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CO_2 Capture by PEI-Impregnated Alumina Sorbents

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Abstract: Direct air capture (DAC) or direct CO_2 extraction from ambient air is a promising approach to reduce greenhouse gas emissions caused by both distributed (location independent) and point sources (location specific). Solid sorbents have been considered as more effective for DAC compared to the liquid counterpart since they have a faster kinetic and avoid volatile and heat losses due to the absence of evaporation of liquids. In this study, the alumina - supported polyethyleneimine (PEI) material was chosen as solid sorbents and their CO_2 capture performance for different PEI loadings (20, 35, 50 wt%), flow rate (15, 30, 45 L/h) and adsorption temperatures (30, 40, 50, 60 °C) was investigated. Sorbents were prepared by using wetness impregnation method and their physical and chemical properties were characterized by several techniques such as N_2 adsorption - desorption (surface area, pore size and volume), Scanning Electron Microscopy - SEM (surface morphology, surface chemical composition). The CO_2 capture performance of sorbents were analyzed under different CO_2 concentrations and the cyclic (adsorption - desorption) behavior of the sorbents were tested. The results show that alumina-supported PEI adsorbents are promising materials for CO_2 capture with high CO_2 adsorption capacity and stability.

Keywords: PEI, Adsorption, CO_2 Capture, DAC, Greenhouse Gas, Alumina

Introduction

Carbon capture and storage (CCS) is crucial in the fight against climate change, which poses an existential threat to our planet. Despite being on the global agenda for decades, progress has been slow, insufficient, and sporadic. Anthropogenic CO_2 emissions are caused by our reliance on fossil fuels, accounting for 68% (or 37.5 $GtCO_2$) of the total greenhouse gas emissions in 2018. Capturing CO_2 at this scale requires resources and technologies that are currently unavailable. C_{O2} capture is an expensive, energy-intensive process that is complicated by diverse emission sources varying in volume, composition, location, type, and industry or sector. However, the diversity of sources highlights the need for a multi-prong strategy that emphasizes the development of a wide range of CCS technologies, materials, and processes tailored to different sources (Gür, 2022).

Direct air capture (DAC) is a method of removing CO_2 directly from the atmosphere to achieve negative emissions. Despite concerns regarding its feasibility, there has been growing interest in exploring this technology as a climate change mitigation strategy. Proponents argue that even if carbon emissions were to stop

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completely, atmospheric CO_2 concentrations must be reduced expeditiously to mitigate the risks of climate change. DAC has the advantage of being able to capture CO_2 emissions from distributed sources, which make up almost half of global CO_2 emissions, unlike other technologies that mostly capture emissions from point sources (Yu et al., 2012).

Various DAC technologies exist including physical absorption, chemical absorption, adsorption, and membrane technologies, but none of them are yet matured for post-combustion power plants due to significant mass transfer limitations and the need to treat a huge amount of flue gas. Among these technologies, chemical absorption using aqueous alkanolamine solutions is proposed to be the most applicable technology for CO_2 capture before 2030, but it has drawbacks such as high equipment corrosion rate, high energy consumption in regeneration, and a large absorber volume required. Solid adsorption processes, such as impregnation or grafting of amines, have been suggested to overcome these problems. Chemical modification of solid materials with high surface area is a key area of research to improve CO_2 adsorption and selectivity for DAC. The use of organic groups such as amines and inorganic metal oxides like alkali or alkali-earth metals has garnered particular interest due to their basic properties. Covalent bonding between the acidic CO_2 molecules and modified basic active sites on the surface enhances CO_2 adsorption. Although amine-based adsorbents have a low heat of regeneration compared to aqueous amines due to the low heat capacity of solid supports, their low CO_2 adsorption capacity and high cost hinder commercialization. To improve amine-based adsorbents, recent approaches include using amine with high nitrogen content, preparing supports with high amine loading, and effective methods for amine introduction. Amine-based adsorbents can be categorized as amine-impregnated and amine-grafted materials based on their interaction with the supports. Typically, amine-grafted adsorbents exhibit higher adsorption rates and stability in cyclic runs than amine-impregnated ones. However, the grafted amount of amine depends on surface silanol groups, which can result in lower amine loading compared to impregnation. Although higher amine loadings can be achieved through impregnation, it can lead to a large diffusion resistance. The feasibility of operating under practical conditions, containing 3-5% water and 10-15% CO_2 at 55°C in coal power plant flue gases, requires evaluating kinetics and heat effects (Yu et al., 2012).

There are several types of amines that are commonly used for solid adsorbents for CO_2 capture. Primary amines such as monoethanolamine (MEA), diethanolamine (DEA) and triethylenetetramine (TETA) contain one amino ($-NH_2$) group and they are well known their high CO_2 affinity whereas secondary amines like piperazine and N-methyldiethanolamine (MDEA) have two amine groups and they have a lower CO_2 affinity compared to primary amines. N, N-dimethylethanolamine (DMEA) and N, N-dimethylcyclohexylamine (DMCHA) are known as tertiary amines that have three amino groups and have the lowest CO_2 affinity in this class. When polymers are functionalized with amine groups which are called as amine-functionalized polymers, their CO_2 adsorption capacity can be increased due to their high surface area (Wang et al., 2015). Polyethyleneimine (PEI) and polyvinylamine (PVAm) are the most known examples of this class. Primary amines and tertiary amines are often used in post-combustion and pre-combustion CO_2 capture, respectively. Amine-functionalized polymers are used in both post- and pre-combustion CO_2 capture processes.

PEI is a high molecular weight polymer with a branched structure and abundant amino groups that allow for strong CO_2 adsorption. The high molecular weight and branched structure provide a large number of amine groups, which increases the CO_2 adsorption capacity of the material. In addition, PEI is known to have excellent stability and resistance to degradation under harsh conditions such as high temperatures and acidic environments, which are commonly encountered in CO_2 capture processes (Li et al., 2021). This stability ensures the material can be used repeatedly without significant loss of CO_2 adsorption capacity. PEI also has low volatility, which means that it does not evaporate or escape easily into the gas stream during CO_2 capture, reducing the possibility of amine emissions and environmental pollution. This low volatility is attributed to the high molecular weight of the polymer and the strong interactions between the amine groups and the support material.

Xu and his colleagues have investigated the impact of several factors on the capacity of polyethylenimine (PEI) for adsorbing carbon dioxide (CO_2) (Xu et al., 2002a). These factors include PEI loading, gas conditions, temperature, moisture, and the type of support used. Results have shown that a higher PEI loading led to a significant increase in CO_2 adsorption capacity, although this was accompanied by a reduction in surface area, pore size, and pore volume. The highest CO_2 adsorption capacity was observed with 75 wt.% PEI loading in PEI-impregnated MCM-41 under pure CO_2 at 75°C. However, the highest amine efficiency was found with 50 wt% PEI loading and decreased with increasing PEI loading. This suggests that amine loading is not directly related to CO_2 adsorption since the formation of aggregated amine on supports can reduce the amine accessible to CO_2.Temperature was also found to affect CO_2 adsorption capacity, with lower temperatures resulting in decreased capacity due to the exothermic nature of CO_2 adsorption. However, at low temperatures, bulk-like

PEI formation inside pores could lead to diffusion-limited CO_2 adsorption. Higher temperatures were associated with higher CO_2 adsorption capacity, likely due to the increased diffusion rate of CO_2 into bulk-like PEI and the faster reaction rate of CO_2 with PEI. Moisture was found to have a positive effect on CO_2 adsorption capacity when present at concentrations lower than that of CO_2 with carbamate and bicarbonate formation under anhydrous and hydrous conditions respectively.

Flow rate is also important parameter that affects the contact time between the CO_2 and the adsorbent, and a higher flow rate typically leads to a shorter contact time. As a result, the CO_2 may not have enough time to adsorb onto the solid adsorbent and the overall capture efficiency may be reduced. On the other hand, a lower flow rate can increase the contact time between the CO_2 and the adsorbent leading to higher capture efficiency. However, a very low flow rate may also lead to a reduced efficiency due to mass transfer limitations. Shafeeyan et al. (Shafeeyan et al., 2015) studied the adsorption of CO_2 onto ammonia-modified activated carbon and measured the breakthrough adsorption of CO_2 on fixed beds of commercial granular activated carbon (GAC) and ammonia-modified GAC (OXA-GAC) adsorbents. They measured the breakthrough curves from dynamic column measurements at temperatures ranging from 30 to 60 °C with a feed gas flow rate that varied from 50 to 100 $mL.min^{-1}$ and a total pressure of 1.0 atm. They found that the breakthrough time of CO_2 adsorption decreased with increasing flow rate indicating that the flow rate has a significant effect on the CO_2 adsorption capacity of the adsorbent. A study by Darunte et al. investigated the effect of flow rate on CO_2 adsorption by a novel amine-functionalized metal-organic framework (MOF), MIL-101(Cr)-NH_2. They found that the CO_2 adsorption capacity of MIL-101(Cr)-NH_2 increased with increasing flow rate and the maximum CO_2 adsorption capacity was achieved at a flow rate of 100 mL/min (Darunte et al., 2016). However, Goeppert and his colleagues found that total CO_2 adsorption capacity of the silica supported PEI adsorbents did not show the high dependency on the flow rate (Goeppert et al., 2014). When they increase the flow rate from 335 to 945 mL min^{-1}, this resulted with decrease in the total adsorption capacity from 50 to 47 mg CO_2 g^{-1} when 33% PEI by weight was used and increase in PEI loading caused to increase in effect of flow rate on the CO_2 adsorption capacity.

Adsorption temperature is another important factor that can affect the CO_2 capture efficiency. At low temperatures, the adsorption of CO_2 onto the adsorbent surface is generally more favorable because the kinetic energy of the CO_2 molecules is lower, which makes them more likely to adsorb onto the surface. This can lead to a higher CO_2 capture capacity at lower temperatures. However, it's worth noting that the rate of adsorption may be slower at low temperatures, which can reduce the overall capture efficiency. At high temperatures, the adsorption of CO_2 onto the adsorbent surface is generally less favorable because the kinetic energy of the CO_2 molecules is higher, which makes them less likely to adsorb onto the surface. As a result, the CO_2 capture capacity may be reduced at higher temperatures. However, high temperatures can also result in desorption of previously adsorbed CO_2, which can be beneficial for the regeneration of the adsorbent and the reusability of the system. Geoppert et al., found that increase in temperature results with the decrease in total CO_2 adsorption from air by silica-supported PEI adsorbents with loading of 33% and 50% by weight (Goeppert et al., 2014). However, increase in temperature from 25 to 35 ^oC slightly increased the total adsorption from air and significantly decreased when the temperature increased up to 85 ^oC when air under 10 ppm was used.

The support material used in direct air capture (DAC) with polyethyleneimine (PEI) sorbents plays a critical role in determining the overall performance of the system. The support material serves as a substrate for the PEI sorbent, providing a large surface area for CO_2 adsorption and facilitating mass transfer between the gas and solid phases. Different support materials can vary in their pore structure, surface chemistry, and other properties that can impact the adsorption capacity, selectivity, and stability of the sorbent. Solid amine sorbents are commonly supported by silica, but alumina and titania could be better options as they can address some of silica's limitations. Silica, for instance, experiences a structural change and loses its CO_2 capture capability when exposed to steam. While PEI-impregnated sorbents can be regenerated through various methods, including temperature-vacuum alternation, hot CO_2 flow, and water vapor, a urea-forming reaction can lead to irreversible PEI decomposition when CO_2 reacts with two amine groups at or above 135 ^oC in dry conditions. Water vapor regeneration can prevent this decomposition to some extent, but it cannot eliminate urea formation. Steam regeneration or steam-stripping is a convenient method for thermal regeneration, especially in industrial processes where waste steam is typically around the temperature required for water vapor regeneration. Nevertheless, porous silica such as MCM41, SBA-15, and MCF may not be stable in water vapor, leading to a loss of CO_2 uptake capacity (Xu et al., 2002b). Alumina supports, however, are more resistant to structural changes and degradation during regeneration with water vapor due to their crystallinity and lower hydrophilicity.

The CO_2 capture performance of PEI-loaded alumina sorbents have been addressed several times in the literature. Goeppert and colleagues described the preparation of an alumina-supported PEI sorbent for DAC

(Goeppert et al., 2011). The sorbent was prepared by impregnating gamma-alumina with a solution of PEI, followed by drying and calcination. The resulting sorbent had a CO_2 adsorption capacity of 73 to 75 mg CO_2/g adsorbent (1.65 to 1.71 mmol/g). However, when they use alpha-alumina supported PEI rather than gamma-alumina supported PEI, the resulting sorbent had a CO_2 adsorption capacity of 1.02 mmol/g at 25 °C and atmospheric pressure and 1.41 mmol/g at 50 °C and atmospheric pressure. All of these studies have been carried out using methanol as a solvent, however, when the resulting supported-PEI were treated with a mixture of acetic acid and acetic anhydride, CO_2 adsorption capacity of the resulting sorbent reached the 1.85 mmol/g (Gargiulo et al., 2007) and Zhang et al.(Zhang et al., 2013) reported that the adsorbent exhibited a high CO_2 adsorption capacity of 2.5 mmol/g for alumina sorbents with PEI loading of 30 wt% and 40 wt%, respectively. Lin et al. (Lin et al., 2013) reported that at 100 wt% PEI loading, the CO_2 adsorption capacity at 0.15 bar reached a very competitive value of 4.2 mmol g^{-1} at 25°C and 3.4 mmol g^{-1} at 50°C, while Chen et al. (Chen et al., 2014) found that the optimal PEI loading was 50 wt% and the adsorbed amount of CO_2 was 2.5 mmol g^{-1} at 25 °C and 1 bar. The literature studies summarized above for the CO_2 capture from ambient air (400-450 ppm CO_2) on PEI-loaded alumina sorbents indicate that CO_2 adsorption capacity of sorbents varies between 1.65-4.2 mmol/g suggesting that PEI-loaded alumina has an important potential as CO_2 sorbent material. However, the significant difference in the CO_2 adsorption capacity and the optimum PEI loading shows that the relation between the CO_2 capture performance of the material and their physical and chemical properties needs to be further addressed to develop high-performance sorbents. In addition, the CO2 capture performance of the related material at higher CO_2 pressure is lacking in the literature. This needs to be investigated to understand the effect of CO_2 concentration on the CO_2 adsorption capacity of the sorbents, which is especially important to determine the performance of sorbents for the CO_2 capture by pressure-swing adsorption (PSA) process.

To address the related issues, the CO_2 capture by the alumina-supported PEI adsorbents with different PEI loadings have been investigated at different CO_2 concentrations (e.g., 1 and 17%), flow rates and adsorption temperatures. Sorbents were prepared by the impregnation method and characterized by several techniques to link sorbent properties with CO_2 capture performance.

Method

Preparation of Adsorbents

PEI-loaded alumina sorbents were prepared by the impregnation method. F-200 activated gamma alumina adsorbent was purchased from BASF. The sorbent preparation process involves several steps. First, alumina pellets were washed with methanol and dried overnight in an oven at 100 °C. Then, the clean alumina spheres were mixed with 20 ml of methanol and kept under stirring for one hour. Next, 20 ml of methanol was mixed with a specific amount of PEI depending on the desired PEI loading and the resulting mixture was stirred for one hour. The PEI-methanol solution was then added dropwise to alumina pellets suspended in 20 mL of methanol and stirred for another hour. The resulting impregnated alumina pellets were then dried using a rotary evaporator at 50 °C under vacuum with a rotation of 100 rpm and a pressure of 100 mbar. The pellets were subsequently dried in a vacuum oven at 60 °C overnight. Finally, the pellets were weighed, and the PEI loading was calculated and recorded. The PEI loadings were 20%, 35% and 50% by weight and 2 g pellets were prepared for each batch.

CO_2 Adsorption and Desorption Experiments

The CO_2 adsorption and desorption studies were performed at two different CO_2 concentrations by using two different experimental setups. The experiments with a CO_2 concentration of 1% were conducted using Micromeritics' AutoChem II 2920 Chemisorption Analyzer equipped with a TCD detector with a U-tube sorbent bed. The sorbents were loaded to the reactor and heated to 110 °C under N_2 atmosphere for 2 hours to remove water and volatile components. The sorbents were then cooled to the adsorption temperature (40, 50, or 60 °C) The adsorption experiments were carried out at 40 °C under 1% CO_2/N_2 atmosphere with a flow rate of 25 ml/min for 1 hour for desorption, at the end of the adsorption period, the gas was switched from CO_2/N_2 to N_2 (inert gas) and left for 0.5 hours with a flow rate of 50 ml/min. Under the inert gas atmosphere, the temperature was increased to 120 °C with a flow rate of 50 ml/min and a heating rate of 5 °C/min and left for 1 hour. The sample was then cooled down to 40 °C under N_2 flow with 50 ml/min flow rate and the experiment was finalized.

The adsorption-desorption experiments with a CO_2 concentration of 17% were performed in a home-built setup containing a quartz reactor (ID: 10 mm), a tubular oven, flow control units and a CO_2 detector. Sorbents were loaded into the reactor and heated to 110 °C under N_2 atmosphere with a flow rate of 20 L/h. The sample was kept at that temperature for 1 hour to remove water and volatile components. The sample was then cooled to the desired adsorption temperature (40, 50, 60 °C) and the gas flow was switched from N_2 to a 17% CO_2 - N_2 gas mixture. Adsorption experiments were carried out under a 17% CO_2-N_2 gas mixture atmosphere with a flow rate of 15 – 30 – 45 L/h CO_2-N_2 for 1 hour. At the end of the adsorption period, the gas was switched from CO_2-N_2 to $N_{2,}$ and the system was left for 1 hour with a flow rate of 20 L/h. Under an inert gas atmosphere, the temperature was increased to 120 °C with a flow rate of 20 L/h and a heating rate of 5 °C/min and the system was left for 1 hour. The system was finally cooled down to 40 °C under an N_2 flow with a flow rate of 20 L/h.

Sorbent Characterization

The amine loading of sorbents was determined by elemental analysis. The Leco Truspec CHN-2007S was utilized and the nitrogen content of sorbents was used to quantify the amine loading. The surface area, pore volume and pore size distribution of sorbents were analyzed by N_2 adsorption-desorption using Micromeritics Tristar II. The surface area of sorbents was determined using the Brunauer – Emmett − Teller (BET) method, while the pore volume and pore size distribution were calculated using the Barrett−Joyner−Halenda (BJH) method. Prior to analysis, alumina-supported PEI adsorbents were degassed at 110 °C for 2 hours, while alumina spheres were degassed at 60 °C for 12 hours. Thermal gravimetric analysis (TGA) was conducted to determine the desorption and decomposition temperature of CO_2, H_2O, and PEI under N_2 environment by using Perkin Elmer Diomand TG/DTA analyzer. The analysis was carried out at 25-900 °C with a heating rate of 10 °C/min and for 2 hours. SEM-EDX analysis was carried out to investigate surface morphology by using FEI QUANTA 250 FEG analyzer.

Results and Discussion

TGA analysis was performed to determine the thermal stability and decomposition behavior of the adsorbent. One of the challenges in direct air capture is the regeneration of the adsorbent after it is saturated with CO_2. Regeneration typically involves heating the absorbent to high temperatures (70-100 °C), but the excessive heating can cause thermal degradation of the adsorbent, leading to a decrease in its performance over time. To prevent thermal degradation of the sorbent and to determine the safe regeneration window, TGA analysis was applied.

Figure 1 shows TGA curve of 50% PEI containing alumina between 25 ^{o}C and 800 ^{o}C. As seen from the Figure, the first weight loss occurs between 25 and 1500 °C, which is related to water and CO_2 removal. This is followed by a stepwise weight loss between 150 and 600°C, which is attributed to the removal of volatiles caused by PEI degradation via the breaking of the polymer chains. This finding suggests that the regeneration temperature needs to be less than 150°C since above 150C PEI on gamma-alumina starts to degrade. The PEI-related weight loss is around 30%, which is less than the expected weight loss (33.3%) based on PEI loading. Since there is no clear division between weight loss related to water and CO2 removal and PEI degradation, it is difficult to determine PEI loading by TGA analysis. Therefore, CHNS analysis was applied to determine the PEI loading of sorbents by the nitrogen contents of sorbents. The PEI loadings determined by CHNS analysis are shown in Table 1. As seen from the Table, the actual PEI loadings of sorbents are 19.6, 27.5 and 27.4 wt% for 20PEI, 35PEI and 50PEI, respectively. The PEI loadings for 35PEI and 50PEI are almost the same suggesting that PEI does not dissolve in methanol completely for PEI loading greater than 30% in the specified PEI/methanol ratio.

It is well known that amine loading directly affects textural properties of sorbents such as surface area, pore volume and size. The extent of this effect for different PEI loading was analyzed by N_2 adsorption-desorption experiments. Results are shown in Table 2 indicating that the surface area and pore volume of sorbents decreases significantly with PEI loading due to the pore-filling effect of the polymer. The degree of reduction is much higher compared to PEI-loaded sorbents with similar PEI loadings. This is related to the poor solubility of PEI in methanol in the specified impregnation conditions. This was also proved by SEM-EDX analysis. SEM-EDX analysis was performed on both alumina and PEI-loaded alumina sorbents to study the morphology and elemental composition of the adsorbent material.

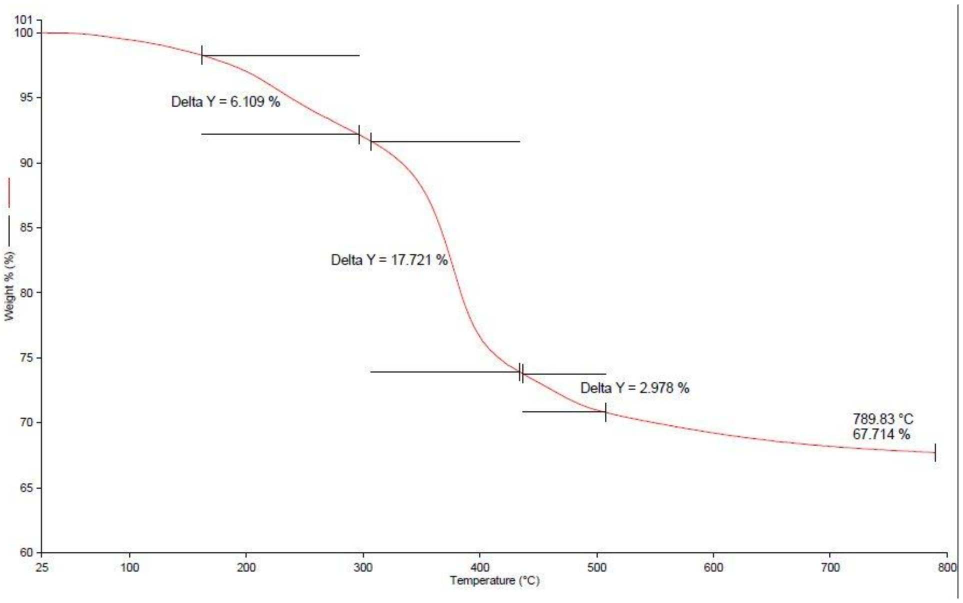

Figure 1. TGA Analysis of PEIM_50 Adsorbent

Figure 2 shows SEM images and elemental map of sorbents. Results show that C, O and N have more uniform distribution on alumina-supported PEI with a loading of 50% by weight contrary to loadings of 20% and 35% (**Figure 2**). However, for all PEI-containing sorbents PEI loading concentrates to specific sites of the support indicating uneven distribution of PEI on the surface. This can be attributed to the poor solubility of PEI in methanol or insufficient mixing process, which supports the findings of N2 adsorption-desorption analysis. Surface composition of carbon and nitrogen was also determined from EDX analysis and listed in **Table 2** in comparison the bulk composition of the related elements. As seen from the Table, surface compositions of carbon and nitrogen are almost doubled compared to bulk composition. This is expected considering that PEI molecules cover surface sites.

Table 1. BET Analysis result of adsorbents

Adsorbents	BET Surface Area (m^2/g)	Volume of Pores (cm^3/g)
Pure Al_2O_3	327.5273	0.291974
PEIM_20	43.2688	0.088509
PEIM_35	21.7087	0.042147
PEIM_50	8.44300	0.013505

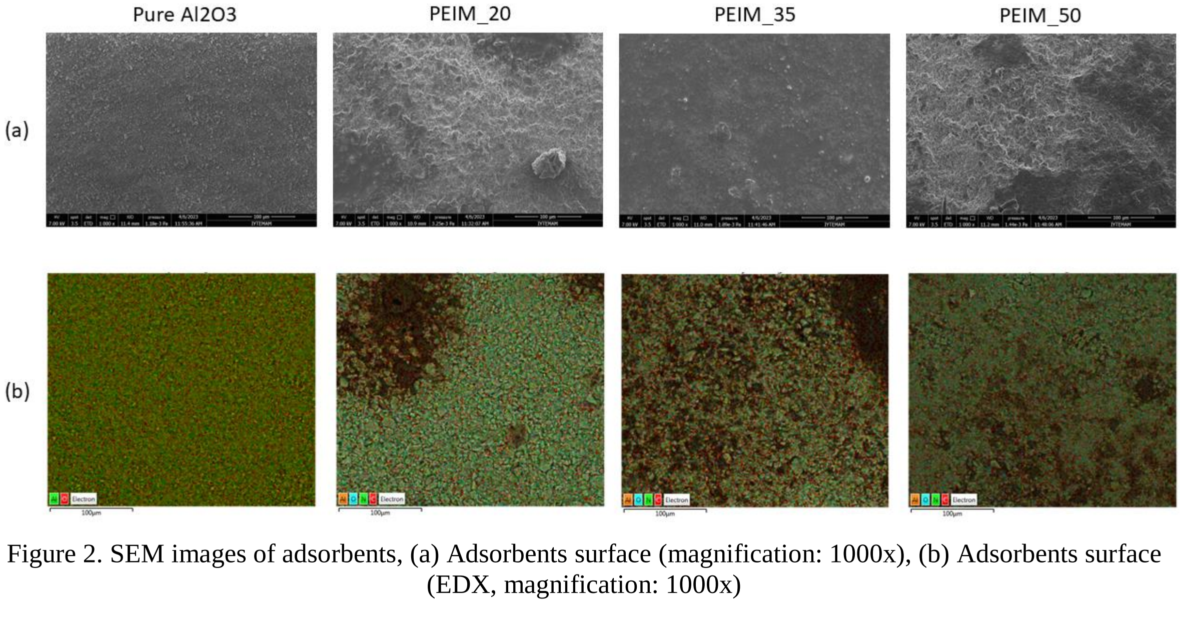

Figure 2. SEM images of adsorbents, (a) Adsorbents surface (magnification: 1000x), (b) Adsorbents surface (EDX, magnification: 1000x)

Table 2. Elemental composition of adsorbents

Adsorbents	Theoretical	CHNS	SEM-EDX
PEIM_20 (wt%)			
C	9.29	13.41	26.76
H	1.96	3.81	NA
N	5.42	5.34	9.68
PEIM_35 (wt%)			
C	14.45	15.51	40.22
H	3.05	4.41	NA
N	8.43	7.03	16.16
PEIM_50 (wt%)			
C	18.57	15.68	44.16
H	3.92	3.94	NA
N	10.83	6.99	17.78

CO_2 adsorption capacity of sorbents were first tested under 1% CO_2 in chemisorption setup by a TCD detector. Since the TCD detector works based on the change in thermal conductivity, it is sensitive to all gases, which complicates obtaining CO_2 adsorption profiles. However, it can still be used to determine the CO2 adsorption capacity of sorbents by using their desorption curves. By using this approach, CO_2 adsorption capacity of sorbents were calculated from desorption peak areas and listed in Table 3. As seen from the table, CO_2 adsorption capacities of PEIM_35, PEIM_50, alumina and PEIM_20 are 90.5, 63.1, 50.3 and 26.2 mg CO_2/g sorbent, respectively. Results show that alumina has a higher CO_2 capture capacity than the sorbent with 20% PEI loading. This can be ascribed to the significant reduction in surface area and pore volume of PEIM_20 compared to pure alumina, which leads to very few active sites for CO2 adsorption. Even if the CO_2 adsorption on PEI is more chemically favored compared to the CO_2 adsorption on alumina, the dramatic decrease in surface area and pore volume of PEIM_20 results in lower CO_2 adsorption. A similar effect was not observed for PEIM_35 and PEIM_50, which show higher CO_2 adsorption compared to pure alumina. The enhancement of CO2 adsorption by PEI for these sorbents are more dominant than the reduction of CO_2 adsorption due to the low surface area and pore volume. PEIM_35 shows higher CO_2 adsorption capability compared to PEIM_50, which can be explained by steric hindrance and a reduction in the accessibility of the amine groups to the CO_2 molecules at high PEI loading. Another possible explanation is that at higher PEI loadings, there may be an increase in the number of free amine groups that are not attached to the surface of the adsorbent. These free amine groups can interact with each other and form bulky PEI aggregates which can reduce the available surface area for CO_2 adsorption and lower the CO_2 adsorption capacity.

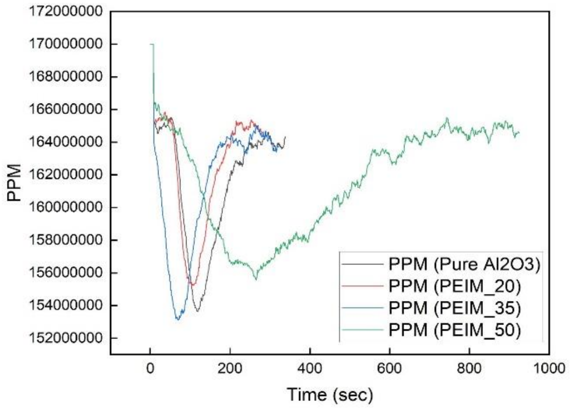

Figure 3. Adsorption of CO_2 by solid adsorbents under 17% CO_2 (ppm) atmosphere.

Table 3. CO_2 adsorption capacities of adsorbents for 1% and 17% CO_2

	Adsorbents	CO_2 Adsorption Capacity (mg CO_2/g adsorbent)
1% CO_2	PEIM_20	26.2
	PEIM_35	90.5
	PEIM_50	63.1
17% CO_2	PEIM_20	6.25
	PEIM_35	6.69
	PEIM_50	24.0

CO_2 adsorption behaviors of sorbent were also studied under 17% CO_2 environment. Figure 3 shows CO_2 adsorption curves for all sorbents. Different from the results obtained at low CO_2 concentration, PEIM_50 exhibits the highest CO_2 adsorption capacity. CO_2 adsorption on the related sorbent occurs in a long adsorption period. The other sorbents behave differently, i.e., they show a fast CO_2 build-up (e.g., sharp decrease in CO_2 concentration) and short adsorption times. Among them, CO_2 adsorption capacity decreases in order by PEIM_35 > alumina > PEIM_20. The CO_2 adsorption capacity of sorbents were also calculated by using areas under the curve and tabulated in Table 3. Calculations indicate that PEIM_50 has almost 4 times higher adsorption capacity than PEIM35 and PEIM_20. The latter two show almost the same performance. The calculated adsorption capacities of sorbents are quite low compared to those obtained at low CO_2 concentrations. This is attributed to high internal mass transfer resistance of sorbents at high flow rate conditions. The gas flow rate for experiments conducted at high CO_2 concentrations is almost 10-fold higher than those performed at low CO_2 concentration. This suggests that the CO_2 adsorption on PEI-loaded sorbents is diffusion limited due to their relatively low pore size.

The effect of diffusion limitation of PEI-loaded sorbents was also evaluated by experiments conducted at different flow rates. Figure 4 shows CO_2 adsorption of the best performance sorbent (PEIM_50) at flow rates of 15, 30 and 45 L/h under 17% CO_2 atmosphere. The figure shows that increase in flow rate results with the decrease in CO_2 capture capacity (Figure 4 and Table 4) and there is a dramatic decrease in adsorption behavior and capacity (Table 4) between the flow rates of 15 and 30 L/h. This indicates that above the flow rate of 15L/h the gas flow rate is so fast that there is not enough time for adsorption due to relatively slow diffusion processes.

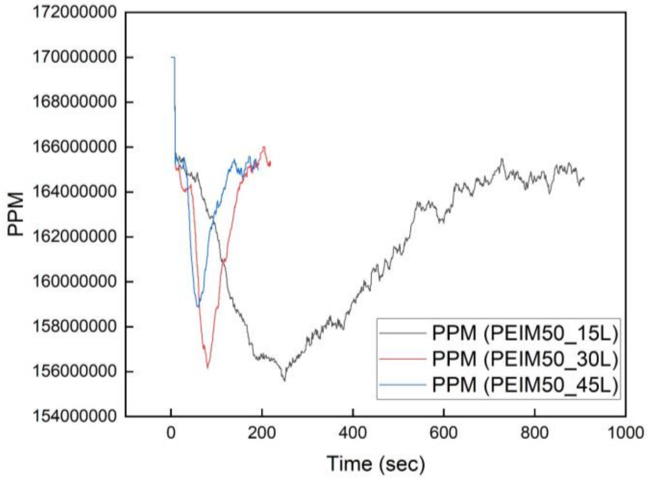

Figure 4. Effect of flow rate on the CO_2 adsorption via the alumina-supported PEI adsorbent with a loading of 50% by weight.

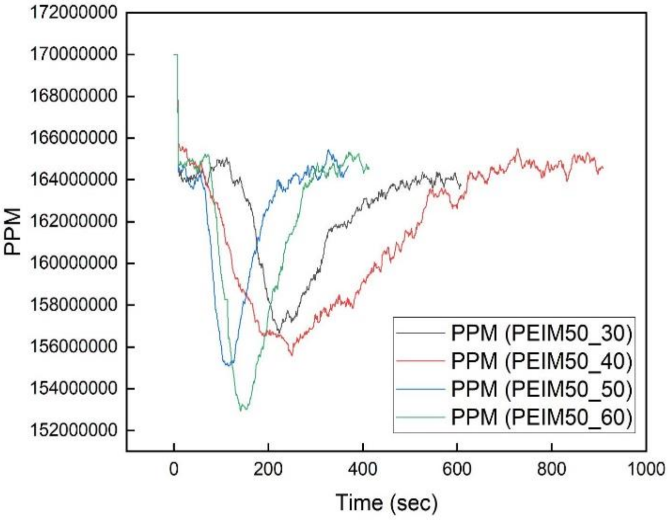

Figure 5. Effect of adsorption temperature on the CO_2 adsorption via the alumina-supported PEI adsorbent with a loading of 50% by weight.

Table 4. Effect of flow rate and adsorption temperature on CO_2 adsorption capacity of PEIM_50

	CO_2 Adsorption Capacity (mg CO_2/g adsorbent)
Flow Rate (L/h)	
15	24.0
30	3.57
45	2.49
Adsorption Temperature (°C)	
30	10.1
40	24.0
50	6.31
60	11.3

The effect of adsorption temperature on the CO_2 adsorption was also studied for the best performing sorbent under 17% CO_2 at 3 different temperatures (e.g. 30, 40, 50 and 60 ^{o}C). The results show that total adsorption capacity increases approximately by two-fold when the temperature increases from 30 to 40 ^{o}C, however, there is a decreasing trend above 40 ^{o}C (Figure 5 and Table 4). This is different from what was observed in the literature, where the adsorption capacity decreases with the adsorption temperature. The related difference can be explained by the excessive reduction of pore size and volume of PEI-loaded sorbents and corresponding diffusion limitation. The diffusion process is accelerated with a small increase in temperature leading to higher adsorption rate while the further increase results in decrease in the adsorption capacity due to the dominating kinetic effect of the desorption process.

Conclusion

Direct air capture (DAC) is a potential method to decrease greenhouse gas emissions from both point sources and distributed sources. Solid sorbents have been considered to be more effective than liquid sorbents for DAC due to their faster kinetics and their ability to avoid volatile and heat losses caused by liquid evaporation. In this investigation, we chose alumina-supported polyethyleneimine (PEI) materials as solid sorbents and examined their CO_2 capturing behaviour for various PEI loadings (20, 35, 50 wt%), flow rates (15, 30, 45 L/h) and adsorption temperatures (30, 40, 50, 60 °C) and at 2 different CO_2 concentration (1% and 17%). The sorbents were prepared using a wetness impregnation technique and were characterized for their physical and chemical properties. Results show that 35% PEI loading has the best CO_2 capture capacity under 1% CO_2 flow with a capacity of 90.5 mg/g sorbent. However, at 17% CO_2 flow, 50% PEI loading was found to be the best choice with a capacity of 24 mg/g sorbent. The significant difference in the CO_2 adsorption capacity of sorbents between 2 different CO_2 concentrations is attributed to the strong diffusion limitation of sorbents caused by the dramatic decrease in their surface area and pore volume. We also found that the flow rate and adsorption temperature have a strong impact on the CO_2 capture capacity. Both have negative effects on the adsorption capacity. One exception was found at 40 ^{o}C, where the adsorption capacity is lower than that observed at 30C. This is also related to diffusion limited adsorption process. The relatively low solvent/PEI ratio and insufficient mixing time results in uneven distribution of PEI on alumina and a high degree of reduction in the surface area and pore volume of sorbent, which leads to the relatively low adsorption capacity due to high diffuison limitation. This issue needs to be solved for further studies.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

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