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Advanced buffer materials for indoor air CO_2 control in commercial buildings

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Abstract

In this study, we evaluated solid sorbents for their ability to passively control indoor CO_2 concentration in buildings or rooms with cyclic occupancy (eg, offices, bedrooms). Silica supported amines were identified as suitable candidates and systematically evaluated in the removal of CO_2 from indoor air by equilibrium and dynamic techniques. In particular, sorbents with various amine loadings were synthesized using tetraethylenepentamine (TEPA), poly(ethyleneimine) (PEI) and a silane coupling agent 3-aminopropyltriethoxysilane (APS). TGA analysis indicates that TEPA impregnated silica not only displays a relatively high adsorption capacity when exposed to ppm level CO_2 concentrations, but also is capable of desorbing the majority of CO_2 by air flow (eg, by concentration gradient). In 10 L flow-through chamber experiments, TEPA-based sorbents reduced outlet CO_2 by up to 5% at 50% RH and up to 93% of CO_2 adsorbed over 8 hours was desorbed within 16 hours. In 8 m^3 flow-through chamber experiments, 18 g of the sorbent powder spread over a 2 m^2 area removed approximately 8% of CO_2 injected. By extrapolating these results to real buildings, we estimate that meaningful reductions in the CO_2 can be achieved, which may help reduce energy requirements for ventilation and/or improve air quality.

KEYWORDS
adsorption, chamber experiments, CO_2 control, indoor air quality, supported amine sorbents

1 | INTRODUCTION

The ambient CO_2 concentration in rural air is about 400 ppm,[1] while in urban areas, ambient CO_2 tends to be somewhat higher than rural air and that of indoor air is typically about 650-700 ppm. According to American Society of Heating, Refrigerating and Air conditioning Engineers (ASHRAE), the CO_2 concentration no greater than ~700 ppm above outdoor air levels will satisfy the occupants inside the buildings with respect to body odor.[2] Studies also show that CO_2 at increased levels is considered as pollutant and affects cognition and productivity. Kajtar et al.[3] found that exposing humans at levels from 2000 to 5000 ppm CO_2 adversely affect proof-reading tasks. In response to these reports, Satish et al.[4] developed a series of human exposure experiments with the goal of identifying reduced productivity. They observed statistically significant decrements in decision-making performance and concluded that reduced productivity would negate any energy and cost-saving benefits of reduced ventilation rates.[4] Moreover, in a recent study by Allen et al.,[5] indoor air conditions in conventional [high concentrations of volatile organic compounds (VOCs)] and green (low concentrations of VOCs) environments were simulated and their impact on human performance (ie, higher-order cognitive function) was evaluated. It was found that cognitive scores are higher under green buildings conditions with a high outdoor air ventilation than in the conventional building conditions.[5] It should also be noted here that recent studies by Zheng et al.[6,7] show that exposure to moderate concentrations of bioeffluents can interfere with cognitive functioning while exposure to pure CO_2 did not result in observable adverse effects on subjects.

Worldwide, buildings are responsible for a large fraction of the total energy budget and consumption is expected to rise about 1.5% every year.[8] In the United States, buildings are responsible for 40% of total energy consumed. Space conditioning accounts for 48% of energy in office buildings. It has been reported that out of the total energy consumed in typical buildings, about 40%-60% is consumed for maintenance of appropriate ventilation and air circulation. Therefore, modern approaches to energy conservation must include improved efficiency in conditioning air in buildings. The cost of space conditioning is influenced by many factors including internal loads, climate, building construction, and ventilation rates.[2,9]

It is suspected that indoor air quality and occupant productivity suffer with low ventilation rates.[10,11] Until recently, it was accepted that in the absence of other pollutant sources, these problems were due primarily to body odor with CO_2 often used as a proxy measure. To ensure sufficient dilution, ASHRAE has developed standards of ventilation for commercial and other building types. Specifically, they recommend a ventilation rate based on a combination of occupancy, which accounts for body odor, and building floor area, which accounts for building material emissions.[2] Yet, this strategy can result in high energy use if ventilation is always set at maximum occupancy. As a response to this problem, CO_2 has been used as a proxy for occupancy. Demand control ventilation (DCV) using CO_2 sensors, in theory, automatically provides sufficient dilution to reduce occupant emissions below odor thresholds. DCV based on CO_2 has been criticized because of variability in CO_2 emissions from people and too few sensors that average CO_2 of multiple zones.[12,13] As an alternative, Gall and Nazaroff suggest that active CO_2 removal (eg, by sorption) from building air can allow for reduced ventilation, and thereby energy consumption, potentially reducing the U.S. building carbon footprint by 10 Tg CO_2/y.[14]

Actively controlling indoor pollutants by traditional means generally requires fan energy associated with recirculating air over filter media. However, several researchers have recommended the use of passive control of outdoor and indoor sourced pollutants. Ozone has been shown to be readily removed at buildings surfaces.[15] Some surfaces, such as brick, concrete, and clay coatings, are particularly good at passively reducing indoor ozone concentrations without generating undesirable byproducts.[16,17] A number of coatings manufacturers have included additives to paints that show promise in reducing indoor concentrations of odorous compounds, formaldehyde, and VOCs.[18,19] Therefore, many internal and external pollutant loads can be controlled without increasing ventilation or filtration rates. These strategies work because the high surface area available for sorption (eg, walls and ceilings) can result in high air cleaning rates.[19] Further, the relatively small mass removal requirements for these pollutants (typically for air concentrations in the μg/m^3 range) allow coatings to be effective sorbents for periods of years or even decades before a new coating is applied.

Passive control by sorption to indoor surface coatings is an attractive possibility for controlling CO_2, when combined with a portfolio of other air cleaning strategies. To effectively control CO_2 in buildings, permanent adsorption to media is unlikely to be practical due to the very large mass of CO_2 generated by occupants (approximately 750 g/person/d for office work). Any reasonable mass of sorbent installed in a building, such as a wall coating, would rapidly become saturated. Instead, we propose that CO_2 can be captured during primary occupancy periods by adsorption, then released passively during low-occupancy periods. In this way, energy associated with thermal or pressure swing adsorption cycles would not be required, eliminating operating costs and minimizing maintenance.

Practical Implications

- This study demonstrates that amine-based sorbents can act to passively reduce CO_2 concentrations under realistic building conditions. When incorporated into coatings, such materials can help reduce CO_2 concentrations to improve air quality and/or reduce ventilation requirements, when combined with other indoor air quality controls.

One of the key advantages of passive control is to save energy through a reduction in the ventilation rate. However, this reduction may result in an increase in the concentration of other indoor pollutants. On the other hand, reduced ventilation can minimize the impact of pollutants of outdoor origin (ozone, NO_x, diesel aerosols, etc.). Thus, the side effects of reduced ventilation rate with respect to both outdoor and indoor air pollutants should be considered in the context of passive CO_2 control.

Adsorption processes for gas separation via selective adsorption on solid media are also well-known.[20-26] To date, there has been a wide variety of sorbent materials investigated for CO_2 capture including conventional materials such as zeolites, carbon-based sorbents, metal oxides, and organic-inorganic hybrids like porous aminosilicates, as well as relatively new materials such as metal organic frameworks (MOFs), porous polymer networks (PPNs), covalently organic frameworks (COFs), and amine-appended MOFs.[27-29] These sorbents can operate via weak physisorption processes or strong chemisorption interactions. The various classes of physisorbents and chemisorbents have unique advantages and disadvantages. For instance, physisorbents are regenerable, but the efficiency of CO_2 adsorption is low, resulting in a long adsorption time while chemisorbents can adsorb CO_2 very quickly and efficiently but are non-regenerable. Indeed, the trade-off that exists between sufficient CO_2 adsorption capacity (ie, steep adsorption isotherms) and regenerability (ie, low sorption enthalpy) at room temperature makes the selection of sorbent candidates for this particular application difficult.[27,30] Competitive water adsorption is another issue which renders most of sorbents impractical despite comparatively high adsorption capacities at low partial pressures. To improve indoor air quality and to efficiently remove CO_2, the candidate sorbent materials should perform low-energy cyclical capture and release of indoor CO_2.

As noted above, this buffering approach has been suggested to help reduce the energy demands of moisture control,[31-33] but to the best of our knowledge, there have not been any studies of the removal of CO_2 from indoor air, aside from a few preliminary investigations. Lee et al.[34] studied the use of Y-type zeolite impregnated amines for CO_2 sorption from indoor air. A variety of zeolite impregnated amines were exposed to 1500 ppm CO_2 at 25°C for 1 hour and a CO_2 capacity of 3.59 mmol/g was reported. However, this particular study was focused on the determination of CO_2 capacity and no information on adsorption/desorption rates or sorbent regeneration was provided. In a recent study,[35] electric-swing adsorption (ESA) process, driven by the electrification and cooling of air flow, was proposed to improve indoor air quality through removal of excess CO_2 from living spaces using carbon monoliths. As demonstrated by the authors, an electrical energy requirement of 57.8 kJ/m^3 air is necessary to treat air containing 3000 ppm CO_2. This energy requirement in addition to complexity of ESA system makes the proposed approach less attractive for practical applications. More recently, Kim et al.[36] studied the performance of a CO_2 adsorption device in the operation of an air ventilation system. The proposed system is based on recirculating indoor air to save energy for a certain period of time. Their simulation results showed that 30%-60% of air ventilation energy for cooling and heating can be saved relative to conventional systems. The study was, however, focused primarily on the evaluation of the performance of the system and the sorbent characteristics and performance were not discussed.

Under typical operating conditions, the sorbent will be exposed to outdoor background CO_2 overnight with the concentration of approximately 400 ppm then CO_2 may rise during the workday to about 1500 ppm, depending on the number of occupants and ventilation rate. The sorbent regeneration and the release of adsorbed CO_2 is driven by concentration gradient between indoor air and the sorbent. Therefore, finding a sorbent material that exhibits relatively high adsorption capacity at such a low concentration while demonstrating a sufficient, fast desorption rate will be an important challenge in managing indoor CO_2. Furthermore, as the regeneration of sorbent is based on the difference in the CO_2 concentration of the sorbent and indoor air, selected sorbents require to not only exhibit high CO_2 adsorption capacity but also exhibit low internal mass transfer resistance in order to demonstrate a fast desorption rate at room temperature. Therefore the textural properties of the porous sorbents play a significant role in effectively adsorbing/desorbing CO_2 under these conditions.

In this study, the feasibility of applying solid sorbents to control indoor CO_2 concentration in buildings was investigated. Specifically, we focused on evaluating various physisorbent and chemisorbent materials for the removal of CO_2 from indoor air. Although the CO_2 sorption characteristics of these materials are well-studied, relatively little quantitative information has been published on their desorption performance at room temperature and at ppm-level concentration. Therefore, this study focuses on systematically exploring CO_2 adsorption and desorption on silica supported amine sorbents under realistic conditions at CO_2 concentrations typical of indoor environments.

2 | EXPERIMENTAL SECTION

2.1 | Material synthesis

The commercial silica, PD09024 from PQ Corporation (named as PD in this study), was used to synthesize supported amine sorbents. The polymeric amines employed, TEPA and PEI, represent aminopolymers previously found to be highly efficient for CO_2 adsorption. The TEPA- and PEI-based sorbents were synthesized using a conventional wet impregnation method.[37] First, a desired amount of TEPA/PEI (10-50 wt%) was dissolved in methanol for 1 hour, and subsequently, dried silica was added and stirred for an additional 12 hours. The methanol solvent was later removed by a rotary evaporator (rotovap), and the resulting adsorbent was further dried under vacuum at 105°C overnight before testing. For preparation of aminosilane-based sorbents containing primary amine moieties (PD-APS), the silica was functionalized through the reaction of APS with surface silanols.[37] First, a desired amount of toluene and silica was mixed for 1 hour and then a desired amount of silane (7, 15, 20 wt%) was added into the mixture. The mixture was kept under vigorous stirring for 24 hours at 85°C. The resulting adsorbent was recovered by filtration, washed with toluene, and then dried under vacuum at 105°C. The aminosilica buffer materials with systematically varied amine loadings were prepared. For the TEPA sorbents, four samples were prepared, namely PD-TEPA-10%, PD-TEPA-20%, PD-TEPA-25%, and PD-TEPA-50%, whereas for the PEI and APS sorbents, the following samples were prepared: PD-PEI-34%, PD-PEI-44%, PD-APS-7%, PD-APS-15%, and PD-APS-20%.

In addition to amine-based sorbents, we also synthesized MOF-74(Mg) via solvothermal method.[38] For this synthesis, desired amounts of DHTA and $Mg(NO_3)_2 \cdot 6H_2O$ were first dissolved in a solution mixture of DMF, ethanol, and DI water. The solution was then mixed rigorously, sealed, and placed in oven for 21 hours at 125°C. After that the solid product was washed, recovered, and finally dried at 250°C under vacuum prior to adsorption experiments. Moreover, commercial zeolites 5A, 13X, and Y as well as activated carbon (AC) were purchased and used in this study without further modification.

2.2 | Materials characterization

Nitrogen physisorption measurements were carried out on a Micromeritics 3Flex at 77 K. The samples were degassed prior to analysis on a Micromeritics SmartVacPrep. Surface areas and pore volumes were calculated from the collected physisorption isotherms. Surface areas were determined using the Brunauer Emmett Teller (BET) method while pore volumes were estimated using the Broekhoff-de Boer-Frenkel Halsey Hill (BdB-FHH) method.[39] Amine loading (mmol N/g) of aminosilica sorbents was estimated from C-H-N elemental analysis tests using PerkinElmer 2400. FTIR spectroscopy measurements were performed on a Nicolet Nexus 470 optical bench to determine the functional groups of the amine-based sorbents.

2.3 | Equilibrium adsorption measurements

The equilibrium adsorption measurements were carried out on a Q500 thermogravimetric analyzer (TA Instruments, New Castle, DE, USA) by directly exposing the buffer materials to the CO_2/N_2 gas mixture. Prior to measurements, the sorbents materials were degassed in flowing N_2 for 30 minutes to remove any preadsorbed humidity or other gases and then exposed to 500 and 3000 ppm CO_2 at room temperature for 4 hours. For all experiments, the gas flow rate was set to 90 mL/min. The desorption step was followed immediately by switching CO_2 to pure N_2 while keeping the temperature constant (ie, room temperature) for 6 hours. The procedure was varied to investigate the impact of desorption time and flow rate of N_2 on the desorption capacity of buffer materials. It should be noted here that although in reality, air is used to desorb CO_2 from the materials, we considered N_2 in the TGA runs instead of air to prevent the interference of other components (such as CO_2 in the air, argon, etc.) with the desorption process.

2.4 | CO_2 breakthrough measurements

The dynamic sorption performance of the amine impregnated silica samples was assessed by performing breakthrough experiments in a fixed-bed column connected to a BEL Mass Spectrometer. Similar to the equilibrium adsorption measurements, the CO_2 and N_2 gases were used alternatively to analyze the desorption capacity along with the adsorption capacity. The feed stream with the composition of 5000 ppm CO_2/N_2 was fed into the column at the flow rate of 40 mL/min. Prior to each sorption experiment, the bed was heated to 110°C under flowing N_2 at 90 mL/min for 1 hour to desorb adventitious CO_2 and water and then cooled to 25°C and exposed to CO_2 for the experimental sorption run. The effluent composition exiting the column was transiently measured by the MS, and after reaching the inlet concentration, the desorption step was started by flowing N_2 to the column at the same flow rate (ie, 40 mL/min).

2.5 | Small chamber measurements

To further evaluate the buffer materials under realistic mass-transport conditions, small chamber tests were carried out in a laboratory-scale chamber setup shown in Figure 1. The setup consists of a small 10 L stainless steel connected to a CO_2 gas analyzer for monitoring the CO_2 concentration at the chamber outlet. A mixture of air and CO_2 at 1400-1500 ppm was fed into the chamber at 1.0 L/min. Half of the inlet air stream was passed through a bubbler to humidify the gas prior to entering to the chamber to control the relative humidity. A 23-cm-diameter disk of painted gypsum drywall was placed inside this chamber. The sorbent material was dusted uniformly over the painted surface of the drywall disk.

Amine-based sorbent performance was tested by varying the sorbent mass in the chamber with the relative humidity fixed at 50 RH%. For these experiments, we loaded 0.0 g (control), 1.0, 2.5, and 4.0 g of the PD-TEPA-25% on the painted drywall disk inside the chamber and exposed it to ~1500 ppm CO_2/air at a flow rate of 1.0 L/min, while recording the CO_2 concentration in the outlet stream. Each experiment consisted of a bypass run followed by adsorption-desorption cycles. The bypass run determines the inlet CO_2 concentration with, and without, added CO_2. First, air with added CO_2 bypasses the chamber and is directed to the CO_2 monitor chamber for 1 hour. Second, air without added CO_2 is directed to the monitor. The bypass is followed by a 7-hour adsorption and 14-hour desorption cycle. The influence of relative humidity (RH) on the sorbent performance was investigated by running the chamber tests at 15%, 50%, and 90% RH, using 2.0 g PD-TEPA-25%.

Due to slight drift in monitor readings from one experiment to the next, the results were normalized, $C_{\text{outlet,norm}}$, based on the inlet,

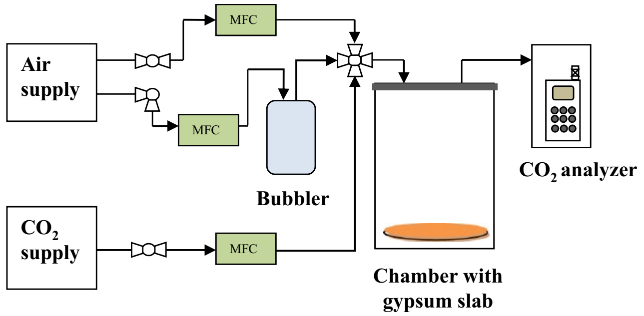

FIGURE 1 Schematic of small chamber setup for indoor air CO_2 control experiments

C_{inlet}, and minimum CO_2 concentrations, C_{min}, measured during that experiment:

$$C_{\text{outlet,norm}} = \frac{(C_{\text{outlet}} - C_{\text{min}})}{(C_{\text{inlet}} - C_{\text{min}})} \tag{1}$$

C_{min} was found at the outlet during the tail of the desorption experiment. The normalized results were then used to estimate the deposition velocity and fraction of adsorbed CO_2 that was released during desorption. During the last 2 hours of an adsorption experiment, the chamber was assumed to act as a steady state, well-mixed chamber, and CO_2 was removed at a constant rate only at the surface of the coated disk. The deposition velocity, v_d, is defined here as:

$$v_d = \frac{Q(C_{\text{inlet}} - C_{\text{min}})(C_{\text{outlet,norm},b} - C_{\text{outlet,norm},i})}{A(C_{\text{outlet,norm},i})} \tag{2}$$

where Q was the volumetric flow rate of the chamber, $C_{\text{outlet,norm},b}$ was the average normalized concentration at the outlet during a control experiment, $C_{\text{outlet,norm},i}$, was the normalized outlet concentration for sorbent run i averaged over the last 2 hours of an adsorption cycle, and A was the cross-sectional area of the coated disk (415 cm^2; we assumed that the sorbent is uniformly distributed across the disk). A transport-limited deposition velocity, v_t, was also calculated using Equation (2) by assuming that the CO_2 concentration adjacent to the sorbent is initially equal to the background concentration, $C_{\text{background}}$, in the supply air (ie, the sorbent is initially at equilibrium with the background air very early in the experiment). To calculate v_t using Equation (2), $C_{\text{outlet,norm},b}$, and $C_{\text{outlet,norm},i}$, were averaged over the period between 30 and 60 minutes after the adsorption cycle starts. This is a compromise between allowing enough time for the chamber to reach pseudo-steady state, but also early enough in the cycle such that a limited amount of CO_2 has adsorbed. As such, the result will slightly underestimate v_t. The percent desorption was determined by integrating mass desorbed and dividing by mass desorbed, using the normalized concentrations.

2.6 | Large chamber measurements

Full-scale testing of dynamic CO_2 concentrations took place in an 8 m^3 chamber shown schematically in Figure 2. This chamber has been used to study ozone-terpene reactions taking place on latex paint.[40]

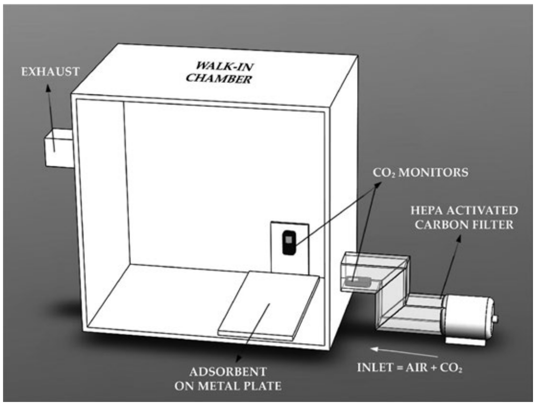

FIGURE 2 Schematic of large chamber setup for indoor air CO_2 control experiments

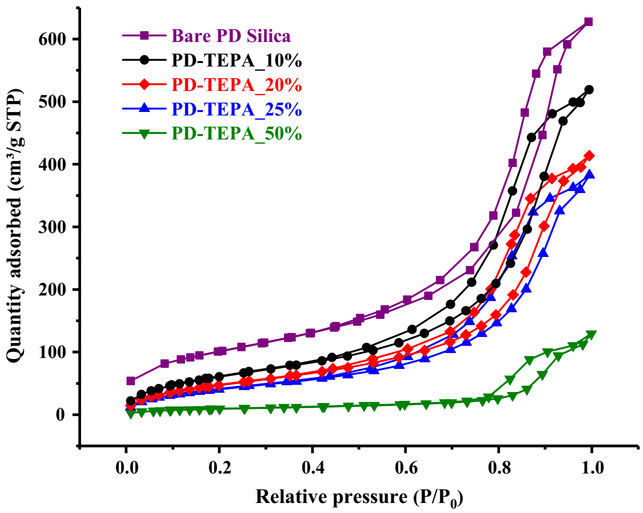

FIGURE 3 Nitrogen physisorption isotherm for tetraethylenepentamine (TEPA)-based buffer materials and bare PD silica

The chamber is an insulated walk-in room with external single-pass, filtered ventilation. The inner surfaces of the chamber are stainless steel, but are clad in drywall panels that have been painted with normal latex paint. Air is passed through a HEPA filter and an activated carbon filter before being introduced into the chamber. CO_2 monitors are positioned at the inlet and at the center of the chamber and monitored continuously during experiments.

Because the current sorbents have not yet been incorporated into wall coatings, we tested the sorbent powder (PD-TEPA-25%) by spreading 18 g as uniformly as possible on a 1.24 m^2 aluminum panel. This sorptive "surface" was placed on the floor of the 8 m^3 chamber described above. Approximately 200 mL/min of CO_2 was introduced into the chamber (operated at an air exchange rate of 1/h) for 8 hours then turned off. This sets the inlet air concentration to about 2100 ppm CO_2. However, due to some uncontrolled air infiltration from the surrounding laboratory, the steady-state chamber air concentration, without adsorbent present, was 1800-1900 ppm. Three cycles were run under these conditions along with three control experiments without the sorbent present. A normalization similar that shown in Equation (1) was used to compare the control experiments and sorbent experiments.

3 | RESULTS AND DISCUSSION

3.1 | Physical properties of materials

N_2 isotherm data collected at 77 K were used to calculate surface areas, pore volumes, and pore size of synthesized materials. The nitrogen adsorption and desorption isotherms are presented in Figure 3 for silica-supported TEPA samples with different amine content. All adsorbents displayed a typical type IV IUPAC isotherm with a type H2 hysteresis loop. Table 1 summarizes the obtained results along with the amine loadings, as determined by elemental analysis. It is apparent from the data that for all materials both surface area and pore volume decreased upon amine functionalization, as expected. For PD-TEPA

TABLE 1 Physical properties of amine adsorbents as well as equilibrium adsorption capacities at 3000 ppm CO_2 and the corresponding desorption rates at 25°C

Adsorbent	Amine loading (mmol N/g)	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	Adsorption capacity (mmol/g)	Desorption capacity (%)
PD-Bare	–	294	1.04	–	–
PD-TEPA-10%	2.02	247	0.76	0.20	89
PD-TEPA-20%	4.96	172	0.59	1.08	40
PD-TEPA-25%	5.79	147	0.54	1.40	31
PD-TEPA-50%	11.25	33	0.16	2.10	8
PD-PEI-34%	7.80	20	0.09	1.23	20
PD-PEI-44%	10.02	8.0	0.04	1.36	10
PD-APS-7%	1.06	196	0.66	0.21	66
PD-APS-15%	2.44	119	0.35	0.81	37
PD-APS-20%	3.00	63	0.23	1.00	31

samples, the surface area decreased from 294 for bare silica support to 247 m^2/g for low-loaded sample (PD-TEPA-10%) while the drop was more pronounced for high-loaded sample (PD-TEPA-50%), reaching 33 m^2/g. The same decreasing trend for pore volume with amine loading was observed for all samples. In the case of TEPA samples, pore volume (obtained at P/P_0 = 0.8-0.9) was decreased from 1.04 to 0.16 cm^3/g. The N_2 physisorption isotherm for PD-PEI and PD-APS samples is presented in Figure S1.

The amine content results presented in Table 1 reveal that for aminopolymers (TEPA and PEI), prepared by physical impregnation method, the amine loading was higher than that for aminosilane-based (APS), synthesized by chemical grafting of monomers onto the silica surface.

All amine-based materials with various amine contents were analyzed using FTIR spectroscopy to assess the surface functional groups. The results are presented in Figures S2 and S3 followed by the corresponding discussion.

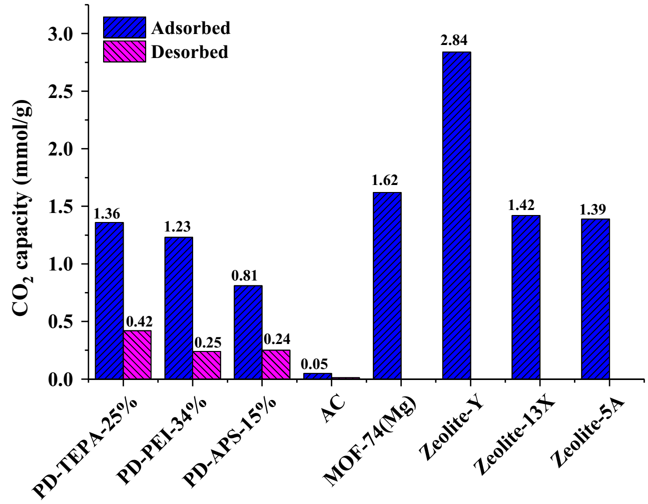

FIGURE 4 Adsorption capacities of buffer materials at 3000 ppm CO_2 and 25°C

3.2 | Equilibrium adsorption measurements

The equilibrium adsorption capacities of buffer materials along with the corresponding desorption amounts are illustrated in Figure 4. All samples were exposed to dry 3000 ppm CO_2 for 4 hours at 25°C and then to pure N_2 for 6 hours at the same temperature. All sorbents reached their equilibrium capacity after 4-hour adsorption. The materials screening results showed that although zeolites and MOF-74 display higher capacity toward CO_2 (2.84 mmol/g for zeolite Y), they do not exhibit any appreciable CO_2 desorption in the flow of nitrogen. Conversely, silica-supported amines exhibited some degree of desorption, as can be seen from this figure. For instance, 31% of adsorbed CO_2 (0.42 mmol/g) was removed by N_2 from PD-TEPA-25% at room temperature, while on PD-PEI-34% and PD-APS-20%, 20% and 31% of CO_2 (0.25 and 0.24 mmol/g) were desorbed, respectively. In the context of identifying the suitable buffer materials for CO_2 management and indoor air quality control, the attention should be paid to both adsorption and desorption performances. The latter is particularly important as CO_2 removal is solely performed as a result of concentration gradient at the interface of sorbent and the indoor air during night, without the aid of temperature or pressure swing.

On the basis of the preliminary screening results, we selected amine-based sorbents for further investigation. A series of silica-TEPA, silica-PEI, and silica-APS sorbents with various amine loadings were investigated and evaluated. Samples of silica-TEPA were synthesized by gradually varying the amine content in each PD-TEPA sample. The corresponding adsorption/desorption capacities are presented in Table 1. It is apparent that for three types of amines investigated here, the adsorption capacity increases with amine content, in agreement with literature data,[30,41-43] while the amount of CO_2 desorbed decreases dramatically. The PD-TEPA sample with 50 wt% TEPA exhibits 2.1 mmol/g CO_2 adsorption, out of which only 8% is desorbed, whereas a low TEPA-content sample (PD-TEPA-20%) displayed a reasonable good uptake and higher desorption capacity (ca. 40%). This trade-off between adsorption capacity and desorption rate

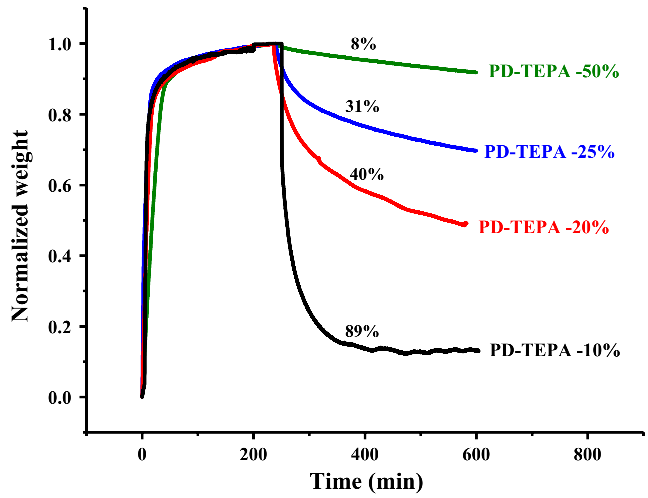

FIGURE 5 Adsorption and desorption performance of silica supported tetraethylenepentamine (TEPA) materials at 3000 ppm CO_2 and 25°C

will influence the total mass of sorbent required for passive CO_2 control in a building.

Figure 5 displays the normalized adsorption/desorption profiles for PD-TEPA samples obtained at 40 mL/min N_2 flow rate. It can be clearly observed that for low amine loading, more CO_2 desorbs readily from the sample at a faster rate under nitrogen flow (characterized by steep weight change), and as amine content increases, it takes longer for CO_2 to desorb and as a result, less desorbs in a same time period. Previous studies of aminosilica materials as CO_2 sorbents mostly focused on adsorption rate and capacity evaluations. Specifically, they demonstrated that medium loading aminosilicas displayed highest CO_2 adsorption ability compared to lower or higher amine loaded samples with faster rate. It has been shown that a higher amine content led to steric constraints making some amine sites inaccessible to CO_2 gas molecules over practical time scales.[44] In accordance with these

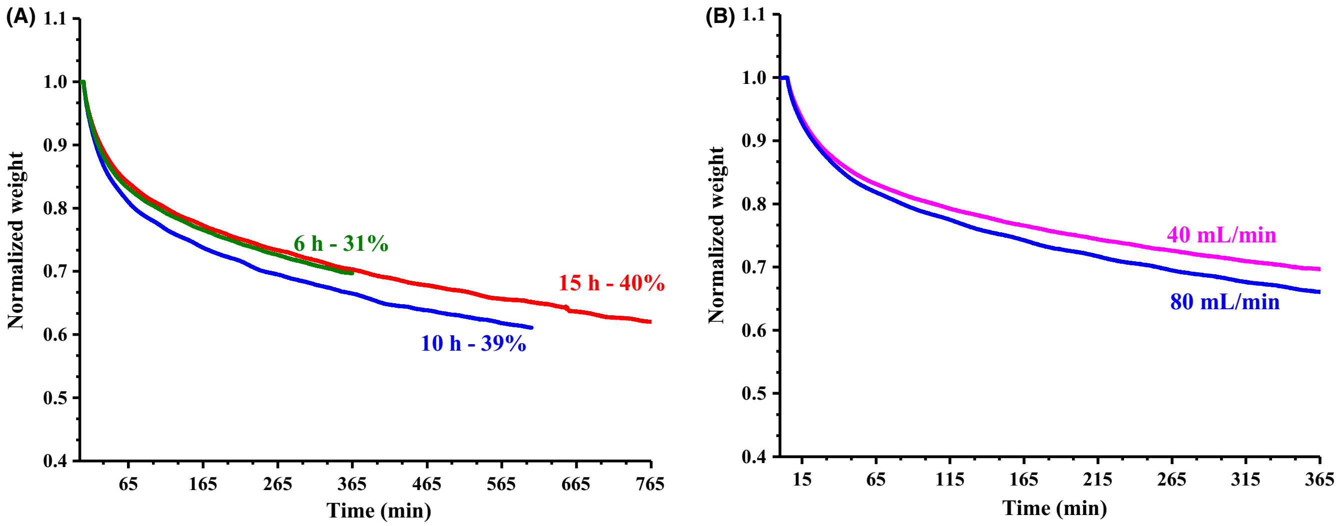

FIGURE 6 Normalized CO_2 desorption profiles for (A) different desorption times, and (B) N_2 flow rates, obtained for PD-tetraethylenepentamine (TEPA)-25% sample at 3000 ppm CO_2 and 25°C

previously reported findings, our results on CO_2 desorption rate and desorbed amount highlight the role of amine content and demonstrate that for a high level of CO_2 uptake and release with relatively fast kinetics at room temperature, the amine content should be optimized. It should be pointed out here that kinetics should also be optimized with respect to the occupancy cycles and ventilation rate.

Furthermore, the effects of desorption time and nitrogen flow rate on the amount of desorbed CO_2 and rate of desorption were investigated by varying the nitrogen flow rate and desorption time. Figure 6A displays the CO_2 desorption profiles for PD-TEPA-25% obtained for different desorption times at 40 mL/min N_2 flow rate. Longer desorption time results in more CO_2 removed from the sorbent by N_2 (39% after 10 hours compared to 31% after 6 hours) but the enhancement was only marginal for prolonged desorption times, showing only 1% enhancement when desorption period increased from 10 to 15 hours. To evaluate the influence of nitrogen flow rate, we kept the desorption time constant (ca. 6 hours) and varied the flow rate from 40 to 80 mL/min. On the basis of these results, it can be inferred that 16-hour desorption time is sufficient to allow sufficient desorption from the buffer material during TGA tests. As can be observed from Figure 6B, upon doubling the N_2 flow rate, the desorption capacity increased only 3% (from 31% to 34%) implying that bulk mass transfer is not rate limiting step during CO_2 desorption from the sorbent particles into the gas phase.

Cyclic adsorption-desorption runs were performed to investigate the stability of materials during consecutive runs. The normalized weight change during three consecutive cycles is shown in Figure 7. The 3-cycle TGA run performed on PD-TEPA-25% revealed no change in the amount of CO_2 desorbed after the third cycle. Additionally, it can be seen that the material adsorbed to its initial capacity during second and third cycles. The cyclic results obtained indicate that the sorbent exhibits short-term stability. Repeatability and stability during CO_2 uptake and release will need to be demonstrated for a buffer material that is effective in managing indoor CO_2.

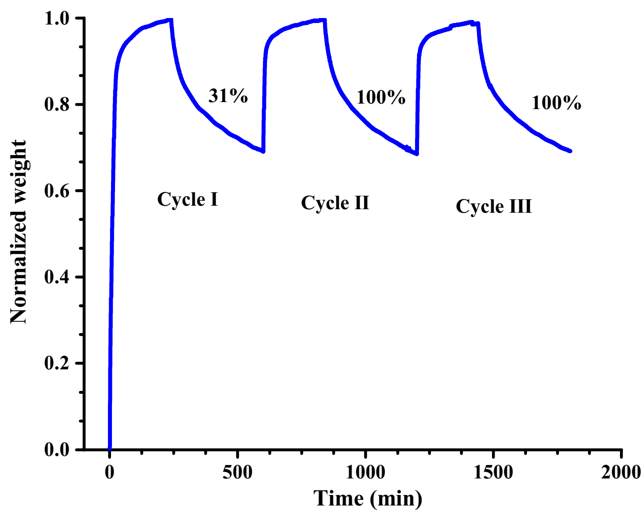

FIGURE 7 Cyclic adsorption-desorption profiles for PD-tetraethylenepentamine (TEA)-25% at 3000 ppm CO_2 and 25°C. While only 31% of CO_2 was desorbed during the first cycle, 100% of CO_2 adsorbed during the second and third cycles was desorbed

3.3 | Breakthrough experiments

The breakthrough profiles for TEPA loaded silica sorbents were performed by exposing the materials to 3000 ppm CO_2 at 25°C, and the results are presented in Figure 8. In agreement with TGA equilibrium capacities, the low-loaded PD-TEPA-10% gave rise to earlier CO_2 breakthrough from the outlet column while the high-loaded PD-TEPA-50% resulted in longer breakthrough. PD-TEPA-50% exhibits a sharper desorption front than its low and medium loaded counterparts, contrary to what we observed earlier from TGA results. We hypothesized that the amount of CO_2 desorbed from PD-TEPA-50% is trivial (as confirmed by TGA); therefore, the concentration of CO_2 in the bulk gas reaches zero very quickly, while for the other materials, more CO_2 desorbs during desorption step. To test this hypothesis,

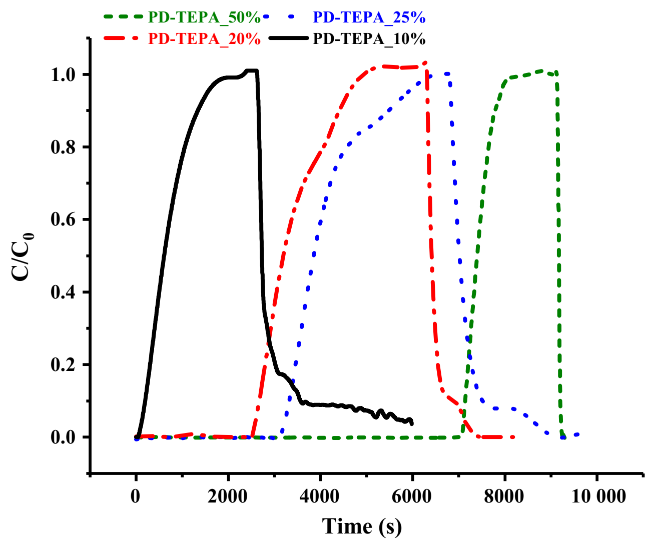

FIGURE 8 Breakthrough profiles for PD-TEA buffer materials using 3000 ppm CO_2 at 25°C

experiment. During the last 2 hours of the adsorption period (approximating steady-state), the CO_2 reduction was small for 1.0 g sorbent but greater for the higher sorbent mass loadings. Based on the normalized results (Figure 9B), the steady-state CO_2 concentration was reduced by <1%, 4.1%, and 5.3% for 1.0, 2.5, and 4.0 g, respectively. In combination, these observations suggest that the sorption for the 1.0-g experiment was nearly depleted, but that 2.5 and 4.0 g retained some sorption capacity at steady state. Under steady-state conditions, the effective deposition velocity for the three experiments was <0.03, 0.12, and 0.14 m/h for 1.0, 2.5, and 4.0 g, respectively. The desorption curves show that more CO_2 was desorbed (more gradual CO_2 decay) for the higher mass sorbent experiments. By integrating the normalized adsorption and desorption curves, and subtracting the dynamic CO_2 concentrations from the control experiment, we found that 83% and 95% of the adsorbed CO_2 was desorbed for the 2.5 and 4.0 g experiments, respectively.

The results for different relative humidity levels are plotted in Figure 10. The reduction in the CO_2 concentration was enhanced as

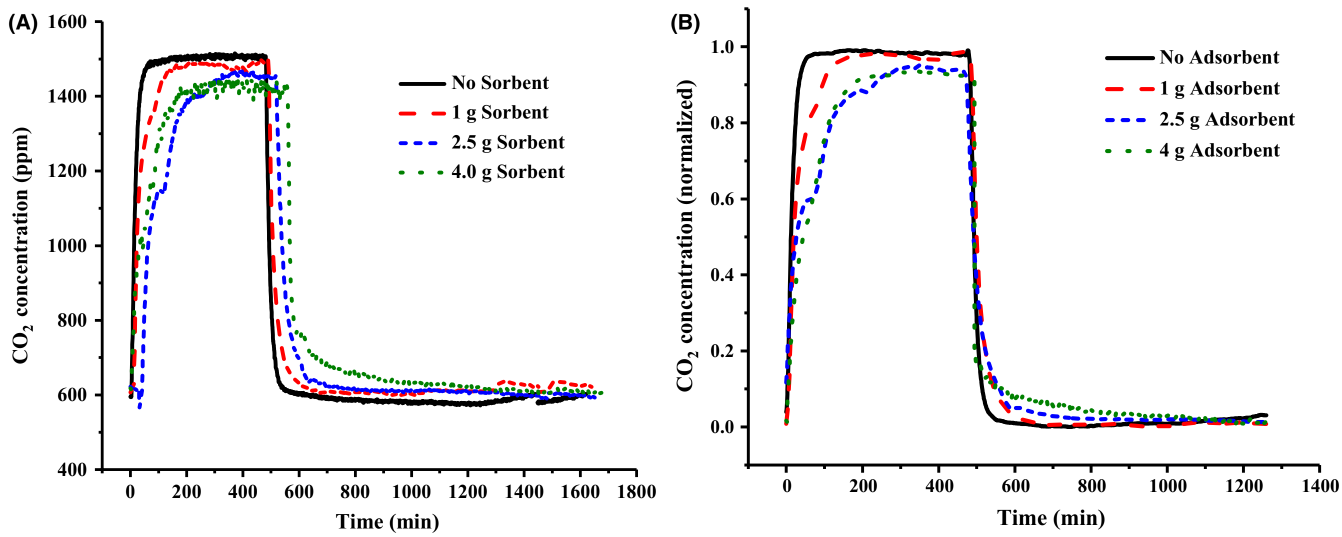

FIGURE 9 Dynamic (A) CO_2 concentration and (B) normalized CO_2 concentration in small chamber experiments as a function of adsorbent mass applied to drywall disk

an additional step was performed following the room temperature desorption in which the PD-TEPA-50% sorbent was regenerated by raising temperature to 110°C. As can be clearly seen from Figure S4, a large amount of CO_2 desorbs from the sorbent into the bulk gas (N_2) which implies that little desorption took place during the previous step at room temperature.

3.4 | Small chamber experiments

On the basis of TGA and fixed-bed results, we chose PD-TEPA-25% for further analysis. As Figure 9A shows, a reduction in the level of CO_2 in air was observed in the presence of the buffer material. In all cases, the presence of sorbent slowed the CO_2 concentration rise, relative to the control experiment. The rate of rise for 2.5 and 4.0 g was qualitatively similar, but slower than for the 1.0 g sorbent

the humidity level increased. There was little difference between the results for 15% and 50% RH. However, there was approximately a 10% reduction in the outlet CO_2 concentration at 90% RH relative to the other two conditions. As expected, higher humidity favored the uptake of CO_2 by the amine-based sorbent, as previously shown by other researchers.[32]

3.5 | Large chamber experiments

Shown in Figure 11A,B are results obtained from the full-chamber runs. The inlet (black) and sorbent run (blue) concentrations for three cycles are shown in Figure 11A. The control experiment results (red) are shown as an average of three experiments, but are only shown once to make it clear that the control experiments do not take place at the same time as the sorbent experiments. As is evident from the

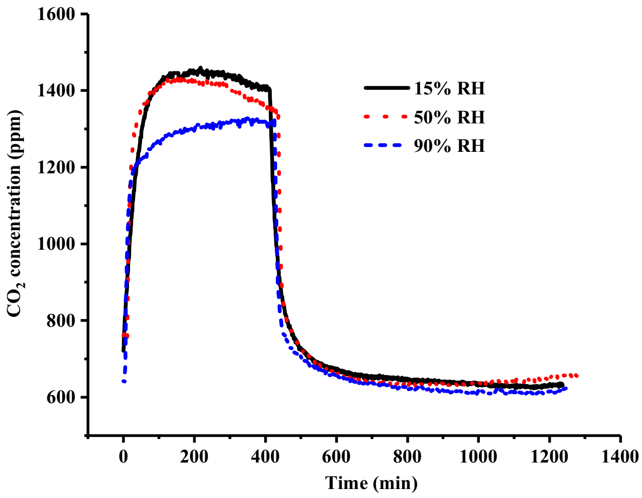

FIGURE 10 Effect of air relative humidity on chamber air CO_2 level control

figures, the CO_2 concentration in the chamber varied more than anticipated during some adsorption and control experiments. This was likely due to some uncontrolled infiltration of CO_2 due to activities taking place in the building. Uncontrolled infiltration also lowered the outlet concentration relative to the inlet concentration. Despite this variability, we were able to conclude that the sorbent reduced concentrations in the chamber relative to control experiments and to estimate other parameters. On average, the steady-state chamber concentration with the sorbent in place was reduced by 84 ppm. Normalized by the inlet and background concentration, the sorbent was responsible for removal of 8.0% of injected CO_2 under steady-state conditions. Integrated over the entire 8-hour adsorption period, the sorbent removed 9.5% of injected CO_2. The steady-state deposition velocity estimated using Equation (2) was 0.5 m/h. We anticipate more practical buffering capacity with larger surface area available by coating walls and ceilings. Incorporated appropriately into coatings, the sorbent can be more fully utilized and sorption kinetics more carefully controlled.

3.6 | Impact on indoor environments

It is not possible to perform detailed simulations of indoor CO_2 concentrations based on the data collected so far. This would require more information on the sorbent dynamic responses over a wide variety of conditions and over a much longer period of time. However, it is possible to estimate the impact on steady-state concentrations, assuming the sorbent performs as observed in the chambers. The indoor air concentration of CO_2, C_{inside}, at steady-state is:

$$C_{inside} = \frac{Q(C_{outside}) + E_p N}{Q + v_d A} \quad (3)$$

where $C_{outside}$ is the outside concentration of CO_2, E_p is the CO_2 emission rate per hour per occupant (assumed to be 34 g/h), N is the number of occupants, A is the surface area coated by the sorbent. Here, we consider a residential bedroom scenario. The residential bedroom has a volume, V, of 30 m^3 and a coated wall area, A, of 30 m^2. The residence is "tight," with a low air exchange rate (Q/V = 0.2/h) and the outdoor concentration is equal to 500 ppm (900 mg/m^3) which is typical of the outdoor CO_2 concentration of urban air. There is one occupant and v_d is assumed to be 0.3 m/h. The resulting steady-state bedroom concentration is 1460 ppm which is much lower than that in the absence of the coating (3650 ppm). Assuming the areal coverage of sorbent required is the same as that used in the chamber experiment, the bedroom would require about 0.27 kg of the sorbent which may be a substantial fraction of the mass of the carrier (eg, paint). Given the large predicted reduction in CO_2, a lower applied mass may be acceptable. For example, for a lower value of v_d corresponding to the small chamber experiments (0.1 m/h), the reduction in the CO_2 concentration is 33%.

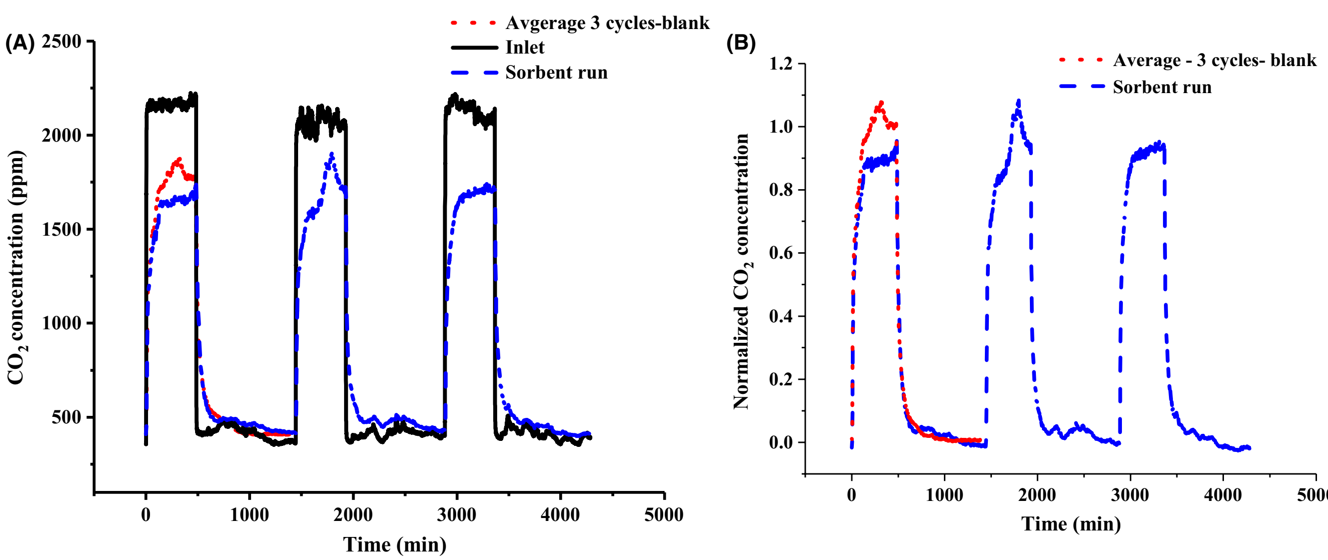

FIGURE 11 Dynamic (A) CO_2 concentration and (B) normalized CO_2 concentration in large chamber experiments in the presence of sorbent, compared with control experiment

4 | CONCLUSIONS

Aminosilica sorbents have been investigated as buffer materials for indoor air CO_2 control. Two different aminopolymers and one aminosilane were used for functionalizing a commercial mesoporous silica support. The initial screening results indicated that TEPA-based silica sorbents were capable of adsorbing and desorbing more amount of CO_2 at room temperature than their PEI and APS counterparts. It was also demonstrated that the amine content dramatically influences both the amount of CO_2 adsorbed and the desorption rate. Chamber experiments suggest that uptake is sufficient to adequately reduce indoor concentrations, and laboratory cyclic sorption experiments show that much of the capacity is regenerated over timeframes useful for the daily cycles of CO_2 sources in buildings. As the concentration gradient between the indoor air and sorbent surface is the solely mode of sorbent regeneration, it will be necessary to optimize these parameters for long-term operation. This preliminary work demonstrates proof of concept for the use of aminosilica buffer materials to reduce the CO_2 concentration inside building environments.

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SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

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