Development of HMMM based Adsorbents by Nanocasting for CO_2 Capture

Dissertation

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By

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Declaration

I, the undersigned, hereby declare that the research work presented in the M. Tech. dissertation entitled "**Development of HMMM based adsorbents by nanocasting for CO_2 capture**" has been carried out by me under the supervision and guidance of Prof. P.K. Bajpai and Dr. Haripada Bhunia, Department of Chemical Engineering, Thapar University, Patiala.

Further, I declare that no part of this Dissertation has been submitted for a degree or any other qualification of any other university or examining body in India/elsewhere.

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Place: Patiala
Date: 14 July 2014

Certificate

This is to certify that dissertation entitled, "**Development of HMMM based adsorbents by nanocasting for CO_2 capture**" submitted by Ms. Harleen Kaur in partial fulfillment of the requirements for the award of Masters of Technology degree in Environmental Science & Technology at Thapar University, Patiala is an authentic work carried out by her under our supervision and guidance.

To the best of our knowledge, the matter embodied in this dissertation has not been submitted to any other university/ institute for award of any Degree or Diploma.

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Abstract

With CO_2 being one of the main contributors to global warming, there is increasing interest in recovery of carbon dioxide (CO_2) from flue gases. Post-combustion CO_2 capture from the flue gases is one of the key technology options to reduce greenhouse gases, because this can be retrofitted to the existing coal-fired power stations. In view of this, in the past few years, several research groups have been involved in the development of new solid sorbents for CO_2 capture from flue gas with superior performance and desired economics. The enhancement of specific adsorption capacity may be carried out by increasing the affinity of the adsorbent surface to CO_2. Nitrogen enrichment is reported to be effective in introducing basic functionalities that enhance specific adsorbate-adsorbent interactions. A variety of promising sorbents such as activated carbonaceous materials, microporous/mesoporous silica or zeolites, carbonates, and polymeric resins loaded with or without nitrogen functionality for the removal of CO_2 from the flue gas streams have been reviewed.

In this work, we report successful synthesis of nitrogen-doped mesoporous carbon by templating or nanocasting method using HMMM as precursor and MCM-41 silica as sacrificial template. The templated carbon with nitrogen containing organic molecules was subjected to carbonization and activation over range of temperatures from 500-800 °C followed by removal of silica template. The resultant adsorbents were characterized for their chemical composition and textural properties. The effect of carbonization and adsorption temperature on CO_2 uptake was studied. Adsorption capacities upto 0.801 mmol g^{-1} of CO_2 at 30 ºC were measured using thermogravimetric analysis and discussed how textural and chemical properties of carbon influence CO_2 capture performance. Finally, the stability and regenerability of the carbons over numerous thermal swing adsorption cycles have been described. Kinetics of adsorption was studied by using pseudo first order and pseudo second order kinetic models.

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Nomenclature

atm	Atmosphere
BJH	Barrett-Joyner-Halenda
CCS	Carbon dioxide Capture & Sequestration
ECBM	Enhanced Coal Bed Methane
EOR	Enhanced Oil Recovery
GHG	Green House Gase
Gt	Giga (billion) tones
HFC	Hydro-fluoro-carbon
HMMM	Hexamethoxymethylmelamine
IPCC	Intergovernmental Panel on Climate Change
MEA	Monoethanolamine
mmol g^{-1}	Milli moles per gram
m^2 g^{-1}	Metre square per gram
Mt	Million Tonnes
nm	Nanometer
PFC	Per-fluoro-carbon
ppm	parts per million
ppmv	parts per million volume
PSA	Pressure Swing Adsorption
SEM	Scanning Electron Microscopy
TSA	Thermal Swing Adsorption
wt%	Weight percentage
XRD	X-Ray Diffraction

CHAPTER 1
INTRODUCTION

1.1. Background and Motivation

Fossil fuel use is integral to the functioning of society at every level: the manufacturing of every aspect of consumer goods, the movement of people and products, the maintenance of shelter from the elements, the production of food, and the provision of water. Today, 80% of global energy use relies on fossil fuel and yet, with every ton of carbon burned, the earth is altered in ways both predictable and unpredictable **[1]**. Owing to the fact that the energy demands of our modern society are primarily met by fossil fuel thermal power plant including coal, oil and gas which produce large quantities of the greenhouse gases. During the last few years, there has been increasing awareness of the impact of greenhouse gases on global climate which has lead to increasing efforts to reduce their environmental influence by applying preventive and remediation methods **[2]**. Preventive methods include renewable energies or energy efficiency programmes while remediation approaches are designed to retrofit existing industrial facilities and current thermal power plants that discharge CO_2 in the atmosphere **[3]**.

GHGs absorb infrared radiation and thereby reduce the energy flow out of the atmosphere, which in turn leads to an increase in the earth's temperature. This phenomenon is known as "Global Warming" **[4]**. The major greenhouse gases are carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), perfluorocarbons (PFCs), hydrofluorocarbons (HFCs) and sulphur hexafluoride (SF_6). Of all the greenhouse gases, CO_2 has the lowest Global Warming Potential but, it has the largest global climate change impact because its total emissions are much greater than the others **[5]**. According to intergovernmental panel on climate change (IPCC), by the year 2100, there will be increase in CO_2 in the atmosphere from its current value of 395 ppmv to 570 ppmv. This will in turn cause rise in mean global temperature of 1.9 ºC and increase in sea level of 0.38 m **[6]**. Thus, to avoid these catastrophic climate changes, stabilization of atmospheric CO_2 concentration is important. According to fifth IPCC Assessment Report, the globally averaged combined land and ocean surface temperature data as calculated by a linear trend (Fig. 1.1), show a warming of 0.85 (0.65 to 1.06) °C, over the period 1880 to 2012. The total increase between the average of the 1850–1900 period and the 2003–2012 period is 0.78 (0.72 to 0.85) °C **[7]**.

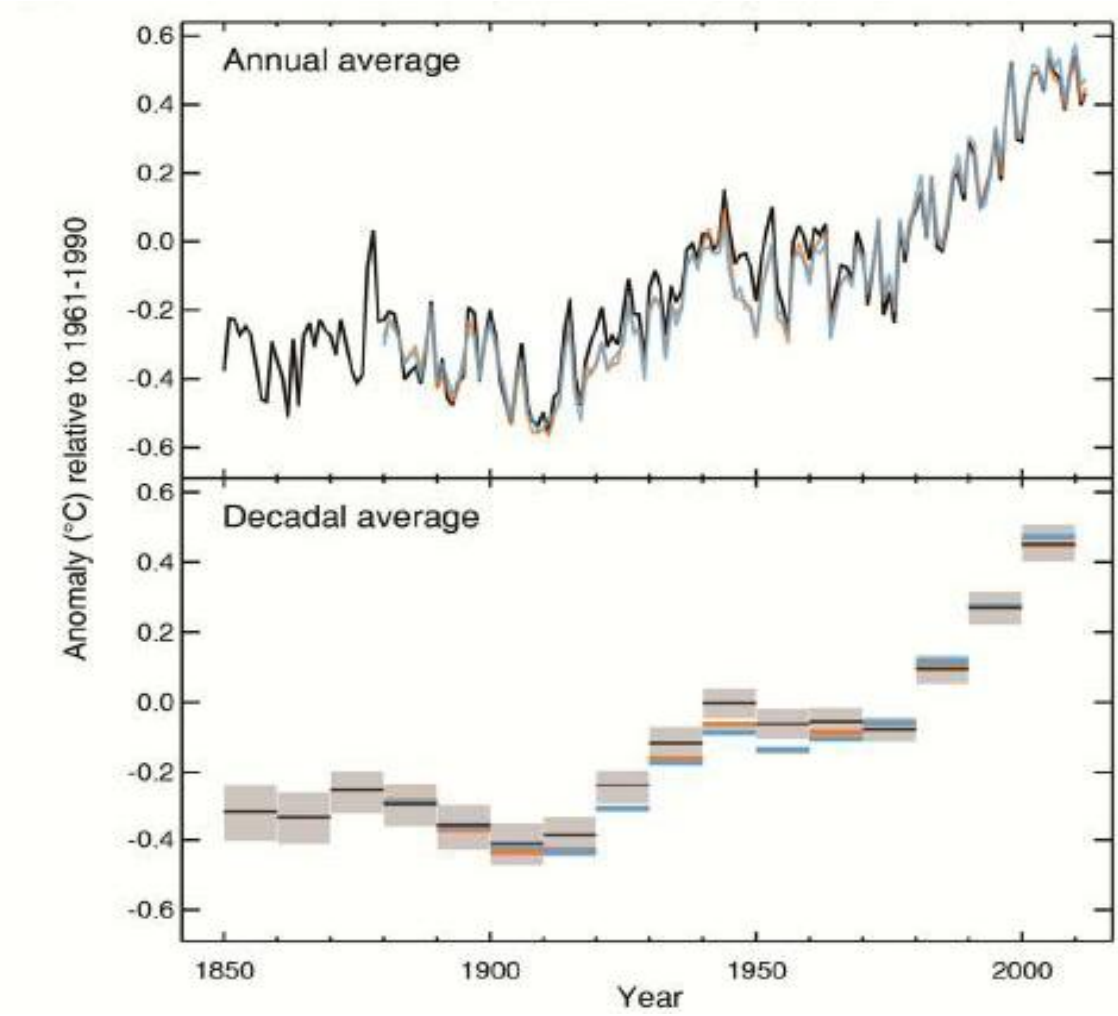


Figure 1.1. The measured global temperature curve from several data sets. Top: annual values. Bottom: averaged values over a decade **[7]**.

Natural sources of carbon dioxide are more than 20 times greater than sources due to human activity. But over periods longer than a few years, natural sources are closely balanced by natural sinks such as weathering of rocks and photosynthesis of carbon compounds by plants and marine plankton. As a result of this balance, the atmospheric concentration of carbon dioxide had remained between 260 and 280 parts per million (ppm) for thousands of years preceding 1850 (approximately the start of industrial revolution) **[8, 9]**. However, a declining trend in the long-term efficiency of these natural sinks in absorbing atmospheric CO_2 is observed. According to fourth IPCC Assessment Report, Figure 1.2 is showing the current atmospheric CO_2 concentration at 388 ppm **[10]**.

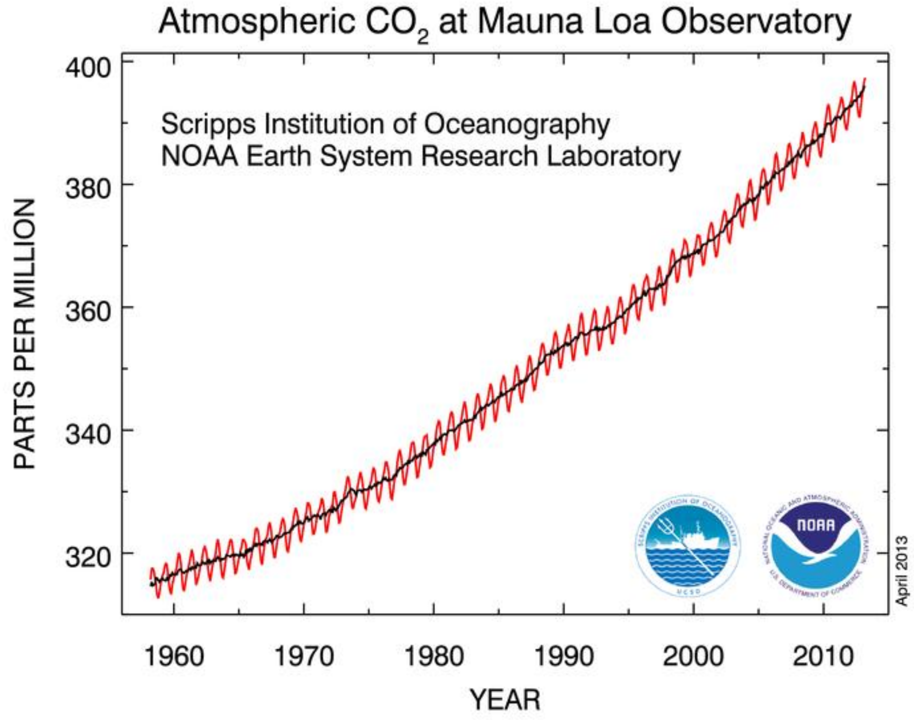


Figure 1.2. CO_2 concentration rise over the years **[10].**

In China and India, rapid economic growth and industrialization have resulted in dramatic emissions increases recently. The buildup of new coal power plants in China and India, and the existing installed base in the U.S. and elsewhere, present a tremendous challenge for reducing global CO_2 emissions over the next several decades **[11]**. India emitted 1751 Mt CO_2 equivalent greenhouse gases (GHGs) in 2005 and coal contributed 56% of these emissions. Indian CO_2 emissions in 2005 were 1229 Mt CO_2, and almost doubled during 1990-2005. It is estimated that total annual CO_2 emissions in India will increase 2.5 times during 2005-2030 to reach 3084 Mt CO_2 in 2030, growing annually at 3.7% **[2]**.

1.2 Need of Mitigating GHGs

Definitive changes in the Earth's global climate, such as increases in the average air and ocean temperatures, increased melting of snow and ice leading to rising sea levels, have already been observed. Additionally, the global emissions of greenhouse gases, in particular CO_2, are projected to grow over the coming decades leading to even greater changes in the Earth's climate **[12]**. GHGs will have effects on climate conditions like changes in the lengths of growing seasons, the availability of water, and the incidence of disturbance regimes like extreme high temperature events, floods, droughts, fires, pest outbreaks etc. Flood magnitude and frequency could increase in many regions as a consequence of increased frequency of heavy precipitation events, which can increase runoff in most of the areas. Systems and activities that are particularly sensitive to climate change and related changes in sea level include: forests, mountain, aquatic and coastal ecosystems, hydrology and water resource management, food and fiber production, human infrastructure and human health. Climate change would degrade water quality through higher water temperatures and increased pollutant load from runoff and overflows of waste facilities **[13]**.

Amid the dire warnings of severe weather perturbations and globally rising temperatures, scientists, engineers, policy makers, and others are searching for ways to reduce the growing threat of climate change **[14]**. There is no single solution, but recognizing the fact that the global dependence on fossil fuels will continue to rise, we need to make strategies and set targets to reduce greenhouse gas emissions. Rapid development and implementation of these strategies will be required so as to evade the warnings of potentially damaging climate change reported by the Intergovernmental Panel on Climate Change **[4]**. Although the magnitude and timing of any impacts from climate change remain uncertain, there is increasing pressure to reduce greenhouse gas emissions now. A major target is CO_2 from fossil energy use **[14]**.

To achieve these ambitious targets for large-scale fossil fuel use such as in coal and gas, power plants, and to avoid their potential adverse impacts from global climate change, the world community has adopted the United Nations Framework Convention on Climate Change (UNFCCC), which has as its objective “stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system” **[15]**.

There are three possible ways to reduce CO_2 emissions:

i. reduce energy consumption by minimizing losses and using more energy efficient programmes, (up to 20% reduction)

ii. reduce dependence on carbonaceous fuels by replacing it with renewable energy source and hydrogen rich fuel, (up to 10%) and

iii. employing carbon capture and storage (CCS) technology which could reduce emissions from power stations by as much as 90%, and the potential to contribute up to 28% of global carbon dioxide mitigation by 2050 **[4, 6]**.

By reducing CO_2 emissions, however, carbon capture and sequestration allow the use of fossil energy to continue, while buying time to make the transition to other energy sources in an orderly fashion **[14]**.

1.3 CO_2 Capture and Sequestration

Carbon capture and sequestration (CCS), is the process of capturing waste carbon dioxide (CO_2) from large point sources such as fossil fuel power plants, transporting it to a storage site, and depositing it where it will not enter the atmosphere, normally an underground geological formations.

Carbon dioxide capture and sequestration is a three step process (Fig. 1.3):

i. Capture of CO_2 from power plants or industrial processes,

ii. Transport of the captured and compressed CO_2 (usually in pipelines),

iii. Underground injection and geologic sequestration (also referred to as storage) of the CO_2 into deep underground rock formations. These formations are often a mile or more beneath the surface and consist of porous rock that holds the CO_2. Overlying these formations are impermeable, non-porous layers of rock that trap the CO_2 and prevent it from migrating upward **[16].**

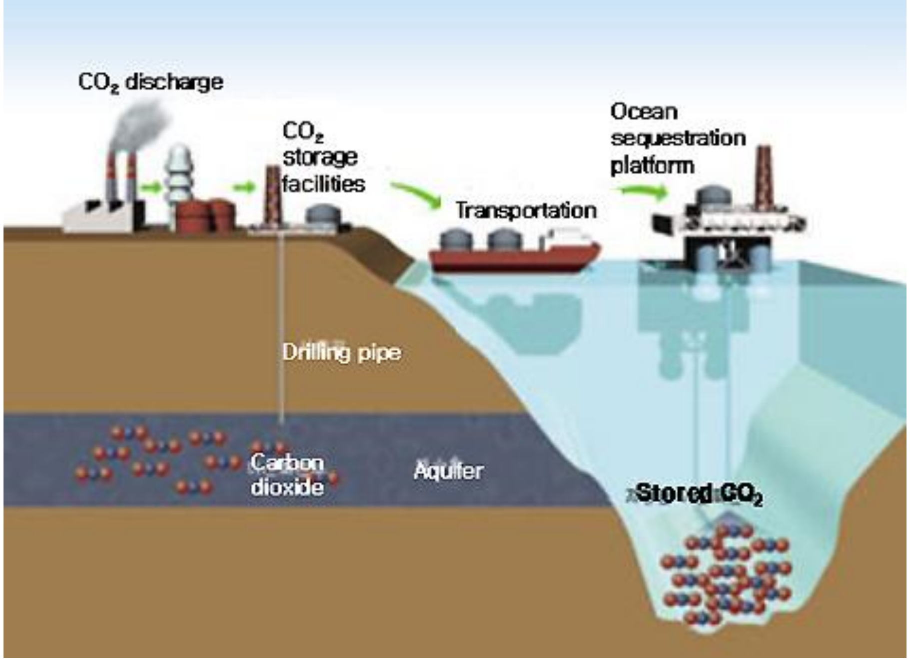


Figure 1.3. The main steps of CCS processes: capture, transportation, storage **[17].**

CCS is not a new or emerging technology. There are decades of operational experience in underground injection of CO_2 for enhanced oil recovery (where CO_2 is injected into the oil reservoirs to increase the mobility of the oil and thereby, increasing the productivity of the reservoir **[11, 18]**, and the use of technologies analogous to CCS, such as acid gas injection and natural gas storage. All the elements of CCS have been separately proven and deployed in various fields of commercial activity. A key step is the successful integration of large-scale CCS systems into commercial-scale power plants which still remains costly affair at current electricity and carbon prices. The costs involved in CCS technology depends on a number of variables and considerations, including the cost of fuel, the technological characteristics of the industrial power plant, the scale of the capture plant, the percentage CO_2 that can be captured, the characteristics of the storage site and the required transportation distance. It has been seen that CO_2 capture from high pressure, high CO_2 concentration streams can potentially be performed at lower cost than from exhaust gases from power production. In general, for CO_2 capture and storage from power station flue gas, the cost of CO_2 separation and compression dominates the CO_2 costs, making up to three-fourth of total specific CO_2 costs across the value chain **[19]**.

1.3.1 CO_2 capture

Capture of CO_2 can be applied to large point sources. Large point sources of CO_2 include large fossil fuel or biomass energy facilities, major CO_2 emitting industries, natural gas production, synthetic fuel plants, oil refineries and fossil fuel-based hydrogen production plants. Capturing CO_2 directly from small and mobile sources in the transportation and residential & commercial building sectors is expected to be more difficult and expensive than from large point sources **[19]**.

There are three basic approaches for capturing carbon dioxide from fossil fuels, namely post-combustion capture, oxy-combustion capture, and pre-combustion capture (Fig. 1.4).

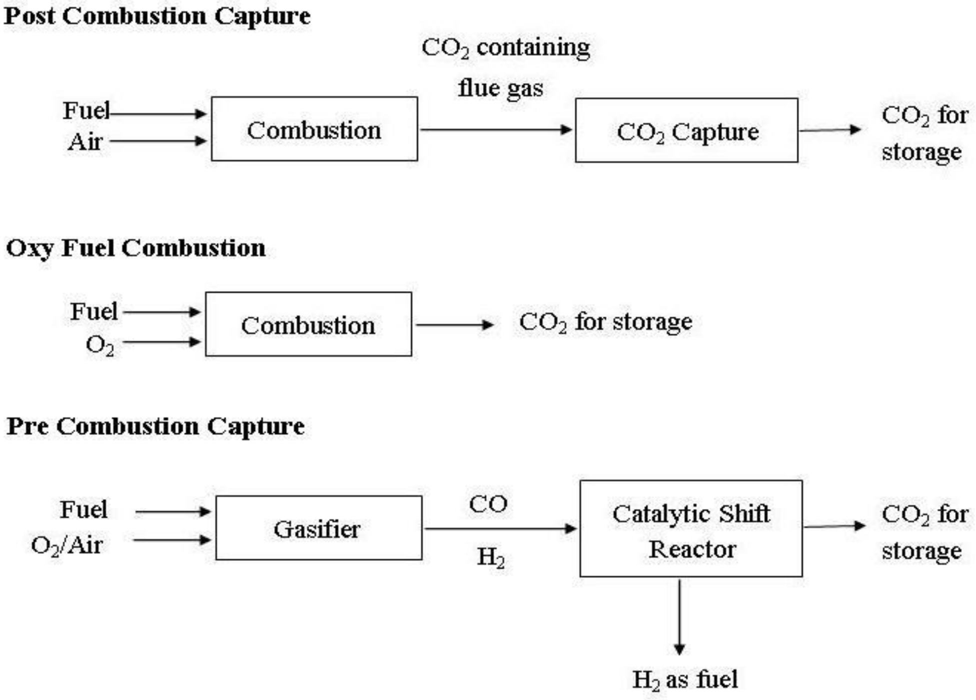


Figure 1.4. Three basic approaches to CO_2 capture **[9]**.

Post-combustion capture is a downstream process that is analogous to flue gas desulfurization and involves the removal of CO_2 from the flue gas after combustion of fuel. Instead of being discharged directly to the atmosphere, the flue gas is passed through equipment which separates/captures most of the CO_2 **[9]**.

In pre-combustion capture, the carbon content of the fuel is reduced prior to combustion, so that upon combustion, a stream of pure CO_2 is produced. An alternative to carbon capture from flue gas is to modify the combustion process so that the flue gas has a high concentration of CO_2. This can be accomplished by burning the fuel in nearly pure oxygen (greater than 95%), referred to as oxy-fuel combustion or simply oxy-combustion, instead of ambient air, thereby eliminating nitrogen and this results in a flue gas that is mainly CO_2 and H_2O. Post-combustion capture applies primarily to coal-fuelled power generators that are air fired. Oxy-combustion can be applied to new plants or retrofitted to existing plants. Pre-combustion capture can be applied to gasification plants **[20]**.

Post-combustion carbon capture has the greatest near-term potential for reducing GHG emissions, because it can be retrofitted to existing units that generate two-thirds of the CO_2 emissions in the power sector **[20]**. A number of methods exist for the post-combustion capture of CO_2 from flue gases.

These include:

i. Absorption
ii. Membrane separation
iii. Adsorption
iv. Cryogenic separation **[21]**.

CO_2 removal by reactive absorption/stripping using aqueous monoethanolamine (MEA) and other blended amine solvents has been established as a mature process, but this technique has various drawbacks such as high energy consumption, solvent evaporation, low cycling capacity, equipment corrosion and flow problems. Cryogenic separation is applied when the gas stream contains high CO_2 concentrations. It is energy intensive process and in case the volume of CO_2 in the exhaust gases is too low and is at atmospheric pressure then it becomes very expensive process. These conditions are usually encountered with typical power generation plants. Membrane separation is a relatively new technique with no moving parts and modularity but the selectivity is generally low and the energy consumption is high. Thus, for flue gas application it can be competitive only if CO_2 flue gas concentration is higher than 10%. On the other hand, adsorption has received much attention for its low energy consumption, low equipment cost, and ease of application **[22]**. It has recently been reported that the cost of the capture or separation step in post combustion CO_2 capture can be reduced by using this technology. Hence it appears to be a promising technology if effective and selective CO_2

adsorbents are developed. It can be performed on naturally occurring substances such as coal or more complex human-made sorbents such as activated carbon, molecular sieves, and zeolite, silica gel and aluminium oxide **[8, 9]**. The sorbents' ability is usually based on the pore size. When CO_2 is the target to be selectively adsorbed, gases smaller than CO_2 can also penetrate the pores. N_2 is the gas that fills up pore space in sorbents (the most common impurity) **[23]**. This makes the process less efficient as a lower degree of CO_2 separation can be achieved in each cycle.

Therefore, solid phase sorption could be a better substitute. A wide range of adsorbent materials like zeolites, activated carbons, molecular sieves, silica gel etc. could be used. However, in these conventional adsorbents physical adsorption plays an important role in adsorption of CO_2 but, these adsorbents need to be modified so as to facilitate chemical adsorption in them.

1.3.2 CO_2 sequestration

Carbon dioxide sequestration can be defined as the secure and fixed storage of CO_2 that would otherwise be emitted. The plan is:

i. to keep carbon emissions produced by human activities from reaching the atmosphere by capturing and diverting them to secure storage, or

ii. to remove carbon from the atmosphere by various means and store it.

Potential technical storage methods are geological storage (in geological formations, such as depleted oil and gas reservoirs, unminable coal seams that are dispersed worldwide and deep saline formations), ocean storage (direct release into the ocean water column or onto the deep seafloor), and industrial fixation of CO_2 into inorganic carbonates. CO_2 sequestration in geologic formations shows great promise because of the large number of potential geologic sinks.

It has been estimated that 1120 to 3400 Gt CO_2 can be sequestered in the formations identified so far **[20]** and the technology to inject CO_2 into the ground is well established.

Sequestration in deep saline formations or in oil and gas reservoirs is achieved by three mechanisms: displacement of the in situ fluids by CO_2, dissolution of CO_2 into the fluids, and chemical reaction of CO_2 with minerals present in the formation to form stable, solid compounds like carbonates. Initially displacement dominates, but dissolution and reaction become more significant over time scales of decades and centuries. Abandoned, uneconomic coal seams are another potential storage site. CO_2 diffuses through the pore structure of coal and is physically adsorbed to it. This process is similar to the way in which activated carbon removes impurities from air or water **[14]**. The combination of CO_2 storage with Enhanced Oil Recovery (EOR) or, potentially, Enhanced Coal Bed Methane (ECBM) recovery could lead to additional revenues from the oil or gas recovery **[19].** CO_2 is widely used fluid for EOR in depleted oil fields and by sequestering CO_2 in such fields oil production can be increased, which would offset the cost of CO_2 sequestration. By far, the ocean represents the largest potential sink for anthropogenic CO_2 seeing that it already contains an estimated 40,000 Gt C (billion metric tons of carbon) compared with only 750 Gt C in the atmosphere and 2200 Gt C in the terrestrial biosphere.

To sequester CO_2 economically, we need to first produce a relatively pure, high-pressure stream of CO_2. This is important because of the following reasons:

i. the economics of transporting CO_2 to any distance will be favorable for concentrated CO_2,
ii. sink capacity is better utilized by injecting pure CO_2 **[14]**.

1.4 Research Objectives

The overall objective of this research work is to develop solid adsorbents that will reduce the cost associated with carbon capture and storage in fossil fuel power plants. The specific objectives are:

i. Synthesis of adsorbents

ii. Characterization of the adsorbents for physico-chemical and other relevant properties

iii. Evaluation of the adsorbents for CO_2 capture and their kinetic studies

iv. Analysis of the results

1.5 Dissertation Structure

This dissertation is divided into five chapters. **Chapter One** introduces and discusses the need to mitigate $CO_{2,}$ systems available for CO_2 capture from fossil fuels, paying more attention to the current state of CCS and the effort towards improving this technology. It also presents the objectives of this work. **Chapter Two** covers the literature review relevant to the research. In this chapter, detailed literature on types of solid adsorbents, their development and modification. **Chapter Three** covers the materials, methods and techniques used in obtaining results presented in this dissertation. It also presents the working principles of the analytical equipment used. **Chapter Four** presents the results obtained by analyzing HMMM resin based adsorbents. In this chapter, the chemical and textural properties, and the CO_2 uptake capacity of the adsorbents were discussed. Finally, the conclusions drawn from the results and recommendations from this work are presented in **Chapter Five**.

CHAPTER-2
LITERATURE REVIEW

Adsorption and separation of CO_2 using porous, solid adsorbents is a promising alternative technique that has received tremendous attention in the past few decades. Adsorption is a heterogeneous process involving interaction between sorbent and foreign molecules. Due to this, CO_2 molecules are attracted and entrapped by surface groups of sorbent or physio-sorbed. Flue gases entering the stack typically contain N_2, CO_2, NO_x, SO_x, CO and particulate matter in various concentrations depending on type of industry and location of sampling point. Because adsorption performs optimally at low CO_2 concentrations (<2%), therefore it is typically used as a final polishing step in a hybrid CO_2 capture system. Regenerable solid adsorbents as an alternative have potential to offer several advantages for post-combustion CO_2 removal.

An ideal adsorbent for CO_2 capture should have following properties:

i. high CO_2 adsorption capacity (>1 mmol g^{-1} of sorbent),

ii. high surface area provides more adsorption sites,

iii. high selectivity for CO_2,

iv. low energy requirement for regeneration,

v. fast adsorption-desorption kinetics,

vi. chemical stability and tolerance to the presence of moisture **[21]**, and

vii. mechanical strength of sorbent particles.

The above mentioned attributes will rarely be optimal in any single adsorbent. However, we need an adsorbent that effectively and economically capture CO_2 from flue gas streams. A large variety of adsorbents are used commercially for CO_2 capture including activated carbon, zeolites or molecular sieves **[8]**, silica gel, and activated alumina and polymeric adsorbents. Others include mesoporous materials such as MCM-41 and SBA-15, oxides, and metal-organic frameworks (MOFs) **[24]**. These materials such as molecular sieves, zeolites and activated carbons have many specific features such as high surface area, thermal and chemical stability, and hydrophobic surface properties. They can be classified according to their pore diameters as microporous (pore size < 2 nm), mesoporous (2 nm < pore size < 50 nm), and macroporous (pore size > 50 nm) **[25].** Pore size controls the maximum dimensions of species than can reside within the material, allowing smaller species to reside in the pores of the adsorbent while rejecting species that are too big.

2.1. Activated-Carbon Based Solid Sorbents

Carbon-based porous materials, especially activated carbon find many applications as adsorbents or supports for various catalysts. Activated carbons have microcrystalline structures. Their adsorptive properties are due to their microporous structure, high surface area and high surface reactivity **[26, 27]**. They have adequate adsorption capacity for CO_2 at ambient temperature and atmospheric pressure. CO_2 adsorption capacity of activated carbon was found to be about 2.5 mmol g^{-1} at 25 °C and CO_2 partial pressure of 1 atm **[8]**. It has been reported that the CO_2 adsorption capacities of activated carbons decrease with increasing adsorption temperature due to the physical nature of the adsorption process. Wang et al. **[28]** in a comparative study reported that water has detrimental effect on CO_2 sorption at low pressure. Adsorption studies with activated carbon exhibit lower heat of adsorption and can be easily regenerated using pressure swing adsorption.

Thus, activated carbons need to be modified so as to facilitate chemical adsorption and hence improve the CO_2 adsorption capacity at high temperatures. The surface chemistry of the activated carbons can be efficiently modified by chemical impregnation which together with the intrinsic nature of the activated carbon can highly increase the adsorption capacity. According to the nature of the adsorbate, the surface chemistry of activated carbon can be modified by creating acidic or basic groups **[26]**. As CO_2 is an acidic gas, the presence of basic species can cause changes in basic character of the carbon surface which promotes the CO_2 capture capacity **[29]**. Increase in basicity can be achieved by various methods such as introducing nitrogen containing groups to the carbon structure, additives through impregnation, alkali metal or alkaline earth on the carbon surface, etc. Introduction of nitrogen groups to the carbon structure can be accomplished by treatment with ammonia or amines. The impregnation of carbon with various compounds may result in some negative effects, such as decrease in surface area and pore blocking in the structure of activated carbon. Instead, nitrogen containing porous carbons can be prepared directly from nitrogen-rich precursors such as acrylonitrile, melamine and cyanamide.

2.2. Zeolites

Zeolites are crystalline aluminosilicates of metals like sodium, potassium, magnesium, or calcium. The framework structure of zeolite is composed of a three dimensional network of basic structural units consisting of SiO_4 and AlO_4 tetrahedra linked through oxygen atoms. The structure contains interstitial voids and connecting channels, which are occupied by cations and water molecules. Commercial molecular sieves are generally of types A and X **[30]**. In general, zeolites have higher adsorption capacity and higher selectivity for CO_2 adsorption as compared to carbon based sorbents. But zeolites have high isosteric heat of adsorption for CO_2 adsorption and very strong nature of adsorption makes desorption difficult. Therefore, instead of pressure swing system it uses energy and time intensive temperature swing system for regeneration. Zeolites adsorption kinetics are extremely favorable for CO_2 adsorption. The most of known zeolites have CO_2 adsorption capacity at high pressures and low temperatures, which varies from 0.15 to 5.5 mmol g^{-1} of CO_2 at 0-60 °C **[31]**. It has been found that CO_2 adsorption capacity of zeolites 13X and 4A was about 3.64 and 3.07 mmol g^{-1} respectively at 25 °C and 1 atm CO_2 partial pressure **[8]**.

2.3. Metal -Organic Frameworks (MOFs)

MOFs are built from metal ions with well-defined coordination geometry and organic bridging ligands. They have ordered structures with high thermal stability, adjustable chemical functionality, extra-high porosity, and the availability of hundreds of crystalline, well-characterized porous structures. They are extended structures with carefully sized cavities that can adsorb CO_2. High storage capacity is possible with less heat requirement for recovery of the adsorbed CO_2. On comparison of gravimetric CO_2 capacities for several MOFs and activated carbon at ambient temperature and pressures up to 42 bars, it was found that MOF-177 had highest adsorption capacity of 33.5 mmol g^{-1}, which was far greater than that of other porous material such as zeolites (7.4 mmol g^{-1} at 32 bars) and activated carbon (25 mmol g^{-1} at 35 bars) **[32]**. The capacity of MOF is reduced in presence of impurities as they will compete with CO_2 for adsorption sites. Water vapor has been shown to pose a serious problem as they will displace ligands and create structural defects in crystalline lattice of the MOF.

Activated carbons give higher additional capacity at pressures greater than atmospheric compared to zeolites and MOFs. Also they are often preferred over zeolites for CO_2 adsorption due to the moderate strength of adsorption which makes desorption process easy and effective. Since CO_2 is strongly adsorbed on zeolites, it cannot be desorbed sufficiently by decreasing pressure **[33]**. A significant adsorption capacity for the CO_2 can be achieved even when the flue gas contains moisture. Most polar adsorbents like zeolites, silica and alumina gels show large decrease in adsorption capacity under such moist conditions. Presence of other gases such as sulphur dioxide and nitrogen dioxide in flue gases greatly affects CO_2 adsorption capacity on activated carbon.

However, in these conventional adsorbents, physical adsorption plays an important role in the adsorption of CO_2 **[8]**. Materials like zeolites and activated carbons have high surface areas (>1500 m^2 g^{-1}) and adsorb selectively different gases depending on their surface area, pore size, pore volume and surface chemistry **[34]**. They can reversibly adsorb a large quantity of CO_2 at room temperature but their capacity diminishes quickly at elevated temperatures. Their selectivity for CO_2 in the presence of water is also poor **[35]**. Thus, these adsorbents need to be modified so as to facilitate chemical adsorption in these adsorbents. Hence, there is an increasing demand to design highly selective adsorbents, which can operate at such high temperatures **[8]**.

Carbonaceous porous solids such as zeolites or activated carbon are good candidates for capturing CO_2 from flue gas through physical adsorption. High porosities endow activated carbon and zeolites with CO_2 capture capacities of 3–4 mmol g^{-1}. However, the CO_2/N_2 selectivity of activated carbon is relatively low, which makes carbon-based systems practical only for CO_2-rich flue gas. Although zeolites offer better CO_2/N_2 selectivities, but their CO_2 capacities degrade significantly, when water vapor is present in the flue gas **[36]**.

2.4. Amine Functionalized Solid Sorbents

At present, CO_2 capture on amines immobilized in porous solid sorbents has been an increasingly active area of research. A variety of amines, supports and immobilizing techniques have been studied with promising results. In contrast to amine scrubbers, solid-supported amine sorbents offer significant advantages for CO_2 capture, including potential elimination of corrosion problems and lower energy cost for sorbent regeneration. Solid-supported amine sorbents exhibit high selectivity and reversibility for CO_2 capture due to the specific CO_2–amine chemistry. Moreover, adsorption on amine functionalized adsorbents occurs via chemisorptions. Unlike zeolites and activated carbon, amine-functionalized sorbents have been proved to be tolerant to moisture during CO_2 capture, thus eliminating the need for strict humidity control prior to CO_2 capture **[31]**.

Because of their numerous advantages, intensive efforts have been directed towards the development of solid-supported amine sorbents in comparison to the liquid phase amine scrubbing technology which suffers from inherently high regeneration cost, equipment corrosion, and amine oxidative degradation. Essentially, two strategies have been used: covalently tethered or physically impregnated amines to solid supports with large surface area such as mesoporous materials.

Jones et al. **[37]** developed a hyper branched aminosilicate material by a one-step reaction between aziridine and SBA-15, and achieved a capacity about 3.1 mmol g^{-1} at 25 ºC in simulated flue gas conditions. Song et al. **[38]** reported the first polyethylenimine impregnated MCM-41 sorbent with a capacity around 3 mmol g^{-1} at 75 ºC in 1 atm dried CO_2. The capacity was further improved to 3.2 mmol g^{-1} using SBA-15 as support in simulated flue gas conditions. Synthesized MCM-41 particles were also tested as support for tetraethylenepentamine and high CO_2 capacity of up to 5.4 mmol g^{-1} was obtained at 75 ºC in 1 atm dried CO_2.

Although solid-supported amine sorbents provide a promising alternative for CO_2 capture, high capture efficiency with good recyclability are required in order to develop an economically feasible industrial-scale process. Schuette et al. **[39]** have evaluated post-combustion CO_2 capture options based on a plant producing 1060 tons CO_2 per day. They compared the cost of capturing 90% CO_2 using 20% MEA solution vs. a solid sorbent based on polyethylenimine impregnated mesoporous silica. According to their calculations, if the CO_2 capture capacity is less than 3 mmol g^{-1} the economics will favor MEA. However, the solid sorbent starts becoming more favorable compared to MEA as the capture capacity increases to more than 4 mmol g^{-1}.

In India, National Environmental Engineering Research Institute (NEERI), Nagpur, is working in this area and the study by Chatti et al. **[8]** describes the feasibility of amine-loaded zeolites for carbon dioxide capture. Novel functionalized adsorbents had been synthesized by immobilization of various amines like monoethanol amine, ethylene diamine etc on synthetic zeolite 13X. Effect of various parameters like effect of solvent, shaking time, synthesis temperature, and wetting of pellets prior to amine loadings was also studied. The adsorption capacities obtained were 0.36 mmol $g^{-1}$of CO_2 for unmodified zeolite 13X and 0.45, and 0.52 mmol g^{-1} of CO_2 for zeolite modified with monoethanol amine, and isopropanol amine respectively **[8]**.

Zeolite 13X had been modified with monoethanol amine using methanol as the solvent. The adsorbent had been characterized for crystallinity, surface area, pore volume, and pore size. The CO_2 adsorption capacity of adsorbents was evaluated using the breakthrough adsorption method in the temperature range of 30–120 °C. The adsorbents showed improvement in CO_2 adsorption capacity over the unmodified zeolite by a factor of ca. 1.6 at 30 °C, whereas at 120 °C the efficiency improved by a factor of 3.5. The adsorbent was also studied for CO_2 selectivity over N_2 at 75 °C. The MEA modified adsorbent had selectivity for CO_2 over N_2 1.4 times more compared to bare zeolite 13X **[40]**.

Xu et al. **[41]** synthesized a new type of composite adsorbents by incorporating monoethanol amine into β-zeolite. The results showed that the structure of zeolite did not deteriorate after MEA modification. In comparison with CH_4 and N_2, CO_2 was preferentially adsorbed on the adsorbents investigated. The introduction of MEA significantly improved the selectivity of both CO_2/CH_4 and CO_2/N_2. Very high selectivity of CO_2/N_2 of 25.67 was obtained on 40 wt% of MEA-functionalized β-zeolite (MEA (40)-β) at 1 atm and 30 °C.

2.5 Templated Porous Carbons

Among all the adsorbents, activated carbons present a series of advantages as CO_2 adsorbents: they are inexpensive, insensitive to moisture, present a high CO_2 adsorption capacity at ambient pressure, easy to design pore structure, surface functionalization, exhibit high surface area and pore volume and ease for regeneration. Besides, almost any carbonaceous material can be converted into an activated carbon by a first step of carbonisation followed by a second step of activation. The properties of the final product will depend upon the nature of the raw material, activating agent, and the conditions of the carbonisation and activation processes. CO_2 is a common activating agent that reacts with carbon at high temperatures releasing gaseous CO. With low CO_2 flow rates and temperatures that are not very high, the consumption of carbon leads to considerable textural development. On the contrary, high flow rates and temperatures cause the external surface of the particle to burn, resulting in a poor porous texture development. The role of CO_2 as a weak Lewis acid is well known and therefore, it is expected that the introduction of Lewis bases onto the surface of an activated carbon may favour the CO_2 capture performance. Several works have already been published indicating enhancement of CO_2 adsorption by incorporating basic nitrogen functionalities. Although the amount of nitrogen in carbon materials is generally low but, it can be incorporated into the carbon structure by causing the carbon to react with gaseous ammonia **[42]**.

Researchers are looking for ways to develop materials with controlled structural characteristics by means of synthetic strategies such as sol–gel technique or micro-emulsion methods. But, these methods require large amounts of organic liquids, expensive reagents (i.e. surfactants), precursors (i.e. organo-metallic), and complex preparation sequences which makes the prediction of resulting mesostructure more difficult. So, to overcome these disadvantages a synthetic strategy based on the nanocasting technique can be used **[43]**.

2.5.1 Principle of nanocasting process

The nanocasting pathway mainly involves three steps: first infiltration of mesopores with a proper precursor, and then thermal treatment of impregnated sample composite under a controlled atmosphere to convert the infiltrated precursor into a rigid framework followed by removal of hard template by chemical reaction method **[44]**. With this synthetic strategy, we can alter the structure of the synthesized inorganic compounds based on the pore characteristics of the selected template **[43].** The beauty of this approach is the enhanced replication of complicated pore phases of the template with defined structural and compositional control **[44].**

2.5.2 Template

Mesoporous silicate materials with highly ordered pore structures and uniform pore size are more ideal templates. Moreover, a 3-D pore structure makes the material interconnect with each other and maintains the topologies of template after removal of template to achieve interesting replica mesostructures. MCM-41is a mesoporous silicate possess 2-D hexagonal symmetry with disconnected cylindrical pores, uniform pore size, but their silicate pore walls are amorphous **[44]**. The pore connectivity of the template directly affects the structure of the mesoporous replicas. Hence, when the template consists of a fully continuous solid phase and connected pore channel system (for instance activated carbons, silica gels or meso-structured silica), the material obtained may retain a 3-D structure containing framework-confined pores. Such a product is an inverse replica of the template structure and may be referred to as a nano-structured material. For the preparation of such nanostructures an extra requirement is necessary, i.e. the filling degree of the porosity of the template by the precursor solution. However for templates whose porosity is made up of non connected pores will produce solids without framework confined pores. When the concentration of infiltrated inorganic species is low or template exhibits non-connected porosity, the inorganic compound formed will have aggregation of non porous nanoparticles **[43]**.

2.5.3 Precursor

To achieve excellent replication, the precursor need to be in situ transformed to the target materials within the mesopores of the template and without escaping out of the pore system. Precursor is dissolved in certain solvent to facilitate easy and sufficient infiltration. The precursor containing solution then enters the open pore system by capillary force and is well distributed into all the vacancies of the template and migrates on the surface during the evaporation of solvent. Besides capillary force, wettability and mobility of precursors on the surface are key factors. They require stronger interaction between precursors than between precursors and pore surface because an over strong interaction between precursors and pore walls will inhibit migration and aggregation of precursors and partially block the channels, leading to failure of infiltration. Moreover if interaction is too weak, impregnation of precursors cannot occur because surfaces are not able to be wetted due to weak capillary force.

2.5.4 Solvent

The choice of solvent plays an important role as the solubility of precursors for the infiltration depends on it. Generally, higher the solubility better precursor filling and higher infiltration efficiency. Solvation of inorganic precursors has an influence on migration and aggregation which affects the surface wettability and hence the capillary force. Ethanol serves as ideal solvent as it has: (1) lower boiling point than water and is more volatile; (2) mild interaction with precursors facilitating facile migration and aggregation of precursors; (3) most inorganic precursors are soluble in ethanol. In addition, ethanol enhances the capillary force due to its amphiphilic property compatible to silica pore wall surface.

2.5.5 Processing

This technique of solvent-evaporation induced capillary condensation is widely used and it includes dissolution of precursor in a volatile solvent to form a dilute solution, then addition of calculated amount of hard template into the solution by moderate stirring, followed by evaporation of the solvent. Owing to the capillary force, the solution is infiltrated into the mesopore channels and finally adsorbed in all the pore vacancy. Upon solvent evaporation the precursors migrate on the surface and aggregate together. The negative aspect of nanocasting is the difficulty for nanochannels of hard templates to become fully filled with precursors, leading to limited mesostucture ordering **[44]**.

From the industrial point of view, where columns packed with adsorbents are mainly utilized for gas separation and purification processes and adsorption is followed by desorption of the strongly adsorbed component in order to regenerate the adsorbent to make the process economically viable. Therefore, we need an adsorbent that has low energy requirements for regeneration. So, to improve the CO_2 adsorption capacity and regeneration capacity, porous carbon with high nitrogen content and high surface area would be highly desirable.

CHAPTER-3
EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals and reagents

Hexamethoxymethylmelamine (HMMM) is methylated melamine formaldehyde resin (fig 3.1). It was procured from M/s Techno Waxchem Pvt. Ltd. It has structural formula $C_{15}H_{30}N_6O_6$ (Mol. Wt.: 390.44 g mol^{-1}) and specific density of 1.192. HMMM containing resins are formed by methylolation of melamine with formaldehyde in the presence of acid or alkali, followed by methylation with methanol in the presence of acid. Commercial methylated melamine formaldehyde resins are complex mixtures of dimers, trimers and higher oligomers. HMMM resins are used as crosslinkers in thermoset coatings. The typical commercial form is either a solid wax or liquid at ambient temperatures.

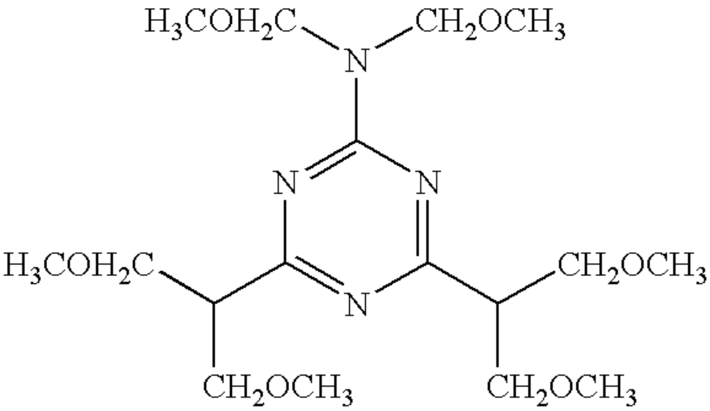


Figure 3.1. Chemical stucture of HMMM

Mesoporous silica (MCM-41) was used as the template. It was procured from M/s Tianjin Chemist Scientific Ltd., Tianjin, China. Its chemical formula is SiO_2. It has surface area in the range of 450 m^2 g^{-1} and average pore diameter of 3.5 nm. Ethanol (100% pure) was used as solvent and was purchased from M/s S. D. Fine Chemicals Ltd., India.

Dry nitrogen and dry carbon dioxide gases were provided by M/s Sigma Gases and Services, India. Nitrogen was Grade-1 (99.995% pure) gas. Carbon dioxide was Instrument Grade (99.999% pure) to exclude the effects of moisture and other impurities.

3.2 Synthesis of Carbon

HMMM was used as carbon precursor and mesoporous silica MCM-41 was used as template. For adsorbent synthesis, HMMM resin was dissolved in ethanol and then mixed with silica particles to form templated resin. The mixture with a mass ratio of SiO_2/HMMM at 2:1 was obtained by evaporating excessive solvent at 120 ºC for 3 hours.

The carbonization was conducted in a horizontal programmable furnace (fig 3.2). The ceramic boats containing templated resin were placed in a quartz tube under N_2 flow of 60 ml min^{-1} and at heating rate of 10 ºC min^{-1} until the desired carbonization temperature is achieved for soaking time of 1 hour, followed by physical activation by switching the gas from N_2 to CO_2 at flow rate of 60 ml min^{-1} for 1 hour under isothermal conditions. Series of adsorbents were prepared by varying carbonization temperature to 500 ºC, 600 ºC, 700 ºC, 800 ºC. After the physical activation the gas flow was switched back to N_2 and sample was allowed to cool down to room temperature. The purpose is to enrich carbon content and to create enhanced porosity and some ordering of the structure.

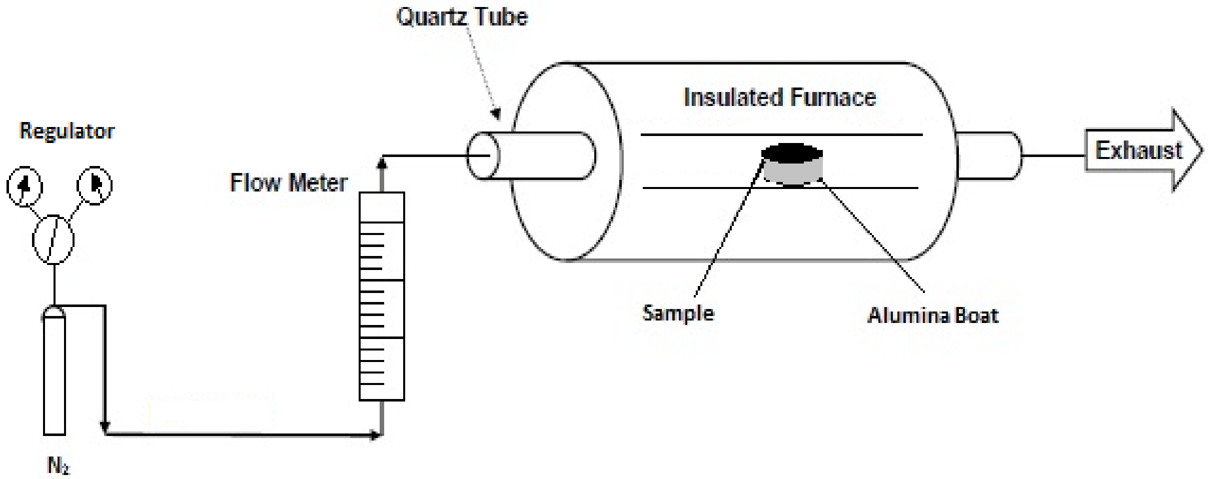


Figure 3.2. Schematic diagram of tubular furnace **[12]**.

The template removal was achieved by dissolution of the samples in 40 wt% NaOH solution for at least 24 hours because silica reacts with it to generate movable gaseous or dissolvable products. The samples were then filtered to remove the template followed by washing with copious amounts of water until neutral pH. After this, the samples were dried in the oven at 100

°C for 3 hours. The carbon samples were designated as C-T, where T stands for the carbonization temperature.

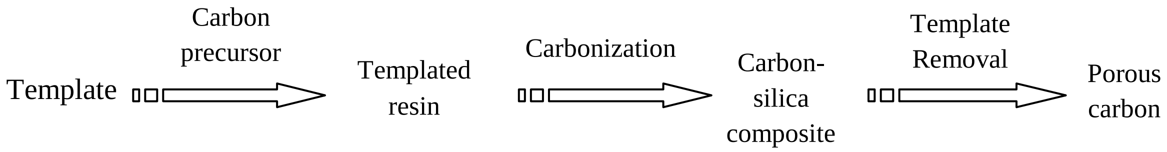


Figure 3.3. Schematic illustration of development of adsorbent by nanocasting.

3.3 Characterization

3.3.1 CHNS analysis

For chemical characterization CHN analysis were carried out to analyze the elemental (H, C, N, O) composition of a chemical compound. It examines the weight percent of each element present in the compound to determine the compound's composition. The elemental analysis of the synthesized adsorbents was conducted using the Thermo scientific (UK) Flash 2000-Organic Elemental Analyzer (CHNS-O analyzer).

3.3.2 Total Kjeldahl nitrogen (TKN)

Nitrogen was estimated by Total Kjeldahl nitrogen (TKN) method as well to determine nitrogen content. The standard procedure was followed according to American public health association (APHA). The method includes 3 steps: digestion, distillation and titration. In the digestion step, amino nitrogen of many organic materials is converted to ammonium in the presence of sulfuric acid (H_2SO_4), potassium sulfate (K_2SO_4), and cupric sulfate ($CuSO_4$) catalyst. Free ammonia is also converted to ammonium. After this, distillation of the samples is carried out with small quantity of sodium hydroxide (NaOH) to distil off ammonia and is absorbed in boric acid. To quantify amount of ammonia, titration is carried out with a standard mineral acid and indicator.

3.3.3 Surface area and pore volume analysis

For textural characterization, the surface area and pore volumes of the adsorbents were evaluated. The specific surface area (S_{BET}) was determined from N_2 isotherms performed at 77 K on a Micrometrics ASAP-2000 volumetric adsorption system using the Brunauer-Emmet-

Teller (BET) equation and the total pore volume (V_{total}) was calculated from amount of N_2 adsorbed at relative pressure of P/Po=0.99. The micropore volume (V_{micro}) was determined by t-plot model and the mesopore volume (V_{meso}) was calculated by the difference of V_{total} and V_{micro}. The pore size distribution curve was obtained from desorption branch by using Barrett-Joyner-Halenda (BJH) method. Prior to any measurement, samples were outgassed 200 ºC for 6 hours under vacuum.

3.3.4 X-ray diffraction (XRD) analysis

Wide-angle X-ray diffraction (WAXD) is an X-ray-diffraction technique that is often used to determine the crystalline structure. This technique specifically refers to the analysis of Bragg peaks scattered to wide angles, which (by Bragg's law) implies that they are caused by sub-nanometer-sized structures. In wide-angle X-ray scattering, the distance from sample to the detector is shorter and thus diffraction maxima at larger angles are observed. According to this method the sample is scanned in a wide-angle X-ray goniometer, and the scattering intensity is plotted as a function of the 2θ angle. X-ray diffraction is a non destructive method of characterization.

The synthesized adsorbents were characterized using an XRD with X'Celerator (X'Pert PRO, PANalytical, Netherlands) with monochromatic Cu Kα radiation. During the analysis, the scanning speed and diffraction angle were 10° min^{-1} and 10–80° (2θ) respectively at 45 kV and with a current of 40 mA.

X- ray diffraction method can also be applied for the measurement of particle size and a particle may consist of several crystallites. The average crystal size can be calculated according to most intense peak of the XRD pattern using the Debay-Scherrer's formula shown in Equation 3.1.

$$D = \frac{0.89\,\lambda}{b\ Cos\ \theta} \tag{3.1}$$

The equation uses the corrected reference peak width at angles θ (º), where λ is wavelength of incident X-ray (nm), b is the corrected width of the XRD peak at half height (º) and D is the average diameter (nm).

3.3.5 Scanning electron microscopy (SEM) analysis

The scanning electron microscope uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens producing a 2-dimensional image that displays spatial variations in the properties of sample. The signals obtained from electron-sample interactions reveal information about those sample properties including surface morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. The signals include scattered electrons emitted by atoms excited by electron beam.

The surface morphology of the samples (synthesized adsorbents) was analyzed by using Scanning Electron Microscope (JEOL, Model JSM 6510 LV). The accelerating voltage was 20 kV. Samples were mounted using conductive carbon double sided sticky tape and were coated with thin (ca. 10 nm) gold film in an automatic sputter coater (Polaron) to avoid charging under an electron beam prior to SEM studies. SEM of all the samples was carried out at 2000 magnification.

3.4 CO_2 Capture Performance

3.4.1 Equipment

TA Instruments Thermo Gravimetric Analyzer (TA, Model Q500) was used to assess the CO_2 adsorption potential of the samples at atmospheric pressure. A thermogravimetric analyzer (TGA) monitors the change in weight of sample as function of temperature (or time) as it is subjected to a specified heating programme in a controlled atmosphere. The equipment consists of sample pan loaded on a highly sensitive mass balance, a furnace and thermocouple. The furnace can be heated upto temperature of 1000 ºC. The system has a capacity of 1.0 g, a sensitivity of 0.1 μg and an accuracy of ± 0.1%. The TGA is linked to a computer having TA instruments universal analysis software which is used to control the equipment and display the TGA data on common axis of time and/ or temperature. Gas cylinders containing nitrogen and carbon dioxide of ultra high purity were connected via gas lines to the equipment. The flow rate of the gases into the equipment was controlled by the software.

3.4.2 Procedure

Prior to TGA study the samples were degassed overnight in oven at 200 ºC. In a typical experiment, ca. 20 mg of sample was loaded onto a platinum pan and subjected to drying process under an inert atmosphere of pure N_2 (flow rate = 50 ml min^{-1}). During this treatment, the samples were heated to 200 ºC at ramp rate of 10 ºC min^{-1}. The temperature was held at this temperature for 60 min until the sample weight was stable and to guarantee removal of any remaining moisture, solvents, or other adsorbates from the sample. Temperature was then decreased to desired adsorption temperature (i.e. 30 ºC) and the gas was switched to CO_2 with flow rate of 50 ml min^{-1}and the balance purge flow of N_2 was held at 1 ml min^{-1} throughout to achieve 100% CO_2 (99.999%) atmosphere in the TGA furnace. Adsorption was carried out till saturation was achieved. After CO_2 adsorption, the gas flow was switched from CO_2 to N_2 for desorption and the temperature was increased to 200 ºC. The change in weight of the adsorbent recorded by TGA analyzer was observed to estimate the adsorption capacity (mmol g^{-1}) of samples. No corrections were performed for buoyancy effects as they are negligible in case of horizontal balance.

3.5 Adsorption Kinetic Models

Studies on CO_2 adsorption/desorption kinetics are desirable to evaluate the performance of adsorbents and to determine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction. Prediction of CO_2 adsorption kinetics is necessary for the rational design and simulation of gas-treating units. To investigate the kinetics of adsorption of CO_2 onto synthesized adsorbents, the following models were considered in this present work:

i. Pseudo-first-order model:

It is the earliest model to describe the adsorption process. The Lagergren's pseudo-first-order rate equation expressed as:

$$\frac{dq_t}{dt} = k_1 \ (q_e - q_t) \tag{3.2}$$

Where, q_t and q_e (mg g^{-1}) are adsorption capacities at time t and at equilibrium respectively and k_1 is the rate constant of the pseudo-first-order adsorption (min^{-1}).

ii. Pseudo-second-order model:

The pseudo second order equation is expressed as:

$$\frac{dq_t}{dt} = k_2 \ (q_e - q_t)^2 \qquad (3.3)$$

where, q_t and q_e have same definitions as for pseudo first order equation and k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order adsorption.

The least squares criterion was used to determine the best fit of kinetic model. To determine the adequacy of model, the coefficient of determination (R^2) and the average absolute percentage deviations according to Eq. (3) indicated the fit between the experimental and calculated data:

$$\mathrm{ABPD}\,\% = \frac{\sum_{i=1}^{n}\left|\left(\frac{(q_{exp}-q_{cal})}{q_{exp}}\right)\right|}{N} \times 100 \qquad (3.4)$$

Where, ABPD (%) is the average absolute percentage deviations, where q_{exp} and q_{cal} are the experimental and calculated adsorption capacity, respectively and N is the total number of experimental points **[45].**

The experimental results were statistically analyzed using Origin 8 software.

CHAPTER-4
RESULTS AND DISCUSSION

4.1 Characterization of Adsorbents

4.1.1 CHNS analysis

The chemical characteristic of the adsorbents is presented in table 4.1. With increase in carbonization temperature, there is decrease in the nitrogen content. This shows that nitrogen is oxidized and more easily removed than carbon because there is no significant change in the latter and appears to be relatively independent of carbonization temperature**.** On the other hand, oxygen content increases, probably due to some chemisorption of oxygen during the heterogeneous reaction between the CO_2 and carbon.

Table 4.1 CHNS analysis of adsorbents.

Samples	**Elemental analysis (wt.%, db)**			
	N	**C**	**H**	**O***
C-500	21.2	63.9	1.9	12.9
C-600	15.9	63.1	2.6	18.4
C-700	13.6	61.7	1.4	23.2
C-800	9.2	64.2	1.9	24.7

db: dry basis

*Calculated by difference

4.1.2 Total Kjeldahl nitrogen (TKN)

The nitrogen content estimated by total Kjeldahl nitrogen (TKN) method was in good agreement with nitrogen content estimated by elemental analysis for all the samples (fig 4.1). This reduction was drastic from 700 to 800 ºC.

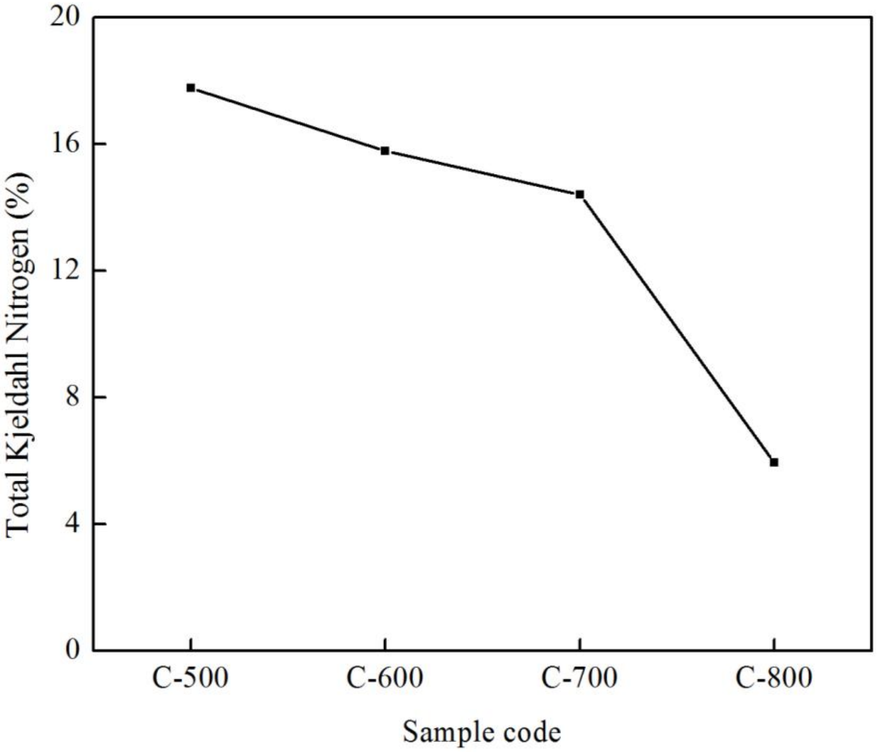


Figure 4.1. The effect of carbonization temperature on TKN of synthesized adsorbents.

4.1.3 Surface area and pore volume analysis

The typical nitrogen adsorption/desorption isotherm at 77 K of the prepared carbon C-700 (fig 4.2) belong to type IV isotherm according to the IUPAC classification of isotherms. It contains sharp capillary condensation step at relative pressures ($P/P_o > 0.9$) and a H4 hysteresis loop, indicating existence of mesopores in the material. As relative pressure further increases to 1, no increase in adsorption is observed, indicating absence of macropores. As shown in table 4.2, the surface area and total pore volume showed a tendency to increase with increasing carbonization temperatures to the C-700 sample but a decrease at higher temperature (C-800 sample). The BET surface area for sample C-700 is 463 $m^2\ g^{-1}$ which is maximum among all the prepared adsorbents. There are many external pores between the particles which facilitate diffusion of gas from the bulk of gas phase to surface of adsorbent. All samples show rapid increase in adsorption isotherms at very low relative pressure indicating presence of micropores that might have developed due to CO_2 activation. The decrease in surface area can be attributed to the portion of pores that were destroyed due to collapse of pore structure at higher temperature.

Table 4.2 Textural parameters of adsorbents.

Sample Code	**S_{BET} (m^2 g^{-1})**	**V_{total} (cm^3 g^{-1})**	**V_{micro} (cm^3 g^{-1})**	**V_{meso} (cm^3 g^{-1})**	**Average pore diameter (nm)**	**Average particle size (nm)**
C-500	321.72	0.36	0.07	0.29	6.13	18.65
C-600	389.93	0.34	0.08	0.26	4.36	15.39
C-700	463.37	0.48	0.09	0.39	5.69	12.95
C-800	111.75	0.12	0.02	0.10	5.47	53.69

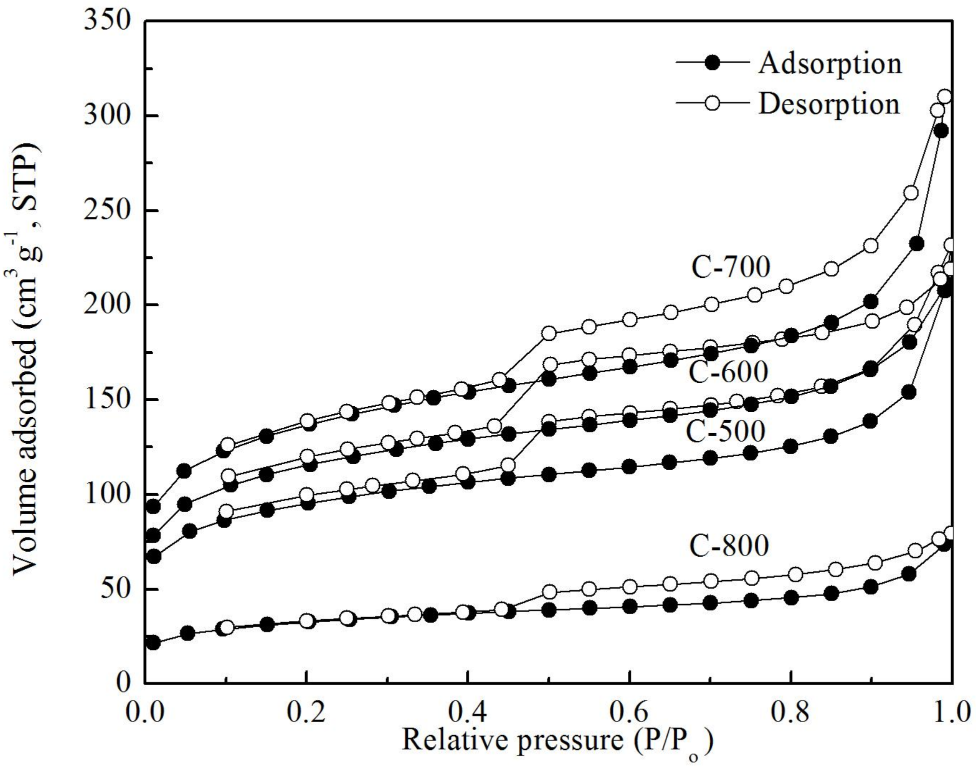


Figure 4.2. Nitrogen adsorption-desorption isotherms for resultant adsorbents.

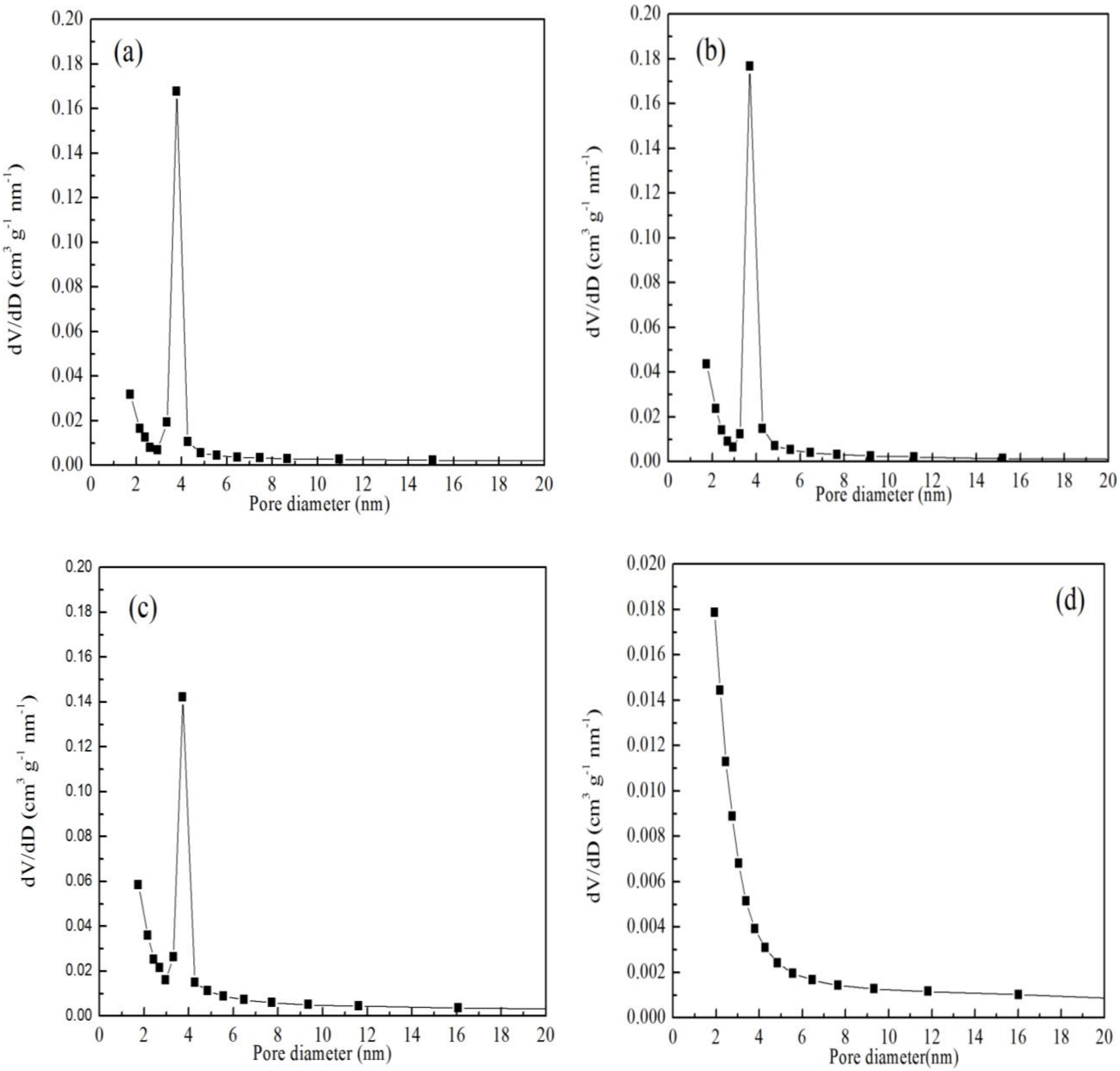


Figure 4.3. BJH pore size distribution of (a) C-500, (b) C-600, (c) C-700, (d) C-800.

The pore volume has trend similar to surface area with highest pore volume of 0.48 cm^3 g^{-1} for sample C-700 (large pore volume means more space is available for CO_2 adsorption). The substantial decrease in pore volume of sample C-800 is probably due to severe gasification reaction along with sintering effect of volatiles resulting in the narrowing and closing up of some pores. Average pore diameter of porous carbons produced in range of 500-800 ºC, was ca. 5-9 nm. As shown in fig 4.3, all samples consisted mainly of mesopores < 50 nm in diameter. Samples C-500, C-600 and C-700 exhibit bimodal and relatively uniform pore size distribution with pore size maxima 1.9 and 4 nm while sample C-800 has unimodal distribution at pore size maxima of 2.7 nm (fig 4.3). Nevertheless, the pore volume of C-800 significantly reduced to 0.12 cm^3 g^{-1} and the pore size distribution shifts from 4 to 2.7 nm. Both trends indicate that the mesostructure of C-800 partially collapses.

4.1.4 X-ray diffraction (XRD) analysis

The XRD patterns of all the adsorbents, synthesized by varying carbonization temperature did not exhibited many diffraction peaks but one intense peak in the range of 2θ = 25-27°, which can be ascribed to (002) diffractions from graphitic pore walls (fig 4.4). In addition, all the samples show a weak broad diffraction at/near 2θ = 43.8° corresponding to superposition of the (100) and (101) reflections of the graphitic carbon which indicate that the material presents disordered stacking of micrographites.

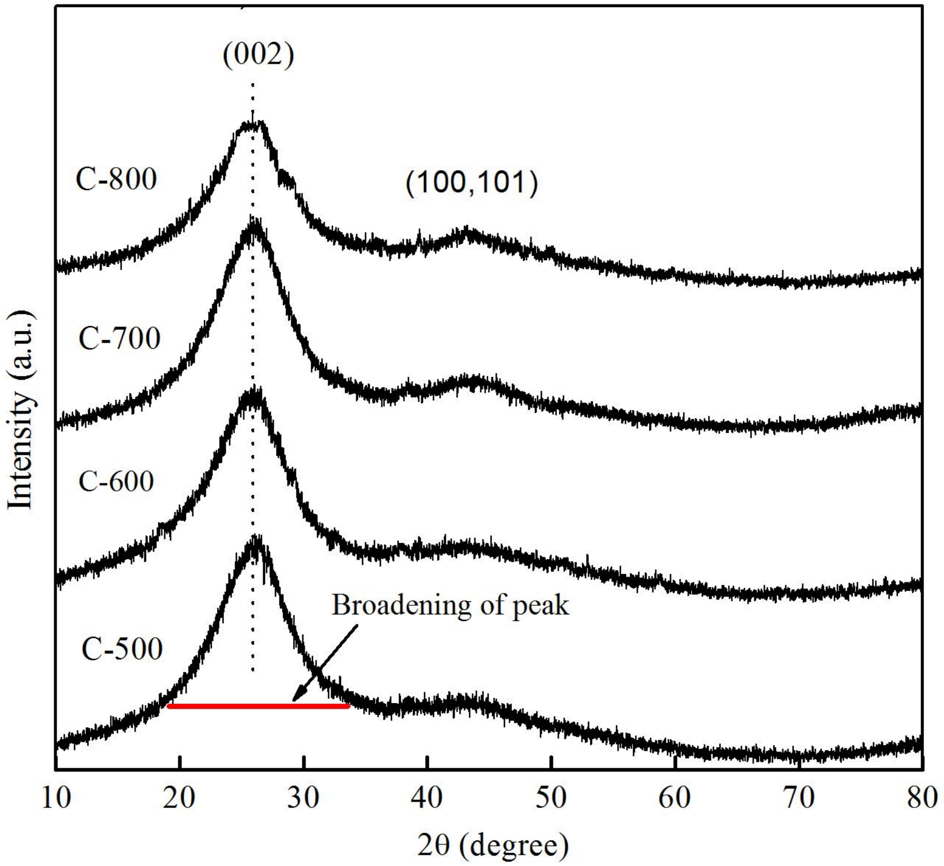


Figure 4.4. The XRD pattern for synthesized adsorbents.

As the most intense peak at 2θ = 25-27° is not very sharp, it indicates that the material is semi crystalline in nature. The structural parameters such as interplanar spacing (d_{002}) and average crystallite size were determined from position and full width at half maxima of peak at (002) diffraction plane respectively. The values of d_{002} were 0.3467, 0.3436, 0.3397, 0.3354 nm for C-500, C-600, C-700 and C-800 respectively. The d-spacing of all the samples are larger than that of ideal graphite (d_{002} = 0.3354 nm) except C-800. This indicates that former samples contained disordered structures and low crystallinity. With an increase in the carbonization temperature the interplanar spacing decreases, and the structure of carbon slowly evolves towards that of ideal graphite.

Table 4.3 Particle diameter obtained from Scherrer's formula.

Sample code	b (º)	2θ (º)	D (nm)
C-500	10.479	25.667	1.371
C-600	11.941	26.544	1.524
C-700	10.231	26.207	1.576
C-800	10.970	26.548	1.662

The mean crystallite size was calculated from XRD line broadening using the Scherrer relationship (equation 3.1). The crystallite size of resultant carbon samples are shown in table 4.3. There is no significant increase in crytallinity with increase in carbonization temperature. The crystallite size ranges from 1.4 to 1.7 nm. Thereby, indicating that the synthesized carbon is nanomaterial.

4.1.5 Scanning electron microscopy (SEM) analysis

SEM photographs (fig 4.5) show the development of pores on the carbon and depicted groups of granular type crystals inter-related by web like structure. The carbon prepared by using MCM-41 as template contained heterogeneous and irregular pores.

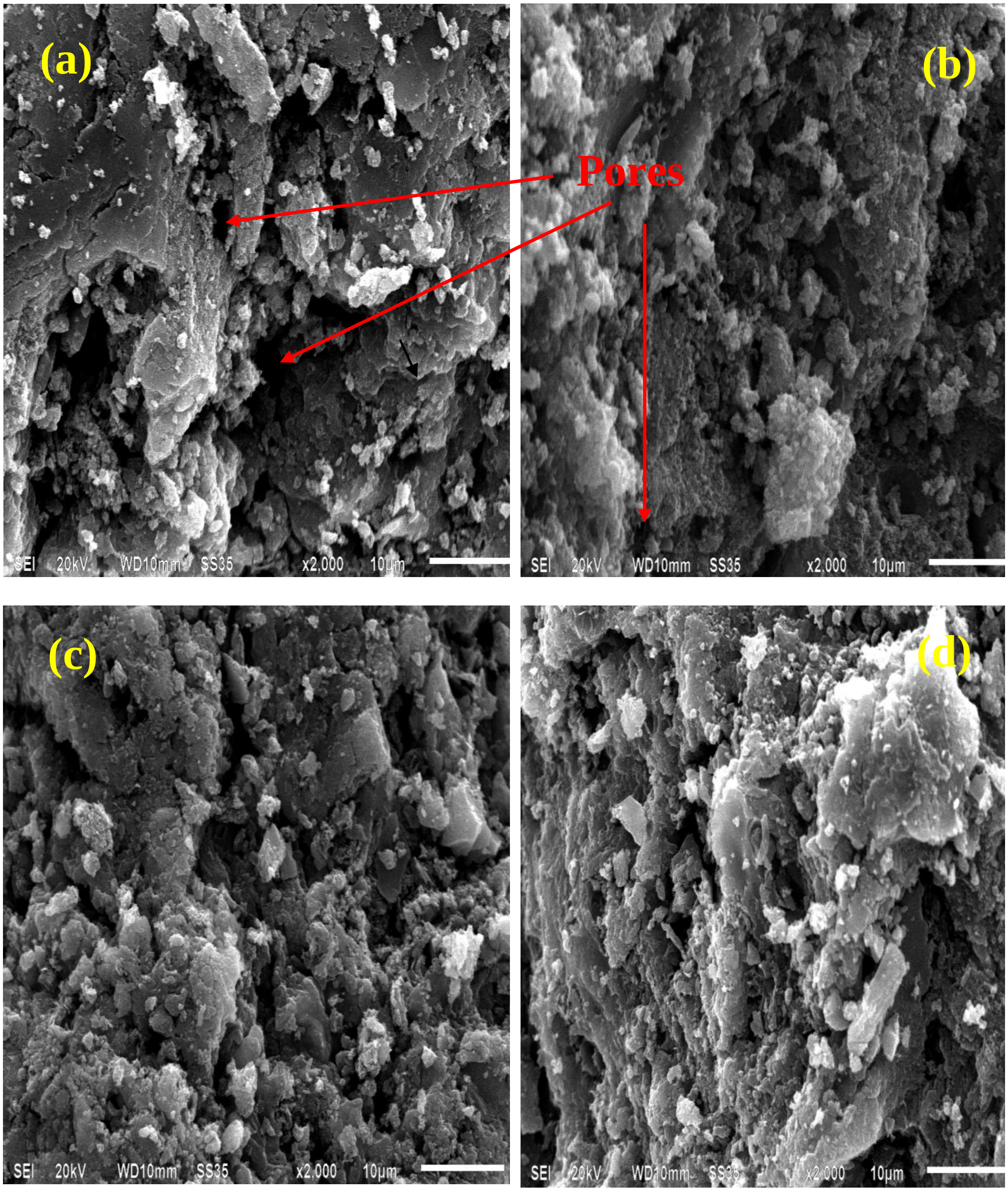


Figure 4.5. Scanning electron micrographs of (a) C-500, (b) C-600, (c) C-700, (d) C-800.

Moreover, the surface appears to be pitted and fragmented having cracks. The micrograph of sample C-800 appears to be more compact with small number of pores indicating that sintering of carbon has occurred due to large amount of volatiles being released from the raw material at high carbonization temperature. The SEM results concur with surface area results.

4.2 CO_2 Adsorption- desorption Study

4.2.1 *Effect of carbonization temperature*

In order to determine equilibrium CO_2 adsorption capacity, CO_2 uptake tests were carried out at 30 ºC under pure CO_2 at atmospheric pressure and held at that temperature for 15 min. The adsorbents presented fast adsorption rates (fig 4.6), more than 95% of the CO_2 being adsorbed in less than 5 min (reaching a plateau). With increasing carbonization temperature from 500 to 600 ºC there is decrease in adsorption capacity (table 4.4) which can be attributed to loss of nitrogen that accounts for decreased CO_2 affinity. But, it is observed that for sample C-700 adsorption capacity increases and is maximum among all. This rise can be attributed to high surface area and pore volume of the sample. Further, sample C-800 exhibits decreased capacity due to significant decrease in surface area and nitrogen. Thus, we can say that both the nitrogen content and surface area are playing important roles in CO_2 adsorption.

Table 4.4 CO_2 adsorption capacity of synthesized adsorbents.

Sample code	**Equilibrium CO_2 adsorption capacity (mmol g^{-1}) 100% CO_2**			
	30 ºC	50 ºC	75 ºC	100 ºC
C-500	0.785	-	-	-
C-600	0.602	-	-	-
C-700	0.801	0. 483	0.423	0.283
C-800	0.694	-	-	-

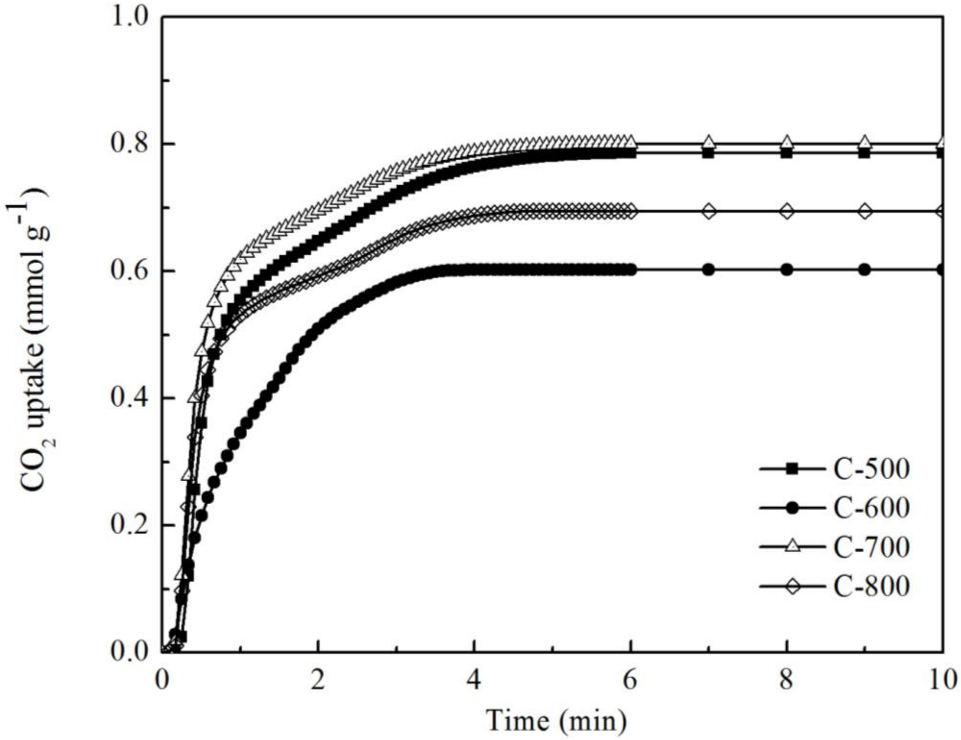


Figure 4.6. Adsorption of CO_2 on synthesized adsorbents at 30 ºC for 100% CO_2.

4.2.2 *Effect of adsorption temperature*

Sample C-700 was studied at different adsorption temperatures of 30, 50, 75 and 100 ºC as it showed maximum CO_2 adsorption capacity at 30 ºC. There is decrease in the adsorption capacity with increase in adsorption temperature (table 4.4). This behavior is typical of physiosorption, where surface energy and molecular diffusion rate increase with increasing adsorption temperature, as a result, the adsorbed gas on the surface of carbon becomes unstable resulting in desorption of adsorbed CO_2 molecules. The interaction between adsorbate and adsorbent for physical adsorption is by relatively weak van der waals forces. Also, in this case adsorption reaches maximum in less than 5 min (fig 4.7) and remains saturated after that. In present study, the CO_2 capture capacity of sample C-700 at 30 ºC is about 3 times than at 100 ºC.

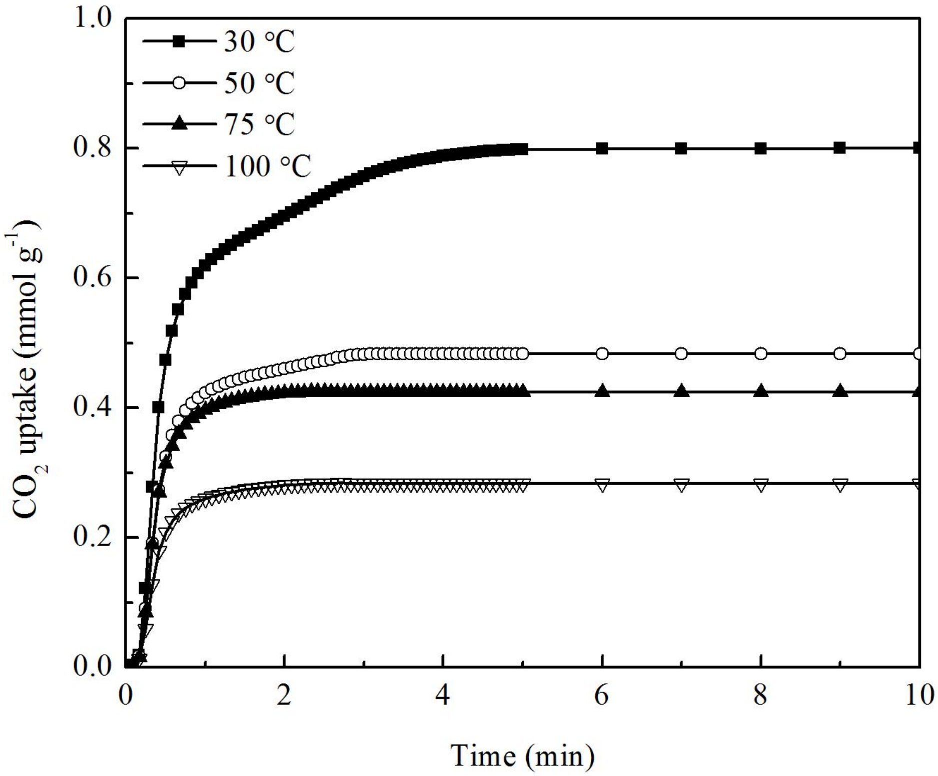


Figure 4.7. CO_2 adsorption on C-700 in pure CO_2 flow at different adsorption temperatures.

Desorption studies were carried out to determine the regeneration capacity of carbon adsorbents by conducting adsorption at 30 ºC and desorption at 200 ºC. The three consecutive adsorption-desorption cycles were carried out at atmospheric pressure. The results are shown in the Figure 4.8. It can be seen that the CO_2 adsorbed is quickly desorbed (~ within 3 min) after the carrier gas is switched from CO_2 to N_2. The adsorption-desorption cycle was repeated three times with no significant changes being observed in the kinetics of CO_2 uptake or desorption. Thus, the adsorbents could be easily regenerated over multiple cycles without any loss of adsorption performance confirming the stability of material.

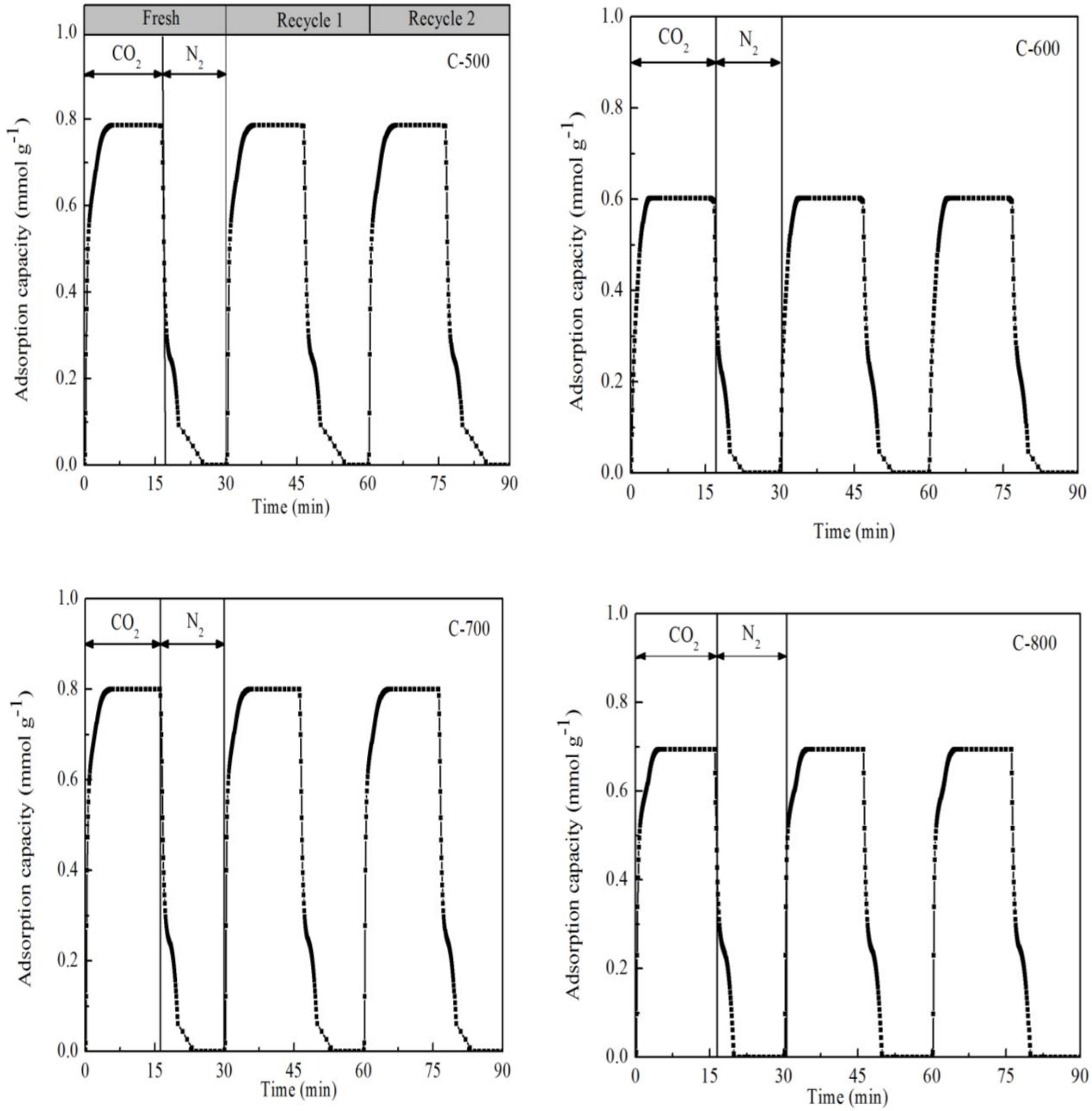


Figure 4.8. Multiple cycles of CO$_2$ adsorption and desorption of samples at 30 ºC.

4.3 Kinetic Studies

The kinetics of CO$_2$ adsorption was studied for all carbon samples at 30 °C and at all adsorption temperatures for sample C-700 using the pseudo first order and pseudo second order models. The parameters in the equations 3.2 and 3.3 are estimated using non linear regression and illustrated in fig 4.9. In this case, the carbon is viewed as a flat surface with specific sites, at which adsorbed molecules (CO$_2$) are located.

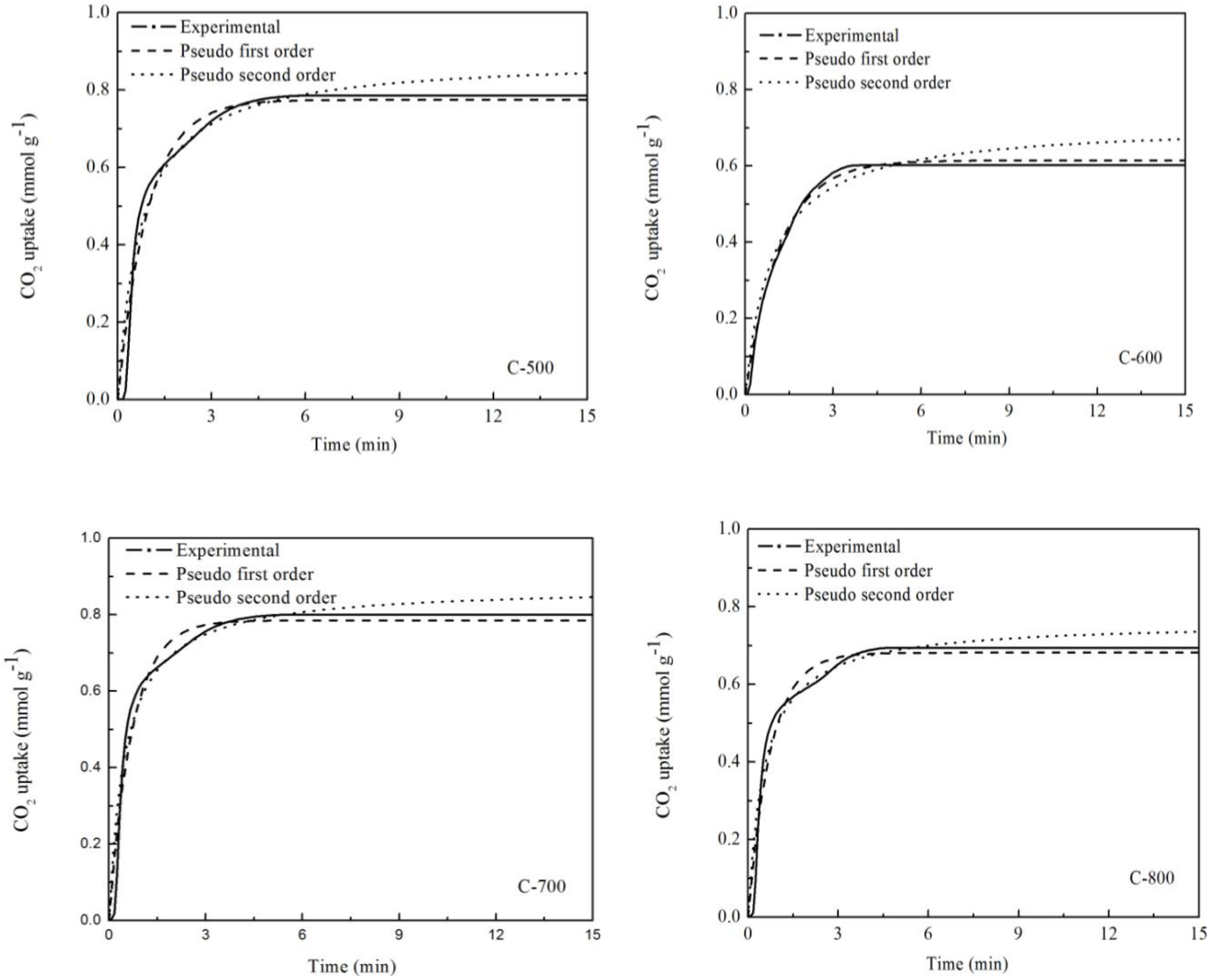


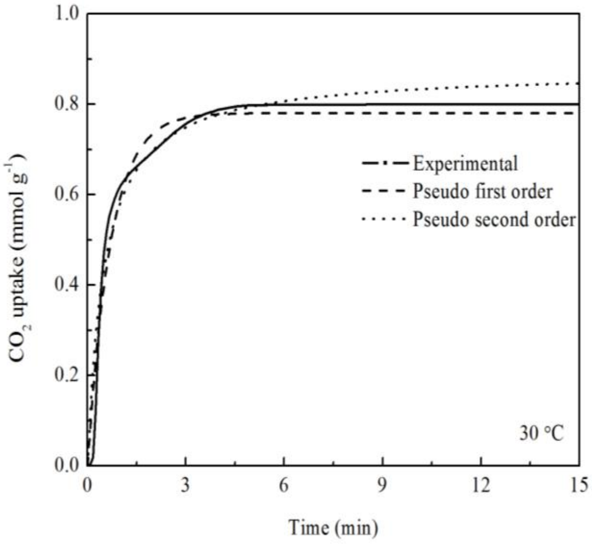
Figure 4.9. Comparison of kinetic models on experimental CO_2 uptake of samples at 100% CO_2 and 30 ºC.

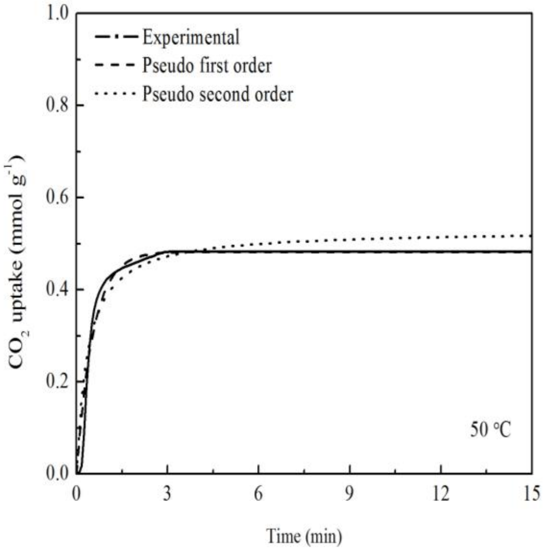
The estimated parameter values and corresponding correlation coefficients are presented in tables 4.5 and 4.6. The pseudo first order model provides the better fit to CO_2 adsorption data for all the samples than the pseudo second order model. This finding is further supported by the R^2 values and error function obtained for both the models. It was observed that the R^2 for the pseudo first order is closer to unity. Also, the experimental and calculated values of q_e are in close agreement for pseudo first order model. This indicates the first order nature of the adsorption process of CO_2 on the templated carbons. Therefore, we can say that according to first order reaction kinetics, the rate of CO_2 diffusion into the carbon surface is faster than the chemical reaction on the carbon surface.

Table 4.5 Kinetic parameters of pseudo-first order and pseudo-second order for synthesized adsorbents.

		C-500	**C-600**	**C-700**	**C-800**
	q_e	0.785	0.602	0.801	0.694
Pseudo first order	k_1 (s^{-1})	1.045	0.854	1.401	1.340
	q_e (mmol g^{-1})	0.774	0.614	0.785	0.681
	R^2	0.963	0.993	0.961	0.956
	Err (%)	4.389	1.687	3.305	3.802
Pseudo second order	k_2 (g $mmol^{-1}$ s^{-1})	1.561	1.534	2.280	2.487
	q_e (mmol g^{-1})	0.884	0.711	0.874	0.761
	R^2	0.952	0.958	0.954	0.952
	Err (%)	4.306	4.738	1.897	2.322

Similarly, kinetic study of sample C-700 followed first order kinetics well with higher R^2 values and corresponding error function in the range of 3.5-1.4 (table 4.6). Also the experimental values are in good agreement with pseudo first order q_e values.





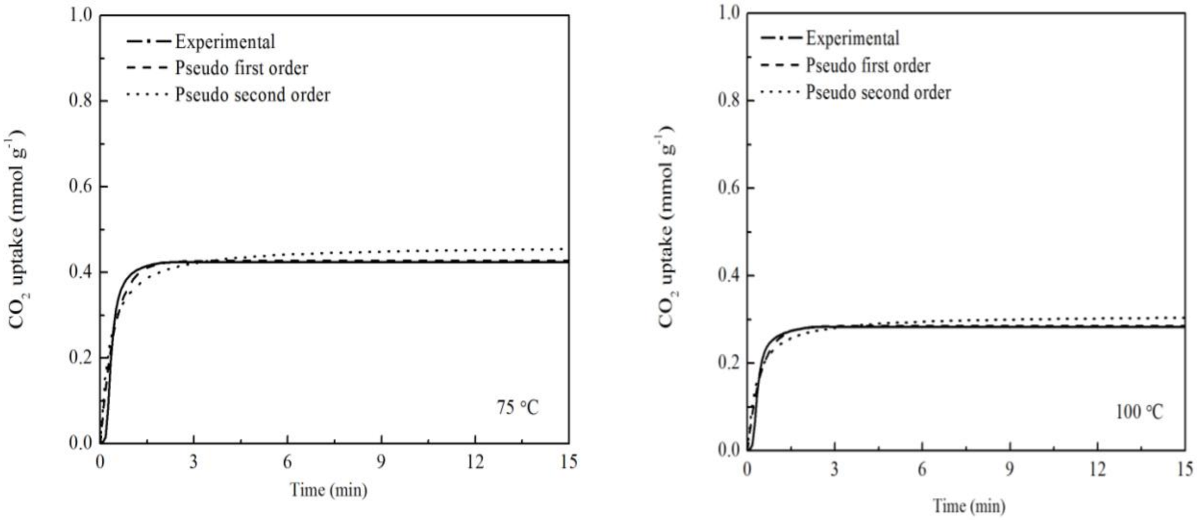


Figure 4.10. Comparison of kinetic models on experimental CO_2 uptake of samples at 100% CO_2 and at different adsorption temperatures.

Table 4.6 Adsorption kinetic model parameters at different temperatures.

C-700		**30 ºC**	**50 ºC**	**75 ºC**	**100 ºC**
	q_e	0.801	0.483	0.423	0.283
Pseudo first order	k_1 (s^{-1})	1.426	1.854	2.172	2.122
	q_e (mmol g^{-1})	0.780	0.482	0.427	0.285
	R^2	0.961	0.961	0.947	0.954
	Err (%)	3.579	1.679	1.822	1.471
Pseudo second order	k_2 (g $mmol^{-1}$ s^{-1})	2.276	5.173	7.197	10.470
	q_e (mmol g^{-1})	0.874	0.530	0.463	0.310
	R^2	0.951	0.913	0.875	0.888
	Err (%)	4.828	3.942	4.681	4.357

CHAPTER 5
CONCLUSIONS

5.1 Conclusions

A series of mesoporous carbon adsorbents were prepared by nanocasting technique. The nitrogen content of the adsorbents decreased with increase in carbonization temperature. Surface area of the adsorbents increased upto carbonization temperature of 700 °C, but further increase led to a drastic reduction due to enhanced gasification of carbon material and hence deteriorating its pore structure. Also, higher carbonization temperature resulted in decrease in adsorption capacity probably because basic sites suitable for adsorption are destroyed. The CO_2 adsorption profiles for all samples illustrate that major CO_2 uptake takes place in less than 5 minutes. Through adsorption-desorption study, we can conclude that the series of porous adsorbents synthesized using HMMM resin has potential to adsorb CO_2 and consecutive adsorption-desorption cycles without significant change in adsorption capacity confirm reproducibility and stability of material. The kinetic studies carried out for resultant adsorbents followed pseudo first order better and the experimental q_e was in good agreement with calculated q_e. Moreover, it was observed that both the surface area and nitrogen content play important roles in the adsorption.

5.2 Recommendations

Typical flue gas temperatures are up to 150 ºC therefore, we need an adsorbent that can operate at high temperatures with good capacities for CO_2. So, further studies can be conducted to maximize CO_2 adsorption capacities.

i. Polymeric materials other than HMMM resin can also be used as precursor like urea-formaldehyde resin and their synthesis processes can be optimized by varying different parameters such as N_2 and CO_2 flow rates, soaking time or heating rate.
ii. The template to resin ratio can also be varied.
iii. The CO_2 capture performance for rest of the samples i.e. C-500, C-600 and C-800 can be studied at different temperatures to determine whether physical and/or chemical sorption is influencing the adsorption.
iv. The effect of different partial pressures of CO_2 on adsorption capacity can also be studied.

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