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Carbon Dioxide Capture Performance Characterization of Mesoporous Carbon Impregnated with Triethylenetetramine

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Mesoporous carbon (MC) impregnated with Triethylenetetramine (TETA) was developed as carbon dioxide (CO_2) capture material to increase the adsorption ability and selectivity towards carbon dioxide. MC was chosen as it has a larger surface area to accommodate a large number of amines compared to the commercial activated carbon, which mainly consists of micropores. The carbon dioxide capture performance of mesoporous carbon impregnated with TETA (MC-TETA) was evaluated by comparing it with commercially available activated carbon and zeolite, which were also impregnated with TETA. Based on the CO_2 adsorption performance results, it can be understood that the appropriate TETA helped to improve the adsorption ability compared to the unmodified MC. Meanwhile, amine impregnation of zeolite reduced the adsorption ability compared with its unmodified form. Therefore, it can be concluded that MC-TETA is the most suitable material for amine impregnation due to its large pore size, which attributes to better accommodate large numbers of amines.

1. Introduction

The increasing world population, followed by increasing energy consumption, leads to an unprecedented increase in the concentration of carbon dioxide in the atmosphere. Carbon Dioxide Capture, Utilization, and Storage (CCUS) technology has a great potential to reduce the impact of increasing carbon dioxide emissions, causing climate change. CCUS is a process of CO_2 separation and capture from stationary sources, followed by transport and storage, or utilization. However, the capture step accounts for 70-80 % of the total CCS cost, which hinders the deployment of CCS technology (Gunawardene et al., 2022). There are several technologies available for CO_2 capture, such as absorption, adsorption, cryogenics, and membrane separation (Raganati et al., 2021). The conventional carbon capture method of absorption by amine solvent poses several limitations, such as high energy consumption for regeneration, corrosiveness to the equipment, and environmental issues. The regeneration of the conventional absorption process using monoethanolamine (MEA) requires energy of 4.1 GJ/t-CO_2 (Kishimoto et al., 2011). In order to reduce the regeneration energy, solid adsorbent has been proposed because it can remove the additional energy requirement for vaporization (Kansha et al., 2016). In addition, adsorption by solid adsorbents is a more environmentally friendly technology and represents a low-energy consumption process. However, solid adsorbent has several drawbacks, such as low CO_2 adsorption capacity and selectivity in the presence of moisture and impurities (Gunawardene et al., 2022). Amine functionalization can improve the adsorption capacity and selectivity towards CO_2. Moreover, amine functionalization of adsorbent can also reduce corrosion problems caused by amine solvents in the absorption process. Out of the available solid adsorbents, carbon-based material offers advantages such as wide availability and low cost compared to other adsorbents such as zeolite, MOF, and silica. Among carbon-based adsorbent, porous carbon material emerged as one of the most versatile adsorbent materials due to its high surface area and selectivity, and ease of surface modification and handling.

Mesoporous carbon is considered the most suitable material for amine functionalization due to its large pore size and high surface area (Chrisnardy and Krisnandi, 2020). Previously, Faisal et al. (2021) synthesized mesoporous carbon impregnated with ethylenediamine (EDA) and triethylenetetramine (TETA) with varying concentrations of 50 %wt and 100 %wt using the impregnation method. From this research, mesoporous carbon modified with EDA 50 %wt and mesoporous carbon with TETA 30 %wt have high CO_2 uptake. As the amount

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of amine groups increases, the adsorption ability of mesoporous carbon also increases. However, the addition of too much amine group leads to clogging or closing of the mesoporous carbon pores, thus decreasing its adsorption ability. Therefore, it is important to find the optimum TETA concentration and operational conditions for the best CO_2 adsorption performance.
In this paper, an environmentally friendly carbon capture material with a higher adsorption capacity than conventional absorption material (MEA) was proposed. Mesoporous carbon impregnated with TETA (MC-TETA) was proposed to enhance CO_2 capture performance by adsorption. This research focuses on evaluating the adsorption ability of MC-TETA by comparing it with commercially available adsorbent such as zeolite. In addition, the desorption process and regeneration stability will be investigated in this research.

2. Experiments

The experiment is divided into three parts: synthesis of MC-TETA, material characterization, and CO_2 capture performance characterization. The mesoporous carbon was synthesized via the soft-template method and impregnated with TETA via the wet impregnation method. The resulting proposed material was investigated by material characterization and pre-experimental study in order to understand the optimum condition for the CO_2 adsorption test. The proposed material's CO_2 adsorption performance and cyclic stability were then investigated.

2.1 Synthesis of MC-TETA

Formaldehyde (HCHO, ACS Reagent, 37 %wt), Pluronic F-127, Triethylenetetramine (≥97.0 %), and Hydrochloric acid (ACS Reagent, 37 %) were purchased from Merck, Sigma Aldrich. Phloroglucinol ($C_6H_6O_3$, Anhydrous, 95 %) and Ethanol (Wako 1st grade, 99.5 %) were purchased from FUJIFILM Wako Pure Chemical Corporation. CO_2 gas (99.5 %) and N_2 gas (99.99 %) were purchased from Suzuki Shokan Co. Ltd., Tokyo, Japan. Zeolite (Zeolum F-9 HA) was purchased from Tosoh Corporation.
The synthesis of mesoporous carbon method employed in this research is the soft template method. This method is chosen due to the simplicity of the procedure. Synthesis of mesoporous carbon using the soft template method had been done before (Górka et al., 2008). Synthesis was done by mixing phloroglucinol and Pluronic F-127 in an ethanol-water 10:9 (w/w) solution. Then, HCl 37 %(w/w) was added and stirred with a magnetic stirrer for 30 min until a slight pink solution was formed. In the next step, formaldehyde 37 % (w/w) was added, and stirring continued for another 30 min. After a cloudy solution was formed, stirring continued for 1-2 h until two phases were formed. The lower part of the two phases was separated and stirred for another 12 h. After 12 h, an elastic and non-sticky monolith was formed. Then, the monolith was transferred to the autoclave and put in the laboratory oven at 100 °C for 24 h. The pre-carbonized sample was then characterized with TG-DTA. The resulting sample was then carbonized under N_2 flow. Carbonization process was done using tubular furnace (ASH Asahi Rikagaku Ceramic Electric Tubular Reactor Openable 500 W ARF-30K, AS ONE) under N_2 flow with temperature profile: 100-400 °C with heating rate 1 °C/min; 400-850 °C with heating rate 5 °C/min; 850 °C for 2 h.
Amine impregnation of MC with TETA was conducted by dispersing mesoporous carbon in amine-ethanol solution (%wt 1:5) and then stirring for 6 h. After that, samples were dried at 100 °C overnight. In addition, commercially available zeolite (Zeo) was also impregnated with TETA to compare its suitability for amine functionalization to be utilized as a carbon capture material.

2.2 Material characterization

Surface properties of the adsorbent, such as total surface area, total pore volume, and pore size distribution of were analyzed with Brunauer-Emmett-Teller (BET). Thermogravimetric Analysis (TGA) is used to investigate the thermal properties of the material by measuring mass change as a function of increasing temperature or time. MC and MC-TETA30 were characterized using TG-DTA instrument (TG-DTA8122, Rigaku) to investigate the thermal stability of the adsorbent and study the effect of amine volatilization. The temperature program of TG analysis of MC and MC-TETA30 was set to 400 °C with a holding time of 10 min.

2.3 CO_2 capture performance characterization

CO_2 adsorption and desorption performance were measured using the reactor shown in Figure 1. Before starting the adsorption test, the sample was pretreated at 100 °C for 90 min under pure N_2 gas (10 cm^3/min) to ensure the removal of any existing gas, such as CO_2, in the system. After pretreatment, the adsorption test was conducted at 25 °C. The gas composition in the exhaust was measured using FTIR spectrometer (Nicolet iS FT-IR Spectrometer, Thermo Fisher Scientific) and analyzed using OMNIC software (Ver. 9.11.706, Thermo Fisher Scientific). The adsorption process was started by introducing CO_2 gas (5 cm^3/minute) and N_2 gas (10 cm^3/minute) into the reactor. During the adsorption process, the exhaust gas composition was measured using FTIR for one hour. After one hour, the oven temperature was increased to 100 °C and the CO_2 gas flow was

stopped while maintaining N_2 gas flow, which marked the start of the desorption process. The CO_2 concentration in exhaust gas was measured for one hour. After completing the desorption test, the oven was turned off, and the N_2 gas flow was stopped.

2.3.1. Pre-experimental study

Before conducting the carbon dioxide capture performance characterization, selecting the appropriate conditions for the experiment is important. The pre-experimental study was also conducted to measure how accurate the CO_2 measurement using FTIR from the adsorption results. The adsorption process was conducted at ambient temperatures (25 °C). According to the TG-DTA results of MC-TETA30, it was found that the mass was stabilized in the range 100-125 °C, which indicates that amine degradation did not occur at this point. In order to find the optimum temperature for the desorption process, the experiment was conducted at 100 °C, 110 °C, and 120 °C. The sample was replaced at each adsorption-desorption test at different desorption temperatures.

2.3.2. Adsorption and Desorption Test

CO_2 adsorption and desorption performance of MC, MC-TETA, Zeo, and Zeo-TETA were measured using the reactor shown in Figure 1. The adsorption test was conducted at 25 °C, and the desorption test was conducted at 100°C based on the finding in the pre-experimental study. The adsorption and desorption performance MC and MC-TETA were compared with commercially available adsorbents, Zeo and Zeo-TETA.

2.3.3. Cyclic Stability Test

In order to study the reusability of the material over several cycles of the adsorption and desorption process, a regeneration stability experiment was conducted using mesoporous carbon, and zeolite. The regeneration test was conducted over two cycles. The adsorption test was conducted at 25 °C for 60 min after pretreatment. The desorption test was conducted directly after the end of the adsorption test. The CO_2 gas supply was stopped while maintaining the N_2 gas supply, and the temperature was increased to 100 °C for 60 min. After one hour, the laboratory oven was turned off, and the temperature decreased to 25 °C for the subsequent adsorption test. After the temperature reached to 25 °C, the adsorption test was started using a similar setup as the first cycle without pretreatment. The resulting spectrum were analyzed with OMNIC Software, and the adsorption capacity was calculated.

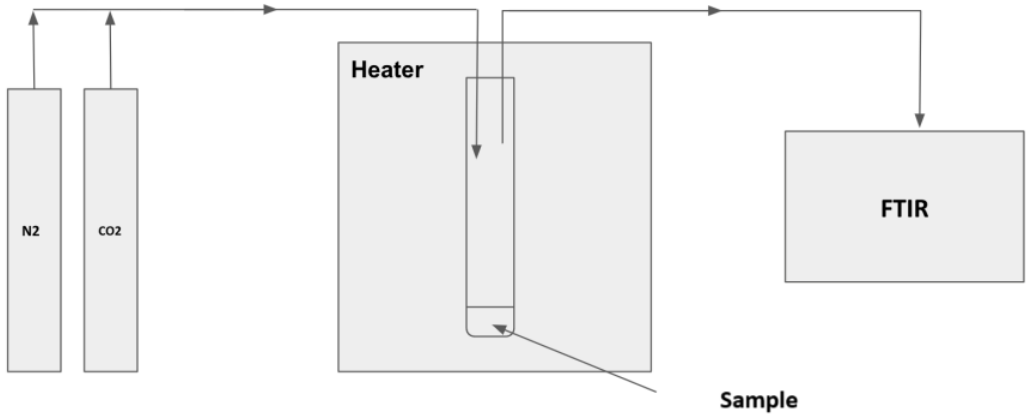

Figure 1: Adsorption and Desorption Setup

3. Results and Discussions

Synthesis method of MC was conducted based on the synthesis method by Gorka et al. (2008). The soft-template method was employed in this research via the self-assembly process of triblock copolymer Pluronic F127 (poly(ethylene oxide)$_x$-poly(propylene oxide)$_y$-poly(ethylene oxide)$_x$) as a template with carbon precursor. The template in the synthesis of mesoporous carbon acts as a structure-directing agent (SDA). Carbon precursors used in the synthesis are phloroglucinol and formaldehyde. A mixture of ethanol-water (10:9) was added as solvent, and HCl 37 %wt acts as a catalyst to increase the rate of the polymerization process of carbon precursor. The amine functionalization method used in this research is the impregnation method.

3.1 Material Characterization

Thermal stabilities of MC and MC-TETA were analyzed using TG in the temperature range 25-400 °C. As shown in Figure 2, the TG curve of MC did not show significant mass change with total weight loss of 1.63 %, which indicates that the material has high thermal stability. However, significant mass change was observed in the TG curve of MC-TETA30. The weight loss can be divided into two stages. The first stage occurred in the temperature range 25-100 °C, MC-TETA30 shows 14.18 % weight loss, which may be attributed to solvent (ethanol) degradation, water, or CO_2, which may be adsorbed in the material. The mass was stable at the temperature of 100-125 °C. The second stage showed a steep decrease in the temperature range 125-400 °C. The observed mass loss is due to TETA volatilization. This result showed similar results of TG measurement of PEI-loaded MCM41 by Xu et al. (2002, 2003), who observed the mass loss from 125 °C.

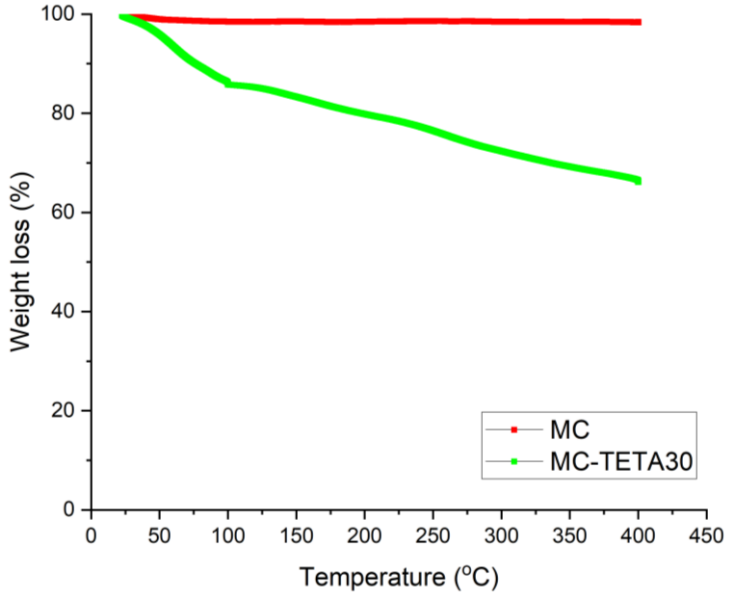

Figure 2: TG curve of MC and MC-TETA30

3.2 CO_2 Capture Performance Characterization

3.2.1. Pre-experimental study

Pre-experimental study was conducted in order to measure the accuracy of CO_2 concentration measurement using FTIR based on the adsorption results using the same sample replaced at each adsorption-desorption experiment. As shown in Figure 3a, the adsorption amount did not show a significant difference with a standard deviation of 0.02. This result indicates that the measurement using FTIR produces results with high precision in the repetitive measurements.

The relationship between desorption temperature and CO_2 desorption amount was also investigated. The desorption amount also did not show a significant difference at different desorption temperatures. This result implies that temperature did not play an important factor in the desorption process of amine-impregnated material within this temperature range. Therefore, for the next CO_2 capture performance characterization, 100 °C will be used as the desorption temperature. High regeneration energy was the main issue of the capture process, therefore, selecting a lower regeneration temperature would help reduce the energy required for the regeneration.

3.2.2. Adsorption of CO_2

The effect of different TETA loadings on CO_2 adsorption performance was investigated. MC was impregnated with TETA with loading from 0-50 %. The CO_2 adsorption temperature was 25 °C, and the CO_2 concentration was 33.33 vol.%. As shown in Figure 3, the CO_2 adsorption capacity varies, and the optimum loading amount of TETA was 20 %, which exhibits an adsorption capacity of 4.43 mmol/g. From this optimum amine loading amount of 20 %, the CO_2 adsorption capacity decreased. Amine impregnation of MC increased the active sites for CO_2 adsorption, which promotes CO_2 adsorption. However, the addition of excess amine blocks the pore of MC. The CO_2 adsorption performance of MC was evaluated by comparing it with the commercialized available adsorbent. In this case, zeolite impregnated with TETA (Zeo-TETA) was used as a comparison. Based on the

results in Figure 3b, the zeolite without modification showed high adsorption capacity compared to Zeo-TETA. This is due to the microporous nature of zeolite, making it difficult for long-chain amine to enter the micropores, therefore, TETA only covers on the surface of the material. This can be proved by decreasing the total surface area data obtained from BET measurement of Zeo-TETA30, as shown in Table 1. The surface area of zeolite decreased from 847.06 m^2/g to 0.7 m^2/g after modification with TETA.

3.2.3. Cyclic Performance

The regeneration stability of the material with and without amine impregnation is investigated over two cycles of the adsorption and desorption experiments. The regenerability of the material is an important aspect in the industry that can estimate how long the material can be used. The cyclic performance of MC-TETA30 was shown in Figure 3c. From this figure, it can be seen that the decrease in the CO_2 adsorption capacity of MC and MC-TETA30 by 7.27 % and 7.52 %, respectively. This may be attributed to volatilization of amine, where amines are leached in high desorption temperature or incomplete desorption, as the desorption time is limited to one hour (Yan et al., 2023).

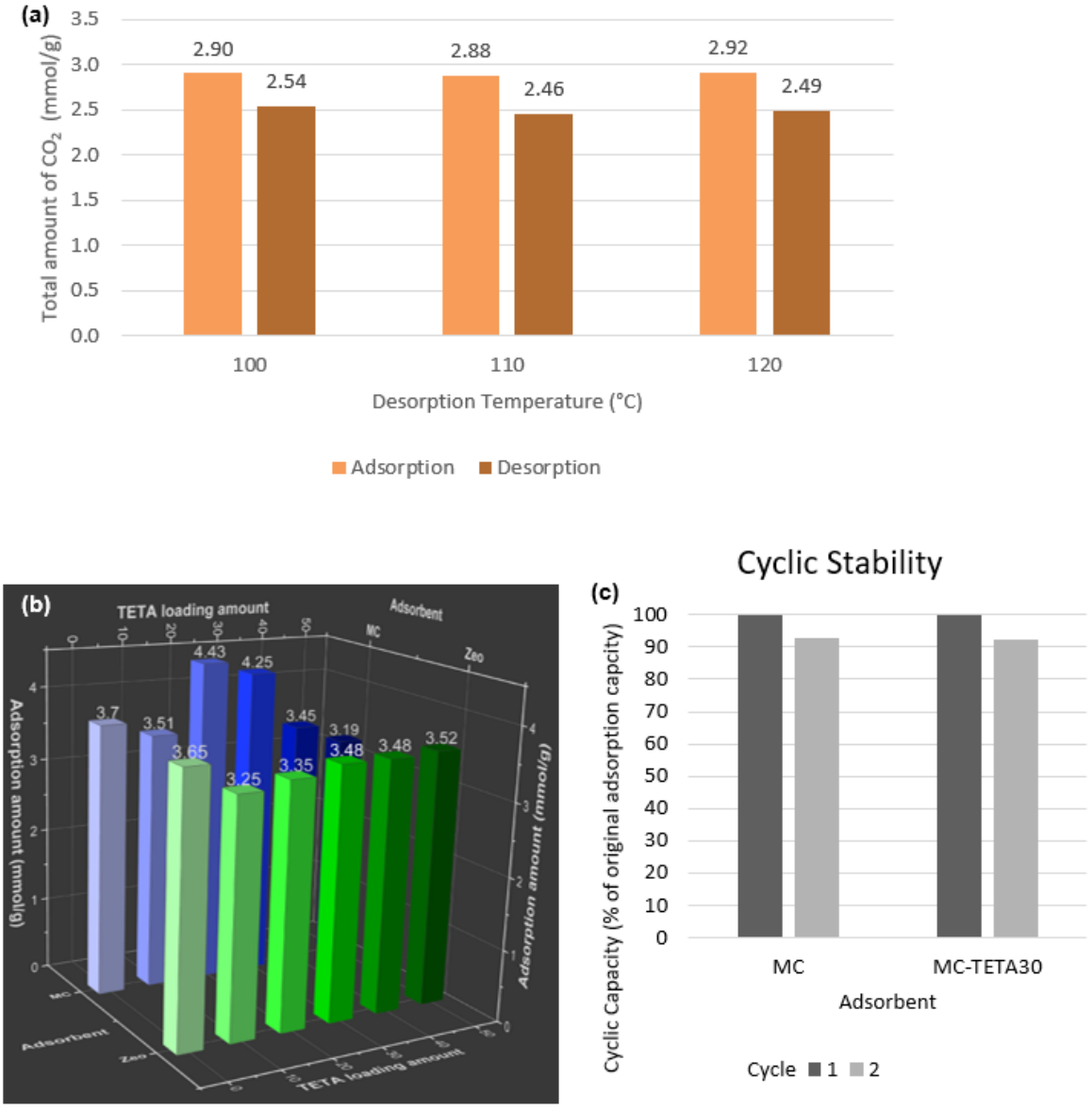

Figure 3: (a) Adsorption and desorption results at different desorption temperature (b) Adsorption capacity of MC-TETA and Zeo-TETA (c) Cyclic Stability of MC and MC-TETA

Table 1: Table summary of total surface area and total pore volume of MC, AC, Zeo and its TETA-impregnated form

Sample	Total Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Volume Monolayer (cm^3 STP/g)	Pore Size Distribution Peak (nm)
MC	423.6	0.470	4.4362	7.37
MC-TETA30	53.924	0.032	2.4001	-
Zeo	858.88	0.336	1.5655	1.67
Zeo-TETA30	0.528	0	0.1213	-

4. Conclusions

In conclusion, mesoporous carbon impregnated with TETA was investigated for its potential as a carbon capture material. Pre-experimental adsorption-desorption study showed that amine-impregnated material can be desorbed at 100 °C. In the adsorption and desorption test, the mesoporous carbon impregnated with TETA adsorption and desorption performance was evaluated by comparing it with commercialized zeolite, which was also impregnated with TETA. Based on this experiment, MC-TETA20 was found to be the optimum concentration for TETA modification of mesoporous carbon, and amine-functionalization of mesoporous carbon successfully improved the adsorption ability towards CO_2. On the contrary, amine-impregnated commercialized adsorbent Zeo-TETA showed a decrease in its adsorption capacity compared to the non-modified material. From these results, it can be concluded that pore size is an important factor for amine modification of solid adsorbents. In addition, mesoporous carbon impregnated with TETA also showed good regenerability, which retains more than 90 % of its original adsorption capacity in the second cycle. Therefore, mesoporous carbon is the most suitable material for amine impregnation and has the potential to be utilized as a carbon capture material due to its high adsorption capacity, selectivity, and reusability.

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