have been widely studied due to their high selectivity towards CO₂ and high thermal stability [32, 33]. Among all of the amines, polyethyleneimine (PEI) is a widely available and economical amine molecule [34-36]. To develop an economical and viable CO₂ adsorption system, a glass fiber that was 7 μm in diameter was introduced as a supporting substrate for polyethyleneimine. The performance of this material for CO₂ capture was investigated under various humidity, temperature, flow rate, bed depth and regeneration conditions.

2 Experimental

2.1 Materials

The glass fiber substrate, which is a nonwoven glass fiber mat with 7 wt% PVA binder (Craneglass 230), was provided by Crane & Co. Inc (Dalton, MA). Polyethylenimine (PEI, $M_n \sim 600$), epichlorohydrin (ECH) and methanol (99.8%) were purchased from Sigma-Aldrich and used as received. The CO₂ and N₂ gases were lab grade and obtained from S.J. Smith Welding, Inc.

2.2 Preparation of PEI-loaded GF

PEI and ECH were dissolved in methanol to yield a homogenous solution. Glass mats were dip-coated with the mixture and dried in air at room temperature overnight followed by curing in a convection oven at 70 °C for a pre-set time.

2.3 Characterization

The morphology of the sorbents was observed using a Hitachi S-4700 scanning electron microscope (SEM). Prior to each characterization, the samples were dried overnight at approximately 70 °C under vacuum followed by conductive coating using a gold-palladium plasma spray for 20 s.

The coating content of PEI on the glass fiber was measured using a Hi-Res TA Instruments 2950 Thermogravimetric Analyzer (TGA) by burning off the coating in air at 800 °C. The surface chemistry functional groups were characterized by Fourier transform infrared spectroscopy (FTIR Nicolet Nexus 670) in diffuse reflectance mode (DRIFTS). The surface charge of the sorbents was

determined through zeta potential measurements using a Zetasizer (Malvern Zetasizer Nano ZS).

2.4 CO₂ adsorption-desorption performance

CO₂ adsorption-desorption breakthrough cycles were conducted using the lab-scale setup shown in Figure 1. The sorbent was loaded into the adsorption column with a fixed bed depth. Prior to each run, the column was purged with N₂ at a humidity level equivalent to the adsorption process. After 15 mins of purging, the CO₂ and N₂ mixture gases were introduced until complete breakthrough was achieved. Then, pure N₂ was used to purge the adsorption column followed by online regeneration. Prior to each run, a blank adsorption experiment was carried without sorbents in the system under the same adsorption conditions. An electrochemical CO₂ sensor (CO₂ Meter, Inc., range of 0-30 vol % CO₂, accuracy of $\pm 0.2 \text{ vol}\% \text{ CO}_2 \pm 3 \text{ vol}\%$ of measured value) was employed to monitor the outlet CO₂ concentration.

Figure 1. Schematic representation of the laboratory scale CO₂ adsorption setup.

Both the adsorption capacity and the desorption rate were used to evaluate the adsorbent. The CO₂ adsorption capacity was calculated using Eq. (1)

$$Q_{\text{CO}_2} = \frac{\int_0^t [(c_0 - c_t) \times V \times \rho_{\text{CO}_2}]}{m} \quad \text{Eq. (1)}$$

where Q_{CO_2} is the CO₂ adsorption capacity ($\text{mg} \cdot \text{g}^{-1}$), c_0 and c_t are the CO₂ concentration in the feed flow and at time t , respectively, (%), V is the flow rate, $\text{L} \cdot \text{min}^{-1}$, ρ_{CO_2} is the CO₂ density ($\text{g} \cdot \text{L}^{-1}$), and m is the weight of sorbent (g).

The desorption rate was calculated using Eq. (2)

$$k_{\text{Desorption}} = \frac{\int_0^t [(c_0 - c_t) \times V \times \rho_{\text{CO}_2}]}{Q_{\text{CO}_2} \times m} \quad \text{Eq. (2)}$$

where Q_{CO_2} is the CO₂ adsorption capacity calculated in the adsorption process ($\text{mg} \cdot \text{g}^{-1}$) and m is the weight of the sorbent (g).

The amine utilization efficiency, which is defined as the moles of CO₂ molecules adsorbed for each mole atom in the amine functional group, was calculated using Eq. (3)

$$E_{\text{Amine}} = \frac{Q_{\text{CO}_2} / M_{\text{WCO}_2}}{r / (1+r) / M_{\text{WN}} \times \frac{M_{\text{WCO}_2}}{M_{\text{WC}_2\text{H}_5\text{N}}}} \times 100\% \quad \text{Eq. (3)}$$

where Q_{CO_2} is the CO₂ adsorption capacity calculated in the adsorption process (mg·g⁻¹) and r is the PEI coating ratio.

3 Results and Discussion

3.1 Morphology

The morphologies of the GF before and after PEI impregnation were investigated by SEM. As shown in Figures 2 (a, b), the GF substrate has a smooth surface with a fiber diameter of 7.0 μm. After coating, a PEI layer with a thickness of ~ 0.5 μm was observed (Figures 2 (c, d)) with a core-shell structure. Theoretically, a relatively smooth diameter dependence exists for the adsorption-desorption activation energy for the symmetric surfactants, and in general, a smaller diameter results in a higher activation energy [37]. In addition, the rate law was also determined based on the interatomic distance and angles during the course of the reaction [38]. Therefore, the core-shell structure of the PEI coated GF with a small reaction diameter could greatly reduce the mass transfer distance and improve surface diffusion, leading to better CO₂ adsorption-desorption kinetics.

Figure 2. SEM images of GF (a, b) and PEI-loaded GF (c, d).

3.2 Characterization

3.2.1 Coating content and thermal stability

The PEI coating content was obtained using TGA by burning the PEI-loaded GF at 800 °C in an air atmosphere. The amount of PEI loaded onto the GF was derived from the weight loss during the TGA test. The coating content of PEI on the glass fiber could be tuned by the concentration of the coating solution. During the course of study, a weight gain of 30% to 400% was observed. In addition, the thermal properties of the adsorbent were investigated using the TGA measurement. As shown in Figure 2, there are three obvious weight loss steps with peak temperatures at approximately 100, 340 and 580 °C, respectively. The first peak was due to the removal of water molecules adsorbed onto the sorbent. In comparison to the TGA results of pure PEI, the latter two peaks are primarily associated with the decomposition of PEI loaded onto the GF. Excluding the effect of moisture, the temperature associated with the 5% weight loss was 97.8 °C, indicating that PEI is an excellent thermally stable media.

Figure 3. TG/TGA curve for the PEI-loaded GF (coating ratio=1.26 g·g⁻¹).

3.2.2 FT-IR Spectroscopy

In the FT-IR spectra of the GF and PEI-loaded GF (Figures 4 (a), (b)), the adsorption peaks at 3349 cm⁻¹, 3284 cm⁻¹ and 914 cm⁻¹ were assigned to the asymmetric bending and stretching vibration of Si-OH, which is the main structure in the GF substrate. In comparison to the GF, the PEI-loaded GF exhibited new peaks located at 2945 cm⁻¹ (symmetric stretching of -CH₂-), 2837 cm⁻¹ (asymmetric stretching of -CH₂-) and 1671 cm⁻¹ (bending vibration of -N(R)H), which indicated that PEI were successfully introduced [39]. The spectra of the PEI-loaded GF before (Figure 4 (b)) and after (Figure 4 (c)) regeneration are nearly identical, indicating that CO₂ was successfully desorbed from PEI.

Figure 4. FT-IR spectra of GF (a) and PEI-loaded GF before (b) and after (c) regeneration.

3.2.3 pH Isotherm and pH_{ZC}

The zeta potential measurements identified the differences in the electrokinetic interactions at the interface between an aqueous electrolyte and material surfaces [40]. As shown in Figure 5, the pH_{ZC} value was $8.58 > 7$, which indicates its weak basic nature, potential to attract weak acidic CO_2 and ease of regeneration. The positive value of the zeta potential (35.73 mV) and the isoelectric point (IEP, the point where the curve crosses pH axis) value of 11.00 were most likely due to the $-\text{NH}_2$ group in the PEI grafted onto the GF.

Figure 5. Zeta potential of PEI coated GF under different pH values.

3.3 CO₂ adsorption of PEI-loaded GF

3.3.1 Effect of PEI content on CO₂ adsorption

The CO₂ adsorption capacity and amine utilization efficiency of the PEI-loaded GF with different PEI coating contents under a 15 vol% CO₂ influent are shown in Figure 6. The results in Figure 6 indicate that the CO₂ adsorption capacity increased from 26.38 mg·g⁻¹ at a 24% weight gain to 58.96 mg·g⁻¹ at a 67% weight gain but decreased to 22.67 mg·g⁻¹ at a 126% weight gain. This trend is consistent with previous results for dynamic adsorption of CO₂ [16, 24]. This result may be due to the dynamic adsorption capacity, which is influenced by two factors as follows: available adsorption sites and accessible sites within the time regime during breakthrough. In general, as the coating content increased, the adsorbent has more interaction sites available for the adsorbate. However, an increase in the coating also creates a thicker coating, which results in a longer diffusion distance that “buries” the sites accessible to CO₂. A substantial increase in the weight without increasing the accessible sites (i.e., capacity) leads to a decrease in the adsorption capacity at higher coating contents.

The amine efficiency exhibits a different pattern compared to the capacity. At a weight gain < 67%, ~ 13.0% of the amine is utilized. Therefore, a weight gain < 67% will not hinder the accessibility of the polymer matrices to CO₂ diffusion. At a 126% weight gain, the amine efficiency is substantially reduced to 4.8% because the coating content falls into the regime where the amines within the inner layer are not available to the CO₂ molecules. Based on the amine efficiency as and adsorption capacity at 18% RH and room temperature, an optimum 67% weight gain was derived at a CO₂ adsorption capacity of 58.96 mg·g⁻¹.

Figure 6. Effect of PEI coating ratio on CO₂ adsorption of the PEI-loaded.

GF Note: Experimental conditions: 18% RH, 25 °C, 18.55 ml·min⁻¹; fix bed dimension: 1.05 cm in length, 1.5 cm in diameter.

3.3.2 Effect of moisture on CO₂ adsorption

Moisture is always present in CO₂-rich fuel. One advantage of amine-containing solid phase adsorbents, such as the PEI-loaded GF, is their tolerance to the presence of moisture in the feed gas compared to other physical adsorbents, including activated carbon and zeolites [41]. The effect of humidity on CO₂ adsorption performance was investigated for the PEI-loaded GF system, and the results are shown in Figure 7.

Moisture plays a critical role in the CO₂ adsorption capacity. As the environment become more humid from 0% to 18%, the adsorption capacity increased from 14.36 mg·g⁻¹ to 49.49 mg·g⁻¹, and the same trend was observed for the amine efficiency. This result suggests that moisture benefits CO₂ adsorption onto the PEI-loaded GF, which is consistent with previously reported results [42, 43].

This phenomena may be due to the different interaction mechanisms between amines and CO₂ under dry and humid conditions. PEI contains primary, secondary and tertiary aliphatic amines (RNH₂, RNH, R₃N), and the adsorption mechanism for CO₂ involves chemisorption [44]. The proposed reaction pathways between CO₂ and primary amine with and without water present are as follows:

Therefore, the CO₂/N stoichiometric retention ratio was 1:2 and 1:1 under dry and humid

conditions, respectively. The decreasing N mass required under humid conditions for the same CO₂ uptake improves the CO₂ adsorption capacity.

However, the data in Figure 7 also indicates that there is a slight decrease in the CO₂ adsorption capacity when the relative humidity exceeds 18% RH (from 49.49 mg·g⁻¹ at 18% RH to 43.19 mg·g⁻¹ at 25% RH). This result is most likely due to excessive water being adsorbed on the surface under high humidity conditions, which results in the formation of dense water films that prohibit CO₂ from diffusing to the active sites. Therefore, CO₂ adsorption was impaired to some degree when the addition of moisture exceeded a certain value (in this case, 18% RH for 0.67 g·g⁻¹ PEI-loaded GF).

Figure 7. Effect of moisture on CO₂ adsorption of the PEI-loaded GF.

Note: Experiment condition: 25 °C, 18.55 ml·min⁻¹; Fix bed dimension: 1.05 cm in length, 1.5 cm in diameter; Materials: 0.67 g (PEI) ·g⁻¹ (GF).

3.3.3 Effect of temperature on CO₂ adsorption

The adsorption temperature also plays a role in CO₂ capture. An increase in temperature leads to more rapid kinetics but worse thermodynamics. Within the tested temperature regime from 0 to 80 °C, the optimum CO₂ adsorption was achieved at 40 °C with a maximum CO₂ adsorption capacity of 60.04 mg·g⁻¹, which is 74.8% higher than at 0 °C, as shown in Figure 8. However, within a temperature range of 25 - 80 °C, the temperature has a minimal effect on the CO₂ capture, and the adsorption capacity varies by only 10%.

At relatively lower temperatures (≤ 40 °C), the diffusion effect dominates the CO₂ adsorption onto the PEI-loaded GF. The carbamates formed with PEI significantly increase the viscosity and density of the PEI coating and inhibit further CO₂ diffusion [45]. An increase in the temperature contributes to a lower PEI viscosity and higher molecular mobility as well as higher CO₂ diffusion, reducing the resistance for CO₂ access to PEI. However, the adsorption effect is important for the exothermic reaction between CO₂ and amines at higher temperatures. In this case, a lower temperature is beneficial for CO₂ adsorption because the equilibrium shifts to desorption when the

temperature continues to increase.

Figure 8. Effect of temperature on CO₂ adsorption of the PEI-loaded GF.

Note: Experiment condition: 18% RH, 18.55 ml·min⁻¹; Fix bed dimension: 1.05 cm in length, 1.5 cm in diameter; Materials: 0.67 g (PEI) ·g⁻¹ (GF).

3.3.4 Effect of flow rate on CO₂ adsorption

The CO₂ adsorption capacity and amine efficiency for the PEI-loaded GF under a 15 vol % CO₂/N₂ atmosphere at 18% RH and room temperature using different CO₂ flow rates are shown in Figure 9.

As the CO₂ flow rate increased, the CO₂ uptake did not vary substantially (i.e., from 39.65 mg·g⁻¹ for 10.51 ml·min⁻¹ to 44.11 mg·g⁻¹ for 22.61 ml·min⁻¹). In general, a higher adsorption capacity is believed to be obtained for various adsorbents at lower flow rates to allow for sufficient contact time between the adsorbate and adsorbent. However, for the PEI-loaded GF, the effect of the flow rate on the CO₂ adsorption capacity was not significant. This counterintuitive result may be due to the core-shell structure of the PEI-loaded GF. The PEI shell layer mitigates the diffusion barriers for CO₂ from the main feed gas stream onto the PEI layer compared to porous materials. Therefore, fast kinetics and an inverse flow rate effect on the CO₂ uptake were observed in the experimental range.

Figure 9 Effect of flow rate on CO₂ adsorption of the PEI-loaded GF.

Note: Experiment condition: 25 °C, 18% RH; Fix bed dimension: 1.05 cm in length, 1.5 cm in diameter; Materials: 0.67 g (PEI) ·g⁻¹ (GF).

3.3.5 Effect of bed depth (H/D) on CO₂ adsorption

Figure 10 shows the CO₂ adsorption capacity of the PEI-loaded GF using various bed depths (H/D) ranging from 0.5 to 1.5. The samples were approximately 0.50 g with different heights (i.e., 0.75, 1.00, 1.50 and 2.25 cm). The ratios of the column height and diameter (H/D) were 0.50, 0.70, 1.00 and 1.50.

Based on the results in Figure 10, H/D=0.70 exhibits the maximum CO₂ adsorption capacity (i.e., 53.67 mg·g⁻¹). When the H/D value is higher than 0.70, the CO₂ adsorption capacity decreased to 17.17 mg·g⁻¹ at H/D=1.50 with an increase in the loading density. Due to the channeling phenomena in fluid dynamics, the feed gas is more likely to get through voids other than those in the absorbent in a fixed bed transfer unit. A low density indicates more voids between the PEI-loaded GF through which CO₂ molecules pass without any contact with the activated sites on PEI, leading to low CO₂ uptake. In summary, an optimum loading density of the PEI-loaded GFs for CO₂ adsorption is important for high operation efficiency in industrial applications, and the optimal value should be 0.70 in this case.

Figure 10. Effect of bed depth on CO₂ adsorption of the PEI-loaded GF.

Note: Experiment condition: 25 °C, 18% RH, 18.55 ml·min⁻¹; Fix bed dimension: 1.5 cm in diameter; Materials: 0.67 g (PEI) ·g⁻¹ (GF).

3.4 Regeneration of PEI-loaded GF

3.4.1 Effect of temperature on PEI-loaded GF regeneration

In practical industrial applications, in addition to a high adsorption capacity, the sorbents should be easily regenerated for economical considerations. After PEI/GF was saturated with CO₂, the media was regenerated at different temperatures (Figure 11). The regeneration rate was calculated and is listed in Table 1. Below 100 °C, PEI/GF was not able to retain its full capacity. However, between 100 and 140 °C, more than 95% of the initial capacity of PEI/GF was regenerate, which indicates that a temperature of 100 °C is necessary and should be employed as the optimum regeneration temperature.

Based on the discussion in section 3.3.3, the adsorption of CO₂ is exothermic. Increasing temperatures promote both the desorption kinetics and thermodynamics, and as the desorption temperature increases, the desorption time is shorter and more CO₂ is concentrated. 100 °C was chosen as the regeneration temperature due to the following reasons: 1) 100% of the initial capacity was retained, 2) at a lower temperature, there is a smaller probability that PEI will degrade or experience physical aging, and 3) this temperature provides a balanced energy efficient solution.

Fig.11 Effect of temperature on CO₂ desorption of the PEI-loaded GF.
Regeneration conditions: 0% RH; 54.8 ml·min⁻¹ purge N₂; Fix bed
dimension: 1.5 cm in diameter; Materials: 0.67 g (PEI) ·g⁻¹ (GF).

Table 1. CO₂ regeneration results at different regeneration temperatures.

Desorption Temperature /°C	60	80	100	120	140
CO ₂ regeneration concentration /%	0.10	0.16	0.30	0.51	0.65
Regeneration rate /%	10.1	32.2	100.0	95.1	100.0

*Note: Regeneration was carried out in 54.8 ml·min⁻¹ N₂ purge. The feed CO₂ concentration was 15%.

3.4.2 Effect of moisture on PEI-loaded GF regeneration

The regeneration of CO₂ was carried out at 100 °C under different RH levels. The calculated CO₂ regeneration ratio under various RH levels is shown in Table 2. The desorbed CO₂ amount increased as the water content decreased, which is consistent with the adsorption effect of moisture when the adsorption capacity of CO₂ increases with an increase in the RH. At a regeneration temperature of 100 °C, a RH lower than 30% does not affect the re-adsorption of CO₂, which indicates direct feed gas circulation without water removal pretreatment, making this absorbent more competitive.

Table 2 CO₂ regeneration results at different regeneration moisture.

Desorption moisture content /%	0	30	45	60	90
CO ₂ regeneration concentration /%	0.46	0.41	0.32	0.30	0.25
Regeneration rate /%	90.4	100.0	90.1	84.2	53.3

*Note: CO₂ regeneration was carried out in 54.8 ml·min⁻¹ N₂ purge. The feed CO₂ concentration was 15%.

3.4.3 Cyclic performance for CO₂ adsorption

To investigate the reusability of the PEI-loaded GF, cyclic CO₂ adsorption-desorption was carried at room temperature for adsorption and 100 °C for desorption using the same samples for 10 consecutive cycles. As shown in Figure 12, the PEI-loaded GF exhibited good cyclic CO₂

adsorption-desorption performance under the experimental conditions. By calculation, the regeneration efficiency was $\sim 90\%$ (similar to literature [17, 44, 45]) even after 10 cycles, indicating reversible CO_2 adsorption-desorption chemistry and the thermal stability of PEI at 100°C . SEM and FTIR analyses (Figure 3 (c)) was before and after the regeneration cycles. The slight decrease between the 1st and 5th cycles may be due to incomplete regenerated cycles or incomplete initial equilibrated states.

In addition, a recovery of the CO_2 adsorption capacity was observed at the 6th cycle after a period of time passed between the 5th and 6th cycle followed by the same pattern of sorbent degradation from the 6th to 10th cycle. The highly hydrophilic property of PEI may contribute to the restored CO_2 adsorption capacity at the 6th cycle. Barely any water molecules remained after regeneration at 100°C . However, the ethylenimine oligomers on the GF surface adsorb ambient water during the extended time period prior to the re-adsorption process. The increased water content is beneficial for the adsorption of CO_2 , leading to a recovery in the CO_2 adsorption capacity.

Figure 12 Regeneration performance of the PEI-loaded GF for CO_2 adsorption. Adsorption conditions: 18% RH, 25°C , $18.55\text{ ml}\cdot\text{min}^{-1}$ 15 vol% CO_2 ; Regeneration conditions: 0% RH; 100°C ; $54.8\text{ ml}\cdot\text{min}^{-1}$ purge N_2 Fix bed dimension: 1.5 cm in diameter; Materials: $0.67\text{ g (PEI)}\cdot\text{g}^{-1}$ (GF).

4 Conclusions

In this study, a facile synthesis of a polyethyleneimine-loaded glass fiber (PEI/GF) system has been developed for CO_2 adsorption. The inexpensive, small-diameter glass fiber serves as an inert substrate, which not only provides a high external surface with a low pressure drop but also a substantially shorter mass transfer distance for CO_2 , which greatly improved its dynamic adsorption performance.

The dynamic breakthrough performance under various conditions (i.e., flow rate, humidity, temperature, and H/D ratio) has been studied. The water content has a significant effect on CO_2

dynamic adsorption. The adsorption is favorable under higher humidity and is less impacted by temperature between 40 and 80 °C, implying its capability of flue gas removal without pretreating the moisture content. The flow rate has a minimum effect on the adsorption capacity, which demonstrates its rapid kinetics due to the core-shell structure. A maximum breakthrough CO₂ adsorption capacity of 60.04 mg·g⁻¹ was obtained with a PEI loading ratio of 0.7 g·g⁻¹ at 40 °C, 18% RH and a bed depth of H/D=0.70.

The regeneration properties of the PEI/GF system were also explored at different regeneration temperatures, humidities, and cycles. After the media was regenerated at 100 °C in multiple cycles, both the morphology and amine chemistry remain unchanged with a minimum loss of adsorption capacity.

Based on both the dynamic breakthrough and regeneration performance, PEI/GF could potentially serve as an excellent solid adsorbent for CO₂ capture.

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