Efficient removal of CO_2 from indoor air using a polyethyleneimine-impregnated resin and its low-temperature regeneration

Wenjing Wang[a], Fenglei Liu[a], Qianxin zhang[a], Gang Yu[a], Shubo Deng[a],*

[a] State Key Joint Laboratory of Environment Simulation and Pollution Control (SKLESPC), Beijing Key Laboratory for Emerging Organic Contaminants Control, School of Environment, Tsinghua University, Beijing 100084, China

HIGHLIGHTS

- A polyethyleneimine-impregnated resin is effective for indoor CO_2 removal.
- Under indoor conditions, the adsorbed amount of CO_2 could reach 128.4 mg/g.
- The spent adsorbent is successfully regenerated by ambient air at 70 °C.
- The desorption equilibrium of CO_2 is almost achieved within 50 min.
- Regeneration efficiency is 66.7% after six adsorption-regeneration cycles.

GRAPHICAL ABSTRACT
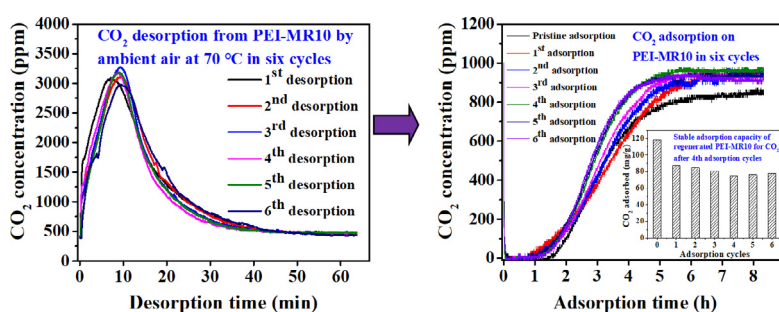
ABSTRACT

Aminated adsorbents are efficient in capturing high concentrations of CO_2, while their efficiency in air purifier for the removal of low concentrations of CO_2 from indoor air remains unclear. In this study, a polyethyleneimine-impregnated resin (PEI-MR10) was prepared and used to remove indoor CO_2, and its regeneration at low temperatures was evaluated. PEI loading narrowed the pore size distribution but increased the average pore size of the PEI-MR10. The PEI-MR10 with small particle size (0.250–0.425 mm) exhibited higher adsorption capacity and faster adsorption rate than the bigger one. The PEI-MR10 was able to remove all CO_2 during the first 2 h with an initial CO_2 concentration of 1000 ppm. Under variable indoor conditions, the adsorbed amounts of CO_2 could maintain high values from 90 to 136 mg/g. At a relative humidity of 50%, the adsorbed amount on the PEI-MR10 for 1000 ppm CO_2 reached 128.4 mg/g. In consideration of real application in air purifier, a cost-effective regeneration method using ambient air was adopted, and the spent PEI-MR10 was regenerated at low temperatures no more than 70 °C. The desorption efficiency of CO_2 increased with increasing temperatures, and the best regeneration was obtained at 70 °C. The adsorbed amount of CO_2 on the first-regenerated PEI-MR10 decreased significantly, but the adsorbent maintained stable adsorption capacity of about 80 mg/g after three adsorption-regeneration cycles. This study demonstrated that PEI-MR10 was an effective adsorbent for CO_2 removal from indoor air.

1. Introduction

Indoor air quality, as an important parameter that is closely related to human health and environmental livability, has always been considered and detected in building assessment processes [1–4]. Carbon dioxide (CO_2) could weaken IAQ [5] and the excessive CO_2 in indoor air

---

* Corresponding author.
  E-mail address: dengshubo@tsinghua.edu.cn (S. Deng).

could affect human activities and health [6–10]. For example, it could reduce people's cognitive level and cause the human body to have neurological symptoms (headache and fatigue). Besides, some latest evidences suggest that the combined effect of CO_2 and some bio-effluent substances may be a new pathogenic factor [11]. The regulatory attention on indoor CO_2 is growing as a result of its influence on indoor air quality. China, Japan, Korea, and Singapore recognized 1000 ppm as the limit value, while United States recognized 600 ppm as a comfortable environmental concentration [5]. Jokl's comprehensive analysis of indoor CO_2 concentrations showed that the indoor CO_2 concentration ranges of residential and public places were 360–1360 and 350–1850 ppm, respectively [12]. In densely populated rooms, the CO_2 concentrations could reach 2000 ppm or even higher. Thus, it is particularly necessary to develop efficient methods for CO_2 removal from indoor air.

Currently, adsorption for CO_2 removal has become a popular research, but research on indoor CO_2 removal is extremely rare and generally lacks applicability. Chu et al. [13] conducted research on indoor CO_2 capture and selected different aminating agents to modify the zeolite, showing high adsorption performance for CO_2. Hu et al. [14] used the impregnation method to modify activated carbon with CaO or MgO, achieving the enhanced adsorption capacity for indoor CO_2. Gall et al. [15] and Lee et al. [16] calculated the performance of alkaline earth metal oxides and activated carbon monomers supplemented by electrochemical methods for indoor CO_2 removal through models. The limited studies on the indoor CO_2 removal were not only lack of systematic studies of adsorption performance in real indoor environments, but also did not involve desorption studies. In all literature about CO_2 capture, many adsorbents such as zeolites, activated carbon, metal organic frameworks (MOFs), metal oxides, SiO_2, and aminated materials have been studied [17–22]. Zeolite has poor selective adsorption for CO_2 in the mixed gases. Activated carbon can achieve rapid and efficient adsorption of high concentration of CO_2 [23], but had low adsorption capacity for low concentration of CO_2. MOFs are not stable and exhibit poor CO_2 adsorption in the presence of water and air. Because their coordination bonds are prone to hydrolysis and their crystallinity are easily changed [18]. Some aminated adsorbents exhibit high CO_2 adsorption capacity, high selectivity, thermal stability and regenerability in the presence of water. Therefore, the polyethyleneimine (PEI)-modified materials may be the excellent candidates for CO_2 capture from indoor air. However, the previous researches on PEI-modified adsorbents were mostly focused on removing high concentrations of CO_2 from flue gases or plant exhaust gases, and very few studies focused on the removal of low-concentration CO_2 [24–29]. When these aminated adsorbents were used to remove CO_2 from indoor air, the adsorbed amounts of CO_2 were in the range of 43.1–139.9 mg/g at 25 °C with 400 ppm CO_2 [24–29]. Besides, to achieve high desorption efficiency, temperatures above 100 °C, vacuum and inert gas (ultra-pure N_2 or He) conditions were usually adopted in their regeneration process. However, these factors are impossible to be applied for the removal of CO_2 from indoor air by air purifiers. For the application of indoor air purification components, high desorption temperatures may bring safety problems, while 70 °C is the upper limit of safe desorption temperatures. Hence, it is necessary to systematically study the efficient adsorbents for removal of low concentration CO_2 and regenerate the spent adsorbents at low temperatures by using ambient air.

In this study, a polyethyleneimine-impregnated resin (PEI-MR10) with high CO_2 adsorption capacity was prepared, and a series of CO_2 adsorption and desorption experiments were carried out to evaluate its performances for the removal of CO_2 from the indoor air. The effect of PEI-MR10 size on CO_2 removal was first investigated, and then the adsorption kinetics of CO_2 under various indoor environmental conditions and the regeneration of PEI-MR10 with ambient air at low temperatures were investigated for CO_2 removal from indoor air. The objectives of this study are to: (1) prepare the efficient PEI-impregnated

resin with high CO_2 adsorption capacity under indoor air condition; (2) clarify the adsorption behaviors of CO_2 on the adsorbent and the regeneration performances of the spent adsorbent, and obtain the optimal adsorption and regeneration conditions for CO_2 removal from indoor air.

2. Materials and methods

2.1. Chemicals and materials

PEI used in this study was purchased from Shanghai Maclean Biochemical Technology Co., Ltd. with an average molecular weight of 600 g/mol and a density of 1.03 g/cm³. The commercial resin MR10 was purchased from a resin company, and was used as porous materials for PEI loading. Methanol (AR grade) was purchased from Shanghai Maclean Biochemical Technology Co., Ltd. CO_2-free air and 10% CO_2 (balanced with nitrogen) were purchased from Praxair (Beijing) Industrial Gas Co., Ltd. N_2 (99.995%) and ambient air were purchased from Beijing Haipu Beifen Gas Industry Co., Ltd.

2.2. Preparation of PEI-MR10

The adsorbent (PEI-MR10) was prepared by a wet impregnation method with slight modification [30–31]. The resins were first sieved to collect the fraction in the range of for PEI loading, and then the resins were vacuum-dried at 105 °C for 12 h to fully remove the adsorbed water [32]. The predetermined amount of PEI was dissolved in moderate amount of methanol and stirred for 15 min, and then the some resins were added into the solution. The mixture was continuously stirred at 150 rpm for 12 h, and then dried at 70 °C for 8 h in a rotary vacuum evaporator. The obtained PEI-impregnated resin was denoted as PEI-MR10. The ratios of PEI/resin were optimized in previous study, and 50% was the optimal one [30].

2.3. Characterization of the PEI-MR10

To obtain the Brunauer-Emmett-Teller (BET) surface areas, total pore volume and pore size distribution, the adsorbents were characterized by N_2 adsorption at 77 K in a gas adsorption instrument (Autosorb iQ, Quantachrome Corp., USA). Scanning electron microscopy and X-ray energy spectrum analysis (SEM-EDS) was used to observe the change of surface morphology before and after impregnation of the resin and qualitatively analyze the relative content of the elements in the samples. The surface functional groups of the pristine and regenerated PEI-MR10 were analyzed by a Fourier Transform Infrared (FTIR) spectrometer (Nicolet 870, USA).

2.4. Experimental setup for CO_2 adsorption

Fig. 1 shows the scheme of adsorption setup for CO_2 adsorption on the PEI-MR10. It was mainly composed of gas source, humidifying device, temperature control device, humidity sensor, adsorption bed, CO_2 analyzer, and flow meters. The CO_2 analyzer (Huayun GXH-3011N) equipped with an IR detector was placed in-line with the adsorption setup for CO_2 measurement. The flow rate of the gas was controlled by gas flow control instrument. The N_2 gas stream was a mixture from two branches, one of which passed through a bubbling device in a water bath at constant temperature to increase the humidity of the gas, and the other was the dry gas stream. The relative humidity (RH) of the gas was controlled by adjusting the ratio of the gas flow. RH was measured upstream of the adsorption column with electronic sensor. The temperature control device was used to monitor and control the temperature of the gas stream in the experiment. The CO_2 adsorption experiments from gas mixtures with different CO_2 concentrations on the adsorbents were conducted in a fixed-bed adsorption column operated at a specified temperature and relative humidity.
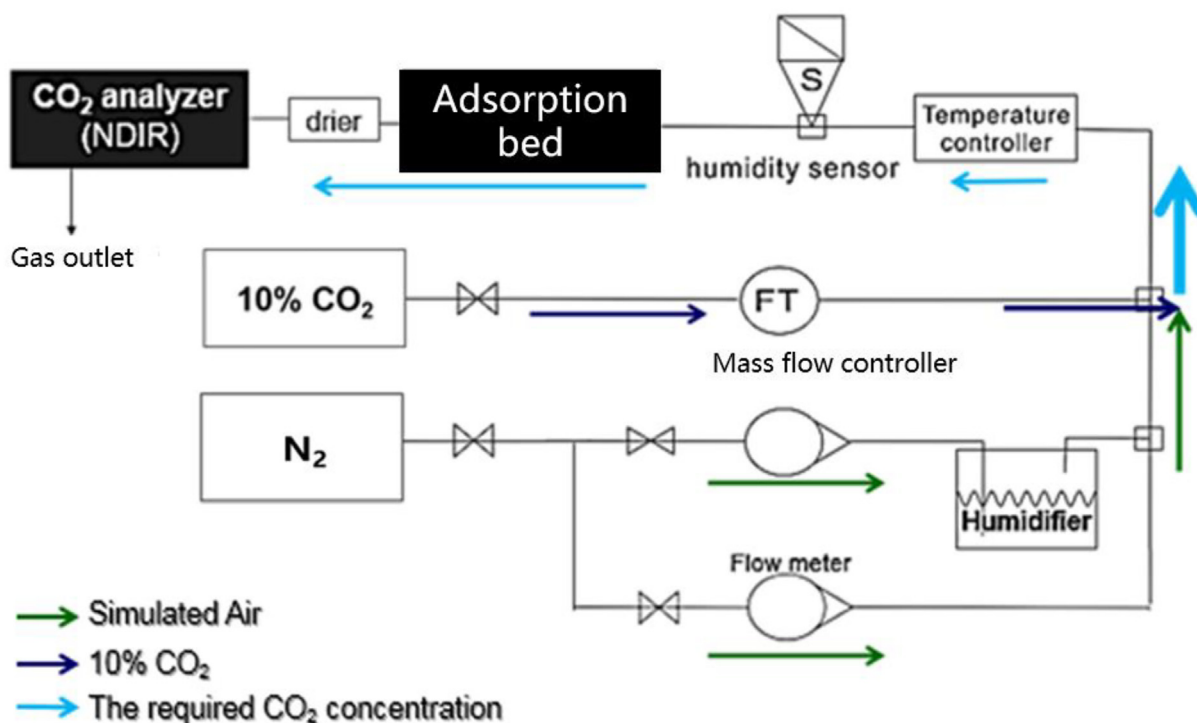
Fig. 1. Flow diagram of CO_2 adsorption on PEI-MR10.

2.5. Adsorption experiments of CO_2

In a typical adsorption process, 14 g of the adsorbent was packed in the middle of the adsorption column supported with quartz wool. The adsorption unit was a transparent polymethyl methacrylate column with inner diameter of 2 cm, and the height of packed adsorbent inside was around 7 cm. Before the adsorption test, the adsorbent was treated at a N_2 flow of 0.1 L/min for 180 min by heating at 105 °C in oil bath, to remove excess moisture and CO_2, and then the dry or moist 10% CO_2 (balanced with nitrogen) and N_2 (99.995%) gas mixture with a certain CO_2 concentration was introduced through the column at an approximate flow rate of 3 L/min. The RH was set at 30% in all the experiments, except for the specific investigation of influence of relative humidity on CO_2 removal, in which the relative humidity was adjusted in the range of 30%–60%. The CO_2 adsorption process was monitored with a CO_2 analyzer, which measures CO_2 concentration with non-disperisive infrared spectrometry. Before each run, the analyzer was calibrated with ultrapure N_2 and 8000 ppm CO_2 to check its stability and accuracy. After calibration, the initial CO_2 concentration in N_2 was determined. After saturation of the adsorbent, the CO_2 concentration reached the inlet value, and the gas flow was stopped. The CO_2 concentrations in the inlet gas, the flow rate, the adsorption time and the mass of the adsorbent were used as the basic calculation parameters, and the adsorbed amount of the adsorbent was calculated by integrating the area above the curve [31]. Q_s denoted the saturated adsorption amount, which was calculated at the saturation time when the outlet concentration was equal to the inlet concentration. Q_b represented the breakthrough adsorption amount which was calculated using the breakthrough time. The breakthrough time meant the adsorption time when the outlet concentration was 5% of the inlet concentration. The CO_2 adsorption amount (mg/g) was calculated using Eq. (1):

$$Q = \frac{1}{m} \cdot \frac{44 \cdot q}{M \cdot 60} \cdot \frac{\int_0^t (C_{in} - C_{out})dt}{C_{in}} \qquad (1)$$

where Q (mg/g) represented Q_s or Q_b, m (g) was the mass of adsorbent, q (L/min) was the gas flow rate, C_{in} and C_{out} (ppm) were the concentrations of CO_2 at the inlet and outlet of the adsorption bed, respectively, M (L/mol) was the CO_2 molar volume at a certain temperature.

2.6. Regeneration and reuse experiments

Regeneration experiment was conducted after adsorption process using hot gas. After the adsorption experiments, CO_2-free air or ambient air (about 400 ppm CO_2) was heated to 70 °C by a heater and was introduced to the column with a flow rate of about 10.6 L/min. The outlet CO_2 concentrations were monitored with the CO_2 analyzer until the concentrations didn't change. Afterwards, the adsorbent was cooled down to 25 °C for the next adsorption cycle. Moisture was introduced to the 70 °C CO_2-free air or ambient air with a relative humidity of 5% [24,33]. The successive adsorption–desorption experiments were repeated six times to investigate the changes of the adsorption capacities and the regeneration stability of the adsorbent. The stability and commercial value of the adsorbent were demonstrated by evaluating the adsorption rate and adsorption capacity of CO_2 on the regenerated adsorbent.

3. Results and discussion

3.1. Characterization of PEI-MR10

Textural characteristics of MR10 may be changed before and after PEI loading, which may affect CO_2 adsorption. The N_2 adsorption-desorption isotherm of the commercial resin MR10 shown in Fig. S1 was a typical IV curve, indicating that the resin had a rich mesopore structure. The N_2 adsorption-desorption isotherms of the two particle sizes of PEI-MR10 showed a significant decrease in nitrogen adsorption, but still conformed to the mesopore curve type. Calculated from the N_2 adsorption-desorption isotherms, the pore structure characteristics and pore size distribution of the MR10 and PEI-MR10 are shown in Table 1 and Fig. 2, respectively. After MR10 resin was loaded with PEI, the specific surface area and pore volume decreased significantly, and its

Table 1
Structure characteristics of MR10 before and after PEI loading.

Samples	Surface area[a] (cm²/g)	Pore volume (cm³/g)	Average pore size[b] (nm)
MR10	590.00	1.30	20.10
PEI-MR10 (0.425–0.060 mm)	17.94	0.34	30.66
PEI-MR10 (0.250–0.425 mm)	16.02	0.30	30.73

[a] BET specific surface area.
[b] BJH average pore size.

pore size distribution range became narrow (Fig. 2). This suggested that PEI molecules were successfully loaded into the pores of the MR10.

Fig. S2 shows the SEM images of the samples the MR10 and PEI-MR10, and no obvious change was observed before and after PEI loading, suggesting that the PEI molecules were mainly loaded in the pores of the resin. The EDS results showed that the N content of the PEI-MR10 increased significantly from 0% to 14.57%, further indicating the successfully loading of PEI into the MR10. (Table S1).

3.2. Effect of adsorbent sizes on CO_2 adsorption

In the preparation process of the PEI-MR10, the effect of resin size on CO_2 adsorption was investigated in this study. The gas containing 1000 ppm CO_2 and 30% relative humidity was introduced into the adsorption bed. It can be seen from Fig. 3 that the small particle size adsorbent (0.25–0.425 mm) shows higher adsorbed amounts for CO_2 than the bigger one (0.425–0.60 mm). Compared to the large particle size adsorbent with the adsorption amount (Q_s) of 101.99 mg/g, the small particle size resin had higher adsorbed amount (Q_s) of 120.48 mg/g and longer breakthrough time. This result is similar to the study by Goeppert et al. [33] that the faster adsorption kinetics was achieved when the small adsorbent was adopted. The adsorbent characterization results showed that there was no significant difference in the specific surface area and the pore size distribution (Fig. 3) between the two particle size adsorbents, and thus the high adsorption capacity and fast adsorption were attributed to the fast diffusion processes in the small resin [34]. With decreasing the size of the adsorbent particles, the diffusion of CO_2 molecules into the internal pores of the PEI-MR10 became easier. The particle size was different and the penetration depth was also different, which directly affected the internal diffusion and indirectly affected the external diffusion [35].

3.3. CO_2 adsorption on PEI-MR10 under different indoor air conditions

Air conditions including temperature, relative humidity, and CO_2 concentrations are the key factors for studying indoor CO_2 removal. In order to study their contributions, the room temperature, the varying indoor relative humidity and the concentration of CO_2 varied from 400 to 2000 ppm were investigated. The adsorption capacities of PEI-MR10 for CO_2 at 25 °C and 35 °C were studied (Fig. 4). In the initial adsorption stage, when the gas stream containing CO_2 was passed into the adsorbent bed and contacted with the PEI-MR10, CO_2 was completely adsorbed on the adsorbent, and no CO_2 was detected. After 1.5 h adsorption, CO_2 began to penetrate through the adsorbents bed and gradually exhibited high concentration in the treated gas. Comparing the experimental results at two temperatures, it could be found that the CO_2 adsorbed amount at 25 °C (116.2 mg/g) was little higher than that at 35 °C (109.8 mg/g) (Fig. 4b), and confirmed that the CO_2 adsorption amount on the PEI-MR10 decreased with increasing temperature, indicating the exothermic adsorption process [36]. In the adsorption process, it is important to make CO_2 diffuse into the adsorbent pores to contact more amine groups in PEI molecules. Although high temperatures are favorable for CO_2 diffusion into PEI phase, the negative effect of exothermic reaction on CO_2 adsorption may be dominant [37,38], resulting in the lower CO_2 adsorption at high temperature.

Moisture is inevitably present in indoor air, which may not only affect the CO_2 adsorption performance, but also be an important condition to assess whether the adsorbent can be applied to an air purifier system. Fig. 5 showed the influence of relative humidity on CO_2 removal in a series of breakthrough experiments using 1000 ppm CO_2 at 25 °C. According to the breakthrough curves (Fig. 5a), it could be seen that the breakthrough time of CO_2 on the PEI-MR10 increased with the increase of relative humidity from 0 to 50%, indicating that the moisture had a positive influence on CO_2 adsorption on the adsorbent. It was reported that moisture promoted the high concentration of CO_2 adsorption on the solid amine adsorbent due to its proton transfer function in the reaction between CO_2 and amine groups [39]. Further research revealed that the surface amine groups interacted with CO_2 to form carbamate with a stoichiometric CO_2/N ratio of 0.5 under dry air condition [40], whereas the stoichiometric CO_2/N ratio was 1 to form bicarbonate under proper humid conditions [41]. In addition, the adsorbed amounts of CO_2 on the PEI-MR10 at different relative humidity were calculated and shown in Fig. 5b. Both Q_s and Q_b increased with the increase of relative humidity, and 50 RH% was the most favorable for CO_2 adsorption under several humidity experimental conditions, and the Q_s and Q_b values were 128.4 mg/g and 75.6 mg/g, respectively, namely, both the amounts of penetration and saturated adsorption increased.

In comparison with industrial flue gas, the concentrations of CO_2 in indoor air are much lower. The different CO_2 concentrations including 500, 1000, 1500 and 2000 ppm were chosen to investigate their effects on the adsorption performances. Fig. 6 showed the breakthrough curve and adsorbed amounts of CO_2 on PEI-MR10 at different CO_2
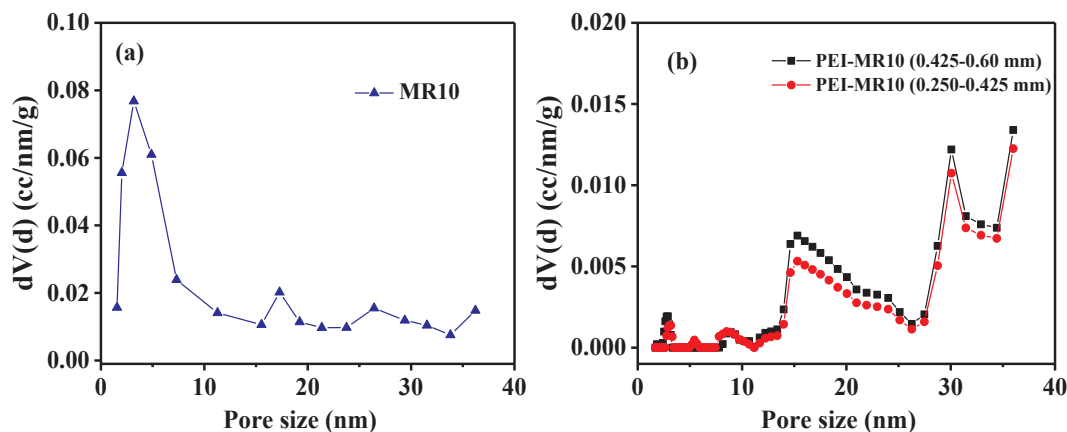

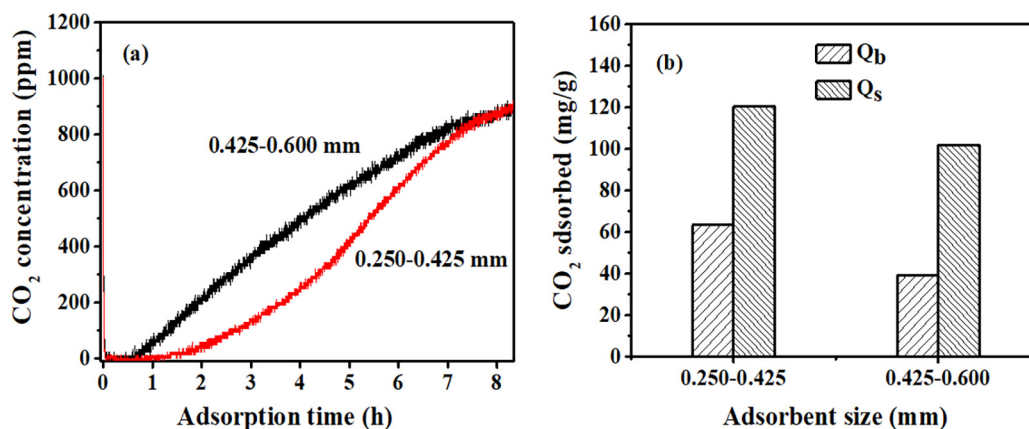**Fig. 2.** Pore size distribution of the MR10 (a) and PEI-MR10 with two different sizes (b).

Fig. 3. Breakthrough adsorption curves (a) and adsorbed amount of CO_2 (b) using different particle size PEI-MR10 with an initial CO_2 concentration of 1000 ppm.
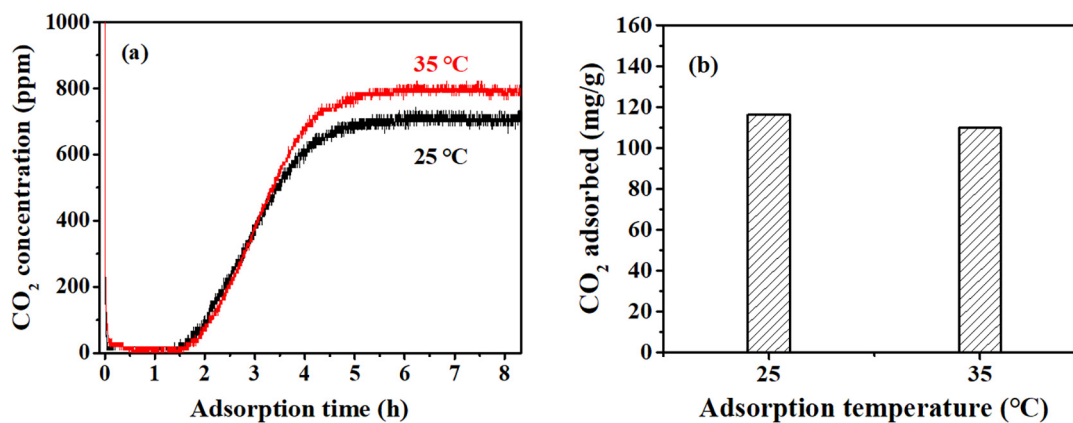

Fig. 4. Influence of temperature on the CO_2 adsorption breakthrough curves (a) and adsorbed amounts (b) of CO_2 on PEI-MR10.

concentrations at 50 RH%. The CO_2 adsorption breakthrough curves showed that breakthrough time became shorter with the increase of CO_2 concentrations from 500 ppm to 2000 ppm (binary CO_2 / N_2 mixture) (Fig. 6a). The breakthrough curve obtained at the extremely low CO_2 concentration (500 ppm) exhibited a longer breakthrough time than others. By calculating the amount of CO_2 penetration and saturated adsorption (Fig. 6b), the saturated adsorption amounts gradually increased from 97.0 to 136.4 mg/g with increasing CO_2 concentration from 500 to 2000 ppm. The adsorbent PEI-MR10 had the highest breakthrough amount of 86.1 mg/g and a saturation adsorption amount of 136.4 mg/g when the CO_2 concentration was 2000 ppm. The high adsorption capacity for CO_2 indicates that the PEI-MR10 adsorbent is suitable for low concentration of CO_2 removal from indoor air.

3.4. CO_2 adsorption kinetics and adsorption isotherms

The adsorption kinetics of CO_2 on the PEI-MR10 was conducted under the typical indoor condition (25 °C, 30% RH, 1000 ppm CO_2), and the adsorbed amounts of CO_2 increased gradually during the 8 h adsorption process (Fig. S3). The pseudo-first order, pseudo-second order and Avrami [42] kinetic models were adopted to describe the kinetic data, and the fitting curves and obtained parameters were shown in Fig. S3 and Table S2. It could be seen that the Avrami kinetic model fitted better than the pseudo-first order and the pseudo-second order kinetic models for the adsorption of CO_2 on PEI-MR10. The correlation coefficient R^2 of the Avrami kinetic model was 0.999, and the fitted theoretical equilibrium adsorption amount was similar to the
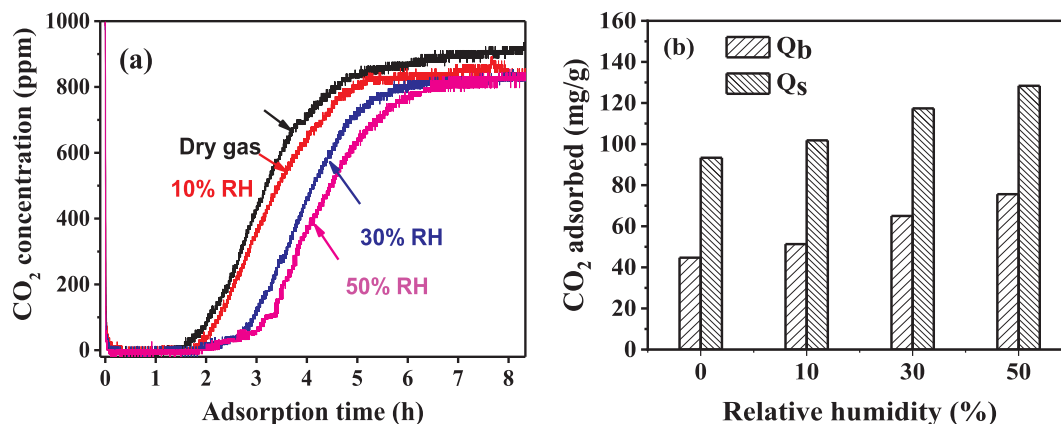

Fig. 5. Influence of relative humidity on the breakthrough curves (a) and adsorbed amounts (b) of CO_2 on PEI-MR10.
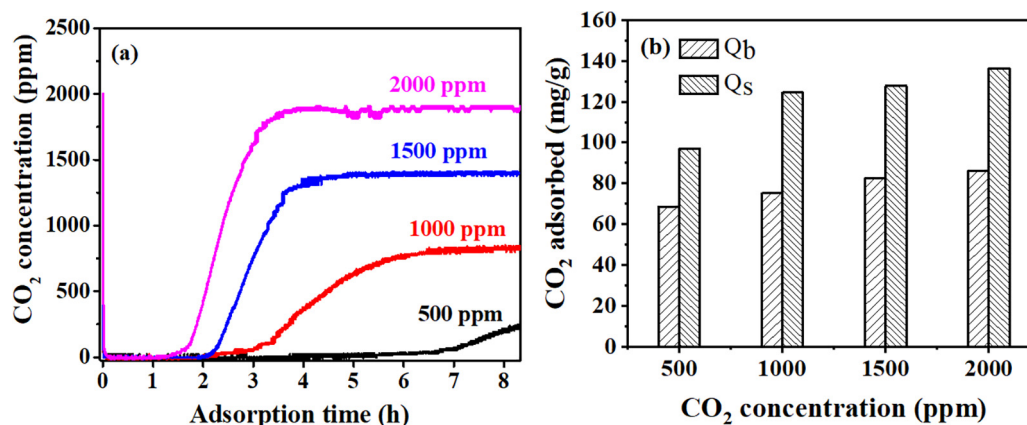
Fig. 6. Influence of CO_2 concentrations on the breakthrough curves (a) and adsorbed amounts (b) of CO_2 on PEI-MR10.

experimental one. The previous adsorption kinetic studies on this type of aminated resin showed that the process of pure CO_2 adsorption conformed to the double-exponential model [30], and the adsorption equilibrium was achieved quickly in the early stage of adsorption. However, the adsorption rate was relatively slow in this study (Fig. S3), due to the very low concentration of CO_2 in indoor air. The adsorption kinetics curve began to approach the adsorption equilibrium after around 5 h, consistent with the change trend shown by the adsorption breakthrough curve. Although the adsorption rate on the PEI-MR10 for low-concentration CO_2 at room temperature was lower than that for pure CO_2 at higher temperatures, PEI-MR10 still showed high adsorption capacity for low-concentration CO_2 in indoor air.

The adsorption isotherms of CO_2 on the PEI-MR10 were shown in Fig. S4. The Langmuir and Freundlich models [43] were used to fit the adsorption isotherm data, and the obtained model parameters were listed in Table S3. It could be seen that the Langmuir model fitted the adsorption isotherm of CO_2 on PEI-MR10 a little better than the Freundlich model in the lower CO_2 partial pressure range, indicating the possible monolayer adsorption of CO_2 on the amine groups on PEI-MR10. According to the Langmuir fitting, the maximum adsorption capacity of CO_2 on the PEI-MR10 was 150.9 mg/g.

3.5. Regeneration of PEI-MR10 at low temperatures

Increasing temperature and decreasing pressure are usually used to desorb CO_2 from spent adsorbents. Decreasing pressure is not applied to adsorbent regeneration in air purifiers, while increasing temperature is an easy and feasible method for CO_2 desorption. However, heating method is an energy-consuming process, and especially the commonly used desorption temperature above 100 °C is impossible for the regeneration of spent adsorbent in air purifiers. In consideration of the safety, the suitable desorption temperatures should be no more than 70 °C in air purifiers. In addition, the flow gas in the regeneration process also affects CO_2 desorption from spent adsorbents, and pure nitrogen and CO_2-free air are commonly used as flow gas, but they are impossible to be used in real application in air purifiers.

The spent PEI-MR10 adsorbent after CO_2 adsorption was regenerated at 70 °C using CO_2-free air or ambient air. Both CO_2-free air and ambient air were tried in the desorption process to clarify the effect of CO_2 in ordinary ambient air generally containing 380–420 ppm CO_2. The CO_2 concentrations in the outlet gases as a function of regeneration time were presented in Fig. 7a. It was noted that the gas used in the desorption process contained some moisture. It was reported that the accumulation of urea can be inhibited in water-contained air [41], that was to say, the formed urea on the adsorbent might be hydrolyzed in the regeneration process so that the regenerated adsorbent could not be deactivated. It could be seen that the CO_2-free air was more favorable for the regeneration of PEI-MR10 than the ambient air and more CO_2

molecules were desorbed from the adsorbent (Fig. 7a). The CO_2 desorption process was conducted within 1 h with a gas flow rate of 10.6 L/ min at 70 °C, and the adsorbed CO_2 molecules were not completely desorbed from the adsorbent. According to the CO_2 adsorbed amounts on the pristine PEI-MR10 (Fig. S5) and on the regenerated ones (Fig. 7b) using the CO_2-free air or ambient air, it could be calculated that the desorption efficiency of CO_2 by the CO_2-free air could reach nearly 90% while the desorption efficiency by the ambient air was about 70%. The adsorbed amounts of CO_2 on the regenerated adsorbent by CO_2-free air and ambient air were reduced from approximately 120 mg/g to 108 mg/g and 87 mg/g, respectively (Fig. 7b).

Compared with CO_2-free air, ambient air had more potential for real application in the removal of CO_2 by air purifiers. Therefore, ambient air was used as flow gas in the regeneration process, and the desorption efficiencies of CO_2 from the spent PEI-MR10 at different temperatures were studied (Fig. S6). The desorption efficiencies of CO_2 increased significantly with increasing temperatures from 40 °C to 70 °C. After the integral calculation of the desorption curves, the desorption efficiencies of CO_2 by the ambient air were around 70% at 70 °C, 45% at 60 °C, 28% at 50 °C, and 17% at 40 °C. It is clear that the adsorbed CO_2 may be easily desorbed from the PEI-MR10 at temperature above 60 °C.

3.6. Successive CO_2 adsorption and desorption

To investigate the reusability of PEI-MR10 for CO_2 removal from indoor air, the successive six CO_2 adsorption–desorption cycles on the adsorbent were conducted with the mixed gas containing 1000 ppm CO_2 at 25 °C, and two different flow gases (CO_2-free air and ambient air) were used as regeneration gas in the desorption experiments at 70 °C to further analyze the desorption behavior. With CO_2-free air as flow gas, the six desorption kinetic curves of CO_2 from the spent adsorbent and the adsorbed amounts of CO_2 in the subsequent adsorption cycles were shown in Fig. 8. The six desorption kinetics curves of CO_2 from the spent adsorbent were similar, and the desorbed CO_2 concentrations first increased and then decreased with increasing desorption time (Fig. 8a). The highest CO_2 concentrations were achieved at about 10 min, and almost no CO_2 were desorbed after 60 min. According to the adsorption kinetic curves (Fig. S7), the adsorbed amount of CO_2 on the pristine PEI-MR10 was calculated to be 121.1 mg/g (Fig. 8b). Since the desorption temperature of 70 °C was not high enough to achieve the complete CO_2 desorption from the adsorbent in the first regeneration process, the adsorbed amount decreased to 108.2 mg/ g after the first desorption, and the desorption efficiency was about 90%. The CO_2 adsorbed amounts on the adsorbent decreased gradually in the first three adsorption cycles, and then remained constant in the following cycles with the adsorbed amount of CO_2 around 100 mg/g (Fig. 8b).

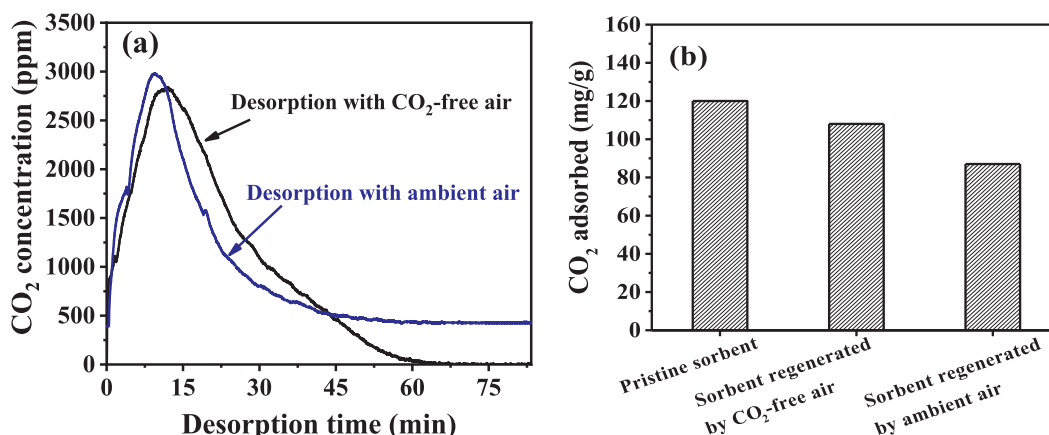Fig. 9 showed the six desorption kinetic curves of CO_2 from the

Fig. 7. Effect of different flow gas on CO_2 desorption at 70 °C (a) and their calculated amount of CO_2 adsorbed on the pristine PEI-MR10 and regenerated ones by CO_2-free air and ambient air (b).

spent PEI-MR10 and the adsorbed amounts of CO_2 in the subsequent adsorption cycles when the ambient air was used as flow gas at 70 °C. Since the ambient air contained approximately 400 ppm CO_2, it also affected the desorption efficiency of CO_2 from the spent adsorbent. It was reported that the polyethyleneimine-impregnated adsorbents could still adsorb CO_2 at 70 °C [30,44,45]. In the successive six adsorption-desorption cycles, the six desorption kinetic curves exhibited the very similar shape and they almost overlapped each other, indicating that almost the same amounts of CO_2 were desorbed from the spent PEI-MR10 (Fig. 9a). After each desorption, the regenerated adsorbent was reused for CO_2 adsorption, and the six adsorption kinetic curves were also similar (Fig. S8). After the first desorption, the adsorbed amounts of CO_2 on the regenerated adsorbent decreased from 118.6 mg/g to 87.2 mg/g, and the desorption efficiency was only about 70%, 20% lower than the desorption by CO_2-free air (Fig. 9b). In the following two adsorption cycles, the CO_2 adsorbed amount decreased slowly, and almost remained stable of about 80 mg/g after the 4th adsorption cycle. Although the ambient air had lower desorption of CO_2 from the spent adsorbent than the CO_2-free air, the regenerated PEI-MR10 could still keep stable adsorption capacity for CO_2 in the successive cycles, suggesting the high reusability of the PEI-MR10 for CO_2 removal from indoor air.

3.7. Desorption mechanism

To investigate the desorption mechanism of CO_2 from the spent adsorbent using two flow gases at 70 °C, the pristine PEI-MR10 and the regenerated PEI-MR10 by CO_2-free air and ambient air were analyzed

by FTIR to deduce the chemical substances formed during the adsorption process. It is generally accepted that the formation of carbamates and bicarbonates from the interaction of amine groups with CO_2 happened in the process of CO_2 on the amine-based adsorbents [36,40,41]. The FTIR spectra of the pristine PEI-MR10 and the regenerated PEI-MR10 by CO_2-free air and ambient air were shown in Fig. 10. The region between 1600 and 1200 cm^{-1} had some recognition peaks including carbonyl and urethane stretching and bending modes. The vibration at 1320, 1431, 1482 cm^{-1} and stretching band at 1565 cm^{-1} indicated the generation of the functional group of $NCOO^-$ associated with carbamate [46]. The C=O stretching vibration at 1657 cm^{-1} and the bicarbonate stretching vibration at 824 cm^{-1} were associated with the formation of bicarbonate [47]. Compared with the pristine PEI-MR10, the regenerated PEI-MR10 by CO_2-free air and ambient air showed stronger peaks at these vibration positions related to the accumulation of carbamate and bicarbonate, indicating that 70 °C was not high enough to achieve complete desorption of CO_2 from the spent adsorbent using CO_2-free air and ambient air. By comparing the amplitudes of the four peaks of 1320, 1431, 1482 and 1565 cm^{-1} related to $NCOO^-$ on the PEI-MR10 regenerated by CO_2-free air and ambient air, it was found that the peaks of PEI-MR10 regenerated by CO_2-free air reduced in amplitude more significantly, suggesting that the adsorbent regenerated by the ambient air had a tendency to form more $NCOO^-$ than the adsorbent regenerated by CO_2-free air. Besides, the accumulation of carbamate and bicarbonates on the regenerated PEI-MR10 by CO_2-free air and ambient air indicated that 70 °C was not high enough to achieve complete desorption of CO_2 from the spent adsorbent. Since CO_2 could be adsorbed at 70 °C [28], it could be
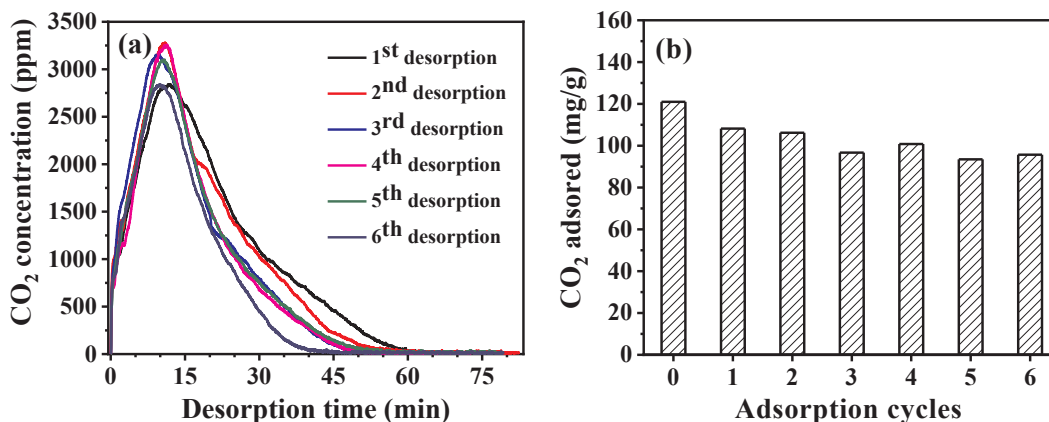

Fig. 8. Desorption curves (a) and adsorbed amounts (b) of CO_2 on the PEI-MR10 regenerated by CO_2-free air in six adsorption-desorption cycles.
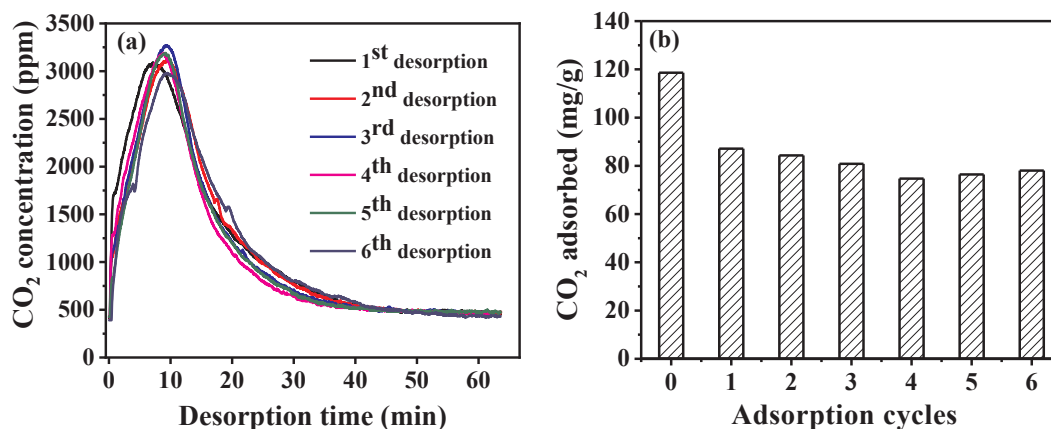
Fig. 9. Desorption curves (a) and adsorbed amounts (b) of CO_2 on the PEI-MR10 regenerated by ambient air in six adsorption-desorption cycles.
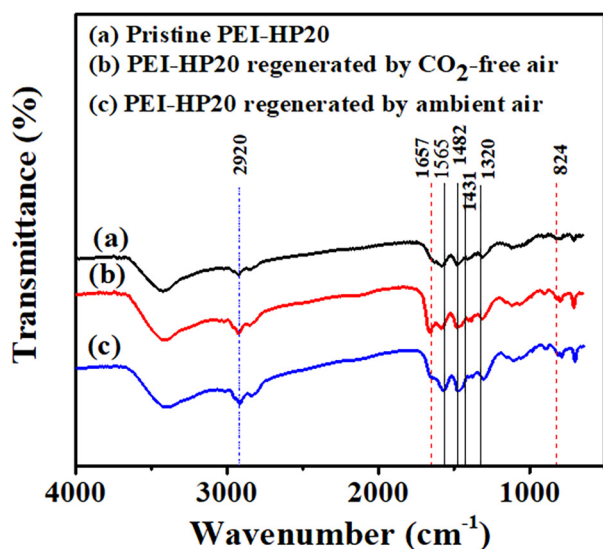

Fig. 10. FTIR spectra of pristine PEI-MR10 (a) and regenerated PEI-MR10 by CO_2-free air (b) and ambient air (c).

reasonably speculated that when the ambient air was used as flow gas, some CO_2 molecules in the air were also adsorbed on the adsorbent. A strong peak at around 2920 cm^{-1} was attributed to the formation of urea [45], which was accumulated in the adsorption process. The adsorbent regenerated by ambient air had a stronger absorption peak at 2920 cm^{-1} than the adsorbent regenerated by CO_2-free air, indicating that more urea was formed under the ambient condition. The difference might be due to the fact that the low concentration of CO_2 still present therein was captured to some extent by the amine groups on the adsorbent when ambient air was used for desorption. It was reported that the desorption gas containing humidity did not cause the accumulation of urea [31]. The incomplete regeneration at 70 °C and the adsorption of CO_2 during the desorption process by ambient air may be a dual reason for the small amount of urea still present after the desorption process of the moisture-containing gas in this study.

4. Conclusions

A PEI-impregnated resin (PEI-MR10) was successfully prepared for efficient removal of low concentrations of CO_2 from indoor air. The PEI-MR10 was able to remove all CO_2 during the first 2 h with an initial CO_2 concentration of 1000 ppm, and exhibited an average saturated adsorption amount of 116.2 mg/g at 25 °C. The adsorbed amounts of CO_2 increased with increasing humidity, and when the relative humidity

was increased to 50%, the adsorbed amount of CO_2 was increased to 128.4 mg/g on the adsorbent. The spent PEI-MR10 could be easily regenerated at 70 °C by using the CO_2-free air or ambient air as the flow gases. The desorption efficiencies of CO_2 decreased significantly with the decrease of regeneration temperatures. The successive adsorption–desorption experiments indicated that the PEI-MR10 adsorbent regenerated by ambient air at 70 °C could be reused for more than 6 times, maintaining stable adsorption ability of about 80 mg/g for low concentration CO_2. The decrease of CO_2 adsorption capacity was attributed to the accumulation of carbamate and bicarbonates on the regenerated PEI-MR10, which were not completely destructed at 70 °C. This study showed that the PEI-impregnated adsorbents had the extraordinary adsorption performance for low concentrations of CO_2 and good regeneration performance at 70 °C, which could be used to effectively remove CO_2 from indoor air. High adsorption capacity for CO_2 at room temperatures and stable regeneration of the spent adsorbent at relatively low temperatures make this efficient adsorbent attractive in real application in the future.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2020.125734.

References

[1] P. Wolkoff, Indoor air pollutants in office environments: assessment of comfort, health, and performance, Int. J. Hyg. Environ. Health. 216 (2013) 371–394.

[2] U. Haverinen-Shaughnessy, R.J. Shaughnessy, E.C. Cole, O. Toyinbo, D.J. Moschandreas, An assessment of indoor environmental quality in schools and its association with health and performance, Build. Environ. 93 (2015) 35–40.

[3] C. Liu, Y.P. Zhang, Relations between indoor and outdoor PM2.5 and constituent concentrations, Front. Environ. Sci. Eng. 13 (2019) 5.

[4] W. Wei, O. Ramalho, M. Derbez, J. Riberon, C. Mandin, Applicability and relevance of six indoor air quality indexes, Build. Environ. 109 (2016) 42–49.

[5] S.A. Abdul-Wahab, S.C.F. En, A. Elkamel, L. Ahmadi, K. Yetilmezsoy, A review of standards and guidelines set by international bodies for the parameters of indoor air quality, Atmos. Pollut. Res. 6 (2015) 751–767.

[6] J. Madureira, M. Alvim-Ferraz, S. Rodrigues, C. Gon-Alves, M. Azevedo, E. Pinto, Indoor air quality in schools and health symptoms among Portuguese teachers, Hum. Ecol. Risk. Assess. 15 (2009) 159–169.

[7] D. Twardella, W. Matzen, T. Lahrz, Effect of classroom air quality on student's concentration: results of a cluster-randomized cross-over experimental study, Indoor Air. 22 (2012) 378–387.

[8] E.J. Griez, A. Colasanti, R. Diest, E. Salamon, K. Schruers, Carbon dioxide inhalation induces dose-dependent and age-related negative affectivity, PLoS ONE 2 (2007) e987.

[9] U. Satish, M.J. Mendell, K. Shekhar, T. Hotchi, W.B.J. Fisk, Is CO_2 an indoor pollutant? Direct effects of low-to-moderate CO_2 concentrations on human decision-making performance, Environ. Health. Persp. 120 (2012) 1671–1677.

[10] T. Vehvilainen, H. Lindholm, H. Rintamaki, R. Pakkonen, A. Hirvonen, O. Niemi, J. Vinha, High indoor CO_2 concentrations in an office environment increases the transcutaneous CO_2 level and sleepiness during cognitive work, J. Occup. Environ. Hyg. 13 (2016) 19–29.

[11] X. Zhang, P. Wargocki, Z. Lian, C. Thyregod, Effects of exposure to carbon dioxide and bioeffluents on perceived air quality, self-assessed acute health symptoms and cognitive performance, Indoor Air. 27 (2017) 47–64.

[12] M.V. Jokl, Evaluation of indoor air quality using the decibel concept based on carbon dioxide and TVOC, Build. Environ. 35 (2000) 677–697.

[13] S.C. Lee, C.C. Hsieh, C.H. Chen, Y.S. Chen, CO_2 adsorption by Y-Type zeolite impregnated with amines in indoor air, Aerosol. Air. Qual. Res. 13 (2013) 360–366.

[14] S.C. Hu, A. Shiue, S.M. Chang, Removal of carbon dioxide in the indoor environment with sorption-type air filters, Int. J. Low-Carbon. Tec. 12 (2017) 330–334.

[15] E.T. Gall, C. Sonat, W.W. Nazaroff, C. Unluer, Investigating CO_2 removal by Ca- and Mg-based sorbents with application to indoor air treatment, Build. Environ. 110 (2016) 161–172.

[16] T.S. Lee, J.H. Cho, S.H. Chi, Carbon dioxide removal using carbon monolith as electric swing adsorption to improve indoor air quality, Build. Environ. 92 (2015) 209–221.

[17] S.B. Deng, T. Chen, T.N. Zhao, X.L. Yao, B. Wang, J. Huang, Y.J. Wang, G. Yu, Role of micropores and nitrogen-containing groups in CO_2 adsorption on indole-3-butyric acid potassium derived carbons, Chem. Eng. J. 286 (2016) 98–105.

[18] J. Liu, Y. Wang, A.I. Benin, CO_2/H_2O adsorption equilibrium and rates on metal-organic frameworks: HKUST-1 and Ni/DOBDC, Langmuir 26 (2010) 14301–14307.

[19] S. Xian, X. Feng, M. Chen, Y. Wu, Q. Xia, H. Wang, Z. Li, Vapor-enhanced CO_2 adsorption mechanism of composite PEI-ZIF-8 modified by polyethyleneimine for CO_2/N_2 separation, Chem. Eng. J. 280 (2015) 363–369.

[20] J. Wang, H. Huang, M. Wang, L. Yao, W. Qiao, D. Long, Direct capture of low-concentration CO_2 on mesoporous carbon-supported solid amine adsorbents at ambient temperature, Ind. Eng. Chem. Res. 54 (2015) 5319–5327.

[21] M. Niu, H. Yang, X. Zhang, Y. Wang, A. Tang, Amine-impregnated mesoporous silica nanotube as an emerging nanocomposite for CO_2 capture, ACS Appl. Mater. Inter. 8 (2016) 17312–17320.

[22] J. Singha, S. Bhuniab, S. Basua, Synthesis of sulphur enriched carbon monoliths for dynamic CO_2 capture, Chem. Eng. J. 374 (2019) 1–9.

[23] J. Singha, S. Basua, H. Bhuniab, Dynamic CO_2 adsorption on activated carbon adsorbents synthesized from polyacrylonitrile (PAN): kinetic and isotherm studies, Micropor. Mesopor. Mat. 280 (2019) 357–366.

[24] J. Wang, M. Wang, W. Li, W. Qiao, D. Long, L. Ling, Application of polyethylenimine-impregnated solid adsorbents for direct capture of low-concentration CO_2, Aiche. J. 61 (2015) 972–980.

[25] W. Chaikittisilp, R. Khunsupat, T. Chen, C.W. Jones, Poly(allylamine)-mesoporous silica composite materials for CO_2 capture from simulated flue gas or ambient air, Ind. Eng. Chem. Res. 50 (2011) 14203–14210.

[26] W. Chaikittisilp, H.J. Kim, C.W. Jones, Mesoporous alumina-supported amines as potential steam-stable adsorbents for capturing CO_2 from simulated flue gas and ambient air, Energ. Fuel. 25 (2011) 5528–5537.

[27] Y. Belmabkhout, R. Serna-Guerrero, A. Sayari, Adsorption of CO_2-containing gas mixtures over amine-bearing pore-expanded MCM-41 silica: application for gas purification, Ind. Eng. Chem. Res. 49 (2010) 359–365.

[28] N. Gargiulo, A. Peluso, P. Aprea, CO_2 Adsorption on polyethylenimine-functiona-lized SBA-15 mesoporous silica: isotherms and modeling, J. Chem. Eng. Data. 59 (2014) 896–902.

[29] R. Veneman, N. Frigka, W. Zhao, Z. Li, Adsorption of CO_2 and H_2O on supported amine sorbents, Int. J. Greenh. Gas. Con. 63 (2014) 2336–2345.

[30] Z. Chen, S. Deng, H. Wei, B. Wang, G. Yu, Polyethylenimine-impregnated resin for high CO_2 adsorption: an efficient adsorbent for CO_2 capture from simulated flue gas and ambient air, ACS Appl. Mater. Inter. 5 (2013) 6937–6945.

[31] X. Wang, X. Ma, X. Xu, L. Sun, C. Song, Mesoporous-molecular-sieve-supported polymer sorbents for removing H_2S from hydrogen gas streams, Top. Catal. 49 (2008) 108–117.

[32] X. Xu, C. Song, J.M. Andresen, B.G. Miller, A.W. Scaroni, Novel polyethylenimine-modified mesoporous molecular sieve of MCM-41 type as high-amount adsorbent for CO_2 capture, Energ. Fuel. 16 (2001) 1463–1469.

[33] A. Goeppert, H. Zhang, M. Czaun, R.B. May, G.K. Surya Prakash, G.A. Olah, Easily regenerable solid adsorbents based on polyaminesfor carbon dioxide capture from the air, Chem. Sus. Chem. 7 (2014) 1386–1397.

[34] R.B. Bird, W.E. Stewart, E.N. Lightfoot, Transport Phenomena, second ed., John Wiley & Sons Ltd, 2007.

[35] M.J. Bos, T. Kreuger, S.R.A. Kersten, D.W.F. Brilman, Study on transport phenomena and intrinsic kinetics for CO_2 adsorption in solid amine sorbent, Chem. Eng. J. 377 (2019) 120374.

[36] A. Sayari, Y. Belmabkhout, Stabilization of amine-containing CO_2 adsorbents: dramatic effect of water vapor, J. Am. Chem. Soc. 132 (2012) 6312–6314.

[37] X. Xu, C. Song, R. Wincek, J. Andresen, B. Miller, A. Scaroni, Separation of CO_2 from power plant flue gas using a novel CO_2 "molecular basket" adsorbent, Fuel. Chem. Div. Prep. 48 (2003) 162–163.

[38] A.L. Kohl, R.B. Nielsen. Gas Purification, fifth ed., 1997.

[39] X. Xu, C. Song, B. Miller, A. Scaroni, Influence of moisture on CO_2 separation from gas mixture by a nanoporous adsorbent based on polyethylenimine-modified molecular sieve MCM-41, Ind. Eng. Chem. Res. 44 (2005) 8113–8119.

[40] N. Hiyoshi, K. Yogo, T. Yashima, Adsorption characteristics of carbon dioxide on organically functionalized SBA-15, Micropor. Mesopor. Mat. 84 (2005) 357–365.

[41] R. Serna-Guerrero, E. Da'na, A. Sayari, New insights into the interactions of CO2 with amine-functionalized silica, Ind. Eng. Chem. Res. 47 (2008) 9406–9412.

[42] X. Wang, L. Chen, Q. Guo, Development of hybrid amine-functionalized MCM-41 sorbents for CO_2 capture, Chem. Eng. J. 260 (2014) 573–581.

[43] H. Ahn, J.H. Moon, S.H. Hyun, Diffusion mechanism of carbon dioxide in zeolite 4A and CaX pellets, Adsorption 10 (2004) 111–128.

[44] W. Chaikittisilp, R. Khunsupat, T.T. Chen, C.W. Jones, Poly(allyl-amine)-mesoporous silica composite materials for CO_2 capture from simulated flue gas or ambient air, Ind. Eng. Chem. Res. 50 (2011) 14203–14210.

[45] R.W. Alesi, J.R. Kitchin, Evaluation of a primary amine-functionalized ion-exchange resin for CO_2 capture, Ind. Eng. Chem. Res. 51 (2012) 6907–6915.

[46] H. He, X. Hou, B. Ma, L. Zhuang, C. Li, S. He, S. Chen, The oxidation of viscose fiber optimized by response surface methodology and its further amination with PEI for CO_2 adsorption, Cellulose 23 (2016) 2539–2548.

[47] M. Parvazinia, S. Garcia, M. Maroto-Valer, CO_2 capture by ion exchange resins as amine functionalised adsorbents, Chem. Eng. J. 331 (2018) 335–342.