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# Carbon Dioxide Capture on Porous Adsorbents containing Surface Amino Groups

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A thesis

presented to

the faculty of the Department of Chemistry

East Tennessee State University

In partial fulfillment

of the requirements for the degree

Master of Science in Chemistry

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by

Odette Amana Esam

December 2013

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Keywords: carbon dioxide, sol-gel, grafting, global warming, greenhouse gases, modification of porous surfaces, amino groups, adsorption, trialkoxysilane

## ABSTRACT

### CO<sub>2</sub> Capture on Porous Adsorbents Containing Surface Amino Groups

by

Odette Amana Esam

The potential impact of carbon dioxide as a major source of global warming has led to extensive research in order to mitigate the greenhouse effect. In this work, four adsorbents were synthesized and studied. The adsorbents were obtained by grafting and sol-gel of amino-containing molecules such as bis[3-(trimethoxysilyl)propyl]amine as monoamine and [3-(2-aminoethylamino)propyl]-trimethoxysilane as diamine on the surface of silica gel. CO<sub>2</sub> passed through adsorbents at room temperature for its capture, then desorbed at moderate heating, and stored in the form of insoluble BaCO<sub>3</sub>. The adsorbent synthesized by sol-gel synthesis was found to be more efficient due to its high content of amino groups. A demonstration experiment on reversible adsorption of CO<sub>2</sub> on mesoporous modified silica gel was developed. This experiment visualizes a technology of post-combustion CO<sub>2</sub> sequestration from industrial emission gases and its storage.

## DEDICATION

This piece of work is dedicated to my family, to all the members of Bread of Life Ministry who have always supported me with their prayers, and also to the Almighty God for being my all in all.

## ACKNOWLEDGEMENTS

I will like to express my deep gratitude to Dr. Aleksey Vasiliev, my research project advisor for his patient guidance, enthusiastic encouragement, professional and constructive help, and planning of this research work. His willingness to give his time and supervision so generously that made this research a success has been very much appreciated. I wish to thank my research committee members - Drs. Ismail Kady and Ningfeng Zhao for their generous advice and assistance in making this work a success. I would also like to thank Dr. Ray Mohseni for providing me with valuable instrumentation training and data analysis. My endless thanks goes to my friends and course mates for their valuable contribution, spiritual and moral support, not leaving out Fredricka Quarshi, Duke Kojo Asante Debrah, Derrick Boateng, Martha Bokete, George Appiah, Seka Petra, just to name a few. I will also like to thank the Chemistry Department of ETSU for providing me with resources to start this research. My sincere gratitude goes to the access and diversity office of ETSU for providing me with a graduate assistance that enabled me to complete this research.

Finally I wish to thank the almighty God for His sufficiency.

## TABLE OF CONTENTS

	Page
ABSTRACT.....	2
DEDICATION.....	3
ACKNOWLEDGEMENTS.....	4
LISTS OF TABLES.....	8
LIST OF FIGURES.....	9
Chapter	
1. INTRODUCTION.....	11
Problem of Global Warming .....	11
Separation of CO <sub>2</sub> from Emission Gases .....	14
Post-combustion capture.....	15
Pre-combustion capture.....	16
Oxy-fuel combustion capture.....	16
Materials used until present times for post-combustion CO <sub>2</sub> capture.....	17
Background on grafting technique and its applications.....	21
Background on sol-gel technique.....	23
Critical comparison of grafting and sol-gel techniques.....	26
Porous structure determination.....	27
Research objectives .....	28
2. EXPERIMENTAL.....	29
Reagents .....	29

Precursors.....	29
Surfactant.....	29
Other chemical reagents used.....	30
Hazards.....	30
Grafting technique.....	31
Preparation of sample 1.....	31
Preparation of sample 2.....	31
Sol-gel technique.....	31
Preparation of sample 3.....	31
Preparation of sample 4.....	32
Preparation of barium hydroxide (Ba(OH) <sub>2</sub> ) solution.....	32
Absorption/desorption setup.....	33
Elemental analysis.....	35
Pore size determination.....	36
3. RESULTS AND DISCUSSION.....	37
Synthesis of adsorbents.....	37
Synthesis by grafting method.....	37
Synthesis by sol-gel method.....	37
Characterization.....	38
Elemental analysis.....	38
Porosity study.....	39
Adsorption/desorption of CO <sub>2</sub> on adsorbents.....	42
Data of adsorption/desorption cycle of CO <sub>2</sub> .....	43

Discussion.....	44
Synthesis of adsorbents.....	44
Adsorption of CO <sub>2</sub> .....	45
Technical impact of this research.....	46
Educational impact of this research.....	47
Conclusion.....	47
REFERENCES.....	49
VITA.....	57



## LIST OF TABLES

Tables	Page
1. Contents of N, % on adsorbent and contents of surface amino compounds, mmol/g on samples 1-4.....	39
2. Surface area ( $\text{m}^2/\text{g}$ ), pore average radius ( $\text{\AA}$ ) and pore volume ( $\text{cm}^3/\text{g}$ ).....	42
3. Results of $\text{CO}_2$ capture by samples 1-4 in three adsorption/desorption cycles.....	44

## LIST OF FIGURES

Figure	Page
1. Anthropogenic release of greenhouse gases into the atmosphere .....	12
2. Rescuers check for survivors in New Orleans, Louisiana, after Hurricane Katrina.....	13
3. CO <sub>2</sub> capture from power plant flue gases.....	15
4. Schematic of the three main methods of CO <sub>2</sub> capture.....	17
5. Structure of a bifunctional anchor consisting of pyrene anchoring group and an amine CO <sub>2</sub> capturing group.....	19
6. Grafting of amino group on a solid support of silica gel.....	22
7. Example of hydrolysis and condensation in sol-gel reaction .....	24
8. Sol-gel reaction in (a) acidic and (b) basic conditions .....	25
9. Simplified representation of condensation of TEOS in sol-gel process.....	26
10. Structure of bis[3-(trimethoxysilyl)propyl]amine .....	29
11. Structure of [3-(2-aminoethylamino)propyl]trimethoxysilane diamine.....	29
12. Structure of dodecylamine .....	29
13. Structure of silica gel.....	30
14. Scheme of CO <sub>2</sub> adsorption/desorption set-up .....	33
15. Photograph of the adsorption/desorption apparatus.....	34
16. Grafting of amines on the silica surface and CO <sub>2</sub> adsorption/desorption.....	35
17. BET isotherm for N <sub>2</sub> adsorption/desorption on sample 1.....	40
18. BET isotherm for N <sub>2</sub> adsorption/desorption on sample 2.....	40
19. BET isotherm for N <sub>2</sub> adsorption/desorption on sample 3.....	41
20. BET isotherm for N <sub>2</sub> adsorption/desorption on sample 4.....	41

21. Receiver for CO <sub>2</sub> capture before (left) and after (right) desorption.....	43
22. (a) Wet adsorption and (b) Dry adsorption of CO <sub>2</sub> .....	45

## CHAPTER 1

### INTRODUCTION

#### Problem of Global Warming

Global warming is the gradual increase of the temperature of the atmosphere that is great enough to cause changes in global climate believed to be caused by an increase in greenhouse effect brought about by an increased level of greenhouse gases. There are essentially three factors that were suspected to be causing today's rapid global warming which include:

1. The sun;
2. Earth's reflectivity;
3. Greenhouse gases.

It has been found that the Sun and the Earth's reflectivity have just a small effect on global warming. Hence, all evidence points at greenhouse effect to be the major cause of global warming. Greenhouse effect is a natural phenomenon by which greenhouse gases emitted into the atmosphere prevent re-emission of heat energy back into space, thereby trapping energy in the atmosphere leading to an increase in the earth's temperature. The main greenhouse gases include carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O), water vapor, hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulphur hexafluoride (SF<sub>6</sub>) [1].

The theory of global warming was first proposed by Svante Arrhenius in 1896. In his theory he stated that carbon dioxide (CO<sub>2</sub>) traps heat from the atmosphere and that the CO<sub>2</sub> was produced mostly from burning coal and oil; the Earth's surface emits IR radiation coming from the electromagnetic spectrum of sunlight, greenhouse gases such as CO<sub>2</sub> and water vapor absorb the IR radiation from the Earth's surface preventing it from being emitted back into the atmosphere. A certain amount of greenhouse gases is naturally present in the atmosphere. They capture heat and

help to keep the Earth's surface warm enough for habitation. Hence life on Earth is a careful balance of the greenhouse gases in the atmosphere.

Before the industrial age in the mid-1700s, there was a balance between the greenhouse gases emitted into the atmosphere and the greenhouse gases absorbed in natural water. But after this period, large amounts of greenhouse gases have been emitted into the atmosphere through deforestation and burning of fossil fuel to run cars, trucks, factories, planes, power plants, etc. (Figure 1).



Figure 1. Anthropogenic release of greenhouse gases into the atmosphere [2]

These gases can last in the atmosphere for nearly a century, accumulating there and creating an extra thick blanket around the Earth. Recent reports have also shown that CO<sub>2</sub> emissions rose by 21.8% from 1990 to 2007 largely due to increased generation of electricity and an uptick in transportation activities. In the same period, CH<sub>4</sub> emission declined by 5% and N<sub>2</sub>O emission dropped by 1%. Better technology and management plans as well as increased collection and burning of CH<sub>4</sub> gas at landfills accounts for most of the reduction in methane emission. If effective majors are not taken to reduce emission of greenhouse gases, the global average temperature will increase on a high end by 5.8 °C and on the low end by 1.4 °C by the year 2100. Be it at the low or

higher end, it will result in changes in climate leading to a rise in sea level as a result of melting glacier hence thermal expansion of water; this rise in sea level and changes in the temperature of water bodies might lead to hurricanes (Figure 2), tornadoes, flooding, intense storms, more pronounced droughts, coastal areas more severely eroded by rising seas, acidic oceans, destruction of ecosystems, cause mass extinctions, generate extreme weather, hinder agriculture, spread tropical diseases into new areas, displace millions of people. Water shortage and expansion of deserts amongst others are also potential risks of global warming [3-5].



Figure 2. Rescuers check for survivors in New Orleans, Louisiana, after hurricane Katrina [6].

According to National Geographic news in March 2013 [7], a recent study has found that hurricanes formed in the Atlantic Ocean are expected to gain considerable strength as the global temperature continues to rise. Hurricane strength is directly related to the heat of the water where the storm forms. This report also says that for every 1 °C rise of the Earth's temperature, the

number of hurricanes in the Atlantic that are as strong as or stronger than hurricane Katrina will increase twofold to sevenfold.

There have been recent records of cold weather in some parts of the world which some people have used to disprove global warming [8]; this is as a result of people confusing weather patterns and climate change. Nevertheless, scientists are no longer debating whether global warming is real or not, but thousands of scientists came together in 2007 to form an association called Intergovernmental Panel on Climate Change (IPCC). From the findings of this union there is a greater than 90% likelihood that the rise in global warming is being caused by human activities [1]. The U.S. Global Change Research program suggest that changes made now will have a bigger impact on curbing global warming than those same changes made at a later date.

Carbon dioxide is one of the major and most influential greenhouse gases emitted to the atmosphere as a result of human activities; it contributes to over 60% of the greenhouse effect. The effect of CO<sub>2</sub> on the Earth climate is determined by a combination of two factors: its ability to remain in the atmosphere for a long time and to absorb energy radiated from the Earth. Among sources of U.S. CO<sub>2</sub> emissions, approximately 40% originate from electric power plants.

#### Separation of CO<sub>2</sub> from emission gases

Separation of CO<sub>2</sub> is widely practiced, although it is currently done at a relatively small scale compared to that required for significant impact on global CO<sub>2</sub> emissions [9]. CO<sub>2</sub> can be separated from other components on the bases of difference in physical and chemical features such as molecular weight, solubility, boiling point and reactivity. Generally CO<sub>2</sub> capture from power plant is classified under the following three broad methods:

## Post-combustion capture

It is the separation of CO<sub>2</sub> from mainly N<sub>2</sub> in flue gas derived from combustion of fossil fuels such as coal, natural gas, or oil in air (Figure 3). CO<sub>2</sub> is captured from flue gas after

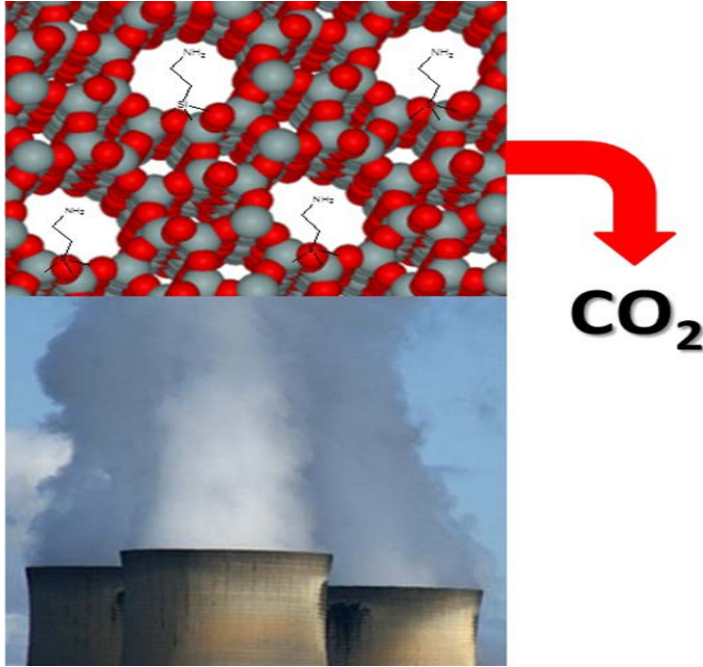


Figure 3. CO<sub>2</sub> capture from power plant flue gases

combustion at low pressure (atmospheric pressure) and low CO<sub>2</sub> content (3-20%). It can be applied at large power plants such as pulverized coal plants, natural gas combined cycles, boilers, furnaces, and stationary fuel cells. It is the most widely used method of CO<sub>2</sub> capture and is the leading candidate for gas fired plants. With this method, the CO<sub>2</sub> can be separated by four main ways:

1. Absorption: fluid dissolves or permeates into a liquid or solid. It can be a chemical or physical process that involves ionic, hydrogen, and covalent bonds or Van der Waals forces.
2. Adsorption: attachment of fluid to a solid surface either chemically or physically involving the different types of chemical bonds or Van der Waals forces.



3. Membranes: separation that makes use of difference in physical or chemical interaction with membrane. The transport mechanism through the membrane is a function of porosity and the membrane characteristics included permeability, selectivity, and stability.
4. Cryogenic (low-temperature distillation): temperature of flue gas is reduced until CO<sub>2</sub> liquefies to the point where it is easily separated from the system. Separation is based on difference in boiling points.

#### Pre-combustion Capture

As the name suggest, it refers to capture of CO<sub>2</sub> prior to combustion. Fossil fuels are first converted to syngas, a mixture consisting mainly of CO and H<sub>2</sub>. CO is further reacted with steam to produce CO<sub>2</sub> and more H<sub>2</sub>. The H<sub>2</sub> rich gas can be distributed for use as an energy source while the CO<sub>2</sub> removed from the system is stored [10-13]. Here CO<sub>2</sub> separation is of less energy and cost-intensive than post-combustion.

#### Oxy-fuel combustion Capture

This method is based on separation of O<sub>2</sub> from N<sub>2</sub>. Fuel is combusted in oxygen instead of separating CO<sub>2</sub> from N<sub>2</sub> as in post-combustion capture; O<sub>2</sub> is separated from N<sub>2</sub> first. Then the flue gas consisting mainly of CO<sub>2</sub> and steam can be separated easily by condensation. Separating O<sub>2</sub> from air is very costly, hence making this method not economically feasible.

The above three methods can be summarized as shown in Figure 4 below.

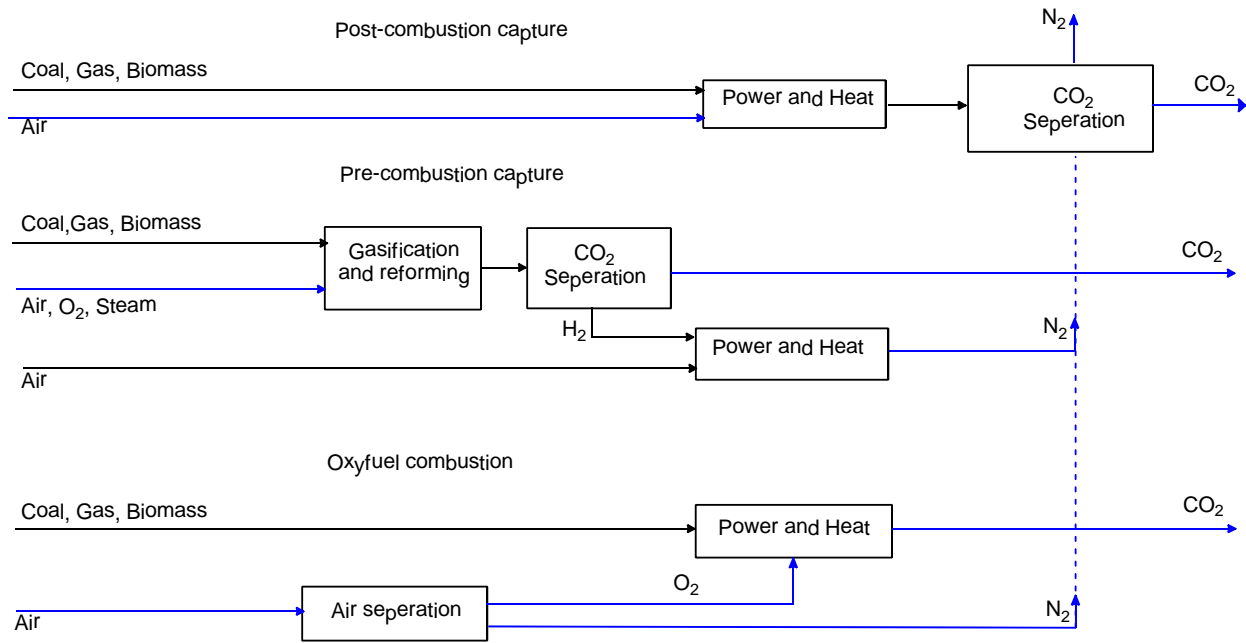


Figure 4. Schematic of the three main methods of CO<sub>2</sub> capture [14]

#### Materials used until present times for post-combustion CO<sub>2</sub> capture

Due to increase of CO<sub>2</sub> emissions from hydrocarbon plants, atmospheric CO<sub>2</sub> levels a century from now are forecasted to double those of a century ago [15]. Hence, the reduction of anthropogenic CO<sub>2</sub> emissions to alleviate the consequences of climate change is a matter of concern for all developed countries. One of the modern approaches to solve this problem is CO<sub>2</sub> sequestration from industrial sources. In the short term, this approach is a viable option for reducing carbon emissions by capturing CO<sub>2</sub> and its storage. Several reviews discussed the problem of carbon capture by different technologies [16-18]. Most common substances used for CO<sub>2</sub> capture in the past were liquid solvents such as amines. The first commercial CO<sub>2</sub> sequestration facility started in Norway in 1996 in response to a Norwegian carbon tax. Nowadays most plants capture CO<sub>2</sub> using processes developed by Fluor Daniel Inc., Dow Chemical Co., and several other companies, and they are based on chemical absorption using monoethanolamine

(MEA) containing solvents. However, the cost of CO<sub>2</sub> capturing by this method is very high (about \$40 per ton) [19]. The amount of heat required to regenerate the solvent is quite high that it significantly reduces the net efficiency of the fossil fuel-based power plants. Part of the solvent is lost during the process. Flue gas impurities (such as O<sub>2</sub>, SO<sub>2</sub>, NO<sub>2</sub>) react with MEA producing thermally stable salts that reduce its absorption capacity. Degradation and oxidation of the solvents over time produces substances that are corrosive and may require hazardous material handling procedures [20]. Thus, MEA reacts with CO<sub>2</sub> producing 2-oxazolidone and other side products [21].

More promising approach to CO<sub>2</sub> capture is based on the use of solid adsorbents. Some porous materials can separate CO<sub>2</sub> by physical adsorption, attracting it to the material surface through weak interactions, i.e., Van der Waals forces. Adsorption of CO<sub>2</sub> can be achieved on activated carbon, metal organic frameworks, or zeolites and hydrotalcites. For example, Konduru suggested use of zeolites as CO<sub>2</sub> adsorbent [22]. However, its capacity was only 40 g/kg, while an active life of the adsorbent was only 8 cycles due to low stability of zeolite structure. Chemical adsorption of CO<sub>2</sub> on solid adsorbents of basic nature is more effective due to high operating temperature and long usage lifetime. Solid-state sorbents are a good option for reversible CO<sub>2</sub> capture. Porous materials with a functionalized surface increase the CO<sub>2</sub> capturing ability and provide a high capacity and large surface area that is gas accessible. CO<sub>2</sub> can react with limestone to form calcium and bicarbonate ions. These products can be deposited into the ocean, short-circuiting the residence of carbon in the atmosphere [23]. However, this method involves large volume of adsorbent that makes it energy- and cost-consuming.

Carbon nanotubes have been used for CO<sub>2</sub> capture. These nanotubes with modified CO<sub>2</sub> capturing capability using molecular anchors such as pyrene-based anchors are an appealing option

for CO<sub>2</sub> capture. Carbon nanotubes have a high surface area and high thermal conductivity. These bifunctional molecules have an anchor part that adheres to nanotubes surfaces through hydrophobic interactions and a functional part to reversibly capture CO<sub>2</sub>. Such molecules with pyrene-based anchors (Figure 5) have low volatility and high relative thermal stability.

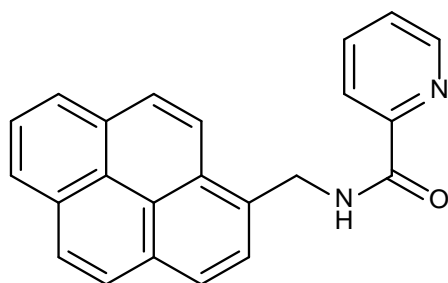


Figure 5. Structure of a bifunctional anchor consisting of a pyrene anchoring group and an amine CO<sub>2</sub> capturing group [24].

According to a report by the U.S. Department of Energy, Carbon Capture and Storage (CCS) technologies have an effective potential in the decrease of the amount of CO<sub>2</sub> emitted, hence reducing global warming without an adverse influence on the use of energy or hindering economic growth. Some materials that have been used by the National Energy Technology Laboratory (NETL) include but not limited to mesoporous (materials with pores of diameter between 2 and 50 nanometers), functionalized solids with highly branched three-dimensional macromolecules of amino-polymers [25].

Bayham et al. reported on March 20<sup>th</sup> 2013 two different types of CO<sub>2</sub> capture termed Syngas Chemical Loop (SCL) and Coal-Direct Chemical Looping (CDCL), which both involve the oxidation of coal [26]. The Syngas involves a sealed chamber without atmospheric oxygen but with oxygen-containing metal compounds that provide oxygen for oxidation, take up coal's energy, release it as heat in a second chamber, and re-circulate back into the first chamber for

another run. The CDCL reports the longest continuous operation time 200 hours. It uses sub-bituminous and lignite coal, which are regarded as the main CO<sub>2</sub> emission source at the U.S coal-fired power plants. The purity of the CO<sub>2</sub> captured was approximately 99.5% [26].

Scientists from the Korean Advanced Institute of Science and Technology (KAIST) reported a new solid material called Azo-COP (a combination of simple organic molecules with nitrogen to create a porous polymer) that is much cheaper to produce and efficient for capturing CO<sub>2</sub> from a mixture of other gases. The capture takes place in hot and humid conditions and this material is stable in these conditions, and maintains its capturing efficiency. It does not need any catalyst and has excellent chemical characteristics like water and structural stability. This material holds on to the gas using weak attractive forces rather than chemical forces, hence reducing the cost of removing CO<sub>2</sub> from the material.

According to Advance Technology Material Inc (ATMI) news on June 28<sup>th</sup> 2012, a high performance adsorbent called Bright Black has been produced. It is made up of microscopic carbon beads that bind with carbon atoms released in the combustion of fossil fuel, such as coal and natural gas. This material is a highly selective adsorbent that can absorb a variety of different gases at the exclusion of others. It was developed for a different purpose but has shown to capture more than 95% of CO<sub>2</sub> from emission source with about 130 hours of operation time. It is less energy consuming than amine-based methods of CO<sub>2</sub> capture. In this technology CO<sub>2</sub> is absorbed in a bed of sorbent pellets and is desorbed in a separate chamber that regenerates the sorbent again back to the absorber with little or no mechanical or chemical degradation of the sorbent [27].

Carbon dioxide Capture and Sequestration (CCS) can also be done geologically. CCS is a set of technologies that helps to reduce CO<sub>2</sub> emissions from large stationary sources such as heavy industrial sources. The CCS process includes three different steps:

1. Firstly is the capture of CO<sub>2</sub> from fire plants;
2. Secondly, the transportation of captured CO<sub>2</sub> that has been compressed (usually transported through pipelines);
3. And thirdly is storage (underground injection) and geologic sequestration of CO<sub>2</sub> into deep underground porous rocks usually a mile or more beneath the earth surface.

Overlying these porous rocks are non-porous layers that help to trap the CO<sub>2</sub> and prevent it from migrating upwards [28]. More than 40% of CO<sub>2</sub> emissions in the U.S. are from electric power generation and CCS can reduce 80-90% of CO<sub>2</sub> emission from power plants. Hence, geologic sequestration is one step in the CCS process. CO<sub>2</sub> can also be captured and stored through terrestrial or biological sequestration, where carbon is stored via agricultural and forestry practices in which plants help to capture carbon dioxide for photosynthesis.

Two major approaches to synthesis of materials for post-combustion CO<sub>2</sub> capture include grafting technique and sol-gel technique.

#### Background on grafting technique and its applications

In the last few years, many researchers were involved in the development and studies of organic/inorganic hybrid materials with amine functionalities to modify the surfaces of these materials [29-32]. Among the various technologies and processes that have been developed and are emerging for the modification of the surfaces of inorganic porous materials, grafting has been one of the most eminent techniques [33]. A typical inorganic precursor used is silica gel and an organic precursor is primary or secondary amine group as shown in Figure 6 below. It uses the mechanism of physical or chemical adsorption. The end result is a new organic/inorganic highly porous hybrid material whose surface has been modified. These modified nanoparticles are applicable in many areas of science not leaving out greenhouse chemistry for the adsorption of CO<sub>2</sub>.

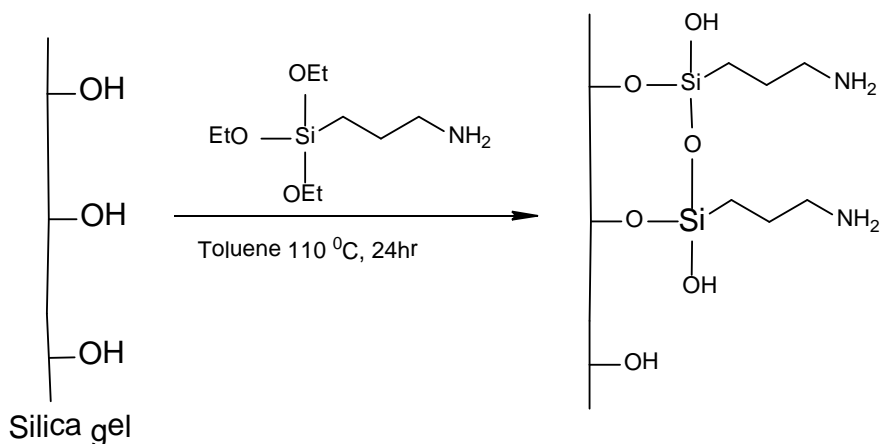


Figure 6. Grafting of amino group on a solid support of silica gel

According to Rajesh et al. [34], CO<sub>2</sub> is adsorbed on diamine grafted SBA-15 as bidentate carbonate and bidentate and monodentate bicarbonates at 25 °C (Figure 8). Desorption revealed that the monodentate and bidentate bicarbonates bound stronger to the diamine grafted SBA-15 surface than the bidentate carbonate. Desorption at 120 °C removes the majority of the captured CO<sub>2</sub> and regenerates the sorbent for CO<sub>2</sub> capture at low temperature.

Pevida et al. reported synthesis of carbon-based sorbents containing NH<sub>2</sub>-groups by high-temperature treatment of activated carbon by ammonia [35]. Their adsorption capacity was 7.0-8.4%. Similar results were obtained by Maroto-Valer et al. [36]. Functionalized polymers provide adsorption of up to 8.19% CO<sub>2</sub> [37].

Many publications are devoted to the use of functionalized silica for CO<sub>2</sub> chemisorption. Synthesis of such functionalized materials containing siloxane structures with incorporated organic molecules is well known as an effective method of obtaining materials with a wide range of structures, compositions, and properties. They can be prepared by grafting of organic molecules on the surface of silica or co-polycondensation of tetraalkoxysilane and trialkoxysilane containing an organic functional group. Several reviews describe these materials and their synthesis [38]. Gray et

al. used silica sorbent prepared with template for synthesis of an amino-containing adsorbent [39]. They functionalized the surface of silica by grafting with (3-aminopropyl)trimethoxysilane, and the obtained material adsorbed up to 8.8% CO<sub>2</sub> in respect to the total weight of the adsorbent. This value is higher than for commercial amine adsorbent that was explained by uniform distribution of aminoalkyl groups in pores increasing their accessibility for CO<sub>2</sub> molecules. Authors suggested that CO<sub>2</sub> forms carbonate and bicarbonate structures on surface amino groups [40].

#### Background on sol-gel technique

Sol-gel process is a chemical technique widely used in material science and ceramic engineering for the fabrication of both glassy and ceramic materials. The precursor involves a metal or metalloid element surrounded by various reactive ligands. The sol-gel process can be described as the formation of an oxide network through polycondensation of molecular precursors in a liquid. This method can be used to prepare materials with a variety of shapes such as porous structures, thin fibers, dense powders, and thin films. The starting material is a colloidal solution (sol) that is a suspension of solid particles in a liquid. It acts as a precursor for an integrated porous, three dimensional, continuous network (or gel) of either discrete particles or network polymers. In this gel a recombination of polymers produces bushy structures that invade the whole volume inside the solvent, reaction by-products and free polymers are trapped. The sol evolves gradually towards the formation of a gel-like network containing both liquid and solid phase after the solution is allowed to precipitate [41-44]. The removal of the remaining liquid requires drying process accompanied by significant amount of shrinkage. The rate at which the solvent can be removed is determined by the distribution of its porosity in the gel. There are two distinct reactions in the sol-gel process, hydrolysis and condensation (Figure 7) of the resulting hydroxyl groups and occur by nucleophilic substitution through the following steps: addition of a nucleophile followed



by proton transfer, then eliminating the proton as water or an alcohol [45]. A well-studied alkoxide is tetraethoxysilane ( $\text{Si}(\text{OC}_2\text{H}_5)_4$ ). Alkoxides are ideal chemical precursors for sol-gel synthesis because they react readily with water. In this hydrolysis reaction, hydroxyl ions become attached to the silicon atoms.

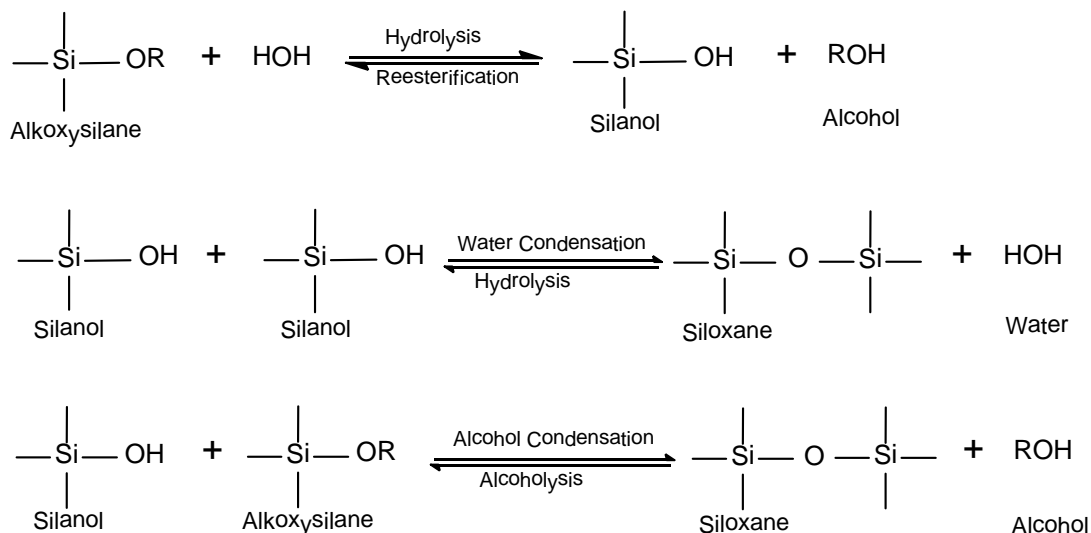


Figure 7. Example of hydrolysis and condensation in sol-gel reaction

Also, the condensation reactions are acid and base specific (Figure 8), hence the final structure of the end product is greatly influenced by the pH condition of the reaction. Mineral acids such as HCl and ammonia are commonly used as catalyst. In acidic condition, the reaction rate decreases as more alkoxy groups are hydrolyzed. Reaction at terminal Si is more favored resulting in a primarily or randomly branched polymer product. In basic conditions, the reaction rate increases as more alkoxy groups are hydrolyzed. Reaction at central Si favored resulting in a

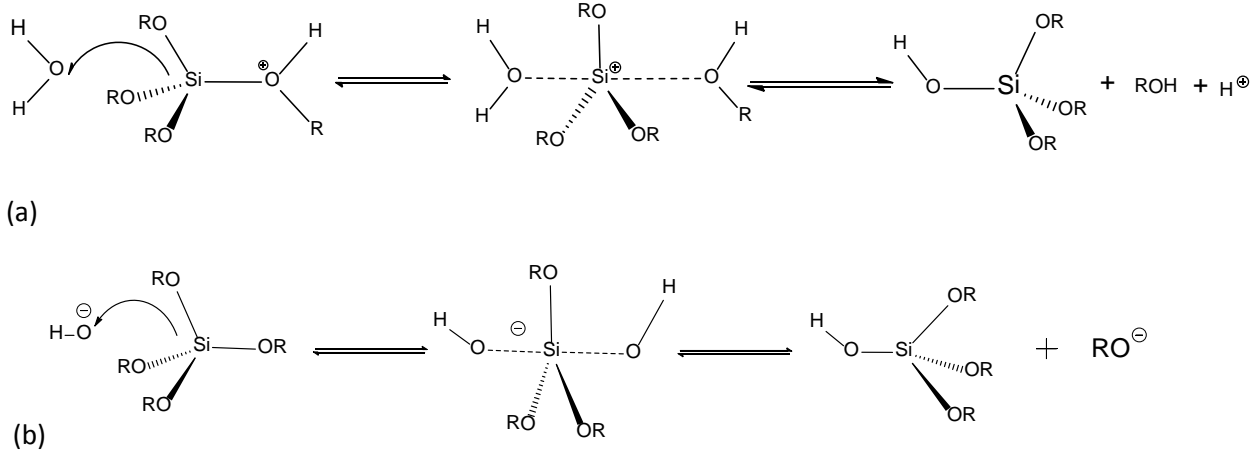


Figure 8. Sol-gel reaction in (a) acidic and (b) basic conditions

highly branched polymer network. Aside the effect of pH, there are other factors that also affect the rate of hydrolysis and condensation that include but not limited to temperature, time of reaction, reagent concentration, catalyst nature, H<sub>2</sub>O/Si molar ratio, and aging temperature and time.

Aging is the structure modification with time depending on temperature, solvent and pH conditions. It leads to the promotion of additional cross linking as unreacted terminal groups (OH and OR) come in contact. The process also helps in further structural changes such as pore formation.

Tetraethylorthosilicate (TEOS) is one of the most commonly used precursors in sol-gel chemistry and results in a highly branched porous network structure as shown in Figure 9 below.

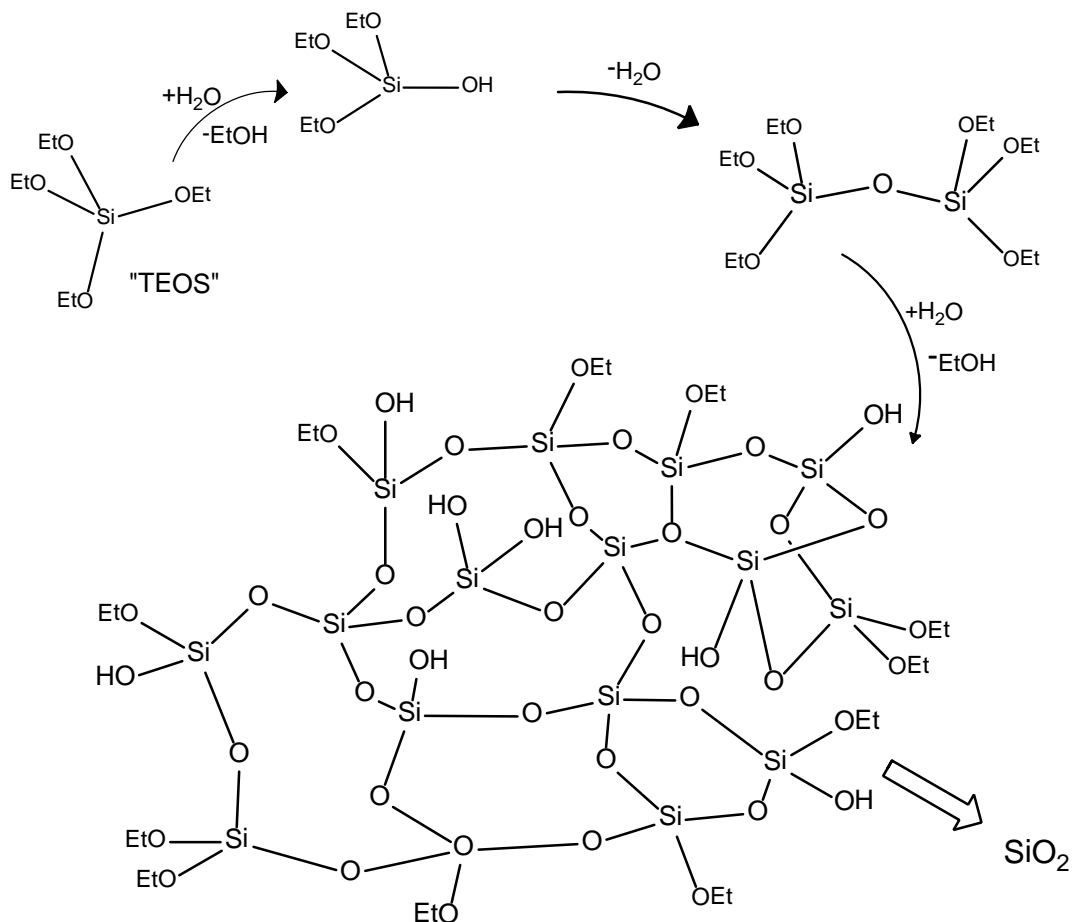


Figure 9. Simplified representation of condensation of TEOS in sol-gel process

### Critical comparison of grafting and sol-gel technique

The modification of silica surface can be done using several different methods amongst which are grafting and sol-gel method. The method used to prepare the adsorbent determines the porosity and the quality of the adsorbent.

Grafting takes place by chemical reaction between silanol groups (Si-OH) from commercial silica with ligands (e.g., chloride or alkoxide). The commercially obtained silica gel is highly porous, but we can introduce only small amount of amino groups because of steric hindrance. Hence, grafting results in a highly porous material that has limited number of amino groups

resulting to a low absorption capacity [46-48]. In the case of sol-gel, Si alkoxides are combined in a two-step reaction: hydrolysis (which leads to the formation of Si-OH bond) followed by condensation (which generates siloxane ie Si-O-Si bond) that results in the bulk skeleton of silica network. We don't need any previously formed silica network, hence we can introduce any amount of amino group during the reaction. The product obtained has a high amount of amino groups but low porosity, hence a low absorption capacity [49]. The material obtained by sol-gel method has a well-defined morphology of spherical particle showing both the lamellar and spherical domains [49].

### Porous Structure Determination

The structural and surface properties of porous materials used in different applications have a great influence on the performance of these materials. These properties can be determined using Porosimetry method, which is an extremely useful characterization technique for porous materials and is one of the few analytical techniques used to determine various quantifiable aspects of a material's porous nature, such as pore diameter, total pore volume, surface area, and absolute density by gas adsorption using a porosimeter. There are many different types of Porosimetry methods such as mercury porosimetry, nitrogen porosimetry, argon porosimetry, etc. [50]. Irrespective of the type of porosimetry method used, the principle behind it is the same. From the volume and partial pressure data, the area of pore at each diameter range can be obtained as well as the total pore volume and average pore diameter. A plot of the volume of gas as a function of pressure called an isotherm is obtained. Surface area can be calculated using the Langmuir or BET (Brunauer-Emmett-Teller) equation. These two equations have two different principles: BET seeks to explain the physical adsorption of gas molecules on a solid surface and is an extension of the Langmuir theory that is based on monolayer molecular adsorption. A variety of methods are

available for the calculation of pore volume and size distribution such as BJH (Barret, Joyer, and Halenda), Horvath-Kowazoe, and DFT (Density Functional Theory) methods [51].

Porosimetry is not only useful in chemistry but also in life sciences as Robinson et al., used it as a technique for comparing the total pore volume and size distribution of the pores in ancient animals represented on European archaeological sites. The measurement of variations in bone porosity is a good potential for contributing to the predictive model of bone diagenesis [51, 52].

#### Research Objective

The main objective of this research is to develop new highly efficient adsorbents for carbon dioxide capture from a stationary source of flue gas. Synthesis of such adsorbents is based on the hybrid and inorganic materials, using bridged amines to achieve high porosity and high amine content; two methods of synthesis were used, namely:- grafting and sol-gel methods.

CHAPTER 2  
EXPERIMENTAL

Reagents

Precursors

Bis[3-(trimethoxysilyl)propyl]amine (BTMSPA,  $C_{12}H_{31}NO_6Si_2$ , MW = 341.55, Figure 10) from Sigma Aldrich (St. Louis, MO).

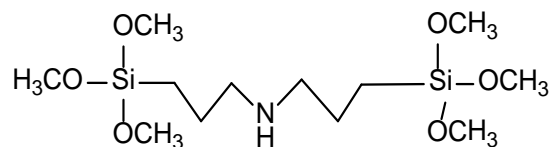


Figure 10. Bis[3-(trimethoxysilyl)propyl]amine

[3-(2-Aminoethylamino)propyl]trimethoxysilane (AEAPTMS,  $C_8H_{22}N_2O_3Si$ , MW = 222.36, Figure 11) from Sigma Aldrich (St. Louis, MO).

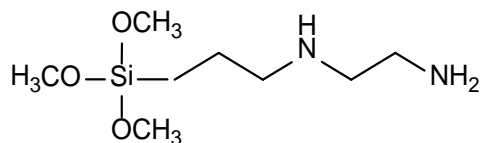


Figure 11. [3-(2-Aminoethylamino)propyl]trimethoxysilane

Surfactant

Dodecylamine (DDA,  $C_{12}H_{27}N$ , MW = 185.35, Figure 12) was obtained from Acros Organics (Morris Plain, NJ)

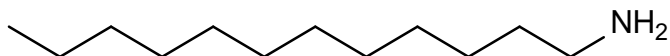


Figure 12. Dodecylamine

### Other chemical reagents used

Silica gel (Figure 13) from TCI America (Portland, OR)

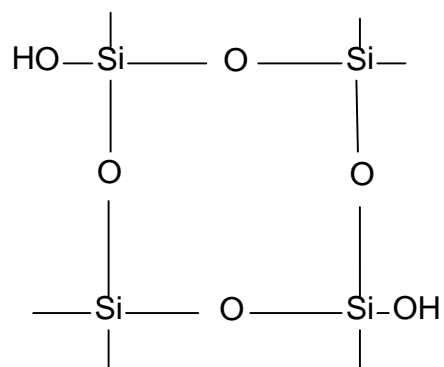


Figure 13. Structure of silica gel

Toluene

Hydrochloric acid (HCl) from Acros Organics (Morris Plains, NJ)

Isopropanol

Sodium bicarbonate (NaHCO<sub>3</sub>)

Acetone

Ether

Barium hydroxide (Ba(OH)<sub>2</sub>) from Fischer Scientific (NJ)

Deionized water

### Hazards

N-[3-(trimethoxysilyl)propyl]ethylenediamine and bis[3-(trimethoxysilyl)-propyl]amine are irritants. Barium hydroxide is corrosive. Toluene is a flammable liquid. It causes skin and eye irritation and is harmful if inhaled. Silica gel is not a dangerous substance. Tube furnace should not be used in presence of flammable materials. Protective gloves, goggles, and clothing must be worn during the experiment.

### Grafting technique

Two samples (1 and 2) were synthesized by grafting method as follows:

#### Preparation of sample 1:

About 3.5 g of bis[3-(trimetoxysilyl)propyl]amine was weighed using a top-loading balance and dissolved in 100 mL of toluene in a beaker. Then, 20 g of silica gel was added to the solution and stirred. The entire solution was then transferred into a round bottom flask in the presence of a magnetic stirrer and then connected to a reflux condenser with a hot plate placed directly under the flask. While stirring the solution was refluxed at 111 °C for 12 hrs. After 24 hours, the solution was allowed to cool down. It was then filtered using a filter paper and washed with acetone to facilitate the drying process. After allowing it to air dry for a few hours, sample 1 was then stored in a closed container to keep it from absorbing moisture because it is hygroscopic. Its final weight was 19.7 g.

#### Preparation of sample 2:

About 3.5 g of [3-(2-Aminoethylamino)propyl]trimethoxysilane was weighed and dissolved in 100 mL of toluene in a beaker. Then, 20 g of silica gel was also added to the solution and stirred. It was then refluxed at 111 °C, filtered, washed, dried, and stored using the same reagents and under the same conditions as sample 1. The final weight of the product was 21.6 g.

### Sol-gel technique

Also, two samples (3 and 4) were synthesized using the sol-gel method as thus:

#### Preparation of sample 3:

Two solutions were prepared at the same time. The first solution consisted of 80 mL of 35% HCl and 10 g of dodecylamine added to 500 mL of distilled water in a 1000 mL beaker. The second solution consisted of 30 g of bis[3-(trimetoxysilyl)propyl]amine dissolved in 50 mL of



isopropanol in a 100 mL beaker. The first solution was heated at 40 °C while stirring with a magnetic stirrer. The second solution was then added drop-wise to the first solution while still heating and stirring. I continued heating and stirring the final solution at 40 °C for 24 hours, then increased the temperature to 80 °C and continued heating and stirring for 24 hours again. Allowed the solution to cool; the solid product was filtered using a funnel. Washed the filtrate with distilled water until all the acid was removed completely (i.e., when the pH = 7). Washed once with a base (NaHCO<sub>3</sub>). Washed again with distilled water until all the base was completely removed, i.e., when the pH = 7. Washed twice with acetone and once with ether. The solid product was then dried in a vacuum desiccator overnight. The weight of the final product obtained was 78.8 g. It was then stored in an air tight container.

#### Preparation of sample 4:

Two individual solutions were prepared at same time. The first solution contained 5 g of dodecylamine and 40 mL of 35% HCl and dissolved in 250 mL of distilled water. The second solution consisted of 15 g of [3-(2-aminoethylamino)propyl]trimethoxysilane in 25 mL of isopropanol. The first solution was heated 40 °C while stirring and the second solution was added drop wise to it. Continued heating at constant temperature for 24 hours. Increased the temperature to 80 °C and heated for 24 hours more. Filtered, washed, and dried using the same method and reagents just as with sample 3. The weight of final product obtained was 3.1 g. It was then stored in an air tight container.

#### Preparation of barium hydroxide (Ba(OH)<sub>2</sub>) solution

One litre Ba(OH)<sub>2</sub> solution that was used to absorb CO<sub>2</sub> from the furnace was prepared by the following procedure. Solubility of Ba(OH)<sub>2</sub> at 20 °C is 3.89 g / 100 mL. A mass of 38.9 g of

Ba(OH)<sub>2</sub> was dissolved in 1 L of distilled water. Stirred until everything dissolves then filtered out any impurities using a filter paper and then stored in a closed container.

Adsorption/desorption setup.

The scheme of CO<sub>2</sub> adsorption/desorption is as shown in Figure 14 below.

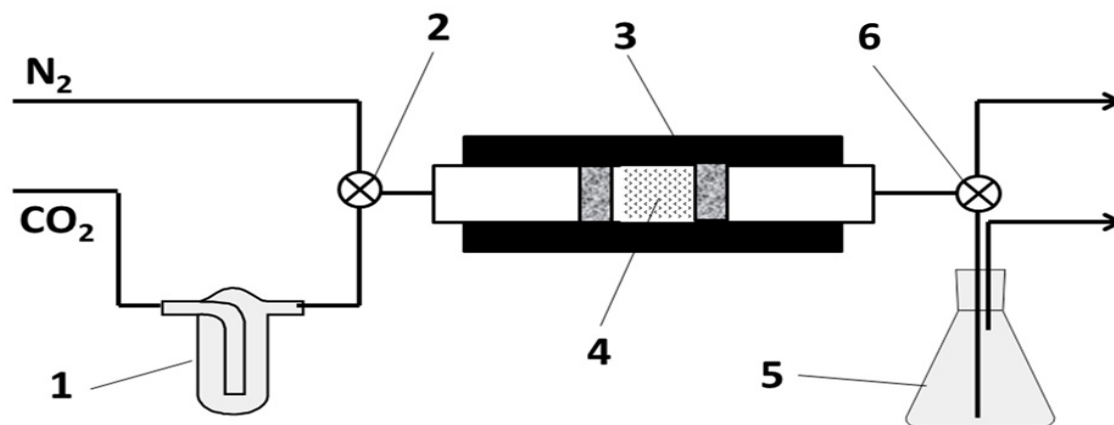


Figure 14. Scheme of CO<sub>2</sub> adsorption/desorption set-up (1 - bubbler (contains water), 2 and 6 - two way valves, 3 - Thermolyne furnace, 4 - adsorber (contains any of the adsorbents prepared), 5 - the receiver containing Ba(OH)<sub>2</sub> solution).

The experiments were conducted on an experimental setup constructed as shown above. A glass distillation column (50 cm x 2 cm) was used as an adsorber 4. The adsorbent (4 g) was loaded in the adsorber between two fiber gaskets, and the adsorber was placed in a furnace. Two gas lines were connected to the setup for: - N<sub>2</sub> and CO<sub>2</sub>. As reported earlier, CO<sub>2</sub> adsorption is higher in the presence of water vapor [19], thus, it bubbled through water in the bubbler 1 prior to entering the adsorber. Saturated solution of Ba(OH)<sub>2</sub> (50 mL) was loaded in the receiver 5. Change of gas flow route was regulated by valves 2 and 6. The image of the adsorption/desorption apparatus including the entire experimental setup is shown in Figure 15 below.

The first step in adsorption/desorption cycle was adsorption of  $\text{CO}_2$  on the sample at room temperature. Gas flow passed through the sample at the rate of 50 mL/min for 30 min and directed to atmosphere by valve 6. Then  $\text{CO}_2$  was switched to  $\text{N}_2$  by valve 2 for additional 30 min until  $\text{CO}_2$  was fully removed from the adsorber. After that, gas flow was turned to the flask 5 by valve 6 and the heating of the sample started. When the temperature reached 120 °C, the solution of  $\text{Ba}(\text{OH})_2$  became cloudy. Desorption of  $\text{CO}_2$  continued for 30 min, then the heating was stopped and white precipitate was collected by filtration on a paper filter.



Figure 15. Photograph of the adsorption/desorption apparatus

The experiment was repeated two more adsorption/desorption cycles to demonstrate recyclability of the adsorbents. The amount of  $\text{CO}_2$  adsorbed was calculated for each cycle.

The reaction of  $\text{CO}_2$  with the adsorbent is shown in Figure 16 below.

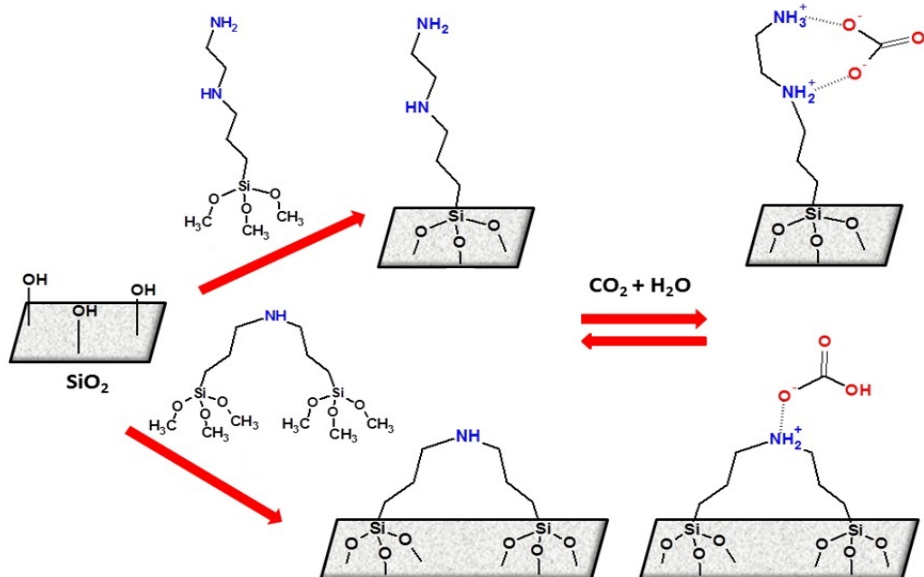


Figure 16. Grafting of amines on the silica surface and CO<sub>2</sub> adsorption/desorption

### Elemental analysis

The content of molecules of amino compounds on the surface of adsorbent were calculated from the data of elemental analysis on nitrogen (provided by Robertson Microlit Laboratories, Ledgewood, NJ) in accordance with the formula (1):

$$C_{(\text{mmol})} = 0.71C_{(\%)/N} \quad (1)$$

[Where  $C_{(\text{mmol})}$  is the content of surface amino groups, mmol/g; C is the content of nitrogen in the samples, mass %; N is the number of nitrogen atom in the molecule].

The molar amounts of CO<sub>2</sub> adsorbed per 1 mmol of surface amino compounds were calculated from the masses of BaCO<sub>3</sub> precipitates in accordance with formula (2):

$$A = 5.08 M / (m \cdot C_{(\text{mmol})}) \quad (2)$$

[Where A is the adsorption of CO<sub>2</sub> per one mmol of surface amino compound, mmol; M is the mass of precipitated BaCO<sub>3</sub>, g;  $C_{(\text{mmol})}$  is contents of surface amino compound, mmol/g; m is the mass of the adsorbent, g].

### Pore size determination

The porosity of the adsorbents synthesized was determined using nitrogen adsorption porosimetry. Nitrogen gas was used as adsorbate because it is an inexpensive and readily obtained gas. The principle behind nitrogen porosimetry is that the analyzer determines pore information by condensing N<sub>2</sub> gas in the pores of the adsorbent and then calculating the pore volume from the quantities of gas required to fill the pores. An estimate of about 0.3 g of adsorbent is placed in a long narrow glass test tube and the test tube is placed in the oven for a few hours to dry the sample. The test tube is then placed in a porosimeter that contains N<sub>2</sub> and pressure is applied to the system. N<sub>2</sub> is being taken up into the pores of the adsorbent as the pressure increases until saturation. The Quantachrome is connected to a computer that automatically plots the volume of N<sub>2</sub> adsorbed/desorbed versus the pressure of adsorption. From the isotherm obtained the pore size is calculated using the Langmuir equation.

## CHAPTER 3

### RESULTS AND DISCUSSION

#### Synthesis of Adsorbents

##### Synthesis by grafting method

The silica gel used served as a solid support on which the amine was incorporated. This commercially obtained silica gel ( $\text{SiO}_2$ ) had a particle size of 63-200  $\mu\text{m}$ , a pore volume of 0.75  $\text{cm}^3/\text{g}$ , a pore size of 60  $\text{\AA}$ , and a surface area of 500  $\text{m}^2/\text{g}$ . After a few hours of refluxing, the solution became thicker and thicker. The rate of modification of the surface of porous silica gel by precursors is increased by heating and stirring. At the end of the heating process, a thick gel-like precipitate was formed. Filtration of the product was very easy. Samples 1 and 2 were easily washed and dried. The resulting weight of sample 1 was 19.65 g, while that of sample 2 was 21.56 g.

##### Synthesis by sol-gel method

The surfactant dodecylamine was used to form a porous system through the formation of micelles, thereby inducing porosity in the system. During synthesis, HCl was added to the reaction mixture in order to catalyze the reaction and convert the surfactant (DDA) to the soluble ammonium salt. Due to the heating of the acid solution and the surface tension reduction effect of the surfactant, the amine dissolved immediately as it was dropped in the acid solution. Because heating was done in an open system, there was fast and continuous loss of water and the need of addition of water into the system every 1.5 – 2 hours. Gelation of the solution started about 20-30 min after both solutions were mixed and increased with time. At the end of the heating when the solution was allowed to cool, they both had precipitates, but the precipitates formed by the diamine was white and had a mesh-like structure suspended at the top of the solution. But the precipitate of

the monoamine was uniformly cloudy with a yellowish color. The surfactant was removed from the product by washing.

At the time of washing the samples, Sample 3 was easily washed and dried though not as easy as the first two samples. But this is not the case with sample 4, it was very unstable because it is a non-bridged amine and also the fact that it was partially soluble in water resulted in the loss of a great part of the sample during washing resulting in a very low yield of 3.088 g while the yield of monoamine was 78.98 g.

Because many chemicals were used during synthesis, it was necessary for all four adsorbents to be washed in order to remove any unreacted amine or other chemicals that might present any interference in the bonding between our product and CO<sub>2</sub>. For samples obtained by sol-gel, washing with acid (HCl) allowed any physically present amine and also surfactant present in pores to form water soluble compounds so they can be washed away easily. But the reaction of acid with surface amino groups produces salts that cannot react with CO<sub>2</sub>. So, further washing with base (NaHCO<sub>3</sub>) converts covalently bonded amino salts to useful amine that can react with CO<sub>2</sub>. At this point we are sure that the amine present in the adsorbents is chemically bonded because physically adsorbed amines should be washed from the surface.

### Characterization

#### Elemental analysis

The contents of amino compounds on the surface of adsorbent were calculated from the data of elemental analysis on nitrogen (provided by Robertson Microlit Laboratories, Ledgewood, NJ) in accordance with the formula (1). The data are as shown in Table 1 below.

Table 1. Content of N, % on adsorbent and contents of surface amino compounds, mmol/g on samples 1-4

Samples	Contents of N, %	Contents of surface amino compound, mmol/g
1	0.68	0.49
2	1.35	0.48
3	5.81	4.13
4	6.23	2.21

#### Porosity study

The BET isotherms for the N<sub>2</sub> adsorption/desorption for samples 1-4 were obtained using porosimetry technique. These isotherms were used to study the porosity and the morphology of the samples. The BET isotherms for each sample are shown in Figures 17-20 below.



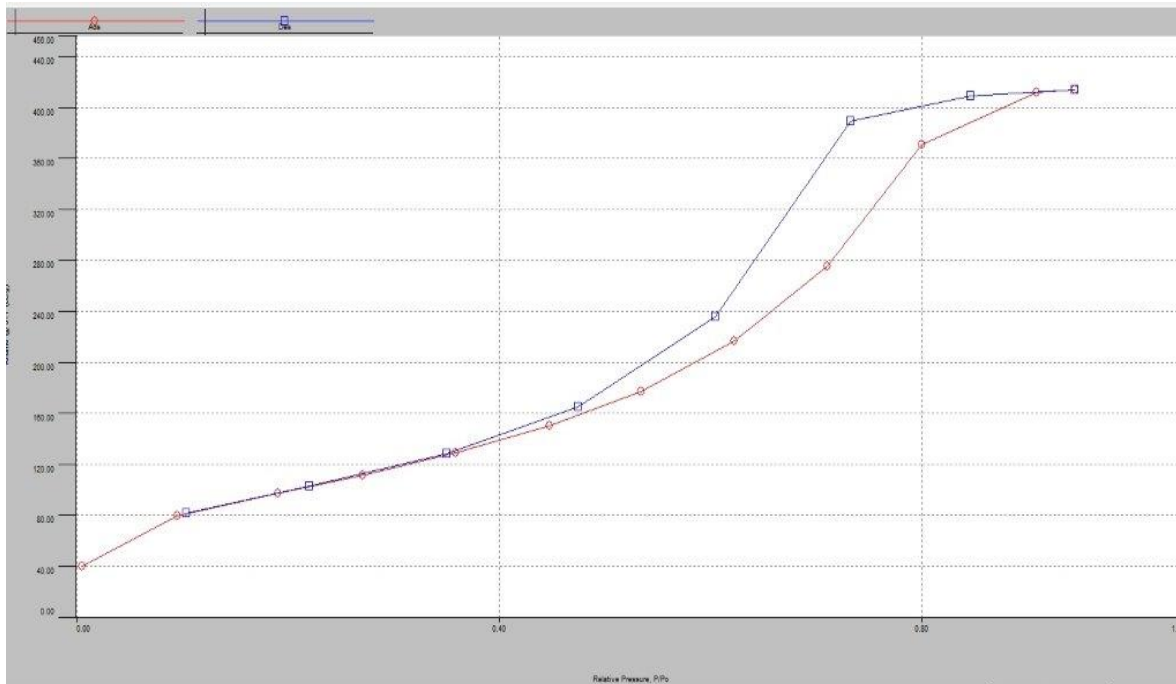


Figure 17 . BET isotherm of N<sub>2</sub> absorption/desorption on sample 1

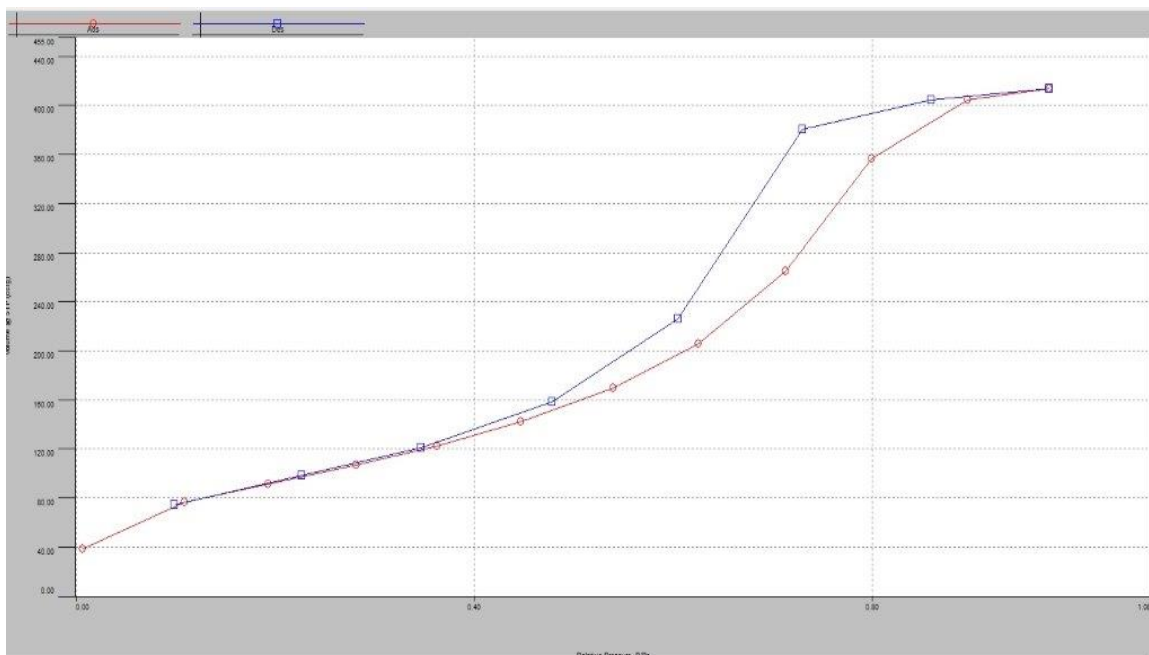


Figure 18. BET isotherm for N<sub>2</sub> absorption/desorption on sample 2

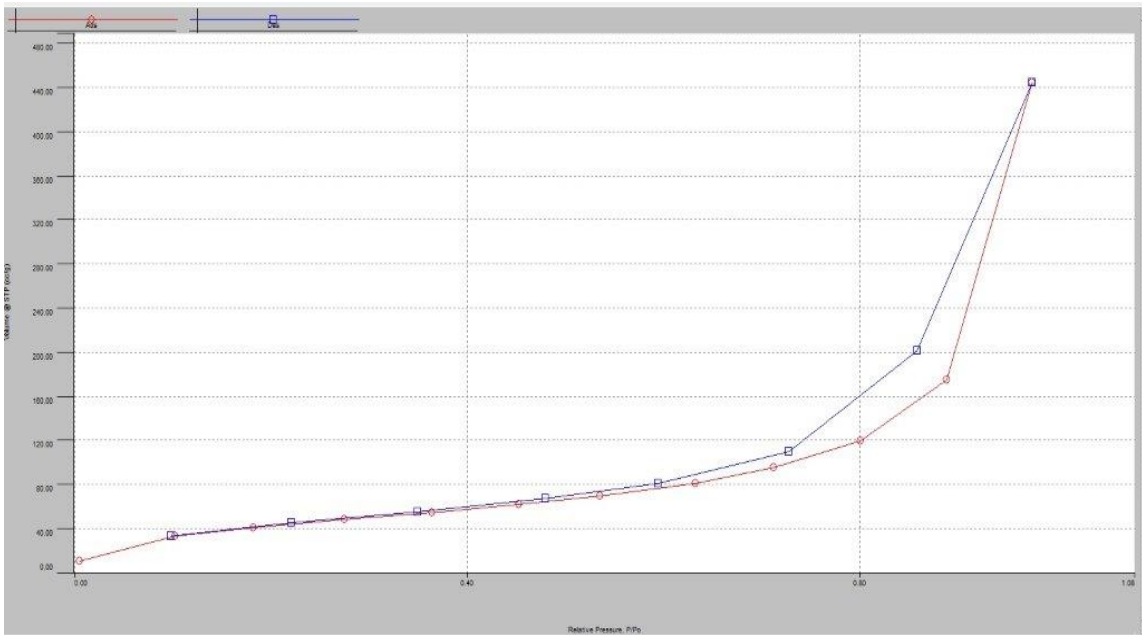


Figure 19. BET isotherm for N<sub>2</sub> absorption/desorption on sample 3

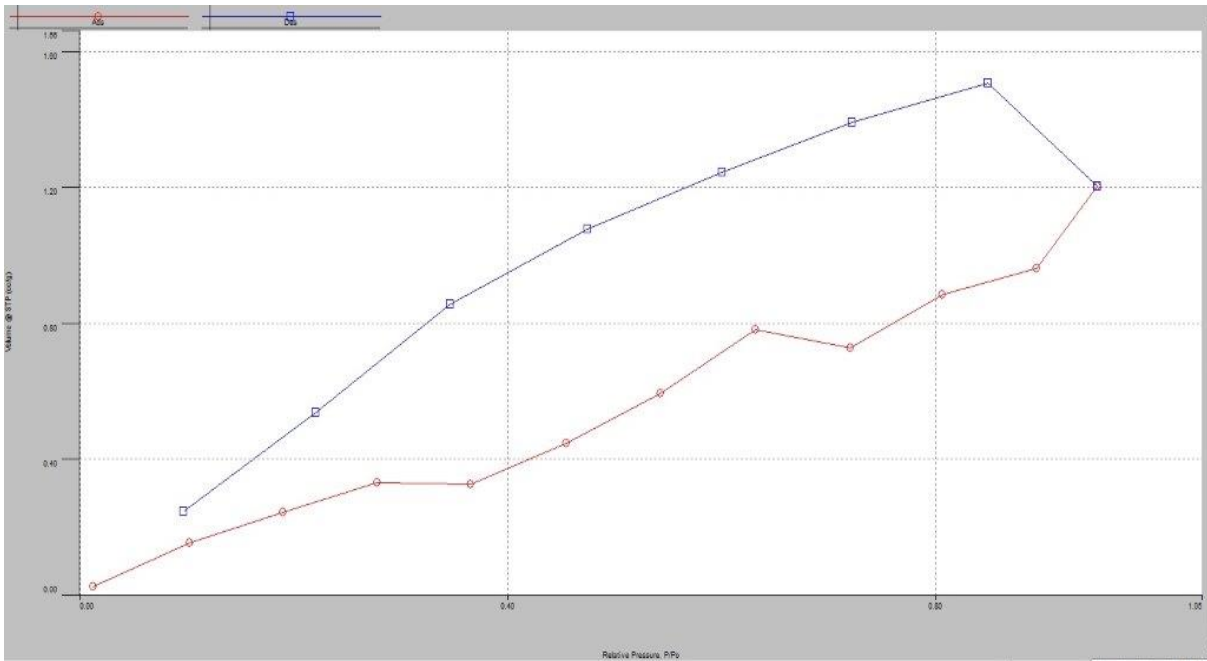


Figure 20. BET isotherm for N<sub>2</sub> absorption/desorption on sample 4

From the isotherms it is obvious that all materials except sample 4 are porous though of different levels of porosity. The isotherms also provided important pore characteristics such as surface area, pore average radius and pore volume as shown in Table 2.

Table 2. Surface area (m<sup>2</sup>/g), pore average radius (Å) and pore volume (cm<sup>3</sup>/g)

Samples	Surface area (m <sup>2</sup> /g)	Pore average radius (Å)	Pore Volume (cm <sup>3</sup> /g)
1	203.56	33.1	0.66
2	125.55	32.8	0.61
3	87.99	56.6	0.67
4	2.46	-	-

#### Adsorption/desorption of CO<sub>2</sub> on adsorbents

The duration of one adsorption/desorption cycle is 1.5 h; however, the experiment was extended to three cycles to demonstrate recyclability of the adsorbent. The carbon dioxide passed through water there by allowing it to form surface carbonate salt that makes the reaction easy and faster. We used N<sub>2</sub> gas as a carrier gas to sweep away the CO<sub>2</sub> that has been physically adsorbed by the adsorbent. The choice of N<sub>2</sub> is because it is an inert gas, hence will not further react with the adsorbent. On the desorption step, thermal decomposition of surface carbonates occurred. The bonding between CO<sub>2</sub> and adsorbents is ionic bonding that is a relatively weak bond hence can be easily broken during the desorption process. The released CO<sub>2</sub> was carried away from the surface of the adsorbent using a carrier gas such as N<sub>2</sub>.

Released  $\text{CO}_2$  reacted with a solution of  $\text{Ba}(\text{OH})_2$  and formed insoluble  $\text{BaCO}_3$ . The color of the  $\text{Ba}(\text{OH})_2$  solution changed from colorless to white confirming the presence of  $\text{CO}_2$  as shown in Figure 21. The molar amount of  $\text{BaCO}_3$  corresponds to the molar amount of  $\text{CO}_2$ , the adsorption of  $\text{CO}_2$  per one amino group was calculated from the amount of  $\text{BaCO}_3$ .

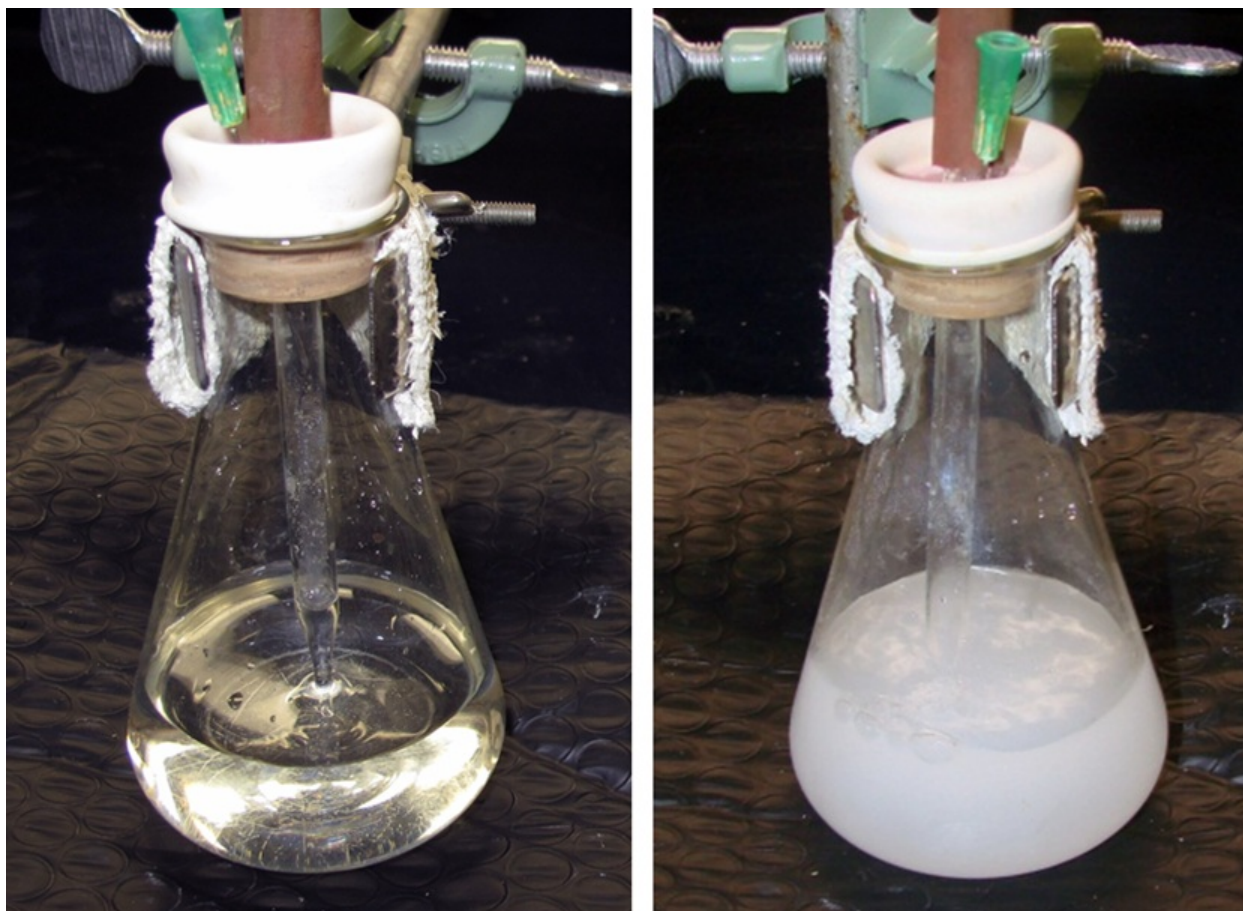


Figure 21. Receiver for  $\text{CO}_2$  capture before (left) and after (right) desorption

#### Data of adsorption/desorption cycle of $\text{CO}_2$

The results for adsorption of  $\text{CO}_2$  per one mmol of surface amino compound for all four samples on each cycle are as shown in Table 3 below.

Table 3. Results of CO<sub>2</sub> capture by samples 1 - 4 in three adsorption/desorption cycles

Samples	Yield of BaCO <sub>3</sub> on each cycle, g			Adsorption of CO <sub>2</sub> per one mmol of surface amino groups		
	1	2	3	1	2	3
1	0.075	0.043	0.083	0.20	0.12	0.22
2	0.154	0.054	0.105	0.41	0.14	0.28
3	0.360	0.139	0.169	0.11	0.04	0.05
4	0.012	-	-	0.01		

## Discussion

### Synthesis of adsorbents

The results obtained for each sample are different due to the different methods used for their synthesis. Grafting method generally requires the use of commercially obtained silica gel that is highly porous, but we can introduce only small amount of amino groups to the surface of silica gel because of steric hindrances. This results in a highly porous product that has limited number of amino groups resulting to a relatively low absorption capacity. Hence, the CO<sub>2</sub> adsorption on samples 1 and 2 can be explained by different numbers of amino groups because both materials are porous. So, sample 2 has a greater adsorption capacity of CO<sub>2</sub> than sample 1, i.e., sample 2 absorbs almost twice as sample 1 because sample 2 has a higher number of amine content than sample 1.

In the case of sol-gel synthesis, there is no previously formed silica network, hence we can introduce any number of amino groups during the bulk silica network reaction. The resulting

product has a high amount of amino groups but low porosity. Hence, the difference in adsorption can be explained using the nature of amines used [53]. The low yield of sample 4 and its inability to absorb much CO<sub>2</sub> is confirmed from literature that explains that non-bridged trialkoxysilanes have only one point of anchor as oppose to the bridged trialkoxysilanes, this makes them less stable. Bridged trialkoxysilanes have two points of anchor on the material, hence making them more stable and the fact that they are also partially porous with a high content of amino groups explains their high absorption capacity. Literature also confirms that non-bridged trialkoxysilanes yield non-porous products partially soluble in water as we observed making them useless [54, 55]. Hence, though bridged alkoxy silanes obtained by sol-gel are not as porous as adsorbents from grafting, but are porous enough and their high content of amino groups makes them adsorb better than grafting products. Among samples 1, 2 and 3, though 3 has the lowest surface area from the isotherm results, it is the most recommended because it has the highest accessibility of amino groups.

### Adsorption of CO<sub>2</sub>

Generally, CO<sub>2</sub> capture can be done either through wet or dry adsorption as shown in Figure 22.

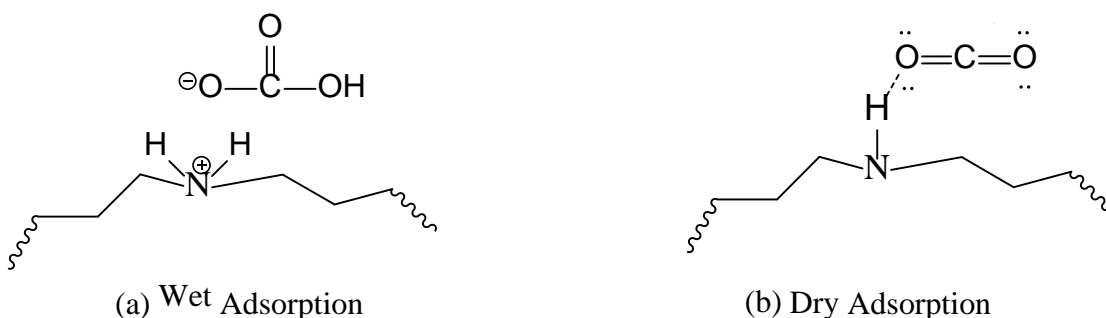


Figure 22. (a) Wet adsorption and (b) Dry adsorption of CO<sub>2</sub>

In wet adsorption, CO<sub>2</sub> passes through water before it reacts with the adsorbent. CO<sub>2</sub> reacts with water to form carbonic acid and the carbonic acid protonates amino group forming ammonium salt

and this involves ionic bonding that is much stronger (Figure 24a). In the case of dry adsorption, i.e., without water, CO<sub>2</sub> C=O bond is polar and the only possibility of bonding is hydrogen bonding formed between H and O that is relatively weak compared to ionic bonding in wet adsorption (Figure 24b). This explains why we preferred using wet absorption (first bubbling of CO<sub>2</sub> through water) in this work to ensure stronger bonding between CO<sub>2</sub> and adsorbent.

On the first step (adsorption), CO<sub>2</sub> reacted with surface amino groups in presence of water producing surface carbonates in the ratio 1 CO<sub>2</sub> : 2 amino groups. This aspect is very important because by using diamine it will be possible to reduce to almost half the amount of amine necessary for the separation of a specific amount of CO<sub>2</sub>. Highly porous silica gel (S = 500 m<sup>2</sup>/g) was used for this experiment. From the data of analysis on nitrogen, surface density of grafted amine in the adsorbents was found about 0.6 molecules per 1 nm<sup>2</sup>. As it can be seen from Table 1, not all amino groups were accessible for CO<sub>2</sub> molecules. Thus, we assumed a necessity of development of adsorbents with high adsorption capacity. From Table 3, there is an inconsistency in the adsorption/desorption values for each sample with the first value always the highest (except for sample 1) followed by the third values then the second.

#### Technical impact of this research

Large-scale implementation of solid adsorbents can provide significant economic benefits because the proposed approach allows reducing the cost of CO<sub>2</sub> capture. In existing absorbers amines are dissolved in water. Regeneration of the amine is a very energy-consuming process because its solution in water has a very high heat capacity. For example, heat capacity of a 10% solution of monoethanolamine in water after absorption of CO<sub>2</sub> is 3.857 J•g<sup>-1</sup>•K<sup>-1</sup> [56]. In contrast, heat capacity of porous silica is 0.7-0.8 J•g<sup>-1</sup>•K<sup>-1</sup>. The adsorbents containing solid adsorbing

materials do not require exhaust gas compression. This additionally reduces the cost of CO<sub>2</sub> capture.

#### Educational impact of this research

A demonstration experiment on reversible adsorption of CO<sub>2</sub> on mesoporous modified silica gel was developed [57-59]. The experiment is simple and does not require any expensive equipment. This experiment visualizes a technology of post-combustion CO<sub>2</sub> sequestration from industrial emission gases and its storage. This demonstration can be included in the course of Industrial Chemistry or Green Chemistry. In this work, one gets to learn about the role of industrial gas emissions in greenhouse effect and the strategies of its reduction. During the demonstration one will gain an understanding of the nature and environmental effect of greenhouse gases. It also discusses the difficulties and shortcomings in the current approaches to management of CO<sub>2</sub> emissions and teaches about chemistry of CO<sub>2</sub> capture.

#### Conclusion

Silica based adsorbents containing surface amino groups were successfully prepared by two methods:-grafting and sol-gel method. Samples obtained by grafting were highly porous; however, they had low contents of amino groups. For samples obtained by sol-gel method, sample 3 (bridged amine structure) was moderately porous but content of amino groups was very high. Sample 4 (non-bridged amine) resulted in very low yield of the product and this product was non porous.

Three porous samples were successfully used for adsorption of CO<sub>2</sub> from gas mixture with N<sub>2</sub>. Reaction of adsorbents of CO<sub>2</sub> was reversible and when CO<sub>2</sub> was adsorbed at room temperature it could be desorbed at moderate heating. Desorbed CO<sub>2</sub> was captured in a solution of Ba(OH)<sub>2</sub> producing insoluble BaCO<sub>3</sub>.



As a result of this work we suggest bridged amine product obtained by sol-gel method as the most promising material for adsorption of CO<sub>2</sub>. In future, adsorption can be improved and adsorption capacity can be increased by improvement of the methodology.

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