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ADVANCED BUFFER MATERIALS FOR INDOOR AIR CO<sub>2</sub> CONTROL  
IN COMMERCIAL BUILDINGS

by

PAVITHRA ETHI RAJAN

A THESIS

Presented to the Faculty of the Graduate School of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements of the Degree

MASTER of SCIENCE IN ENVIRONMENTAL ENGINEERING

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Approved by

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## ABSTRACT

The following describes a novel passive approach to control the indoor CO<sub>2</sub> levels in enclosed spaces, primarily focusing on commercial buildings. Amine impregnated silica sorbents were identified as suitable candidates and synthesized; the amine loading ratio was varied to create a range of materials. These samples along with other commercial zeolite candidates have been tested over a range of CO<sub>2</sub> concentrations to determine the CO<sub>2</sub> adsorption capacity in laboratory systems and under simulated room conditions. The research work also focuses on the CO<sub>2</sub> desorption capacity of the candidate adsorbents. The desorption is allowed to occur gradually over time with the concentration gradient as its sole driving force; usually a pressure or temperature swing is applied to desorb CO<sub>2</sub> from the adsorbents. Results have shown TEPA impregnated silica to have a good adsorption capacity (1.5 mmol/g); and by decreasing the amine content, the silica-TEPA samples showed good initial desorption of almost 31% of the adsorbed CO<sub>2</sub>. They exhibited lower capacity but a greater desorption percentage with repeated cycles. At room temperature and pressure conditions, cyclic tests were conducted in a small chamber simulating real indoor environment. The adsorbent reduced the CO<sub>2</sub> concentration by almost 8% reduction. Further studies conducted to investigate the effect of adsorbent weight showed that adsorption increased from 3% to 8% on increasing the quantity of adsorbent used. Similarly, the effect of relative humidity of chamber air was studied. Results showed a 4% decrease in CO<sub>2</sub> uptake when the RH was dropped to 15% from 50%; and an increase of 10% uptake was observed at 90% RH.

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## LIST OF ABBREVIATIONS

<b>SYMBOL</b>	<b>DESCRIPTION</b>
CO <sub>2</sub>	- Carbon dioxide
PD	- Commercial silica
TEPA	- Tetraethylenepentamine
APS	- 3-aminopropyltriethoxysilane
PEI	- Poly(ethyleneimine)
ASHRAE	- American Society of Heating, Refrigerating and Air conditioning Engineers
VOCs	- Volatile Organic Compounds
DCV	- Demand Control Ventilation
BET	- Brunauer Emmett Teller
BdB-FHH	- Broekhoff-de Boer-Frenkel Halsey Hill
C-H-N	- Carbon–Hydrogen–Nitrogen
FTIR	- Fourier Transform Infra Red spectroscopy
TGA	- Thermo Gravimetric Analysis
HEPA	- High Efficiency Particulate Arrestance
RH	- Relative Humidity

# 1. INTRODUCTION

## 1.1 THE RESEARCH PROBLEM DEFINITION

The ambient CO<sub>2</sub> concentration in outdoor air is about 400 ppm<sup>36, 37</sup> and that of indoor air is typically about 650-700 ppm. American Society of Heating, Refrigerating and Air conditioning Engineers (ASHRAE) recommend safe levels of CO<sub>2</sub> to be 1000-1100 ppm<sup>1</sup>. Studies also show that CO<sub>2</sub> at increased levels are considered as pollutants and affect cognition and productivity. At slightly higher levels, CO<sub>2</sub> induces stiffness and drowsiness; at greater levels the functioning of central nervous system is damaged. This affects and impairs decision making performance<sup>39</sup>. Laszlo Kajtar and Usha Satish have conducted extensive studies relating increased CO<sub>2</sub> levels to decreased brain productivity. Kajtar et al.<sup>2</sup> found that exposing humans at levels from 2000 to 5000 ppm CO<sub>2</sub> adversely affected proof – reading tasks. Satish et al.<sup>3</sup> developed a series of human exposure experiments to identify reduced productivity. They observed significant decrease in decision – making performance and concluded that reduced productivity would negate the cost saved by reduced ventilation rates<sup>3, 38</sup>.

Ventilation is required to dilute air pollution generated indoors, but the energy used to condition this air is responsible for a large fraction of energy consumption. The total energy budget and energy consumption is expected to rise about 1.5% every year<sup>4</sup>. In the United States, buildings consume 40% of total energy out of which 48% goes into space conditioning<sup>40</sup>. Improved efficiency in space conditioning can benefit energy conservation

to a huge extent. The cost of space conditioning is influenced by factors such as internal load, climate, building construction, ventilation rates and many more<sup>5,6</sup>.

Indoor air quality and occupant productivity suffers with low ventilation rates<sup>7,8</sup>. ASHRAE has developed standards of ventilation for buildings based on their types. The ventilation rate depends on the occupancy, which accounts for body odor and the floor area of the building which accounts for the building material emissions<sup>6</sup>. Demand control ventilation (DCV) using CO<sub>2</sub> sensors, in theory, automatically provides sufficient dilution to reduce occupant emissions below odor thresholds. DCV based on CO<sub>2</sub> has been criticized because of variability in CO<sub>2</sub> emissions from people and too few sensors that average CO<sub>2</sub> of multiple zones<sup>1,9</sup>. As an alternative, Gall and Nazaroff suggest that active CO<sub>2</sub> removal (e.g. by adsorption) from building air can allow for reduced ventilation, and thereby energy consumption, potentially reducing the US building carbon footprint by 10 Tg CO<sub>2</sub> /y.<sup>10</sup>

## **1.2 PASSIVE CO<sub>2</sub> CONTROL STRATEGY**

Indoor air pollutants can be controlled using active as well as passive methods. Active control methods involve using fan energy associated with recirculating air over filter media. Passive control methods involve adsorption and / or absorption techniques to control pollutants. Adsorption techniques have been proved effective in the past. Ozone has been readily removed from building surfaces using such techniques<sup>11</sup>. Surfaces such as brick, concrete and clay coatings are good at passively reducing indoor ozone concentrations without generating undesirable by products<sup>12,13</sup>. M. Pinto, et.al, studied the characterization of adsorbent materials supported on polyurethane foams by nitrogen and

toluene adsorption. This study showed the possibility of selective adsorption where activated carbons (pellets) presented the best results with a decrease of about 20% in the nitrogen adsorption capacity but maintaining the same toluene adsorption capacity<sup>48</sup>. Similarly, a number of coating manufacturers included additives to paints that show promise in reducing indoor concentrations of odorous compounds and formaldehyde. Therefore, many internal and external pollutant loads can be controlled without increasing ventilation or filtration rates. These strategies work efficiently because of the availability of large surface area available for sorption (e.g. walls and ceilings). Further, the relatively small mass removal requirements for these pollutants (typically for air concentrations in the  $\mu\text{g}/\text{m}^3$  range) allow coatings to be effective sorbents for periods of years or even decades before a new coating is applied.

Due to the large production of  $\text{CO}_2$  by occupants, permanent adsorption to media is neither an effective nor a practical approach. Any reasonable mass of sorbent installed in a building, such as a wall coating, would rapidly become saturated. Considering these aspects, the idea, to capture  $\text{CO}_2$  during primary occupancy periods by adsorption and passively release  $\text{CO}_2$  during low – occupancy period, was developed. Here, temperature and pressure swings would not be required for desorption; this is predicted to reduce ventilation requirements, thereby reducing energy consumption necessary to condition outdoor air.

Adsorption processes for gas separation via selective adsorption on solid media are also well-known<sup>14</sup>. 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<sub>2</sub> adsorption is low, resulting in a long adsorption time while chemisorbents can adsorb CO<sub>2</sub> very quickly and efficiently but are non-regenerable. Indeed, the trade-off that exists between sufficient CO<sub>2</sub> adsorption capacity (*i.e.*, steep adsorption isotherms) and regenerability (*i.e.*, low sorption enthalpy) at room temperature makes the selection of sorbent candidates for this particular application difficult<sup>15</sup>. Competitive water adsorption is another issue which renders most adsorbents impractical despite comparatively high adsorption capacities at low partial pressures. To improve indoor air quality and to efficiently remove CO<sub>2</sub>, the candidate adsorbent materials should perform low-energy cyclical capture and release of indoor CO<sub>2</sub>.

Based on the Review of research on air – conditioning systems and indoor air quality control for human health conducted by B.F. Yu, et.al<sup>49</sup>, the adsorbents used to purify air mainly include activated carbon, zeolite, activated alumina, silica gel and molecular sieves. Adsorption on activated carbon is an extensive method of purifying indoor air due to its large specific area and high adsorption capacity. At low concentration level, the advantages of activated carbon with abundant micro – pores are more prominent<sup>50</sup>. Activated carbon fibres exhibit a higher adsorption capacity and have faster adsorption kinetics than granular activated carbon, 2 to 20 times faster than granular activated carbon<sup>51</sup>. Moreover, activated carbon fibers are easier to use than granular activated carbon; hence more suitable as an adsorbent for removing indoor gaseous pollutants<sup>52</sup>. However, activated carbon has known to lose its capacity after used for a period of time and its activity also to decrease after regeneration. Moreover, activated carbon fibers are very expensive.

As noted above, this buffering approach has been suggested for helping reduce the energy demands of moisture control,<sup>16-18</sup> but to the best of our knowledge, there have not

been any studies of the removal of CO<sub>2</sub> from indoor air, aside from a preliminary investigation by Lee et al.<sup>19</sup> The authors studied the use of Y-type zeolite impregnated amines for CO<sub>2</sub> adsorption from indoor air. A variety of zeolite impregnated amines were exposed to 1500 ppm CO<sub>2</sub> at 25°C for 1 h and a CO<sub>2</sub> capacity of 3.59 mmol/g was reported. However, this particular study was focused on the determination of CO<sub>2</sub> capacity and no information on adsorption/desorption rates or sorbent regeneration was provided. In a recent study,<sup>20</sup> 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<sub>2</sub> from living spaces using carbon monoliths. As demonstrated by the authors, an electrical energy requirement of 57.8 kJ/m<sup>3</sup>-air is necessary to treat air containing 3000 ppm CO<sub>2</sub>. This energy requirement in addition to complexity of an ESA system makes the proposed approach less attractive for practical applications. More recently, Kim et al.<sup>21</sup> studied the performance of a CO<sub>2</sub> 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 mainly on the performance of the system and the adsorbent characteristics and performance were not discussed.

Under typical operating conditions, the sorbent developed in this research would be exposed to outdoor background CO<sub>2</sub> overnight with the concentration of approximately 400 ppm then CO<sub>2</sub> will rise during the work day to about 1500 ppm. The sorbent regeneration and the release of adsorbed CO<sub>2</sub> is driven by a 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 CO<sub>2</sub>. Furthermore, as the regeneration of sorbent is based on the difference in the CO<sub>2</sub> concentration of the sorbent and indoor air, selected sorbents require to not only bind weakly with CO<sub>2</sub> molecules 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<sub>2</sub> under these conditions.

### **1.3 SUITABLE BUFFER MATERIALS - SYNTHESIS & CHARACTERIZATION**

In this study, the feasibility of applying solid sorbents to control indoor CO<sub>2</sub> concentration in buildings was investigated. Specifically, we focused on evaluating various physisorbent and chemisorbent materials (mainly silica-supported amine powders) for the removal of CO<sub>2</sub> from indoor air. Although the CO<sub>2</sub> sorption characteristics of these materials is well-studied, relatively little quantitative information has been published on their desorption performance at room temperature, and thus, this study focuses on systematically exploring the ppm level CO<sub>2</sub> adsorption and desorption on silica supported amine adsorbents under realistic conditions.

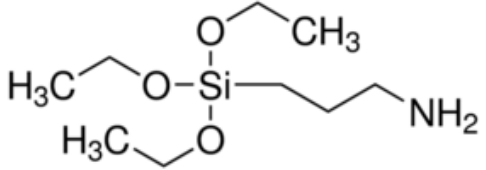
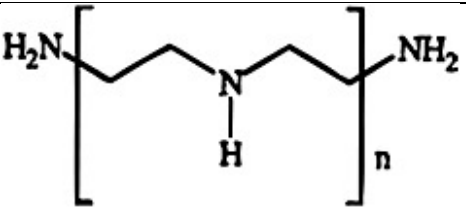
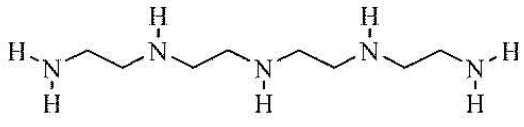
The first leg of this research is about understanding and studying amine impregnated silica and their adsorption capacity. There are quite a few CO<sub>2</sub> sorbents typically preferred for these studies, activated carbon, zeolites, silica supported amino polymers, and several metal-organic frameworks were among those. Silica functionalized with amines are very promising sorbents for CO<sub>2</sub> capture. Amines owe their high adsorption capacities to the presence of high density of active sites per unit mass. Silica – amines can be categorized into three groups: primary, secondary and tertiary amines<sup>19</sup>. Diamine functional groups

and hyperbranched aminosilica were found to have good adsorption capacities<sup>15,41</sup>. The candidates selected suitable for this study were tetraethylenepentamine (TEPA), polyethyleneimine (PEI), (3-aminopropyl) triethoxysilane (APS) (Table 1.1) and a commercial silica (PD, from PQ-corporation) was used as a mesoporous support. TEPA-impregnated silica has been widely accepted as a good candidate in studies involving CO<sub>2</sub> capture. The preliminary tests of this research also prove the above statement. Out of the three amine candidates synthesized, PD-TEPA samples have high adsorption capacities and also display good desorption rates. Apart from the amine candidates, Mg-MOF-74 was also considered for this study. Although MOFs are typically very good adsorbents, they are expensive and have stability issues. As the main objective of this study is to compare different materials to select a few suitable candidates as buffer material, activated carbon and zeolite 13X were also considered as potential buffer materials.

The next phase was the synthesis and characterization of the selected candidates, which included testing them for their adsorptive performance. The silica - amine samples were synthesized at varying ratios to generate a wide set of materials. Characterization included inspecting all the potential buffer materials by Fourier Transform Infrared Spectroscopy (FTIR). The Thermogravimetric Analysis (TGA) helped find out the CO<sub>2</sub> equilibrium adsorption capacity of each sample. For this, the sample is exposed to CO<sub>2</sub> gas for a specific period of time. Consecutively, purging nitrogen after CO<sub>2</sub> gas, the desorption rate too was studied. The samples were exposed at both low (500 ppm) and high (3000 ppm) concentration of CO<sub>2</sub>. The dynamic adsorptive performance of the material was assessed with the help of a fixed bed column by performing CO<sub>2</sub> breakthrough measurements. The

material should adsorb CO<sub>2</sub> rapidly but also desorb readily. More importantly, this happens without the supply of heat or pressure.

Table 1.1 Amines (buffer materials) used in this study

AMINE	CHEMICAL FORMULA	STRUCTURE
APS	C <sub>9</sub> H <sub>23</sub> NO <sub>3</sub> Si	
PEI	(C <sub>2</sub> H <sub>5</sub> N) <sub>n</sub>	
TEPA	(NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NHCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NH	

#### 1.4 CHAMBER STUDIES

The primary goal of this research work is to make a comparative study analyzing the adsorption and desorption capacities of promising amino polymers of differing classes. Cyclic runs are studied to study and analyze the change in capacity (if any) of the adsorbent with each cycle.

A small scale chamber test was arranged and run to study the adsorption and desorption capacity of the selected adsorbents. This set up consisted of a small confined chamber (10

L); a mixture of CO<sub>2</sub> and air was first purged to determine the adsorption capacity of the adsorbents, followed by purging just air to determine the desorption capacity. On comparing runs with and without the adsorbent material, it was observed that a considerable amount of CO<sub>2</sub> was reduced in presence of adsorbents.

The novelty of this research is in studying the desorption capacities of the adsorbents along with the adsorption capacities; having concentration gradient is the sole driving force here. Also, studies at low concentrations of CO<sub>2</sub> are rare. This study generates data on CO<sub>2</sub> buffering under realistic conditions which can be extrapolated for multiple building types and conditions; also this data can be used to generate predictions about the applicability and energy consequences of CO<sub>2</sub> buffering for building stock across the U.S.

## 2. OBJECTIVES

The main objectives of this research work are the following.

- To identify suitable materials that can act as buffer materials for controlling CO<sub>2</sub> in indoor air
- To synthesize a few chosen amine materials with varying silica: amine ratios to determine the best ratio of silica: amine for this work
- To perform a series of equilibrium and dynamic experiments to screen for the most suitable material from the set of synthesized buffer materials
- To investigate adsorption – desorption performance in a small chamber set – up
- To conduct full – chamber runs for preliminary studies

### 3. EXPERIMENTAL SECTION

#### 3.1 MATERIAL SYNTHESIS

The silica – amine samples and the MOF samples were synthesized in the lab. Commercial silica, PD09024 from PQ Corporation was used to synthesize the silica supported amine adsorbents. The initial step for all amine sorbents was drying silica overnight (for 12 h) in a vacuum oven at about 105 °C. Previous studies found aminopolymers TEPA and PEI to be highly efficient for CO<sub>2</sub> adsorption. These aminopolymers were synthesized using a conventional wet impregnation method<sup>44,45</sup>. A desired amount of the amine was dissolved with methanol for 1 h. The dried silica was then added to this solution and was stirred continuously for 16 h. The methanol solvent was later removed by a rotary evaporator (rotovap) and the adsorbent sample was recovered after drying in vacuum oven at 60 °C for 2 h. The synthesis of aminosilane based sorbents containing primary amine moieties (PD–APS)<sup>46</sup> slightly differed from the synthesis of aminopolymers (PD–TEPA and PD–PEI). In the synthesis of aminosilane based adsorbents, the silica was functionalized through the reaction of APS with surface silanols. For this, a desired amount of toluene was degassed and mixed with the dried silica. After 1 h of constant stirring, deionized water was added to the mixture and let to equilibrate for 2 h. a desired amount of silane was then added to the above solution and was kept under vigorous stirring at 80 °C for 24 h. The resulting adsorbent was recovered by filtration, washed with toluene and later dried under vacuum at 60 °C for 2 h. Adsorbents with different amine loadings were prepared for each material type. Table 1.1 summarizes the amine materials synthesized and their corresponding nomenclature.

Apart from the amine – based adsorbents, MOF-74(Mg)<sup>42,43</sup> was also synthesized. Solvothermal method was applied for synthesizing this MOF. A desired amount of DHTA and Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was dissolved in a solution mixture of DMF, ethanol and deionized water. This solution was sonicated to aid mixing. The resulting solution was sealed and placed in oven for 21 h at 125 °C. The mother liquor was decanted and replaced with methanol after cooling it down to room temperature. This methanol solvent was decanted for about 5 times, repeatedly, over the next 2 days. The solid product recovered was then dried at 250 °C under vacuum. Also, commercial zeolite 13X and activated carbon were purchased and used in this study.

### **3.2. MATERIAL CHARACTERIZATION**

Nitrogen physisorption measurements were carried out on a Micrometrics 3Flex at 77 K. The samples were degassed in a Micrometrics SmartVacPrep, prior to analysis. The surface area and pore volume of all adsorbents were calculated from the isotherm data collected. Surface area calculation was using BET method<sup>47</sup> and pore diameter calculations were based on BdB-FHH method<sup>22</sup>. FTIR spectroscopy characterizations were performed on a Nicolet Nexus 470 optical bench. EZ-OMNIC software was used to plot and observe the spikes/peaks of the samples tested. Each sample was analyzed at 16 scans per test. A TA Instrument Q500 thermogravimetric analyzer (TGA) was used to determine the organic loading of the amine materials. Amine loading (mmolN/g) of each sample was estimated from C-H-N analysis tests using Perkin Elmer 2400 Elemental analysis.

### 3.3. EQUILIBRIUM ADSORPTION MEASUREMENTS

The equilibrium adsorption measurements were carried out in the Q500 thermogravimetric analyzer (TA Instruments). This was performed by directly exposing the material to the CO<sub>2</sub> – N<sub>2</sub> gas mixture. The initial step was degassing the sample in flowing nitrogen at 110 °C (250 °C for MOF-74(Mg) and zeolite 13X) for 30 min. This step ensured regeneration of the adsorbent as any remnant gas adsorbed on the sample surface was pulled out. After the degassing step, the sample was exposed to 500 ppm and 3000 ppm CO<sub>2</sub> for 4 h at room temperature. The desorption step quickly followed the adsorption step, where the CO<sub>2</sub> was switched to pure N<sub>2</sub> while keeping the temperature constant and this was 6 h long. Here, the first half determined the adsorption capacity of the sample and the second half showed the desorption capacity of the adsorbent. This procedure was varied to understand the effect of desorption time and flowrate of nitrogen on the desorption capacity of the buffer materials.

### 3.4. CO<sub>2</sub> BREAKTHROUGH MEASUREMENTS

The dynamic adsorption performance of the amine impregnated silica samples were assessed by performing experiments in a fixed-bed column with a BEL Mass Spectrometer. A schematic representation of the breakthrough setup is shown in Figure 3.1. Similar to the equilibrium adsorption measurements, the CO<sub>2</sub> and nitrogen gases were purged alternatively to analyze the adsorption and desorption capacity. The inlet stream composed of 5000 ppm CO<sub>2</sub> – N<sub>2</sub> was fed to the column at a flowrate of 40 mL/min. Prior to each sorption experiment, the bed was heated to 110 °C under flowing N<sub>2</sub> at 80 mL/min for 1 h to desorb adventitious CO<sub>2</sub> and water. It was then cooled to room temperature (25 °C) and exposed to CO<sub>2</sub> for the experimental sorption run. The effluent composition exiting



the column was transiently measured by the MS. After reaching the inlet concentration, desorption step was started by flowing N<sub>2</sub> to the column at the same flowrate (40 mL/min).

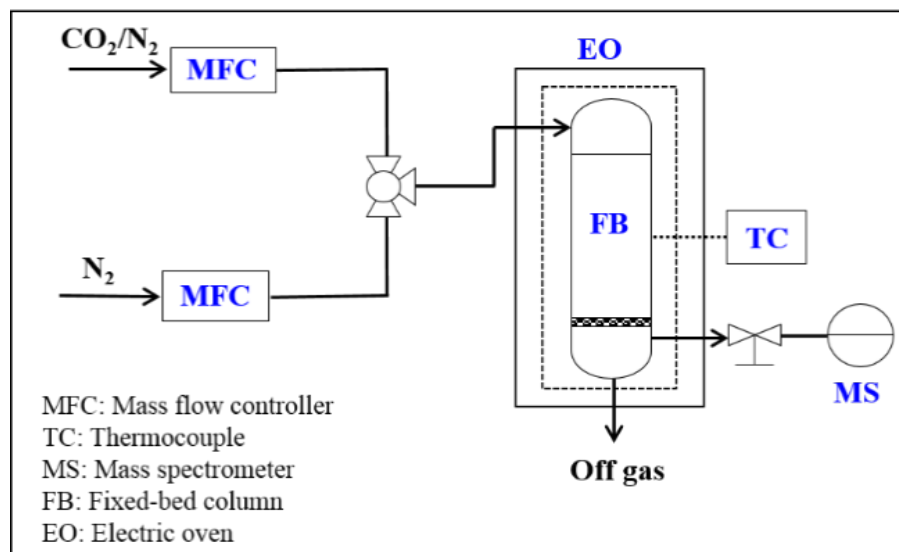


Figure 3.1 General Scheme of the Breakthrough Setup

### 3.5. CHAMBER EXPERIMENTS

To understand the functioning of the buffer materials better, the samples were tested in the lab scale chamber setup shown in Figure 3.2. The setup consisted of a small stainless steel chamber with a volume of 10 L connected to a CO<sub>2</sub> gas analyzer for monitoring CO<sub>2</sub> concentration at the chamber outlet at regular intervals of time. A 23cm diameter disk of gypsum drywall was placed inside the chamber and the adsorbent material was dusted uniformly over it. The inlet gas was a mixture of air and CO<sub>2</sub> with an overall CO<sub>2</sub> concentration of about 1500 ppm. The flow rate of the inlet stream was maintained at 1 L/min. Each experiment consisted of a by-pass run, followed by adsorption-desorption cycles. The by-pass run determined the inlet CO<sub>2</sub> concentration with, and without, added

CO<sub>2</sub>. First air with added CO<sub>2</sub> bypassed the chamber and was directed to the CO<sub>2</sub> monitor chamber for 2 h. Second, air without added CO<sub>2</sub> was directed to the monitor for 1 h. The by-pass was followed by a 7 h adsorption and 14 h desorption-cycle. A part of the air stream was passed through a bubbler to humidify the air before mixing with the inlet stream. This provision was used to modify the humidity over a range (15 – 90%) to study the effect of humidity on the adsorption – desorption process. Results of the chamber experiments were analyzed to understand the effect of external factors affecting the capacity of the adsorbent.

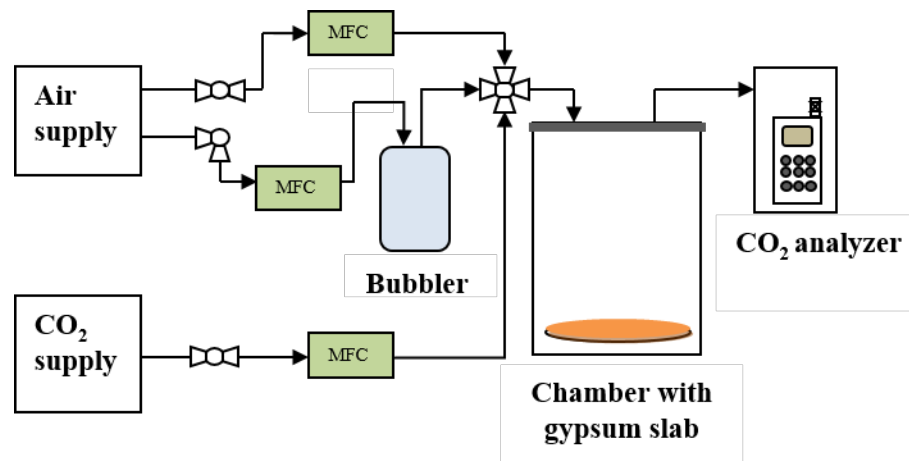


Figure 3.2 Schematic representation of the small chamber setup for indoor air CO<sub>2</sub> control experiments

Due to slight drift in monitor readings from one experiment to the next, the results were normalized,  $C_{outlet,norm}$ , based on the inlet,  $C_{inlet}$ , and minimum CO<sub>2</sub> concentrations,  $C_{min}$ , measured during that experiment:

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

$C_{min}$  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<sub>2</sub> 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<sub>2</sub> is removed at a constant rate only at the surface of the coated disk.

## 4. RESULTS AND DISCUSSION

### 4.1 PHYSICAL PROPERTIES OF MATERIALS

Nitrogen Physisorption isotherm data was used to calculate the surface areas, pore volumes and pore sizes of the samples tested. Brunauer Emmett Teller (BET) method was followed to determine the surface areas and the Broekhoff – de Boer – Frenkel Hasley Hill (BdB – FHH) method was used to calculate the pore volumes. The nitrogen adsorption and desorption isotherms obtained for silica supported TEPA samples are presented in Figure 4.1; and those for silica supported PEI and silica supported APS are presented in Figure 4.2. All adsorbents displayed a typical type IV IUPAC isotherm with a type H2 hysteresis loop. Table 4.1 summarizes the results obtained 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 samples, the surface area decreased from 294 m<sup>2</sup>/g for bare silica support to 247 m<sup>2</sup>/g for low-loaded sample (PD-TEPA-10%) while the drop was more pronounced for high-loaded sample (PD-TEPA-50%), reaching 33 m<sup>2</sup>/g. The same decreasing trend for pore volume with amine loading was observed for all samples, with PD-PEI displaying the most striking decrease in the surface area upon amine loading. The low-loaded PD-PEI sample (PD-PEI-30%) had a surface area of 20 m<sup>2</sup>/g and this reduced to 8 m<sup>2</sup>/g in the high-loaded PD-PEI sample (PD-PEI-50%). On the other hand PD-APS too showed a decrease in the surface area with the increase in amine loading, but it was less distinct compared to PD-PEI. For the low-loaded PD-APS sample (PD-APS-10%), the surface

area was  $196 \text{ m}^2/\text{g}$  and this value decreased to  $63 \text{ m}^2/\text{g}$  for the high-loaded PD-APS sample (PD-PEI-50%).

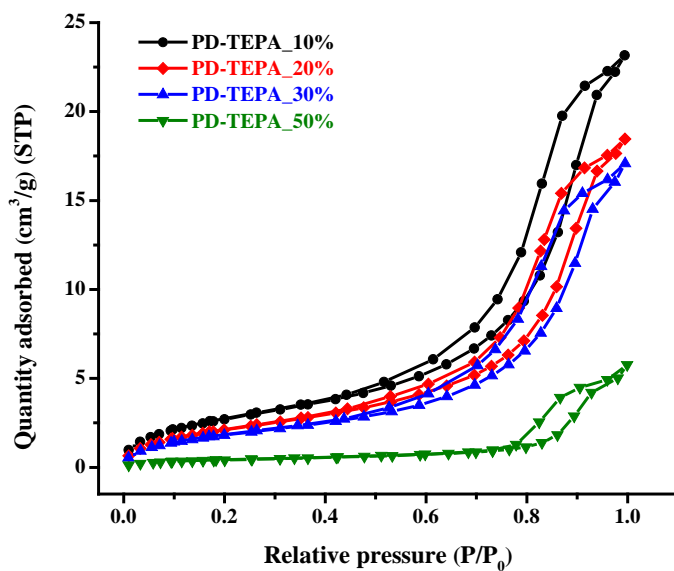


Figure 4.1 Nitrogen physisorption isotherm for TEPA-based buffer materials

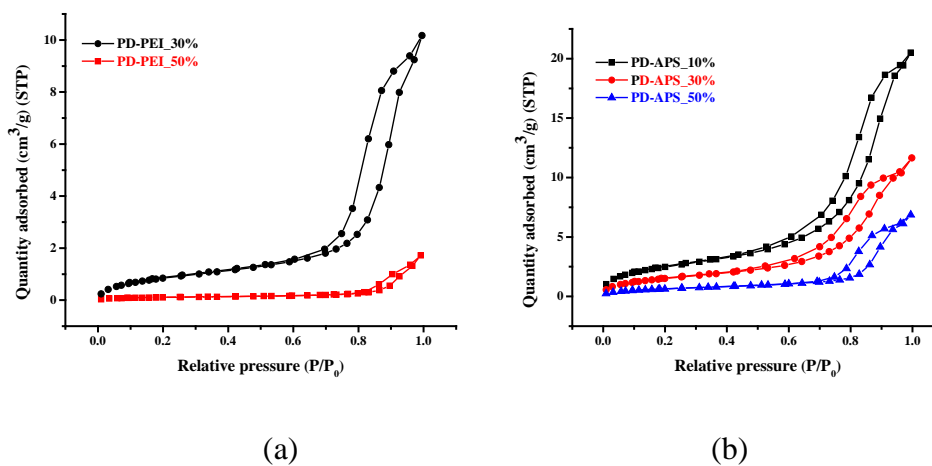


Figure 4.2 Nitrogen physisorption isotherm for (a) PEI – and (b) APS – based buffer materials

In the case of pore volumes (obtained at  $P/P_0 = 0.8-0.9$ ), TEPA samples showed a decrease from 1.04 to 0.16  $\text{cm}^3/\text{g}$  when observed from low-loading to high-loading. Similarly, the other silica-amine samples too showed decrease in the pore volume as the amine loading was increased. Here, the decrease was very marginal while comparing the low-loaded and high-loaded PD-PEI (from 0.09 – 0.04  $\text{cm}^3/\text{g}$ ). And the low – loaded PD-PEI recorded a pore volume of 0.66  $\text{cm}^3/\text{g}$  and this pore volume decreased to 0.23  $\text{cm}^3/\text{g}$  when the amine loading was increased.

Table 4.1 presents the amine – content of the adsorbent samples which were determined by the Elemental analysis. As can be seen, the aminosilica buffer materials with systematically varied amine loadings were prepared. It should be noted 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 adsorbents were analyzed using FTIR spectroscopy to assess the surface functional groups. Figure 4.3 shows the FTIR spectra of the TEPA-based buffer materials. The major peak at around 1200  $\text{cm}^{-1}$  belonged to Si-O-Si while the peak at 3000 – 3100  $\text{cm}^{-1}$  corresponded to O-H stretching vibration. In addition, Si-CH<sub>3</sub> stretching vibration was recognized by sharp peaks at 1260  $\text{cm}^{-1}$  and 750-865  $\text{cm}^{-1}$ . The spectral region associated with silica support was dominated by a band at 460-480  $\text{cm}^{-1}$  while the appearance of 1600-1650  $\text{cm}^{-1}$  band was attributed to N-H functional group of amines. The FTIR spectra of TEPA-loaded sorbents were almost identical which further confirmed that TEPA was loaded on the mesoporous silica support. The corresponding FTIR spectra of

PEI and APS samples are presented in Figure 4.4. And as it can be observed, all silica – amine adsorbents showed similar peaks in the FTIR analysis.

Table 4.1 Physical properties of amine adsorbents

Adsorbent	Amine Loading [mmolN/g]	S <sub>BET</sub> [m <sup>2</sup> /g]	V <sub>pore</sub> [cm <sup>3</sup> /g]
PD-Bare	-	294	1.04
PD-TEPA-10%	2.02	247	0.76
PD-TEPA-20%	4.96	172	0.59
PD-TEPA-30%	5.79	147	0.54
PD-TEPA-50%	11.25	33	0.16
PD-PEI-30%	7.80	20	0.09
PD-PEI-50%	10.02	8.0	0.04
PD-APS-10%	1.06	196	0.66
PD-APS-30%	2.44	119	0.35
PD-APS-50%	3.00	63	0.23

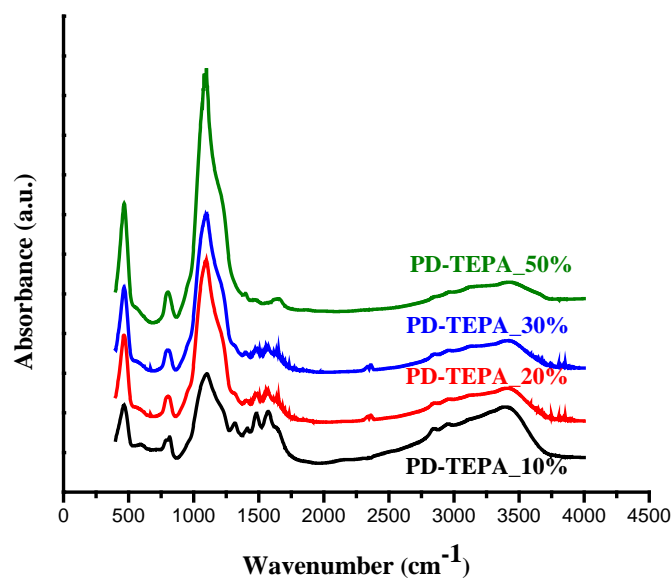


Figure 4.3 FTIR patterns for TEPA – based buffer materials

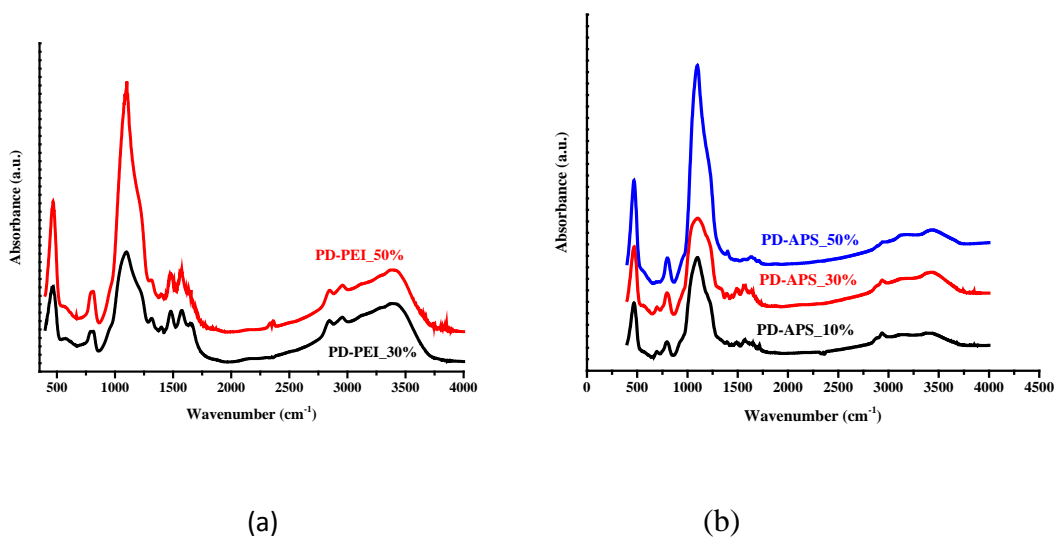


Figure 4.4 FTIR patterns for (a) PEI – and (b) APS – based buffer materials

## 4.2. EQUILIBRIUM ADSORPTION MEASUREMENTS

The equilibrium adsorption capacities of buffer materials along with the corresponding desorption amounts are illustrated in Figure 4.5. All samples were exposed to dry 3000 ppm CO<sub>2</sub> for 4 h at 25 °C and then to pure N<sub>2</sub> for 6 h at the same temperature.



All adsorbents reached their equilibrium capacities after 4 h adsorption. The materials screening results showed that although zeolites and MOF-74 display higher capacity toward CO<sub>2</sub> (2.84 mmol/g for zeolite-Y), however, they did not exhibit any appreciable CO<sub>2</sub> desorption in the flow of nitrogen. Conversely, silica supported amines exhibit some degree of desorption, as can be seen from this Figure 4.5. For example, 31% of adsorbed CO<sub>2</sub> (0.42 mmol/g) was removed by N<sub>2</sub> from PD-TEPA-30% at room temperature, while on PD-PEI-30% and PD-APS-30%, 20 and 30% of CO<sub>2</sub> (0.25 and 0.24 mmol/g) were desorbed, respectively. In the context of identifying the suitable buffer materials for CO<sub>2</sub> management and indoor air quality control, attention should be paid to both adsorption and desorption performances. The latter is particularly important as CO<sub>2</sub> removal will be the result of a concentration gradient from the interface of adsorbent to the bulk air indoors during the evening, without the aid of a temperature or pressure swing.

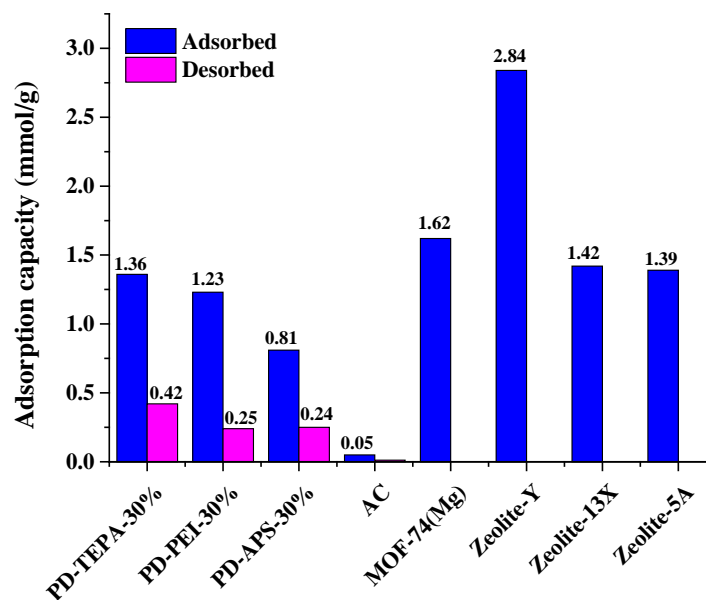


Figure 4.5 Adsorption capacities of buffer materials at 3000 ppm CO<sub>2</sub> and 25 °C.

On the basis of the preliminary screening results, amine-based adsorbents were selected for further investigation. A series of silica-TEPA, -PEI and -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 4.2. It was apparent that for the three types of amines investigated, the adsorption capacity increased, in agreement with literature data,<sup>15,23–25</sup> while the amount of CO<sub>2</sub> desorbed decreased dramatically. The PD-TEPA sample with 50 wt% TEPA exhibits 2.1 mmol/g CO<sub>2</sub> 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 should be taken into account.

The normalized adsorption/desorption profiles for PD-TEPA samples obtained at 40 mL/min N<sub>2</sub> flowrate are shown in Figure 4.6. It can be clearly observed that for low amine loading, more CO<sub>2</sub> 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<sub>2</sub> to desorb and as a result, less desorbs in a same time period. Previous studies of aminosilica materials as CO<sub>2</sub> adsorbents mostly focused on adsorption rate and capacity evaluations. Specifically, it was demonstrated that medium loading aminosilicas displayed highest CO<sub>2</sub> 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<sub>2</sub> gas molecules over practical time scales.<sup>26</sup> In accordance with these previously reported findings, the results of this research work on

CO<sub>2</sub> desorption rate and desorbed amount highlight the role of amine content and demonstrate that for a high level of CO<sub>2</sub> uptake and release at room temperature, the amine content should be optimized.

Table 4.2 Equilibrium adsorption capacities at 3000 ppm CO<sub>2</sub> and the corresponding percentage desorption at 25 °C

Adsorbent	Adsorption	
	capacity [mmol/g]	Desorption [%]
PD-TEPA-14%	0.20	89
PD-TEPA-20%	1.08	40
PD-TEPA-30%	1.40	31
PD-TEPA-50%	2.10	8
PD-PEI-20%	1.23	20
PD-PEI-50%	1.36	10
PD-APS-10%	0.21	66
PD-APS-20%	0.81	37
PD-APS-30%	1.00	31

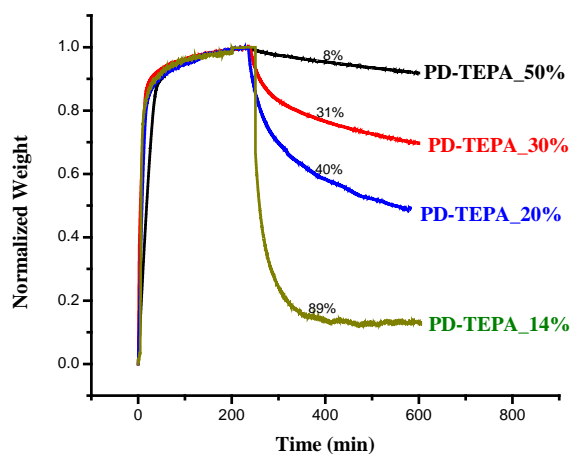


Figure 4.6 Adsorption and desorption performance of silica supported TEPA materials at 3000 ppm CO<sub>2</sub> and 25 °C.

Furthermore, the effects of desorption time and nitrogen flowrate on the amount of desorbed CO<sub>2</sub> and rate of desorption were investigated by varying the nitrogen flowrate and desorption time. Figure 4.7 (a) displays the CO<sub>2</sub> desorption profiles for PD-TEPA-30% obtained for different desorption times at 40 mL/min N<sub>2</sub> flowrate. Longer desorption time results in more CO<sub>2</sub> removed from the adsorbent by N<sub>2</sub> (37% after 10 h compared to 31% after 6 h), however, the enhancement was only marginal for prolonged desorption times, showing only 2% enhancement when desorption period increased from 10 h to 15 h. To evaluate the influence of nitrogen flowrate, the desorption time was kept constant (6 h) and varied the flowrate from 40 to 80 mL/min. On the basis of these results, it could be inferred that 16 h desorption time is sufficient to allow sufficient desorption from the buffer material during chamber tests. As can be observed from Figure 4.7 (b), upon doubling the N<sub>2</sub> flowrate, the desorption capacity increased only 3% (from 31 to 34%) implying that bulk mass transfer is not rate limiting step during CO<sub>2</sub> desorption from the adsorbent particles into the gas phase.

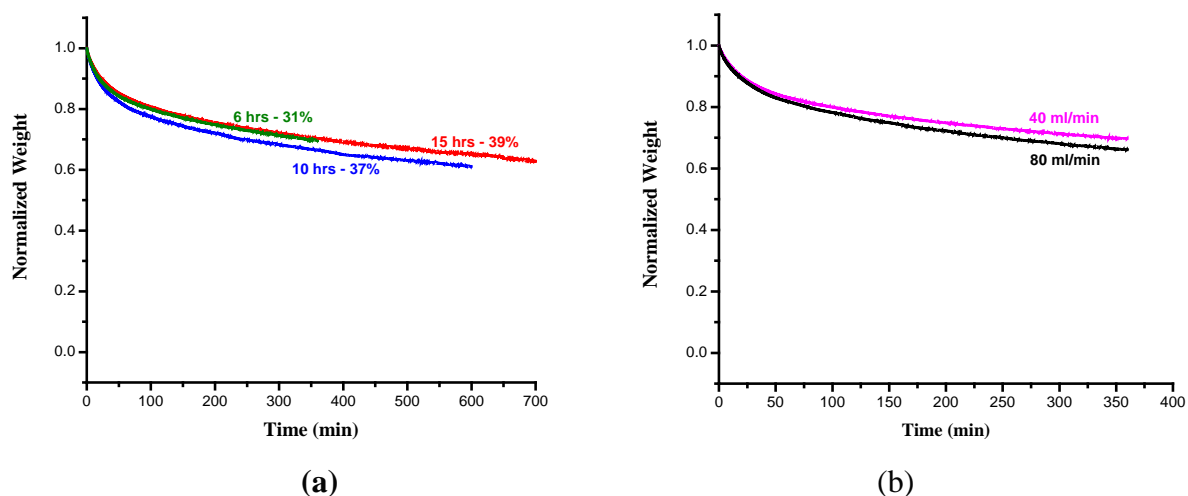


Figure 4.7 Normalized CO<sub>2</sub> desorption profiles for (a) different desorption times, and (b) N<sub>2</sub> flowrates, obtained for PD-TEPA-30% sample at 3000 ppm CO<sub>2</sub> and 25 °C.

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 4.8. The 3-cycle TGA run performed on PD-TEPA revealed no change in the amount of CO<sub>2</sub> desorbed after the third cycle.

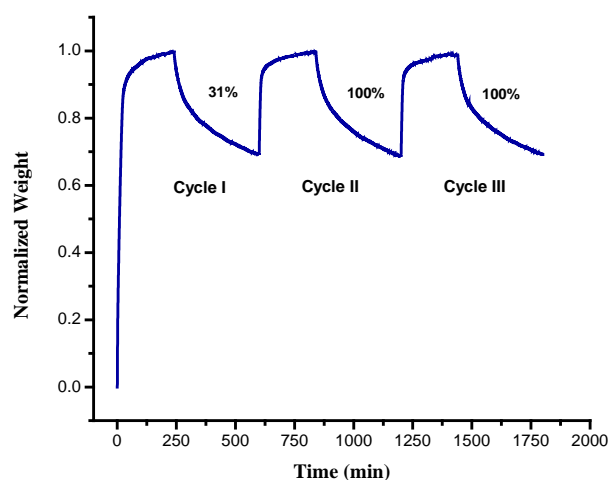


Figure 4.8 Cyclic adsorption – desorption profiles for PD-TEPA\_30% at 3000 ppm CO<sub>2</sub> and 25 °C. (Desorption% shown is based on amount adsorbed during prior adsorption cycle)

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 adsorbent exhibits short term stability. Repeatability and stability during CO<sub>2</sub> uptake and release will need to be demonstrated for a buffer material that is effective at managing indoor CO<sub>2</sub>.

### 4.3. BREAKTHROUGH EXPERIMENTS

The breakthrough profiles for TEPA loaded silica sorbents were performed by exposing the materials to 3000 ppm CO<sub>2</sub> at 25 °C and the results are presented in Figure 4.9. In agreement with TGA equilibrium capacities, the low-loaded PD-TEPA-10% gave rise to earlier CO<sub>2</sub> 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 was observed earlier from TGA results.

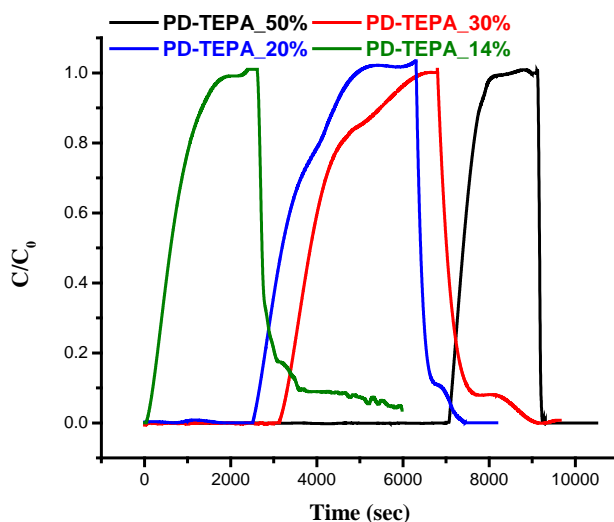


Figure 4.9 Breakthrough profiles for PD-TEPA buffer materials using 3000 ppm CO<sub>2</sub> at 25 °C

From the above result, it was hypothesized that the amount of CO<sub>2</sub> desorbed from PD-TEPA-50% was trivial (as confirmed by TGA), therefore the concentration of CO<sub>2</sub> in

the bulk gas reached zero very quickly, while for the other materials, more CO<sub>2</sub> desorbed during the desorption step. To test this hypothesis, an additional step was performed following the room-temperature desorption in which the PD-TEPA-50% adsorbent was regenerated by raising the temperature to 110 °C. As can be clearly seen from Figure 4.10, a large amount of CO<sub>2</sub> desorbed from the adsorbent onto the bulk gas (N<sub>2</sub>) which implied that no desorption took place in previous step at room temperature.

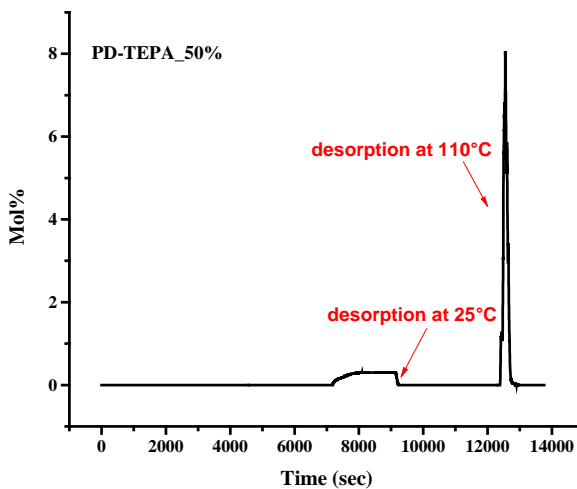


Figure 4.10 Breakthrough profiles for PD-TEA-50% using 3000 ppm CO<sub>2</sub>, adsorption at 25 °C, desorption-1 at 25 °C, desorption-2 at 110 °C

#### 4.4. CHAMBER EXPERIMENTS

The initial chamber tests were performed by varying the adsorbent quantity in the chamber. For these measurements, 1.0 g, 2.5 g and 4 g of the PD-TEPA-30% was loaded on the slab inside the chamber and exposed to ~1500 ppm CO<sub>2</sub>/air with a flowrate of 1000 mL/min, while recording the CO<sub>2</sub> concentration in the outlet stream. Each run consisted of

a by-pass run, followed by adsorption-desorption cycles. The by-pass is of two parts, initially the CO<sub>2</sub> along with air is allowed to flow through the by-pass directly to the CO<sub>2</sub> monitor chamber followed by 1 h of air supply (without CO<sub>2</sub>); this step helped to determine and monitor the inlet flow concentration before each run. The by-pass was followed by a 7 h adsorption and 14 h desorption - cycle. As a control experiment, the CO<sub>2</sub> concentration was recorded for an empty chamber. As Figure 4.11 shows, a reduction in the level of air in CO<sub>2</sub> was observed in the presence of buffer materials. The reduction was marginal when 1 g adsorbent (only 4-5% reduction, reaching 1470 ppm) was tested. But interestingly, the CO<sub>2</sub> level dropped to ~1400 ppm when 2.5 g and 4 g adsorbent was used, compared to no-adsorbent run. In addition to the reduced outlet concentration, it was observed that the rate at which the CO<sub>2</sub> initially increased reduced with an increasing mass of adsorbent. As the adsorbent quantity was increased, the amount of CO<sub>2</sub> adsorbed in the initial adsorption phase increased. Moreover, it was also observed that the CO<sub>2</sub> level did not rapidly decrease after turning off the CO<sub>2</sub> supply; this was because the CO<sub>2</sub> adsorbed by the material was released back in to the air and then flushed out of the chamber. With an increase in the amount of material, a greater delay in the concentration drop was observed.

After studying the effect of buffer material quantity, the influence of relative humidity on the CO<sub>2</sub> control ability of the amine-based buffer material was investigated by running the chamber tests at different humidity levels (RH), namely, 15, 50 and 90% RH, using 2 g PD-TEPA-30% with the inlet air/CO<sub>2</sub> flow rate of 1000 mL/min (1500 ppm inlet CO<sub>2</sub>). The adsorption – desorption cycle of CO<sub>2</sub> in the chamber air is plotted in Figure 4.12. As expected, higher humidity favored the uptake of CO<sub>2</sub> by the amine-based



adsorbent, as previously shown by other researchers<sup>14,26</sup>, as characterized by lower CO<sub>2</sub> level and longer desorption time at higher RH levels.

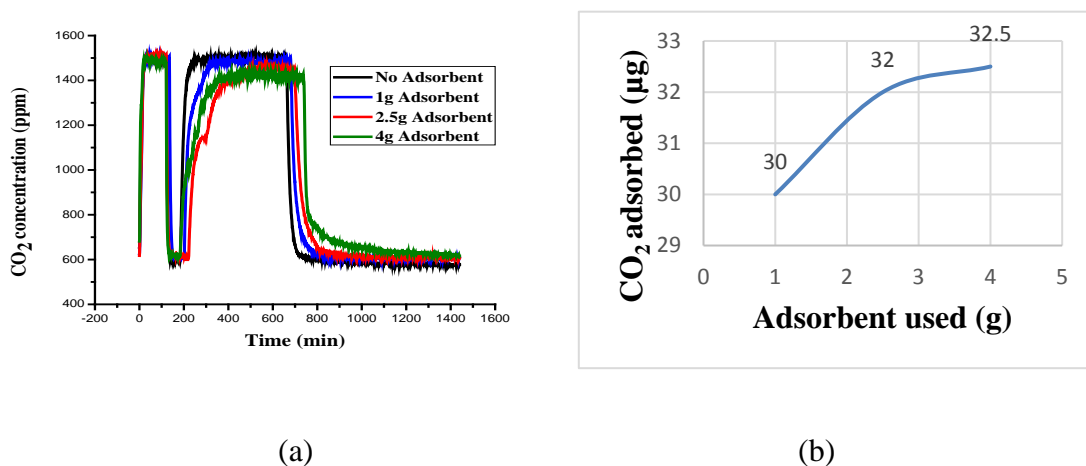


Figure 4.11 Adsorbent quantity studies (a) Effect of buffer material quantity on chamber air CO<sub>2</sub> level control (b) CO<sub>2</sub> adsorption variation with increase in buffer material quantity

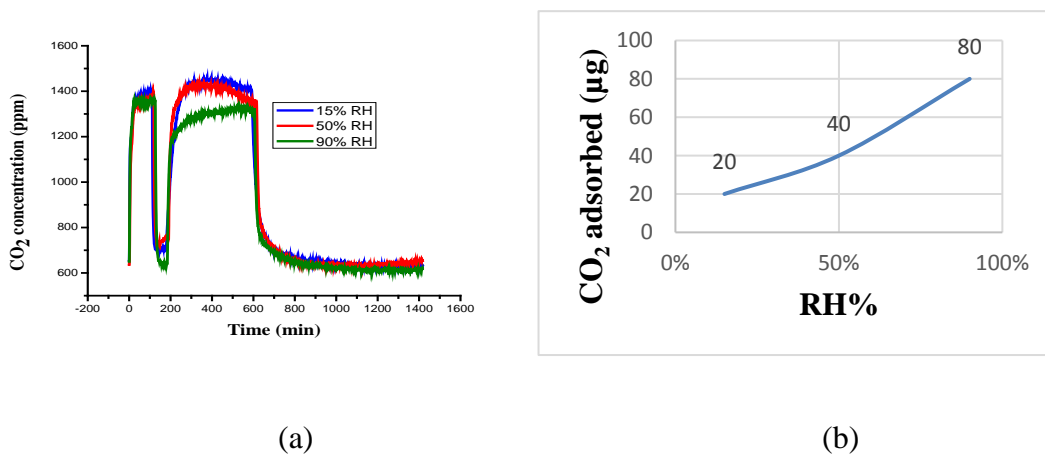


Figure 4.12 Humidity Studies (a) Effect of air relative humidity on chamber air CO<sub>2</sub> level control (b) CO<sub>2</sub> adsorption variation with increase in relative humidity

On the basis of these preliminary chamber tests results, it was concluded that the adsorption ability of the buffer material to control CO<sub>2</sub> level was significantly influenced

by the humidity in inlet air flow as well as the amount of adsorbent present. For large-scale chambers that resemble the actual commercial buildings, the quantity of buffer material and the air flow rate should be optimized based on the volume of the air and the level of CO<sub>2</sub>.

After studying the variation of different parameters influencing the CO<sub>2</sub> adsorption rate and capacity, repeatability was studied through cyclic runs. Figure 4.13 showed the data collected over 3 cyclic runs performed in the small chamber. For this, 2.5 g of the PD-TEPA-30% was dusted on the slab inside the chamber and exposed to ~1500 ppm CO<sub>2</sub>/air with a flowrate of 1000 mL/min, while recording the CO<sub>2</sub> concentration in the outlet stream. Similar to the initial runs conducted, each run consisted of a by-pass run, followed by adsorption-desorption cycles. As it can be seen from the results, consistency was maintained for the 3 runs that were performed.

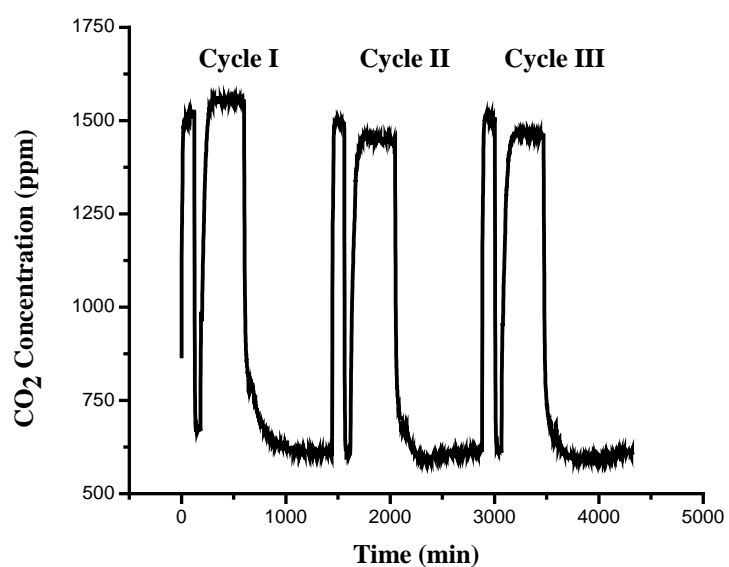


Figure 4.13 Cyclic runs in small chamber

#### 4.5. IMPACT ON INDOOR ENVIRONMENTS

It was not possible to perform detailed simulations of indoor CO<sub>2</sub> 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 was possible to estimate the impact on steady-state concentrations, assuming the sorbent to perform as observed in the chambers. The indoor air concentration of CO<sub>2</sub>,  $C_{inside}$ , at steady-state is given by:

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

where  $C_{outside}$  was taken to be the outside concentration of CO<sub>2</sub>,  $E_p$ , the CO<sub>2</sub> emission rate per hour per occupant (assumed to be 34 g/h),  $N$  as the number of occupants,  $A$  to be the surface area coated by the adsorbent. Here a residential bedroom scenario was considered. The residential bedroom was considered to have a volume,  $V$ , of 30 m<sup>3</sup> and a coated wall area,  $A$ , of 30 m<sup>2</sup>. The residence was also considered as “tight”, with a low air exchange rate ( $Q/V = 0.2/h$ ) and the outdoor concentration to be equal to 500 ppm (900 mg/m<sup>3</sup>) which is typical of the outdoor CO<sub>2</sub> concentration of urban air. There was one occupant and  $v_d$  was assumed to be 0.3 m/h. The resulting steady-state bedroom concentration was 1460 ppm which was much lower than that in the absence of the coating (3650 ppm). Assuming the areal coverage of sorbent required to be 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 (e.g. paint).

Given the large predicted reduction in CO<sub>2</sub>, 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<sub>2</sub> concentration would be 33%.

## 5. CONCLUSIONS

Several buffer materials were identified to be suitable for controlling CO<sub>2</sub> in indoor air. Aminosilica sorbents showed better efficiency as buffer materials and were explored in this study. Two different aminopolymers and one aminosilane were used for functionalizing a commercial mesoporous silica support. Each aminosilica sorbent was synthesized with varying silica: amine ratios to find out the best ratio for this study. The initial screening results indicated that TEPA-based silica sorbents were capable of adsorbing and desorbing more amount of CO<sub>2</sub> at room temperature than their PEI and APS counterparts. It was also demonstrated that the amine content dramatically influences both the amount of CO<sub>2</sub> 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<sub>2</sub> sources in buildings. Since the concentration gradient between the indoor air and sorbent surface is the sole mode of sorbent regeneration, it will be necessary to optimize these parameters for long-term operation. This preliminary full – chamber studies demonstrate proof of concept for the use of aminosilica buffer materials to reduce the CO<sub>2</sub> concentration inside building environments while occupants are present.

## 6. PRELIMINARY FULL – CHAMBER STUDIES

### 6.1 BACKGROUND

Full-scale chamber testing of coatings is necessary to simulate CO<sub>2</sub> buffering at the appropriate physical scale; for this, tests were run to measure dynamic CO<sub>2</sub> concentrations in an 8 m<sup>3</sup> (small room-size) chamber. This chamber has been used to study ozone–terpene reactions taking place on latex paint. After formulating the sorbents into coating films, their efficacy was investigated by performing a set of controlled dynamic experiments. Human subjects were not be used in these experiments.

### 6.2 CHAMBER SETUP

Full-scale testing of dynamic CO<sub>2</sub> concentrations took place in the chamber shown in Figure 6.1. The chamber is an insulated walk-in room with external single-pass, filtered ventilation. The inner surface of the chamber is stainless steel, but was clad in drywall panels that have been painted with normal latex paint or sorbent coatings developed in this project. Air is passed through a HEPA (High Efficiency Particulate Arrestance) filter and an activated carbon filter before being introduced into the chamber. CO<sub>2</sub> monitors were positioned at the inlet and center of the chamber and monitored continuously during experiments.

Sorptive coatings have not yet been developed for this application. In lieu of wall and ceiling coatings, the sorbent powders (Silica-TEPA-30%) were tested by spreading the powder on a 2 m<sup>2</sup> aluminum panel. This sorptive “surface” was placed in the 8 m<sup>3</sup> chamber

described above. The material was observed to adsorb a considerable amount of  $\text{CO}_2$  over an 8 h period. The equilibrium air concentration was set at about 2200ppm  $\text{CO}_2$ . Approximately 200 mL/min of pure  $\text{CO}_2$  was introduced into the chamber (operated at an air exchange rate of 0.7/h) for 8 h then turned off.

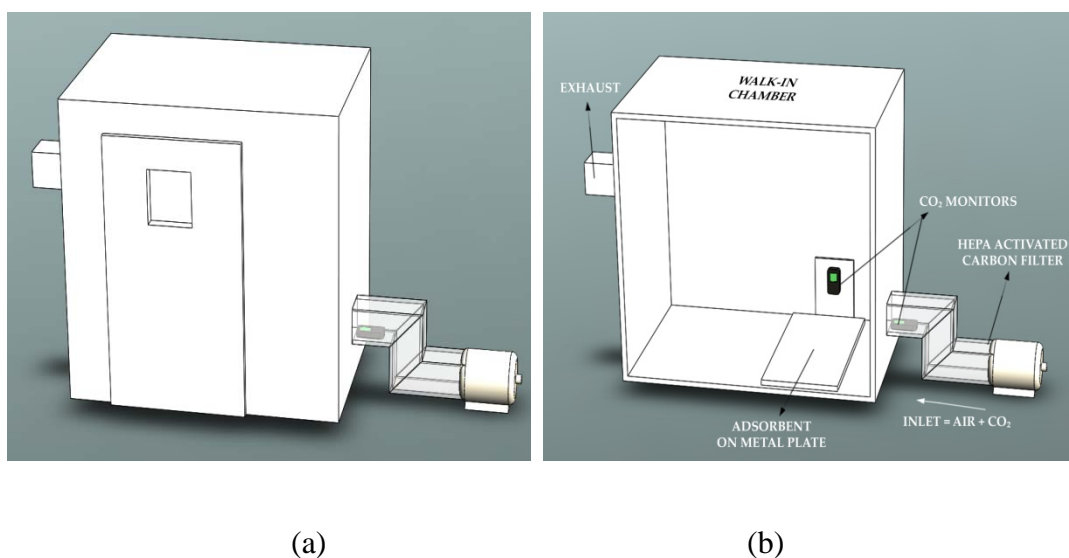


Figure 6.1 Full Chamber set up (a) Front view, and (b) Cross – sectional view

### 6.3 FULL – CHAMBER PRELIMINARY RESULTS

Two monitors were placed in different parts of the chamber to measure the  $\text{CO}_2$  concentration at that given condition. One of the monitors was placed in the duct, to measure the inlet  $\text{CO}_2$  concentration; and the other was placed inside the chamber to monitor the  $\text{CO}_2$  level in the chamber. Shown in Figure 6.2. are the initial results obtained from the full-chamber runs. In black is the  $\text{CO}_2$  level that was supplied to the chamber, this reading was recorded by the monitor placed in the duct. In red is the  $\text{CO}_2$  level recorded inside the chamber when the chamber was empty (in the absence of adsorbent). In blue is

the CO<sub>2</sub> level recorded inside the chamber in the presence of adsorbent material. When the ‘with and without adsorbent’ plots are compared, it can be observed that the adsorbent acts as a good buffer material and controls CO<sub>2</sub> levels in the given space. Under these conditions, a relatively high degree of buffering (10%) was observed.

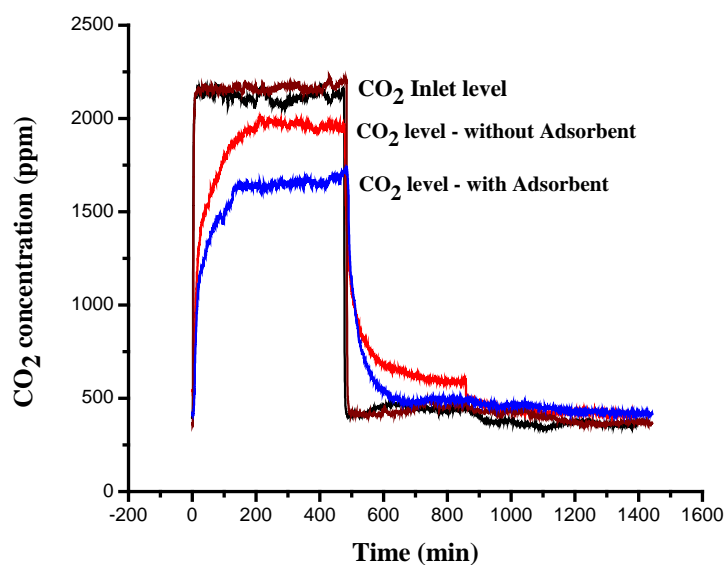


Figure 6.2 CO<sub>2</sub> concentration reduction in the presence of adsorbent – Full Chamber runs

However, more practical buffering capacity can be anticipated with larger surface area available by coating walls and ceilings. Under this scenario, only a fraction of the total capacity of the sorbent is used, and it may be advantageous to alter the sorbent, or amount of sorbent applied, to have a lower sorption capacity. Also, there is a difference in the rate of CO<sub>2</sub> increase between the CO<sub>2</sub> in the duct and the CO<sub>2</sub> in the blank run because, in the duct, the increase is sharp and the volume surrounding the monitor is very small; whereas it takes longer time for the CO<sub>2</sub> to diffuse evenly in the chamber and to reach its maximum. Similarly, a small portion of the CO<sub>2</sub> is lost in the chamber, hence the difference in the concentration between the inlet and the blank run plots.



## 6.4 FUTURE WORK

More studies to be conducted to determine the right amount of adsorbent material required for the given space. This data will help in scaling the amount of adsorbent material to be used for bigger rooms/office spaces.

Once the right adsorbent and the appropriate quantity of the adsorbent has been determined, the next stage would be to find suitable coating materials on which the selected silica amine samples (PD-TEPA) can be incorporated. These coatings would then be run through similar set of tests to study the adsorptive and desorptive capacities of the silica amines when combined with coating materials. Cyclic runs study for multiple cycles should be conducted to study long term capacities of the buffer materials. Also, the effect of material regeneration must be studied.

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