Preparation of Adsorbent(s) using Nano-Casting Technique for Carbon Dioxide Capture from Flue Gases

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By:

CHITRAKSHI GOEL

M. Tech. 2nd year

(Roll No. 600901005)

Under the guidance of

Dr. P. K. Bajpai
Distinguished Professor
Department of Chemical Engg.

Dr. Haripada Bhunia
Assistant Professor
Department of Chemical Engg.

Department of Biotechnology and Environmental Science
THAPAR UNIVERSITY
Patiala, Punjab

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CERTIFICATE

This is to certify that the thesis entitled **"Preparation of Adsorbent(s) using Nano-Casting Technique for Carbon Dioxide Capture from Flue Gases"**, is an authentic record of my own work carried out as requirements for the award of degree of Master of Technology in Environmental Science & Technology from Thapar University, Patiala, under the guidance of Dr. Pramod K. Bajpai (Distinguished Professor, ChED) and Dr. Haripada Bhunia (Assistant Professor, ChED) during January to June 2011.

Chitrakshi Goel.

Date: 14th July, 2011

Chitrakshi Goel
(Roll No: 600901005)

It is certified that the above statement made by the student is correct to the best of our knowledge and belief.

Dr. P. K. Bajpai
Distinguished Professor
Department of Chemical Engineering
Thapar University, Patiala

Dr. Haripada Bhunia
Assistant Professor
Department of Chemical Engineering
Thapar University, Patiala

Countersigned by:

Dr. M. S. Reddy
Head, and Department of Biotech & Env Sciences
Thapar University, Patiala

Dr. S. K. Mohapatra
Dean, Academic Affairs
Thapar University, Patiala

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Chitrakshi Goel.

Chitrakshi Goel
(Roll No: 600901005)

ABSTRACT

Increasing awareness of the influence of greenhouse gases on global climate change has led to recent efforts to develop strategies for the reduction of CO_2 emissions. CO_2 capture and storage (CCS) technology is therefore being developed for application to power plants and in CO_2-intensive industries to reduce the carbon footprint of these activities and mitigate the potentially harmful effects of climate change. CO_2 capture from large point sources, such as power plants, can be achieved through continued research, development and demonstration. The main challenge in CO_2 capture technology is to reduce the overall cost by lowering both the energy and the capital cost requirements. While costs and energy requirements for today's capture processes are high, the opportunities for significant reductions exist, since researchers have only recently started to address these needs.

Adsorption has received much attention for its low energy consumption, low equipment cost, and ease of application. Efficient adsorbents and well designed reactor will further improve the process economics. Adsorption of CO_2 using basic adsorbents requires high pressure operation, hence modified adsorption routes need to be developed with higher adsorption capacity, less energy and cost intensive. This can be achieved by two ways, namely (i) modification of adsorbents and (ii) development/modification of nano-structured adsorbents. The focus of the present work is to develop the nano-structured adsorbents and evaluate the CO_2 adsorption capacity.

For the development of nano-structured adsorbents, melamine-formaldehyde resin was used as the precursor and mesoporous silica was used as the template. Development of adsorbent included two steps namely synthesis of resin (precursor) and carbonization of the templated resin samples. The process conditions for the resin synthesis were optimized. After this, carbonization was done at 500 °C for 1 hour, resulting in the thermal degradation of the precursor. Five porous carbon adsorbents were obtained having different template to precursor ratio. X-ray diffraction analysis was done from 2• = 10–80° which showed that the synthesized material is nano-structured carbon. Surface morphological changes were observed by scanning electron microscopy. Irregular and heterogeneous types of pores were observed. FTIR spectra were taken to identify the

functional groups present in the synthesized adsorbents. No peak for nitrogen was observed. Absence of nitrogen in the synthesized adsorbents was confirmed by Kjeldahl test. Both texture and surface chemistry influence the CO_2 capture performance of the prepared adsorbents. If an adequate and well developed porosity is joined to a favorable chemistry, the CO_2 adsorption capacity is considerably enhanced. Porous and nano-structured adsorbents are obtained but due to the loss of nitrogen, CO_2 did not adsorb on the synthesized materials when a mixture of CO_2 and N_2 is passed over them at room temperature. To confirm the integrity of the new adsorption study set up, CO_2 adsorption study was carried out for zeolite 13X at room temperature.

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ABBREVIATIONS

atm	Atmosphere
CCS	Carbon dioxide Capture & Sequestration
DEA	Diethanolamine
DETA	Diethylenetriamine
FT-ATR	Fourier Transform-Attenuated Total Reflectance spectroscopy
FTIR	Fourier Transform Infrared spectroscopy
GC	Gas Chromatograph
GHG	Green House Gases
HFC	Hydro-fluoro-carbon
MEA	Monoethanolamine
mmol/g	Milli moles per gram
Mt	Million Tonnes
nm	Nanometer
PEHA	Pentaethylenehexamine
PEI	Polyethylenimine
PFC	Per-fluoro-carbon
ppm	parts per million
SEM	Scanning Electron Microscopy
TEPA	Tetraethylenepentaamine
TEPAN	Tetraethylene-pentaamineacrylonitrile
TRI-PE-MCM-41	Triamine-grafted Pore-Expanded Mesoporous Silica
TSA	Thermal Swing Adsorption
wt%	Weight percentage
XRD	X-Ray Diffraction

CHEMICAL FORMULAE

CH_4	Methane
CO	Carbon Monoxide
CO_2	Carbon Dioxide
H_2	Hydrogen
H_2O	Water
H_2SO_4	Sulphuric Acid
K_2CO_3	Potassium Carbonate
N_2	Nitrogen
N_2O	Nitrous Oxide
$NaOH$	Sodium Hydroxide
NH_3	Ammonia
O_2	Oxygen
SF_6	Sulphur Hexafluoride

CHAPTER 1

INTRODUCTION

People in the rapidly developing economic world are dependent on fossil fuels for 85% of their energy. Fossil fuels will remain the main source of global energy for a long time to come (Figueroa et al., 2008; Li et al., 2008a). But the use of fossil fuels exacerbates global climate change (Garg and Shukla, 2009).

At present, global climate change is one of the most prominent environmental and energy policy issues. Through the burning of fossil fuels, certain industrial processes, and various land use practices, we are contributing greatly to the accumulation of so-called greenhouse gases (GHGs) in the atmosphere (Anderson and Newell, 2004). 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) (Chatti et al., 2009; Rogner et al., 2007). GHGs act as a blanket to trap the infrared radiations coming from the earth’s atmosphere, thus resulting in warming of the earth’s surface and rise in surface temperature (Chatti et al., 2009). Of all the greenhouse gases, CO_2 is the principal greenhouse gas of interest because of its large current greenhouse forcing, and its long persistence in the atmosphere.

Natural sinks available, balanced the atmospheric concentration of carbon dioxide, between 260 and 280 parts per million (ppm), for thousands of years (Chatti et al., 2009; Houghton, 2007; Plasynski et al., 2009; Thiruvenkatachari et al., 2009). However, a declining trend in the long-term efficiency of these natural sinks in absorbing atmospheric CO_2 is observed, with major implications for current and future growth of atmospheric CO_2. In 2005, the concentration of atmospheric CO_2 reached nearly 380 ppm, an increase of ~35% above the preindustrial concentration of CO_2 in the atmosphere (275–285 ppm) (Chatti et al., 2009; Houghton, 2007). 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% (Garg and Shukla, 2009).

The rapid economic growth and industrialization have resulted in dramatic increase in emissions in the recent times. Since the industrial revolution, CO_2 emissions from fuel combustion have risen exponentially (fig 1.1) and this presents a tremendous challenge for reducing global CO_2 emissions over the next several decades (Herzog et al., 2009).

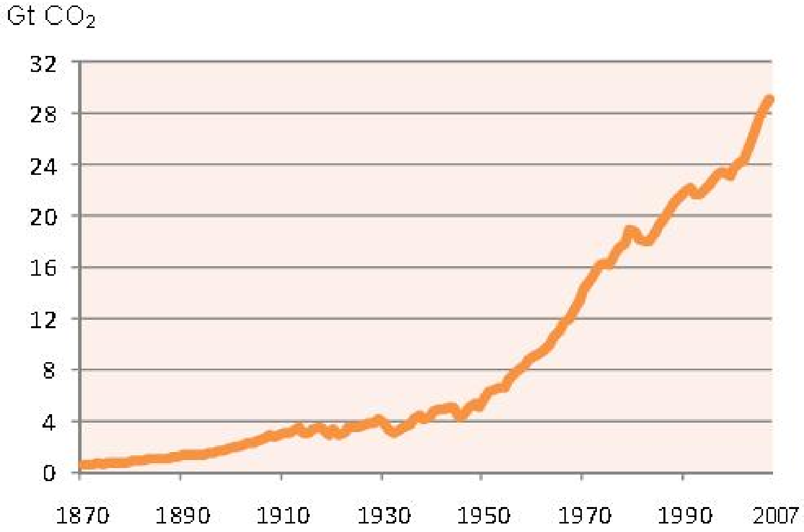


Figure 1.1 Trend in CO_2 emissions from fossil fuel combustion (IEA, 2010)

1.1 Environmental Problems Associated with Greenhouse Gases, Especially CO_2

Atmospheric enrichment of CO_2 and other GHGs is increasing the global temperature (Lal, 2009; Plasynski et al., 2009). This is one of the major concerns relative to increasing atmospheric CO_2. One manifestation of this is the melting of glaciers and the disappearance of sea ice in the polar regions of the earth. Melting of the Greenland and Antarctic ice caps could result in a rise in sea level, threatening millions of people living in coastal areas (Plasynski et al., 2009).

Researchers estimate that the global average surface temperature has increased between 0.6 and 1.0 °C during the last 150 years and will increase by 1.4 to 5.8 °C from 1990 to 2100. The Intergovernmental Panel on Climate Change (IPCC) predicts that the sea level will rise by 0.09 to 0.88 meters from 1990 to 2100, which will affect 25% of the world’s population living less than 1.1 m above sea level (Berger, 2002). Other probable consequences of global warming include droughts, expanding deserts, heat waves, ecosystem disruption, increasingly severe weather, and loss of agriculture productivity.

GHGs will cause 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 (IPCC, 1997; IPCC, 2001). Also as the CO_2 content of the atmosphere increases, more CO_2 will dissolve in the ocean and increase its acidity, resulting in unknown consequences for marine life (Plasynski et al., 2009).

1.2 Requirement of CO_2 Capture and Sequestration

Increasing awareness of the influence of GHGs on global climate change has led to recent efforts to develop strategies for the reduction of carbon dioxide (CO_2) emissions (Drage et al., 2008; Pevida et al., 2009; Plasynski et al., 2009). Although future transition to other energy sources such as hydrogen is required to slow the accumulation of greenhouse gases in the atmosphere, there is a growing understanding that in the meantime fossil fuel will continue to increase the atmospheric CO_2 levels. Therefore, urgent technological solutions need to be applied in order to control increasing CO_2 emissions (Pevida et al., 2008). Various approaches that can be followed in order to reduce emissions associated with fossil fuel combustion are reducing the energy demand by increasing the efficiency of energy conversion and/or utilization devices, de-carbonizing energy supplies either by switching to less carbon-intensive fuels (for example from coal to natural gas), and/or by increasing the use of renewable energy sources and/or nuclear energy (each of which, on balance, emit little or no CO_2), reducing non-CO_2 greenhouse gases, and capture of CO_2 followed by its storage in geological formations (CCS) is viewed as an important strategy for achieving substantial reduction in the emission levels (Herzog et al., 2009; IPCC, 2005; Pevida et al., 2008; Plasynski et al., 2009; Steeneveldt et al., 2006).

Carbon dioxide capture and sequestration (CCS) is the only pathway that can allow the world to continue to enjoy the benefits of using fossil fuel while drastically reducing the emissions associated with its combustion (Herzog et al., 2009; Li et al., 2008b). At a minimum, CCS can be a bridging strategy to provide time for alternatives to fossil fuels (coal) to be developed (Herzog et al., 2009; Yang et al. 2008). Unlike indirect forms of sequestration (afforestation or enhanced ocean uptake of CO_2), which rely on removing CO_2 from the atmosphere, CCS intends to avoid atmospheric emissions altogether (Anderson and Newell, 2004). It has the potential to reduce the overall mitigation costs and increase flexibility in achieving greenhouse gas emission reductions (IPCC, 2005; Plasynski et al., 2009).

1.3 CO_2 Capture and Sequestration

Carbon dioxide (CO_2) capture and sequestration (CCS) is a process consisting of the separation of CO_2 from industrial and energy-related sources, transport to a storage location and long-term isolation from the atmosphere (IPCC, 2005; Plasynski et al., 2009).

Carbon dioxide capture and sequestration is a three step process:

i. capture of CO_2 from a power plant, industrial process, or other source
ii. transport to a storage site, and
iii. injection into a geologic formation (Holloway, 2001; Plasynski et al., 2009; Thiruvenkatachari et al., 2009).

Carbon dioxide sequestration can be defined as the secure storage of CO_2 that would otherwise be emitted to or remain in the atmosphere. Potential technical storage methods are geological storage (in geological formations, such as oil and gas fields, unminable coal beds 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 (IPCC, 2005; Rao and Rubin, 2002). CO_2 sequestration in geologic formations shows great promise because of the large number of potential geologic sinks (Figueroa et al., 2008).

To sequester CO_2 economically, one must first produce a relatively pure, high-pressure stream of CO_2. The process of producing this high purity, high pressure CO_2 stream is referred to as separation and capture of CO_2 (Herzog, 1999).

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 (DOE, 1999; IPCC, 2005; Steeneveldt et al., 2006).

CO_2 capture from a power plant is the most expensive step, accounting for approximately 75% of the total cost (Holloway, 2001; Plasynski et al., 2009; Thiruvenkatachari et al., 2009). Therefore, the development of an efficient and cost-effective CO_2 capture technique is considered to be one of the highest priorities in the field of CCS (Thiruvenkatachari et al., 2009). There are three basic approaches for capturing carbon dioxide from fossil fuels, namely post-combustion capture, oxy-combustion capture, and pre-combustion capture (figure 1.2) (Balat et al., 2009; Kanniche et al., 2009; Plasynski et al., 2009; Thiruvenkatachari et al., 2009).

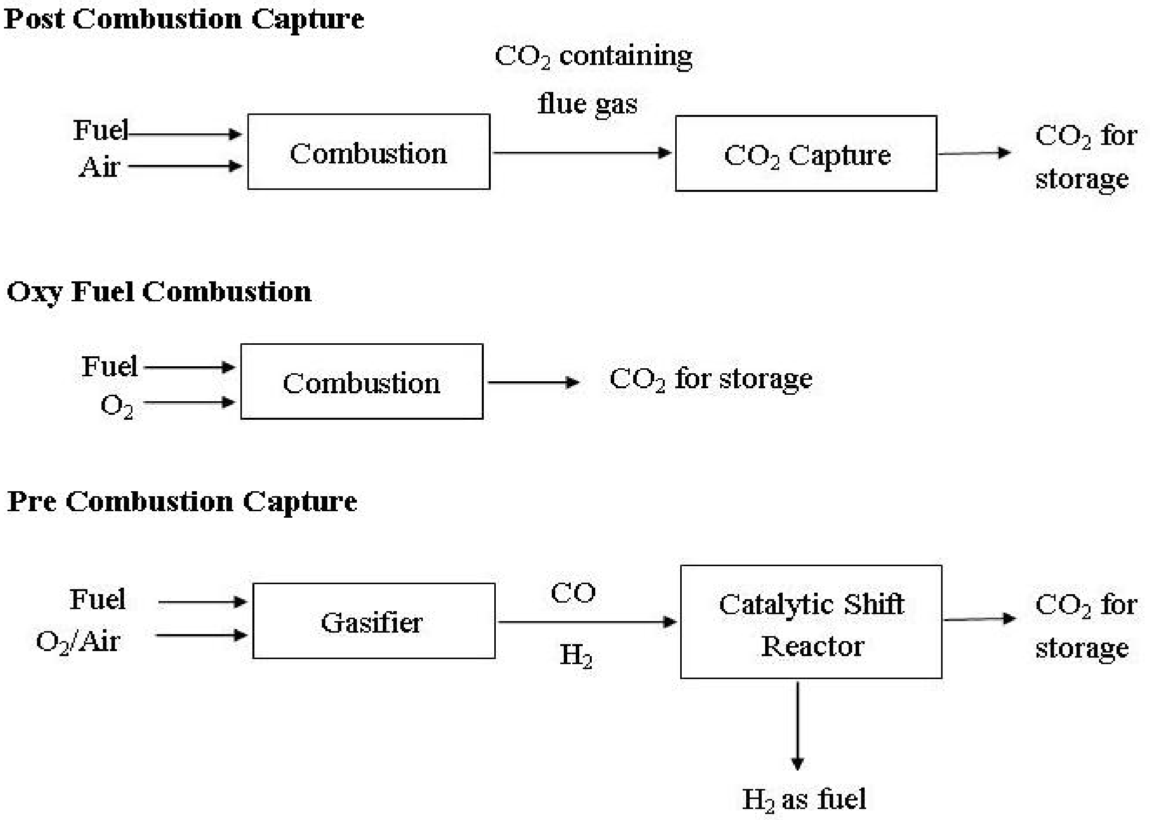


Figure 1.2 Three basic approaches to CO_2 capture (Thiruvenkatachari et al., 2009)

Post-combustion capture involves the removal of CO_2 from the flue gas after combustion (Plasynski et al., 2009; Thiruvenkatachari et al., 2009). Instead of being discharged directly to the atmosphere, the flue gas is passed through equipment which separates/captures most of the CO_2 (Thiruvenkatachari et al., 2009). Pre-combustion CO_2 capture refers to the capture of CO_2 prior to combustion (Herzog et al., 2009). An alternative to capturing carbon 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 (Figueroa et al., 2008).

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 (Figueroa et al., 2008 and Plasynski et al., 2009). There are several post combustion gas separation and capture technologies being investigated, namely:

i. absorption,
ii. cryogenic separation,
iii. membrane separation, and
iv. adsorption (Kanniche et al., 2009; Seo et al., 2007; Thiruvenkatachari et al., 2009).

Although mature, the liquid phase amine scrubbing technology suffers from inherently high regeneration cost, equipment corrosion, and amine oxidative degradation (Romeo et al., 2007; Sayari and Belmabkhout, 2010). Cryogenic separation is applied to CO_2 capture where the gas stream contains high CO_2 concentrations. It requires large amount of energy and is too expensive when the volume of CO_2 in the exhaust gases is too low and is at atmospheric pressure (Al-Shalchi, 2008; Kanniche et al., 2009) such as those encountered with typical power generation plants (Thiruvenkatachari et al., 2009). Membrane separation is a relatively new technique and the selectivity is generally low while the energy consumption is high. For flue gas application, it can be competitive only if CO_2 flue gas concentration is higher than 10% (Aaron and Tsouris, 2005; Meisen and Shuai, 1997).

Adsorption is another method that can be used to separate CO_2 from flue gases generated by fossil fuel power plants (Aaron and Tsouris, 2005). 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 (Aaron and Tsouris, 2005; Chatti et al., 2009; Thiruvenkatachari et al., 2009). 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 most commonly fills up pore space in sorbents. This makes the process less efficient as a lower degree of CO_2 separation can be achieved in each cycle. The purity of the CO_2 stream is affected by the sorbent used, since various sorbents will adsorb varying amounts of N_2 (the most common impurity) (Aaron and Tsouris, 2005).

Adsorption has received much attention for its low energy consumption, low equipment cost, and ease of application (Li et al., 2008b). 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 (Plaza et al., 2009). Hence it appears to be a promising technology if effective and selective CO_2 adsorbents are developed (Pevida et al., 2008).

CHAPTER 2

LITERATURE REVIEW

Adsorption and separation of CO_2 using porous, solid adsorbents has received tremendous attention in the past few decades, mostly in the area of energy and environment. Because adsorption performs optimally at low CO_2 concentrations (<2%), adsorption is typically used as a final polishing step in a hybrid CO_2 capture system. Regenerable solid adsorbents as an alternative can potentially offer several advantages for post-combustion CO_2 removal (Pevida et al., 2008).

An ideal adsorbent for CO_2 capture should have following properties:

i. high CO_2 adsorption capacity (>1.0 mmol/g),
ii. high selectivity towards CO_2,
iii. low energy requirement for regeneration,
iv. stability to prolonged adsorption-desorption cycling, and
v. tolerance to the presence of moisture (Khatri et al., 2006; Serna-Guerrero et al., 2010)

2.1 Adsorbents for CO_2 Capture

A large variety of adsorbents are found for CO_2 capture including activated carbon, zeolites or molecular sieves (Chatti et al., 2009), silica gel, and activated alumina. Others include mesoporous materials such as MCM-41 (Zhao et al., 2007) and SBA-15 (Chang et al., 2003), oxides, and metal-organic frameworks (MOFs) (Belmabkhout et al., 2010).

Carbon-based porous materials, especially activated carbon find many applications as adsorbents or supports for various catalysts. Activated carbons have microcrystalline structures and their adsorptive properties are due to their microporous structure, high surface area and high surface reactivity (Somy et al., 2009; Yong et al., 2002). They have adequate adsorption capacity for CO_2 at ambient temperature and atmospheric pressure (Yong et al., 2002). Zeolites are crystalline aluminosilicates of metals like sodium, potassium, magnesium, or calcium. The framework structure of zeolites are composed of a three dimensional network of basic structural units consisting SiO_4 and AlO_4 tetrahedra linked through oxygen atoms (Dutta, 2007). 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.

CO_2 adsorption capacity of activated carbon was found to be about 2.5 mmol/g at 25 °C and 1 atm CO_2 partial pressure (Chatti et al., 2009). 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 (Siriwardane et al., 2001). Thus, activated carbons need to be modified so as to facilitate chemical adsorption and hence improve the CO_2 adsorption capacity at high temperatures. Their surface chemistry can be efficiently modified by chemical impregnation which together with the intrinsic nature of the activated carbon can highly increase the adsorption capacity (Somy et al., 2009). 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. But there is an increase in the adsorption capacity of activated carbons at high temperatures.

The most of known zeolites have a capacity of CO_2 adsorption at high pressures and low temperatures, which varies from 0.15 to 5.5 mmol/g of CO_2 at 0-60 °C (Bonenfant et al., 2008). It has been found that CO_2 adsorption capacity of zeolites 13X and 4A was about 3.64 and 3.07 mmol/g respectively at 25 °C and 1 atm CO_2 partial pressure (Chatti et al., 2009). Activated carbons 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 (Park et al., 1998).

However, in these conventional adsorbents, physical adsorption plays an important role in the adsorption of CO_2 (Chatti et al., 2009). Materials like zeolites and activated carbons have high surface areas (>1500 m^2/g) and adsorb selectively different gases depending on their surface area, pore size, pore volume and surface chemistry (Maroto-Valer et al., 2008). 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 (Hutson et al., 2004; Pevida et al., 2008). They require large pressure and/ or temperature gradient between the adsorption and desorption stages to enable both efficient adsorption performances and near complete desorption of CO_2. 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 (Chatti et al., 2009). This can be achieved by two ways, namely (i) modification of adsorbents (Drage et al., 2009), and (ii) development/modification of nano-structured adsorbents.

2.2 Modification of Adsorbents

A promising approach for CO_2 adsorbents that has been successfully developed in recent years is the incorporation of amines into a high surface area support, combining good capacity and selectivity at moderate temperature. Adsorbents containing basic nitrogen functional groups have increased adsorbent/adsorbate interaction, thereby providing such materials with a selective affinity for CO_2 via the formation of ammonium carbamate species under anhydrous conditions and, in addition, via transformation to ammonium bicarbonate and carbonate species in the presence of water (Pevida et al., 2008 and 2009).

Zeolite 13X had been modified with monoethanol amine (MEA) using methanol as the solvent (Jadhav et al., 2007). 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. The performance of the adsorbent was also satisfactory in repeated cycles of adsorption (Jadhav et al., 2007). In another work, novel functionalized adsorbents had been synthesized by immobilization of various amines like monoethanol amine, ethylene diamine and isopropanol amine on synthetic zeolite 13X (Chatti et al., 2009). 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 of CO_2 for unmodified zeolite 13X and 0.45, and 0.52 mmol/g of CO_2 for zeolite modified with monoethanol amine, and isopropanol amine (Chatti et al., 2009).

A new type of composite adsorbent was synthesized by incorporating monoethanol amine into •-zeolite (Xu et al., 2009). The adsorption behavior of carbon dioxide, methane, and nitrogen on these adsorbents was investigated at 30 ºC. The results showed that the structure of zeolite did not deteoriate 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 •-zeolite (MEA(40)-•) at 1 atm and 30 °C. Steric effect and chemical adsorbate-adsorbent interaction were responsible for such high adsorption selectivity of CO_2. The adsorption capacity was constant after 6 cycles of adsorption and desorption (Xu et al., 2009).

Different alkylamines were evaluated as a potential source of basic sites for CO_2 capture, and a commercial activated carbon was used as a preliminary support in order to study the effect of the impregnation (Plaza et al., 2007). Diethylentriamine (DETA), pentaethylenehexamine (PEHA), and polyethylenimine (PEI) were used for impregnation. The amine coating increased the basicity and nitrogen content of the carbon. However, it drastically reduced the microporous volume of the activated carbon, which was chiefly responsible for CO_2 physisorption, thus decreasing the capacity of raw carbon at room temperature. Vacuum swing adsorption was applied to the prepared impregnated carbons. They do not achieve complete regeneration because of the chemisorption character of these adsorbents (Plaza et al., 2007).

Impregnation of activated carbons by metal oxides can be an efficient way to improve the surface adsorption characteristics of activated carbons. The effect of impregnation of activated carbon with Cr_2O and Fe_2O_3 and promotion by Zn^{2+} on its adsorptive properties of CO_2 was studied by Somy et al. (2009). Slurry and solution impregnation methods were used to compare CO_2 capture capacity of the impregnated activated carbon promoted by Zinc. The results showed that the amount of CO_2 adsorbed on the samples impregnated by Cr_2O was increased about 20% at 20 °C as compared to raw activated carbon. It was found that Fe_2O_3 was not an effective impregnating species for activated carbon modification. Also slurry impregnation method showed higher CO_2 adsorption capacity in comparison with solution impregnation method. Samples prepared by co-impregnation of two metal species showed more adsorption capacity than samples impregnated by just one metal species individually (Somy et al., 2009).

High capacity CO_2 adsorbents were prepared from a biomass residue, almond shells (Plaza et al., 2009). Two different methods for producing these adsorbents were compared: activation with carbon dioxide and heat treatment with ammonia gas (amination and ammoxidation). The prepared carbons were physically and chemically characterised. Amination and ammoxidation introduced nitrogen into the carbon structure, up to a 5 wt%, turning the carbon surface more basic, without the need of carrying out a preoxidation treatment. On the other hand, activation with carbon dioxide led to a significantly higher development of the texture of the samples. Amination and activation showed to be suitable methods for the production of CO_2 adsorbents. The prepared adsorbents presented a high CO_2 capture capacity, comparable to that of commercial activated carbons, and showed fully reversible adsorption (Plaza et al., 2009).

Monolith silica with a hierarchical pore structure was prepared and was impregnated with polyethylenimine (PEI) and tetraethylenepentaamine (TEPA) (Chen et al., 2009). Amine-impregnated monolith silica exhibited significantly higher CO_2 adsorption capacity than other silica-supported amine sorbents, and produced a reversible and durable sorption performance. In particular, the PEI/monolith exhibited very reversible and durable CO_2 capturing performance (4.77 mmol/g of CO_2 at 75 °C), and also showed excellent performances in both diluted and moisture-containing CO_2 conditions (Chen et al., 2009).

A novel adsorbent was developed by coating polyethylenimine (PEI) on glass fiber matrix and using epichlorohydrin as cross-linking agent (Li et al., 2008a). The physicochemical properties of the fibrous adsorbent were characterized. The experimental results showed that this fibrous PEI adsorbent exhibited much higher adsorption capacity of 3.98 mmol CO_2/g of adsorbent at 30 °C. Factors that affect the adsorption capacity of the fibrous adsorbent were studied.The adsorbent can be completely regenerated at 120 °C. This PEI-modified fibrous adsorbent had high thermal stability (about 250 °C) and is stable in the presence of moisture (Li et al., 2008a). In another work, adsorbent for CO_2 capture was prepared by coating polyethylenimine (PEI) on a glass fiber matrix, using epoxy resin (EP) as crosslinking agent (Li et al., 2008b). Factors that affected the adsorption capacity of the fibrous adsorbent were studied, including the crosslinking agent dosage, coating weight, moisture, adsorption temperature, and CO_2 concentration of the simulated flue gas. The experimental results indicate that the properly crosslinked fibrous adsorbent had a high thermal stability at about 280 °C. Adsorption capacity of 2.02 mmol/g CO_2 was obtained at 30 °C. Moisture had a promoting influence on the adsorption of CO_2 from flue gas. The CO_2 adsorption capacity of the fibrous adsorbent in the presence of moisture could be 19 times higher than that in dry conditions. The fibrous adsorbent could be completely regenerated at 120 °C (Li et al., 2008b).

Two approaches, thermal swing adsorption (TSA) cycles over a range of temperatures and time in an atmosphere of CO_2 and thermally assisted pressure swing desorption, are explored for the regeneration of the polyethylenimine (PEI) based adsorbents (Drage et al., 2008). Thermal swing regeneration was demonstrated to give good cyclic regeneration capacities (2 mmol/g). The reactions occurring during the TSA regeneration of PEI based adsorbents in an atmosphere of CO_2, especially the formation of a thermostable complex between PEI and CO_2 above 130 °C are described. However, further reaction of the regenerable carbamate ion to form urea linkages, significantly reduces cyclic capacity and therefore the lifetime of the adsorbent. Regeneration of this secondary reaction product at elevated temperatures was attempted in a nitrogen atmosphere, and whilst recovering some of the original capacity did not fully regenerate the adsorbent. Adsorbent regeneration with nitrogen as a stripping gas was used as an alternative regeneration method, the results of which suggest that steam stripping may be a potential method for adsorbent regeneration (Drage et al., 2007 and 2008).

2.3 Development/Modification of Nano-Structured Adsorbents

Even after modification of the adsorbent by different techniques, the desirable adsorbent characteristics could not be obtained. So, another approach would be to prepare altogether new adsorbents which will have desirable characteristics in terms of capacity, selectivity and regenerability. For higher selectivity of adsorbent towards CO_2, these new adsorbents can be modified further using various amines. Some work has already been initiated by few research groups in this area.

2.3.1 Development of Nano-Structured Adsorbents

High-surface area inorganic materials have attracted widespread attention in diverse areas such as heterogeneous catalysis, adsorption, gas sensing, energy storage, drug delivery, biomedical applications, electrochemistry, etc. Because of this broad range of applications, a great effort has been made to prepare materials with controlled structural characteristics by means of synthetic strategies based on the sol–gel technique or micro-emulsion methods. In general, these methods require large amounts of organic liquids, expensive reagents (i.e. surfactants) and/or precursors (i.e. organometallic), and complex preparation sequences. However, these disadvantages can be overcome by using a synthetic strategy based on the nano-casting technique.

The application of the nano-casting technique to the fabrication of inorganic compounds implies that the fabrication of these products takes place in the nano-spaces provided by the pores of a porous solid (hard template). After the synthesis of the material, the template framework is selectively removed and the inorganic product is obtained. Basically, the nano-casting route comprises three steps: (i) infiltration of the porosity of the template with a solution containing the precursors of the inorganic compound; (ii) heat treatment under a controlled atmosphere of the impregnated template to convert the infiltrated precursor into the inorganic material and (iii) removal of the template framework, by dissolution (i.e. silica) or by oxidation at high temperatures (i.e. carbon). Due to the fact that the synthesis takes place in a confined nano-space, the sintering of the particles is restricted and the preparation of high surface area materials (nano-structures or nano-particles) is achieved. In this way, numerous compounds of high-surface area can be obtained, although high-temperatures are required to synthesize them. Moreover, this synthetic strategy clearly suggests that the structure of the synthesized inorganic compounds can be tailored depending on the pore characteristics of the selected template (Valdes-Solis and Fuertes, 2006).

An inorganic diluent such as silica is used to shape the in-growing polymer. On dissolution of the inorganic template the polymer remains as a mirror image, inheriting the porosity of the template (Pevida et al., 2009). The connectivity of the porous template directly affects the structure of the solid formed. Hence, when the template consists of a fully continuous solid phase and a continuous porous system (for instance activated carbons, silica gels or meso-structured silica), the material obtained may retain a 3D 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 must be sufficiently high.

The preparation of high surface area materials is illustrated in figure 2.1 (Valdes-Solis and Fuertes, 2006).

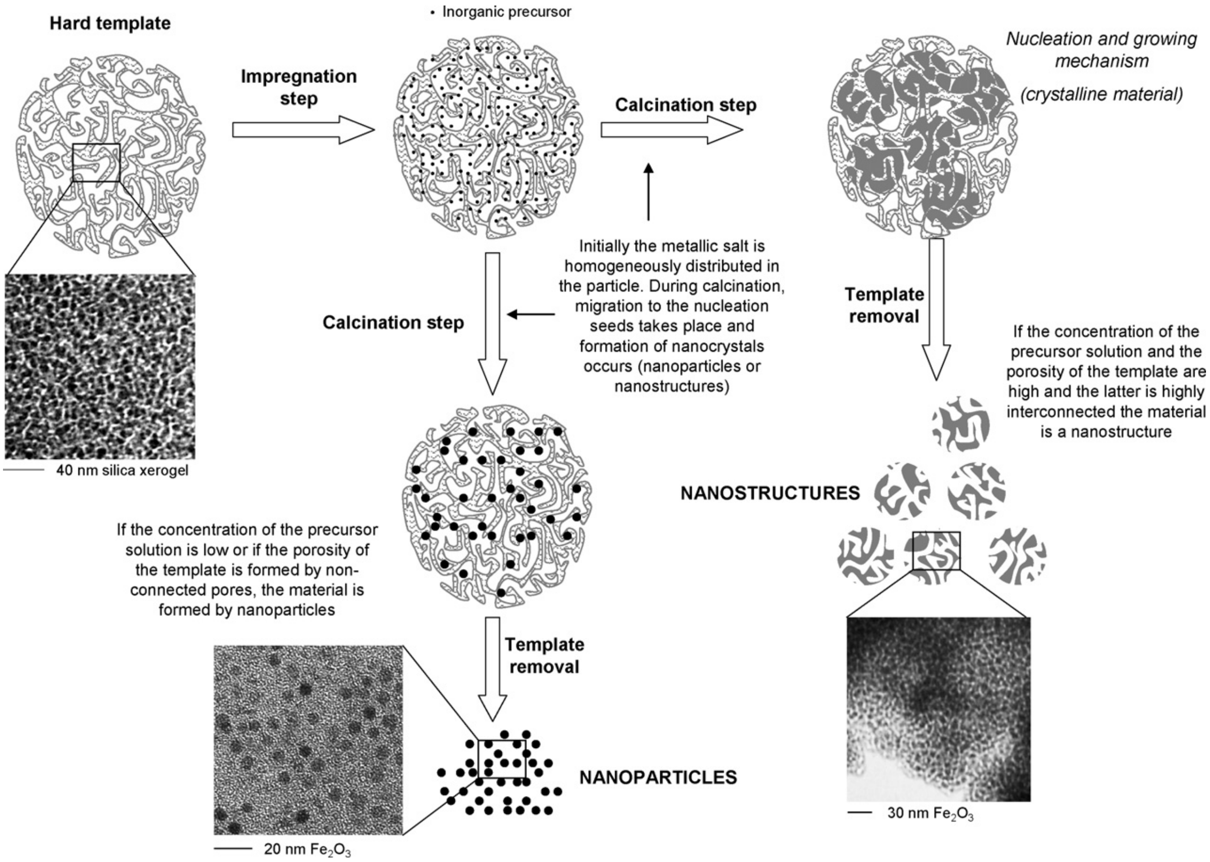


Figure 2.1 Nano-casting routes for the preparation of nano-structured materials (Valdes-Solis and Fuertes, 2006)

Templating technique was used by which a removable inorganic template was used to generate porous polymers with high surface area. A range of adsorbents had been synthesized by templating melamine–formaldehyde resin with silica followed by activation over a range of temperatures from 400–700 °C (Pevida et al., 2009). Nitrogen incorporated into the polymer matrix resulted in the greater stability of the adsorbents in terms of volatile and thermal loss of nitrogen. CO_2 capture performances were evaluated between 25 °C and 75 °C. CO_2 adsorption capacities up to 2.25 mmol/g of CO_2 at 25 °C were achieved which was 2.5 times higher than activated carbon (0.89 mmol/g of CO_2 at 25 °C). Both texture and surface chemistry influenced the CO_2 capture performance of the adsorbents (Pevida et al., 2008 and 2009). Drage et al. (2007) used the templating or nanocasting technique to produce nitrogen enriched carbons from urea-formaldehyde and melamine–formaldehyde resins polymerized in the presence of K_2CO_3 as a chemical activation agent followed by thermal activation over a range of temperatures. Adsorbents capable of capturing 1.86 and 1.03 mmol/g of CO2 at 25 °C were produced from the thermal activation of urea-formaldehyde resin and melamine-formaldehyde resin respectively at 500 °C compared to 0.16 and 0.26 mmol/g of urea-formaldehyde resin and melamine-formaldehyde resin respectively. Activation temperature had control over both textural and surface chemistry of the adsorbents (Drage et al., 2007).

In situ nitrogen enriched carbon for carbon dioxide capture was synthesized by Thote et al. (2010), from low cost soybean as the proteinaceous source. The material was synthesized by chemical activation using zinc chloride followed by physical activation using CO_2. The surface area of synthesized nitrogen enriched carbon was found to be 811 m^2/g which was comparable with commercially available activated carbon (920 m^2/g). The nitrogen enriched carbon was having a breakthrough adsorption capacity of 23 mg/g at 120 °C which was almost three times higher in comparison with the commercially available activated carbon for a gas mixture comprising 15% CO_2 balanced with helium. This high adsorption capacity was attributed to the presence of nitrogen group within the carbon matrix. Multi cycle adsorption-desorption studies were carried out at 30 °C and 75 °C in binary mixture of CO_2/N_2. Adsorption capacity was retained in 5 consecutive adsorption-desorption cycles for adsorption at 30 °C but the capacity was not retained for adsorption at 75 °C (Thote et al., 2010).

Carbon dioxide adsorption measurements were performed on MCM-41 silica samples at different temperatures from 60 °C to 120 °C. Adsorption of dry CO_2 was investigated at room temperature up to 45 bar. The most promising MCM-41 sample in terms of CO_2 adsorption capacity, i.e., MCM-41-100 prepared at 100 °C, was compared to a number of typical CO_2 adsorbents. At high pressure (e.g., 45 bar), MCM-41-100 exhibited higher volumetric capacity than activated carbons and 13X zeolite. Moreover, adsorption of pure CO_2 on MCM-41 at ambient temperature was completely reversible and exceedingly fast (Belmabkhout et al., 2009).

2.3.2 Modification of Nano-Structured Adsorbents

Further modification of the prepared nano-structured adsorbents was also done, in order to have higher selectivity of the adsorbent towards CO_2 over N_2. Surface chemistry of the nano-structured materials like MCM-41, SBA-15 etc. had been modified by impregnation with various amine polymers. Along with the adsorption capacity, the adsorbents were also studied for the selectivity of CO_2 over N_2, CH_4 etc.

Activated fly ash derived sorbents were developed for CO_2 capture. Fly ash carbon samples were steam activated at 850 °C, resulting in a significant increase of the surface area (1075 m^2/g) (Maroto-Valer et al., 2008). The activated samples were impregnated with different amine compounds like monoethanol amine (MEA), diethanol amine (DEA), methyldiethanol amine (MDEA), and the resultant samples were tested for CO_2 capture at different temperatures. The CO_2 adsorption of the parent and activated samples is typical of a physical adsorption process. The impregnation process results in a decrease of the surface areas, indicating a blocking of the porosity. The highest adsorption capacity at 30 and 70 °C for the amine impregnated activated carbons was probably due to a combination of physical adsorption inherent from the parent sample and chemical adsorption of the loaded amine groups. The CO_2 adsorption capacities for the activated amine impregnated samples are higher than fly ash carbons without activation (Maroto-Valer et al., 2008).

Low-cost carbon materials derived from fly ash were studied by Arenillas et al. (2005) for CO_2 adsorption through impregnation with organic bases like polyethylenimine aided by polyethylene glycol, tetraethylene-pentaamineacrylonitrile (TEPAN) and diethanolamine (DEA). The results showed that for same substrate, impregnated with different amines, the CO_2 adsorption capacities were relatively high (from 4 to 6 wt%) especially at high temperatures (75 °C), where commercial active carbons relying on physi-sorption had low capacities. Adsorbent retained the capacity after an adsorption-desorption cycle (Arenillas et al., 2005).

Adsorption of CO_2 on triamine-grafted pore-expanded mesoporous silica, TRI-PE-MCM-41, was investigated by Belmabkhout et al. (2010) and Serna-Guerrero et al. (2010) from very low pressure to 1 bar at four temperatures. TRI-PE-MCM-41 exhibited one of the highest equilibrium capacities compared to other typical CO_2 adsorbents such as zeolites, activated carbons, and metal-organic frameworks. Also TRI-PE-MCM-41 exhibited very small uptakes of N_2, CH_4, H_2, and O_2 showing high selectivity of CO_2 over other species even at very low CO_2 concentrations. Unlike most physical adsorbents the CO_2 adsorption capacity of TRI-PE-MCM-41 was improved in the presence of moisture. Adsorption-desorption cyclic measurements using pure CO_2 and CO_2-N_2 mixture showed excellent stability of the adsorbent upto 120 °C (Belmabkhout et al., 2010; Serna-Guerrero et al., 2010). Chang et al. (2009) examined the characteristics and CO_2 adsorption capacity of mesoporous silicas including MCM-41, SBA-15, and pore expanded MCM-41 with pore size in a range of 2–17 nm. These mesoporous silicas were modified by mono-, di-, and tri-aminosilanes. SBA-15 was found to be a better support than MCM-41 and pore expanded SBA-15 for grafting amine onto the mesoporous silicas. SBA-15, possessing a proper pore size, accommodated amines and exhibited the best CO_2 adsorption capacity as 2.41 mmol/g of CO_2 at 60 °C. Selectivity of CO_2/N_2 of 0.66 at 30 °C was obtained for tri-amine grafted SBA-15 (Chang et al., 2009).

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

3.1.1 Chemicals and reagents

The chemicals used were melamine, formaldehyde solution (37-41% w/v), potassium carbonate anhydrous, methanol, di-sodium tetra borate (borax), ammonia solution, sodium hydroxide pellets and sulphuric acid. All chemicals used were of A.R. grade. These were purchased from S-D Fine Chemicals Ltd., and Qualigens Fine Chemical. Distilled water was used to make solutions.

Gas cylinders of dry nitrogen, helium, carbon dioxide gases were provided by Sigma Gases and Services, India. Nitrogen and helium were Grade-1 (99.995% pure) gases. Carbon dioxide was Instrument Grade (99.999% pure). A gas mixture of 6% carbon dioxide and balance nitrogen was used for the calibration of gas chromatograph. Sigma Gases and Services, India also provided this gas mixture.

Mesoporous silica (CTF-04S) was used as the template. It was procured from Tianji Chemist Scientific Ltd., Tianjin, China. Its chemical formula is SiO_2. It has surface area in the range of 900-1000 m^2/g and average pore diameter of 3.5 nm.

3.2 Instruments/Equipments

3.2.1 Set-up for resin synthesis

The setup for the resin synthesis includes a heating mantle, a 3-neck round bottomed flask connected to a condenser, a mechanical stirrer and a dropping funnel (figure 3.1). Condenser was used for the refluxing of the reaction mixture. Dropping funnel was used to add formaldehyde solution slowly to the reaction mixture over a period of time.

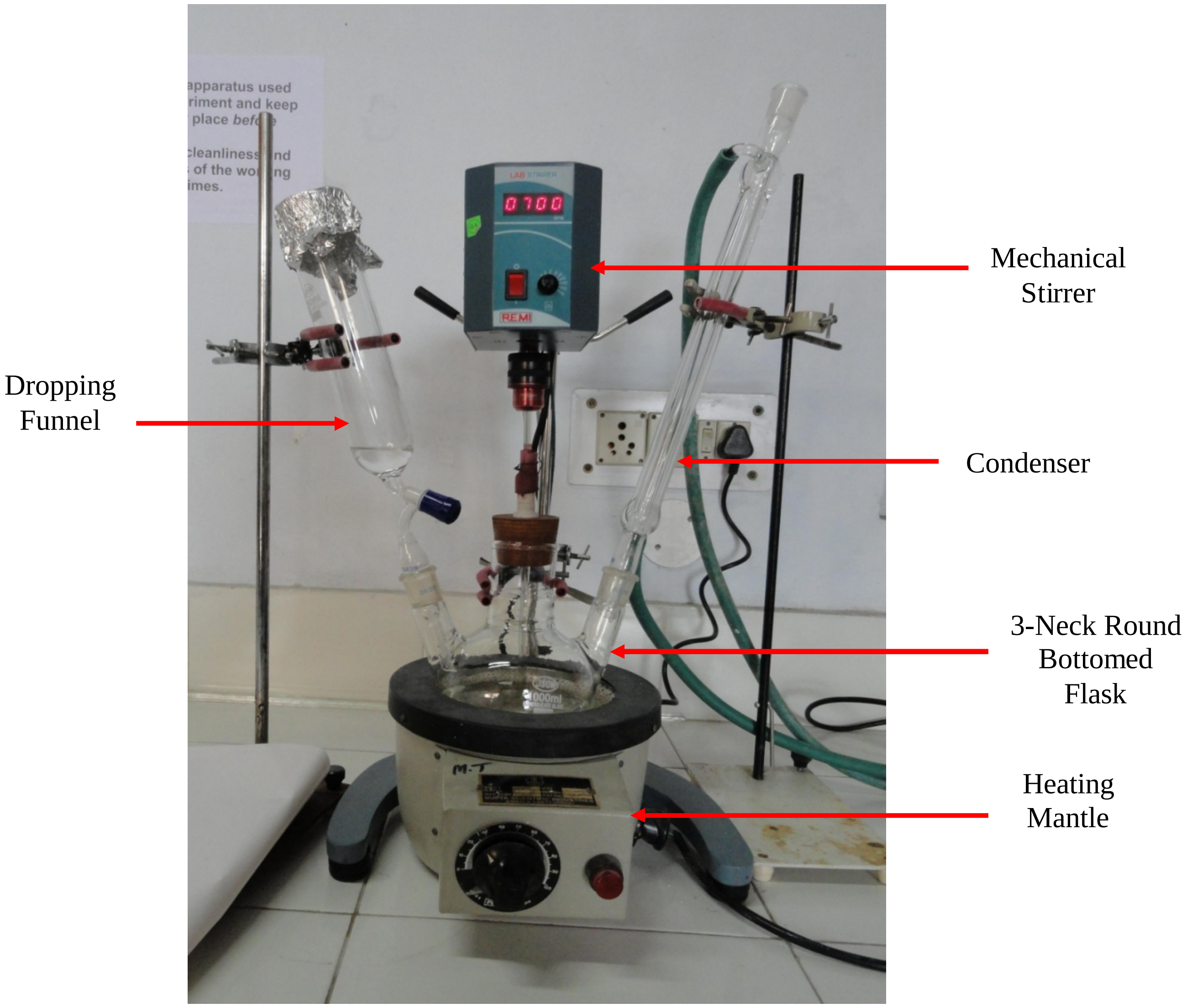
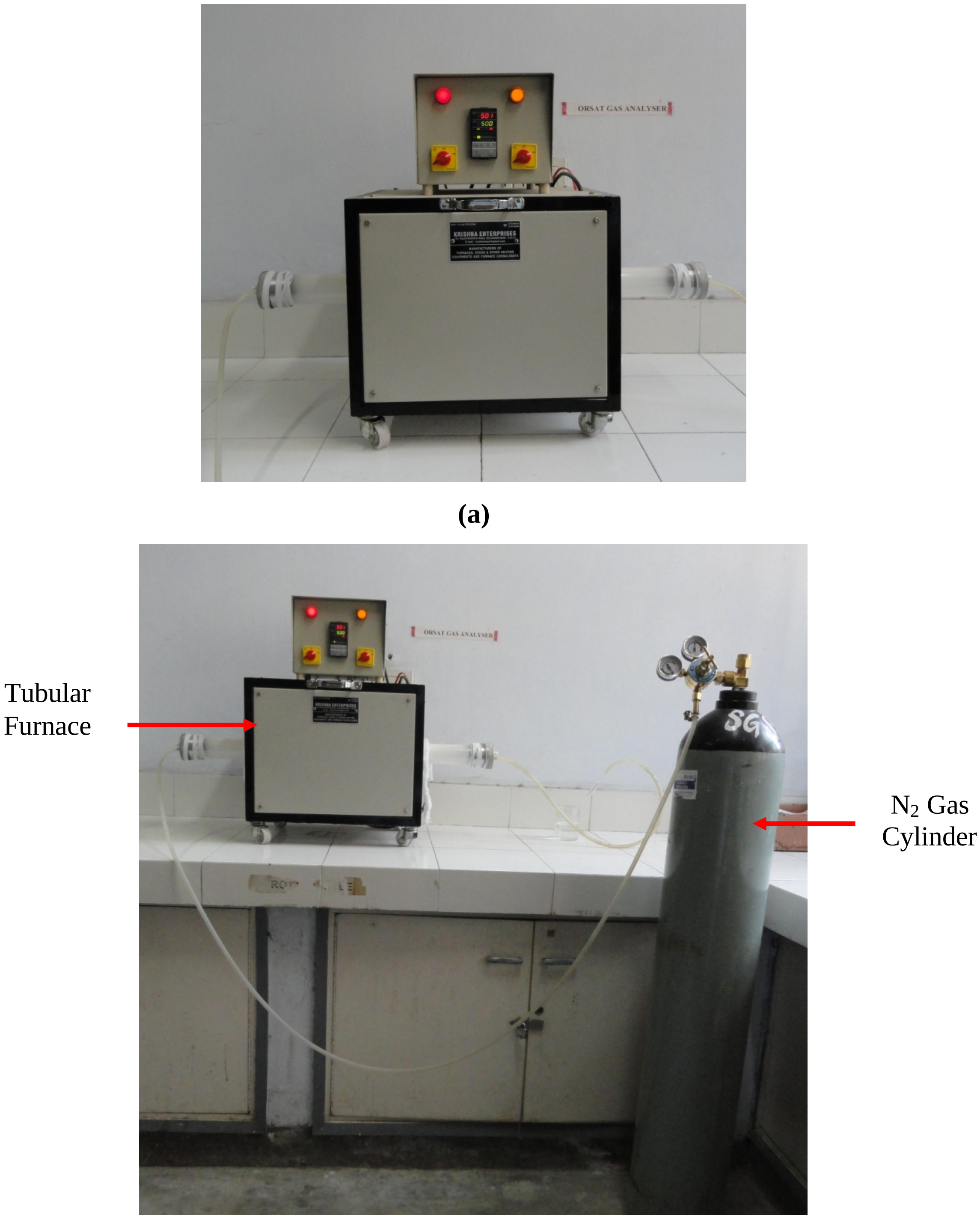


Figure 3.1 Set up for resin synthesis

3.2.2 Tubular furnace

The quartz tube furnace was provided by Krishna Enterprises, Secunderabad, India. It was used for the carbonization of the templated samples (figure 3.2). The samples were loaded in the ceramic buckets. Nitrogen gas was used for maintaining the inert atmosphere during carbonization.



(a)

(b)

Figure 3.2 Tubular furnace

3.2.3 Adsorption study set-up

The adsorption study set-up was designed and got fabricated & assembled by Chemito Technologies Pvt. Ltd., Mumbai (figure 3.3). Adsorption study set up was followed by a Gas Chromatograph, purchased from Agilent Technologies, India, for the quantitative analysis of the gas mixtures. Carbon dioxide and nitrogen were used for the adsorption study. The gas flow rates are controlled by the separate mass flow controllers. These gases are mixed in a mixer provided before the adsorption bed. They can bypass the adsorption bed or can be passed through the adsorption bed as per the requirements. The outlet stream either from the adsorption bed or from the bypass is analyzed using Gas Chromatograph. Helium gas is used as the carrier gas for GC. The adsorption study can be carried out up to the temperature of 350 °C.

(a) Adsorption set-up alone

(b) Adsorption set-up and gas chromatograph together

Figure 3.3 Adsorption study set-up

3.3 Experimental Procedure

3.3.1 Preparation of nano-structured adsorbent

Preparation of nano-structured adsorbent involved two steps: first synthesis of the resin and second carbonization of the templated resin samples. Melamine-formaldehyde resin was used as the precursor and mesoporous silica was used as the template.

3.3.1.1 Resin synthesis

Melamine 46.6 g and 200 ml of 5 wt% methanol solution were added to a 3-neck round bottom flask. The solution was heated to 80 °C. Continuous stirring was done using a mechanical stirrer. 200 ml of formaldehyde solution (37% w/v) was added slowly over 3 hours to the mixture to form hexamethylomelamine. The pH of the solution was adjusted to 8–9 by adding 1.2 g of K_2CO_3. Condensation reaction was initiated by raising the reaction temperature to 85 °C and adjusting the solution to pH to 7-8 by the addition of N/10 NaOH solution and 0.4 g of di-sodium tetra borate (borax). The reaction mixture was stirred for further 2 hours. After this, the reaction mixture was cooled to room temperature followed by addition of 6 ml of 48% H_2SO_4 solution. This reaction mixture was divided into 5 equal parts. To each part, varying amounts (1.0 g, 1.5 g, 2.0 g, 2.5 g, 3.0 g) of the template i.e. mesoporous silica (CTF-04S) were added and thoroughly mixed into the solution. The resultant mixtures were cured at 60 °C for 2 hours and then left at room temperature until complete solidification had occurred. Templated samples were powdered and were neutralized with 5% NH_3 solution. The template removal was achieved by dissolution of the templated samples in 40 wt% NaOH solution for at least 24 hours. The samples were filtered to remove the template followed by washing with copious amounts of water. After this, the samples were dried in the oven at 100 °C for 2 hours. The process for the resin synthesis is shown in the figure 3.4.

3.3.1.2 Carbonization

Carbonization is the process in which carbon-containing organic compounds are heat-treated in an inert atmosphere in order to produce carbon material. During carbonization, the precursor undergoes pyrolysis. Pyrolysis can be defined as the thermal decomposition of materials in the absence of oxygen**.** Generally, pyrolysis is carried out in inert atmosphere (most often in N_2 or Argon) at high temperatures.

Carbonization of the templated samples was done to generate the carbon adsorbents. It was carried out in ceramic buckets loaded into a quartz tubular furnace. Carbonization was undertaken by heating the samples at 10 °C min^{-1} to 500 °C for 1 hour under the flow of dry nitrogen gas.

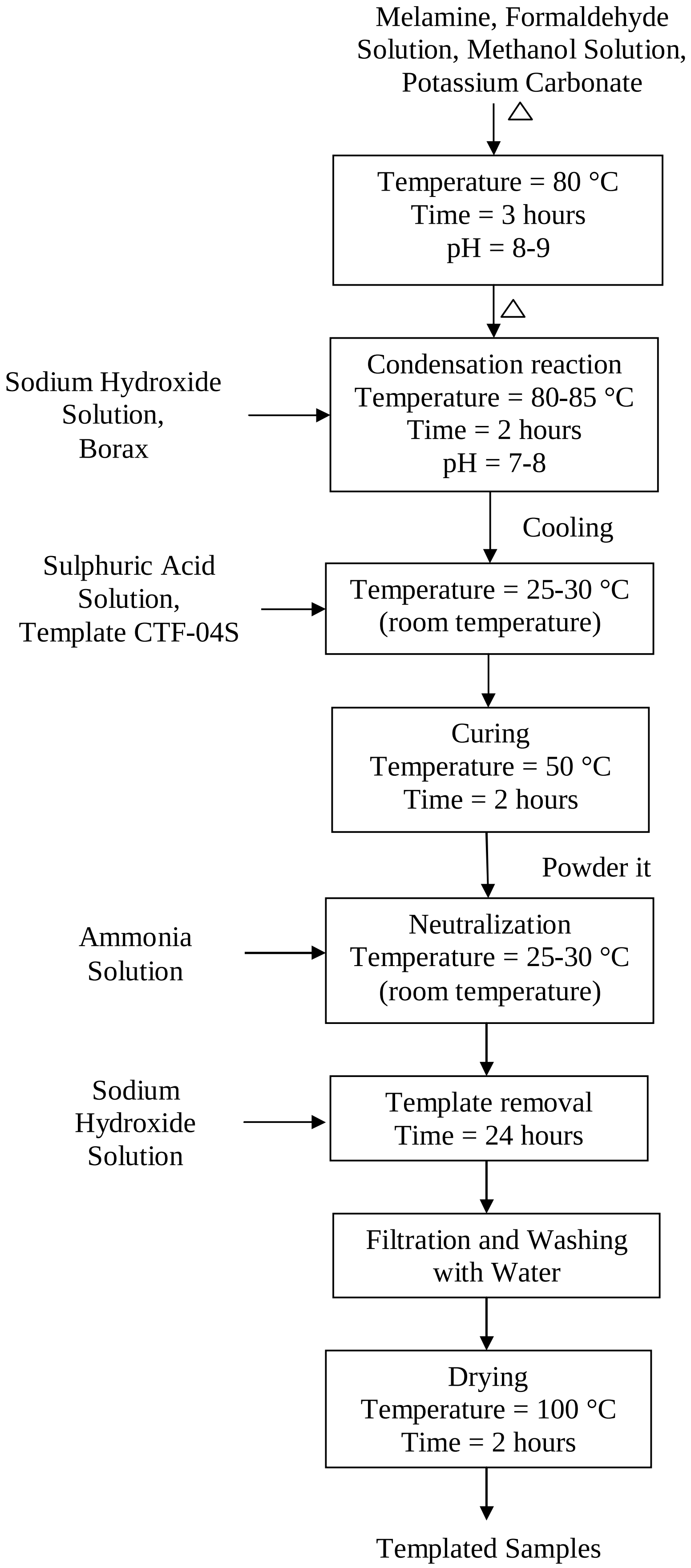


Figure 3.4 Resin synthesis process

3.4 Characterization of Adsorbents

3.4.1 X-ray diffraction (XRD) analysis

The synthesized adsorbents were characterized using an XRD with X’Celerator (X’Pert PRO, PANalytical, Netherlands) with monochromatic Cu K• radiation. During the analysis, the scanning speed and diffraction angle were 10°/min and 10–80° (2•) at 45 kV and with a current of 40 mA.

3.4.2 Scanning electron microscopy (SEM)

The surface morphology and microstructure of the samples before carbonization and after carbonization (synthesized adsorbents) were analyzed by using Scanning Electron Microscope (JEOL, Model JSM 6510 LV). The accelerating voltage was 20 kV. The specimens were coated with 50 µm of thick 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 3 magnifications of 500, 1000 and 2000.

3.4.3 Fourier transform infrared (FTIR) spectroscopy

FTIR analysis is a useful tool to determine the formation of new or disappearance of functional groups in an organic compound. Fourier transform-attenuated total reflectance (FT-ATR) infrared spectroscopic studies were carried out for the synthesized adsorbents using a Thermo Scientific FT-IR Spectrophotometer (Model Nicolet iS10) in the horizontal ATR mode in the range of 4000-400 cm^{-1}, using a ZnSe crystal. FTIR scans were taken with a resolution of 4 cm^{-1}.

3.4.4 Nitrogen content determination by Kjeldahl method

Nitrogen content of the synthesized adsorbents was estimated by Kjeldahl method. This method includes 3 steps: digestion, distillation and titration. In the digestion step, amino nitrogen of many organic materials is converted to ammonium. Free ammonia is also converted to ammonium. For the digestion of the synthesized adsorbents, a digestion reagent was prepared by mixing 100 g of potassium sulphate, 10 g of ferrous sulphate and 2 g of copper sulphate. 10 g digestion reagent and 0.5 g of the sample were added to the Kjeldahl flask. To this, 30 ml of concentrated sulphuric acid was added and the Kjeldahl flask was kept on the hot plate for the digestion of the sample. After the complete digestion of the samples, they were allowed to cool down to room temperature. 300 ml of distilled water was added to each sample and was shaken. Then it was allowed to settle down. The supernatant was decanted and transferred to a clean Kjeldahl flask. After this, distillation of the samples along with a blank was carried out to distil off ammonia from an alkaline medium. To each sample and blank, 50 ml solution of sodium thiosulphate and sodium hydroxide was added. Boric acid was used as the absorbent on the receiving end. Distillation was carried out till around 200 ml of the sample was obtained on the receiving end. Now titration was carried out to quantify the amount of ammonia in the receiving solution by using 0.1 N H_2SO_4 solution and mixed indicator.

3.5 CO_2 Adsorption Study

The adsorption study set-up was designed as per the research's requirements and was a new set-up. Hence initially standardization of the adsorption study set-up was done using bare zeolite 13X as the adsorbent. Adsorption studies for CO_2 were conducted in the adsorption study set-up containing a packed bed column, in which the known amount of the adsorbent was placed. The adsorbents were dried in oven at 140 °C for 2 hours prior to adsorption study to remove any moisture. A layer of glass wool was used to support the adsorbent bed. A PID temperature controlled oven maintained the temperature in the adsorption bed. A gas mixture with flow of 15.4% by volume of CO_2 and balance N_2 was passed through the adsorption bed. Total feed rate was maintained at 26 ml/min (CO_2 = 4 ml/min and N_2 = 22 ml/min). The exit gas stream from the adsorption bed was analysed by gas chromatograph. The adsorption was carried out at room temperature of 30 °C. Analysis was continued till the concentration of CO_2 in the product was found to be equal to that in the feed, i.e. up to saturation of adsorbent bed.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Preparation of Nano-Structured Adsorbent

With the addition of formaldehyde solution to melamine over a period of time, there is a drop in the pH of the reaction mixture. Initially pH is above 10 and it decreases to around 8 with the addition of formaldehyde solution. Addition of formaldehyde to melamine results in the formation of hexamethylomelamine as shown in fig 4.1.

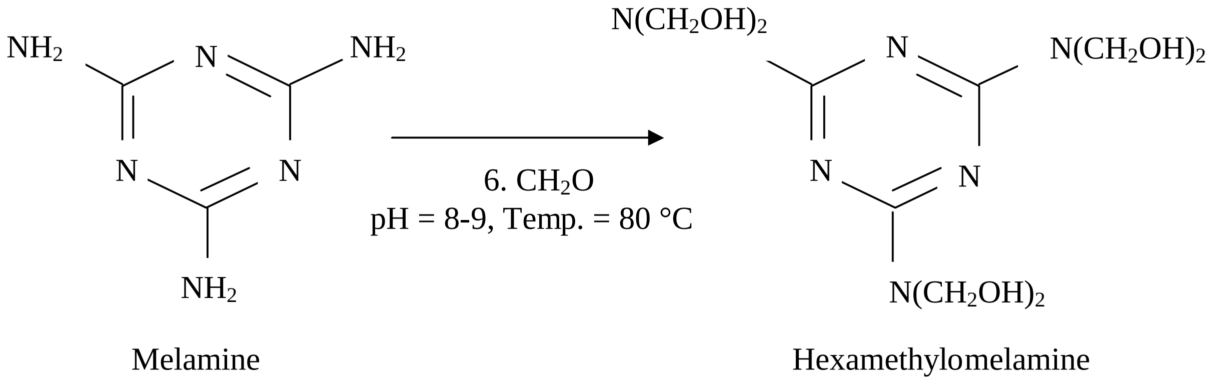


Figure 4.1 Formation of hexamethylomelamine

The second reaction step involves condensation. During the condensation reaction, there is further decrease in pH with increase in temperature. Solidification of the reaction mixture takes place if the pH drops below 7. Hence, pH is maintained above 7 by the addition of NaOH solution and di-sodium tetraborate (borax), which acts as the buffering agent. This step involves bridge formation between the hexamethylomelamine molecules. Two different types of linkages i.e. ether linkage ($-N-CH_2-O-CH_2-N-$) or methylene linkage ($-N-CH_2-N-$) may form during the condensation step, the ratio of which depends strongly on the pH. The two types of linkages are shown in figure 4.2. The cross-linking reaction involves the formation of both ether and methylene linkage. Melamine formaldehyde cross-linked network is shown in figure 4.3.

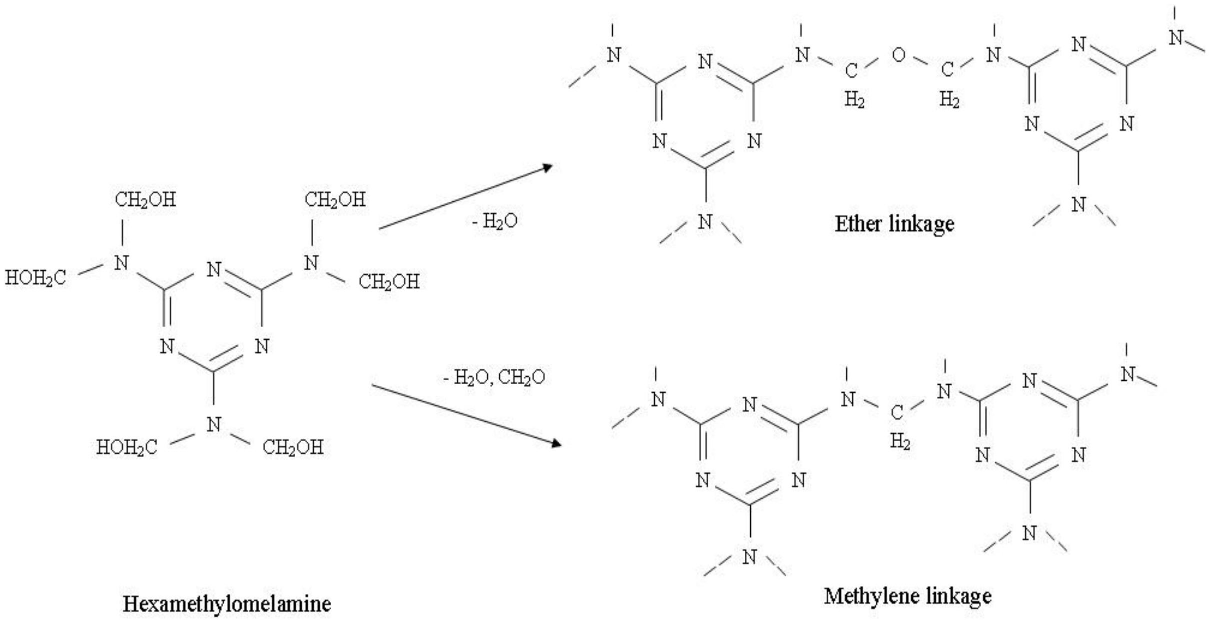


Figure 4.2 Bridge formation during condensation reaction

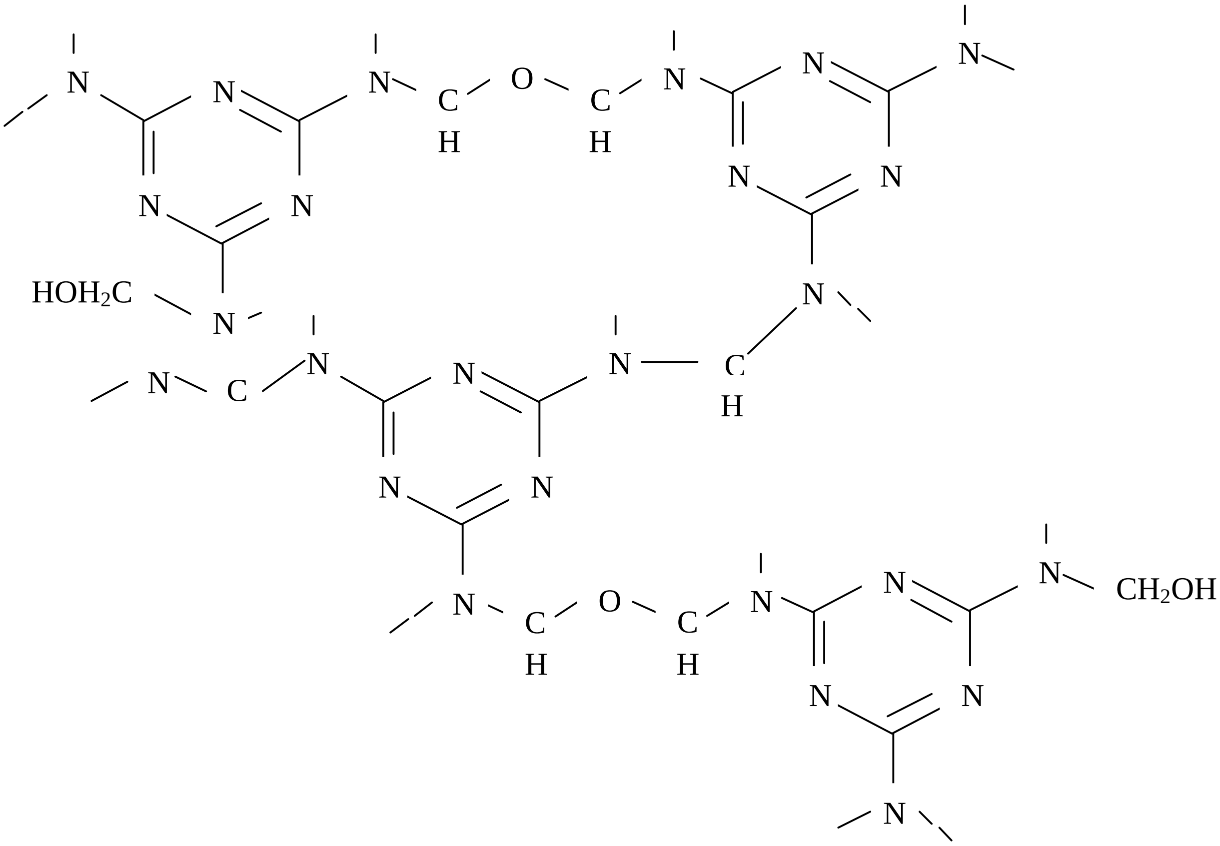


Figure 4.3 Melamine formaldehyde cross-linked network

After the addition of H_2SO_4 solution to the reaction mixture, solidification starts occurring. Hence to ensure proper mixing of the template and the reaction mixture, template has to be added immediately after adding H_2SO_4 solution. The samples obtained after template removal and filtration are shown in figure 4.4.

Figure 4.4 Samples after template removal

Carbonization leads to the thermal decomposition of the precursor, wherein the precursor is reduced to carbon having nitrogen in the structure. Swelling of the material was observed, which shows the pore formation during carbonization. After carbonization, white powdered samples are reduced to black colored carbon as shown in figure 4.5.

Figure 4.5 Samples after carbonization

4.2 Characterization of Adsorbents

4.2.1 X-ray diffraction (XRD) analysis

The XRD patterns of all the synthesized adsorbents, with different template to precursor ratio, have 4 peaks in the 2• range of 10-80° (figures 4.6 – 4.10). The most intense peak is in the range of 2• = 26-27° (table 4.1), which coincides with the peak for graphitic carbon having hexagonal structure (as per index JCPDS X-ray Powder Diffraction Database No. 75-1621).

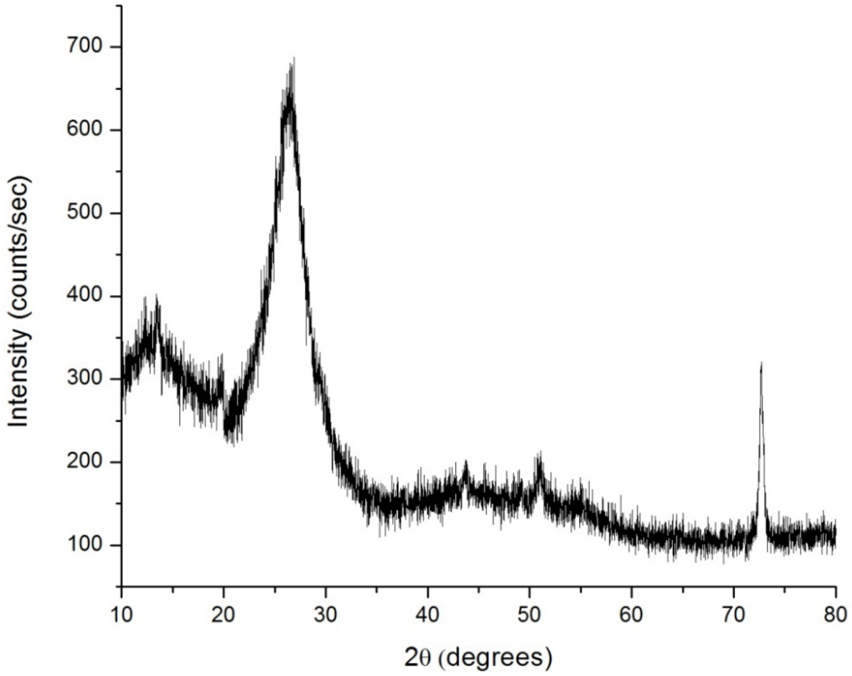


Figure 4.6 XRD pattern of synthesized adsorbent having template to precursor ratio of 1:6

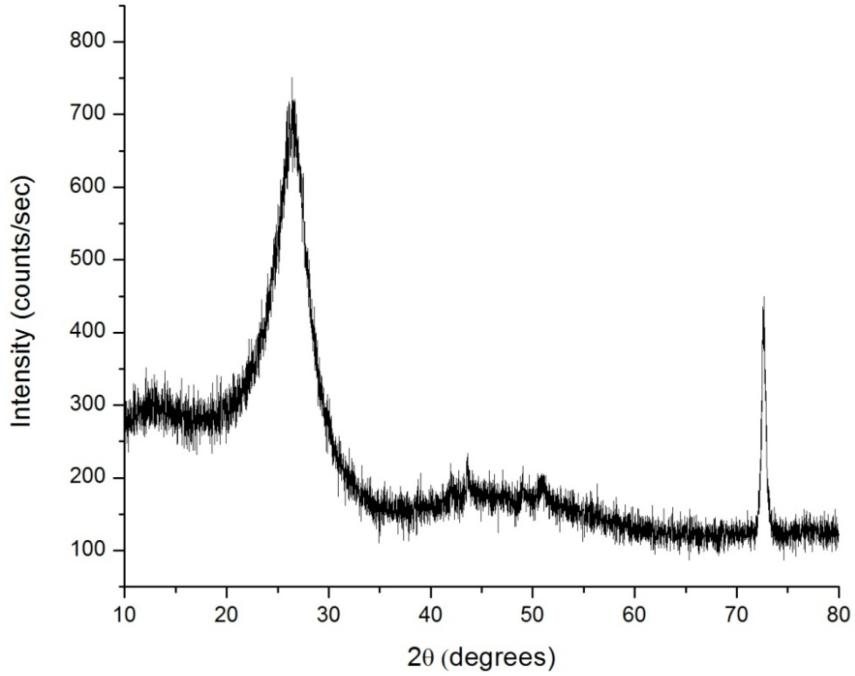


Figure 4.7 XRD pattern of synthesized adsorbent having template to precursor ratio of 1:4

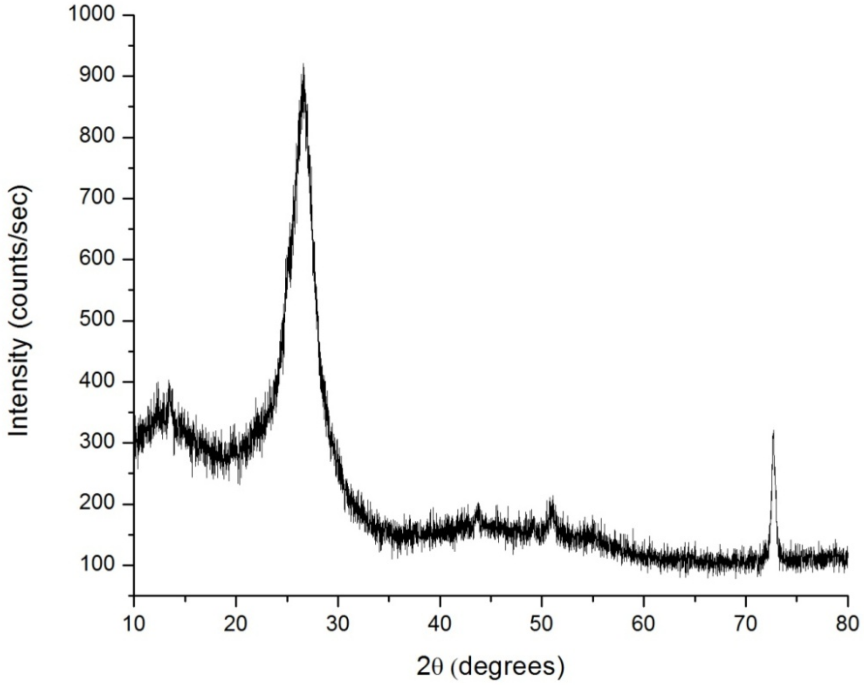


Figure 4.8 XRD pattern of synthesized adsorbent having template to precursor ratio of 1:3

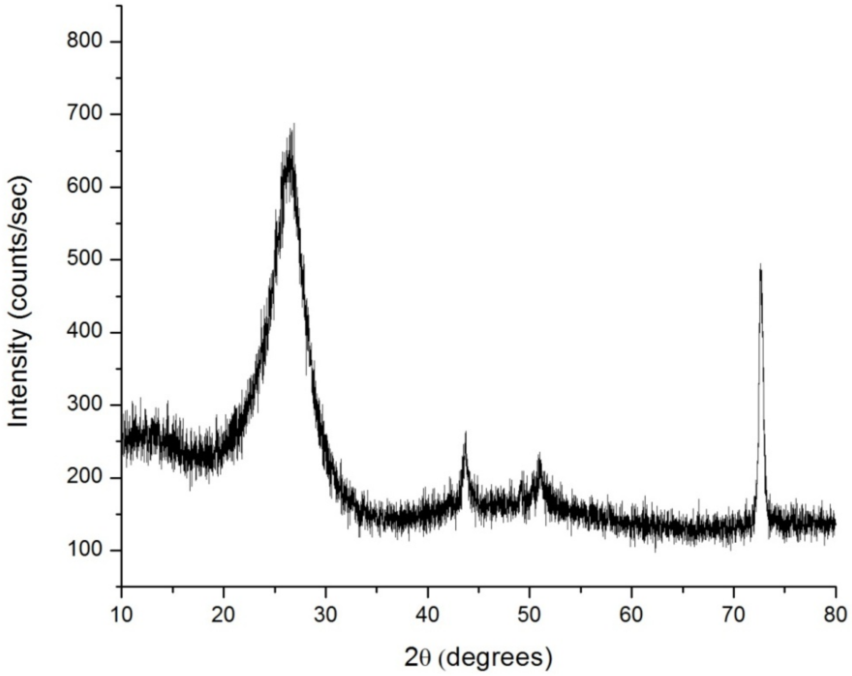


Figure 4.9 XRD pattern of synthesized adsorbent having template to precursor ratio of 1:2.4

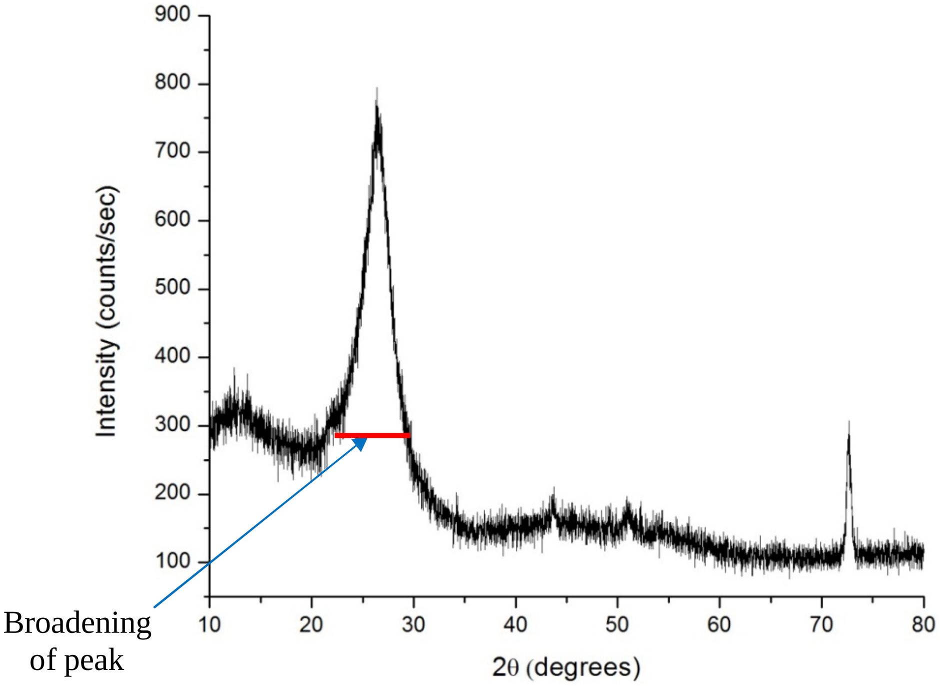


Figure 4.10 XRD pattern of synthesized adsorbent having template to precursor ratio of 1:2

Table 4.1 XRD-2• values for various synthesized adsorbents

S. No.	Template to Precursor Ratio in Synthesized Adsorbent	2• (°)
1.	1:6	26.6274
2.	1:4	26.5446
3.	1:3	26.7056
4.	1:2.4	26.5452
5.	1:2	26.4666

In the XRD patterns of the synthesized adsorbents, there are 3 more peaks for 2• = 43 – 44°, 2• = 49-51° and 2• = 72-73°. These 3 peaks are due to the sample holder used in XRD. The material of the sample holder is aluminium. XRD pattern for the sample holder is shown in figure 4.11. For the sample holder, peaks are obtained at above mentioned 2• values. Hence for the synthesized adsorbents, only one intense peak is obtained at the Bragg angle (2•) of 26-27° (table 4.1).

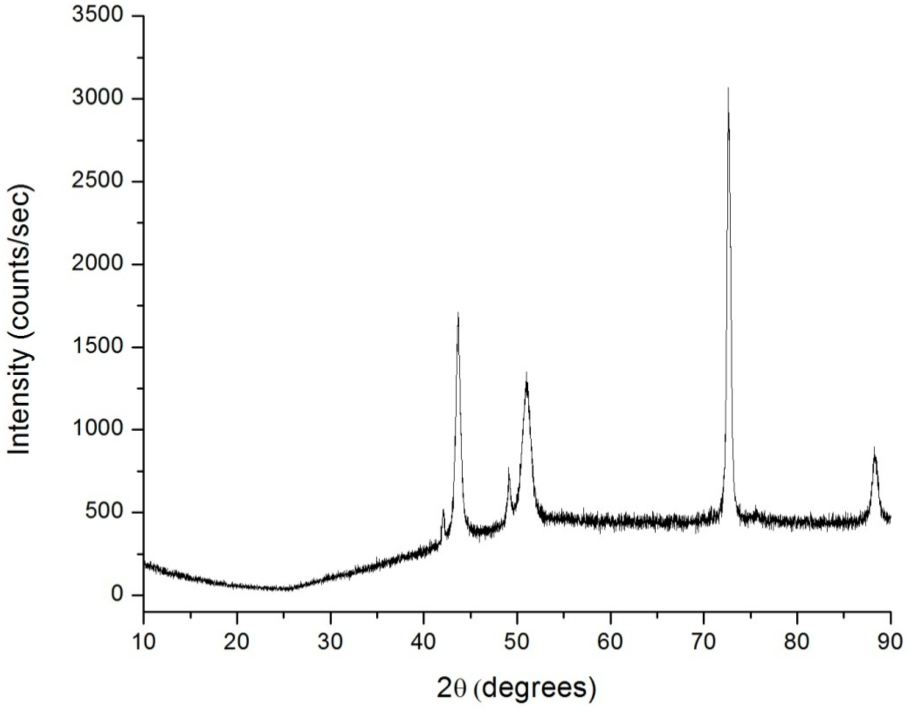


Figure 4.11 XRD pattern of the sample holder

The peak at 2• = 26-27° is from (002) diffraction plane of hexagonal graphitic carbon. Also the line broadening of XRD peaks is observed for all the synthesized adsorbents (figure 4.10). This is primarily due to the very small crystallite size. This is an apparent property of the nano-materials and causes broadening of diffraction peaks (Matej et al., 2009 and Andhariya et al., 2011). Hence the synthesized material is nano-structured.

4.2.2 Scanning electron microscopy (SEM)

SEM images for the samples before carbonization show that the particles have spherical shapes (figure 4.12). The white area represents silica left in the samples. Hence complete removal of silica has to be ensured for further studies.

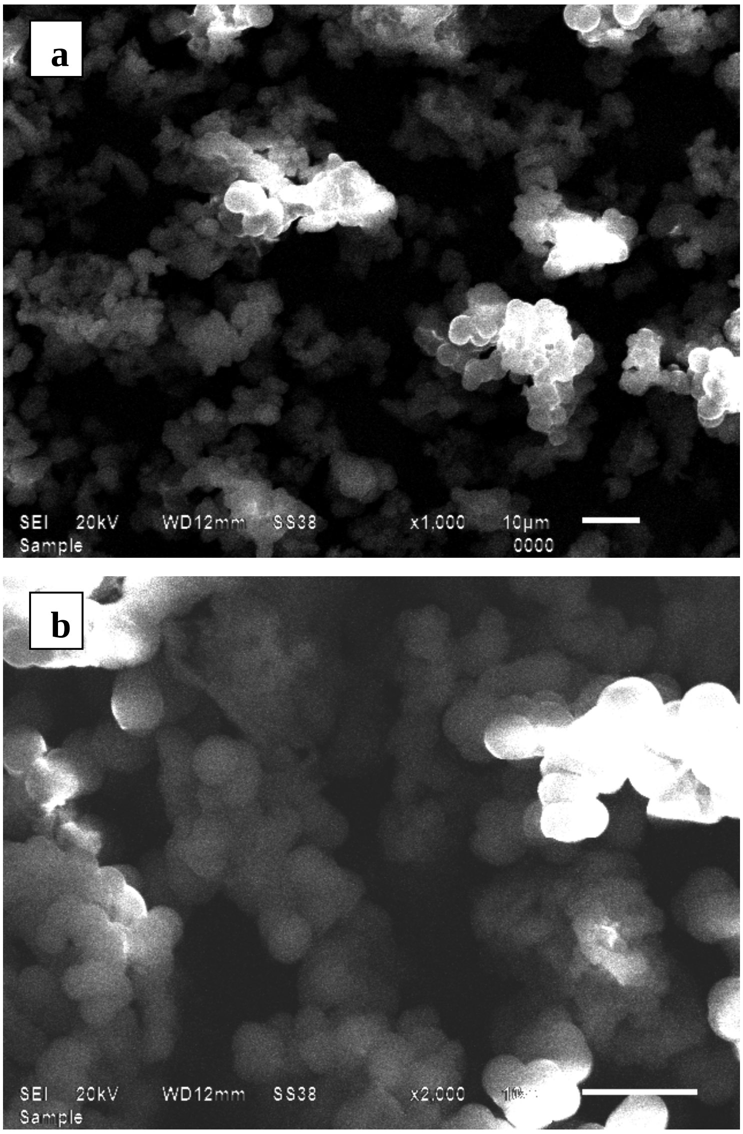


Figure 4.12 SEM images of the samples before carbonization, **a)** having template to precursor ratio of 1:2 at 1000 magnification and **b)** having template to precursor ratio of 1:2.4 at 2000 magnification

After carbonization, the texture of the material has transformed and SEM image of the synthesized adsorbent (figure 4.13) clearly indicates the formation of irregular and heterogeneous type of pores.

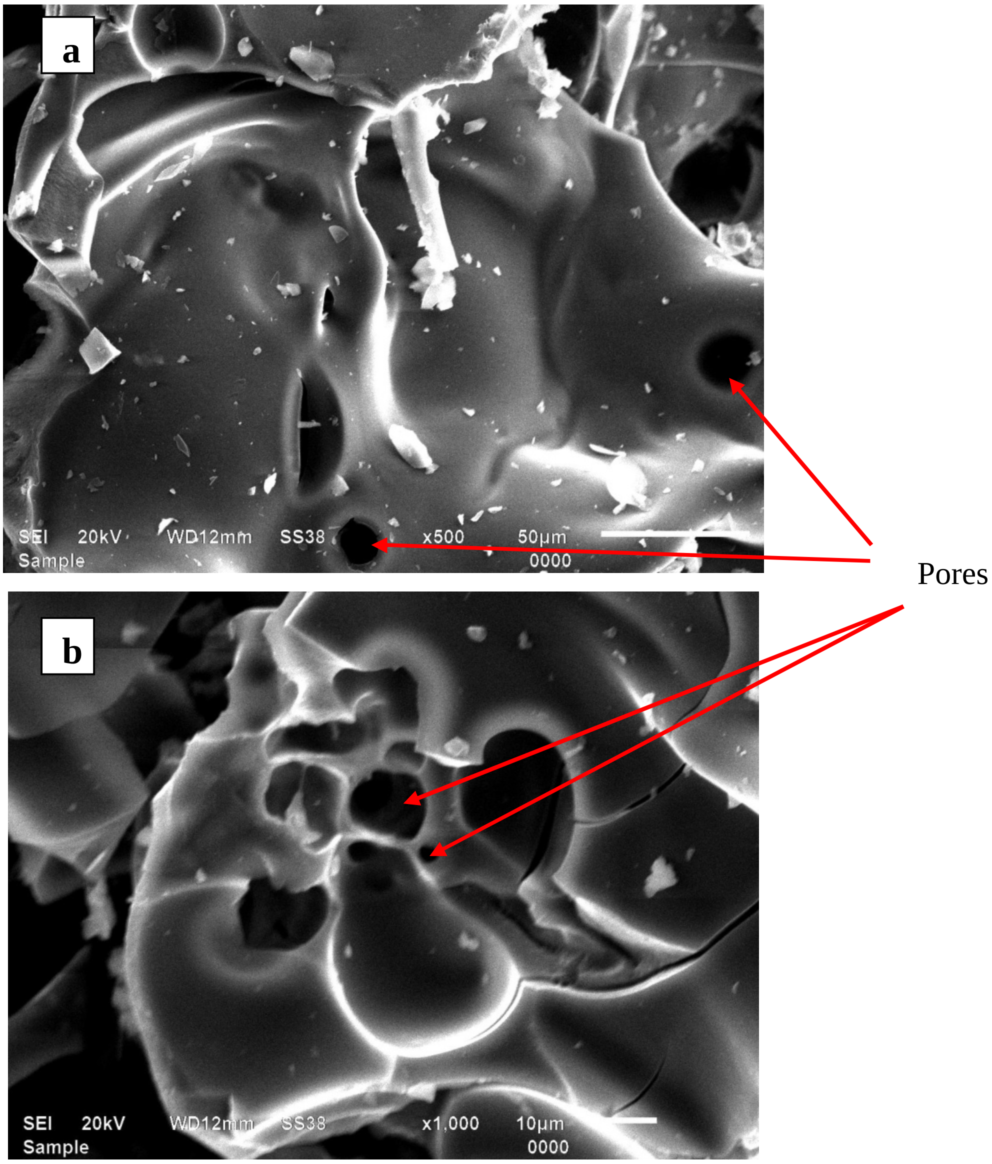


Figure 4.13 SEM images of the synthesized samples, **a)** having template to precursor ratio of 1:2 at 500 magnification, and **b)** having template to precursor ratio of 1:2.4 at 1000 magnification

4.2.3 Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared (FTIR) spectroscopy is a useful tool to determine the formation of new or disappearance of functional groups. The carbonization of the template samples results in the thermal degradation of the precursor i.e. melamine formaldehyde resin. The FTIR spectra of the synthesized adsorbents are shown in figures 4.14 – 4.18.

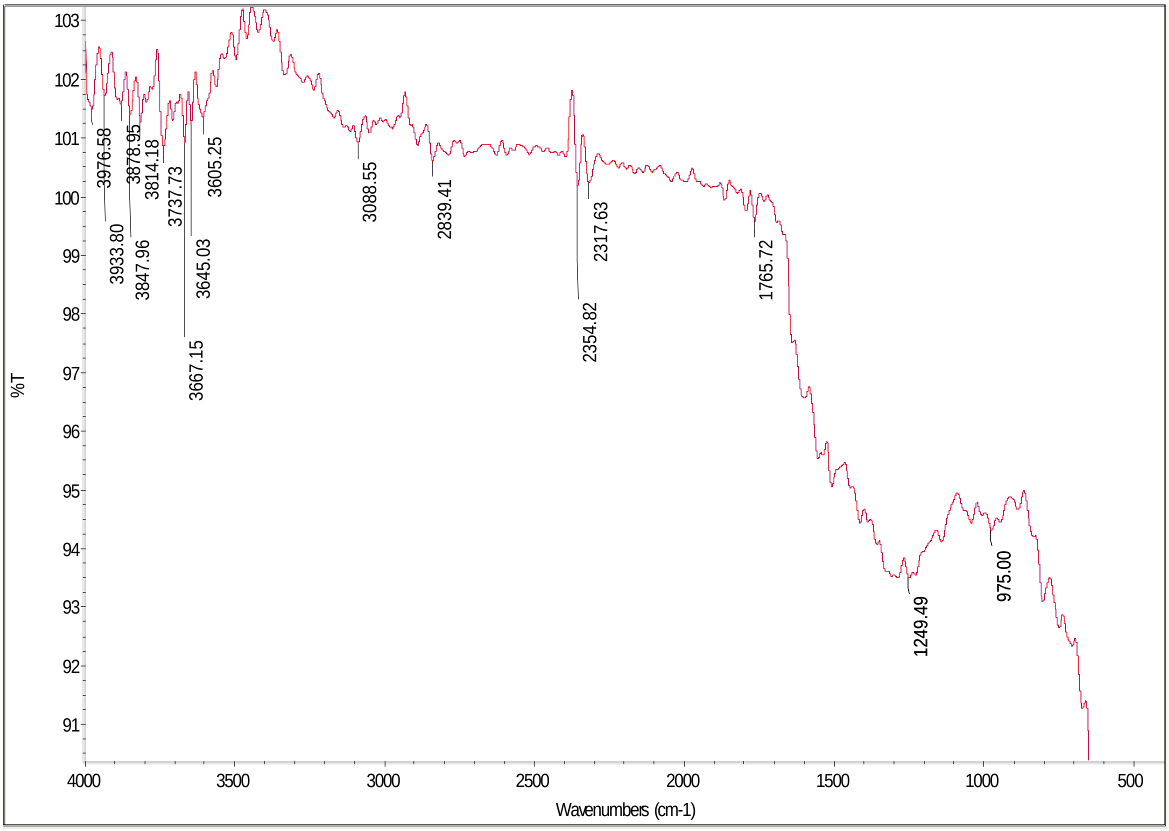


Figure 4.14 FTIR spectrum of synthesized adsorbent having template to precursor ratio of 1:6

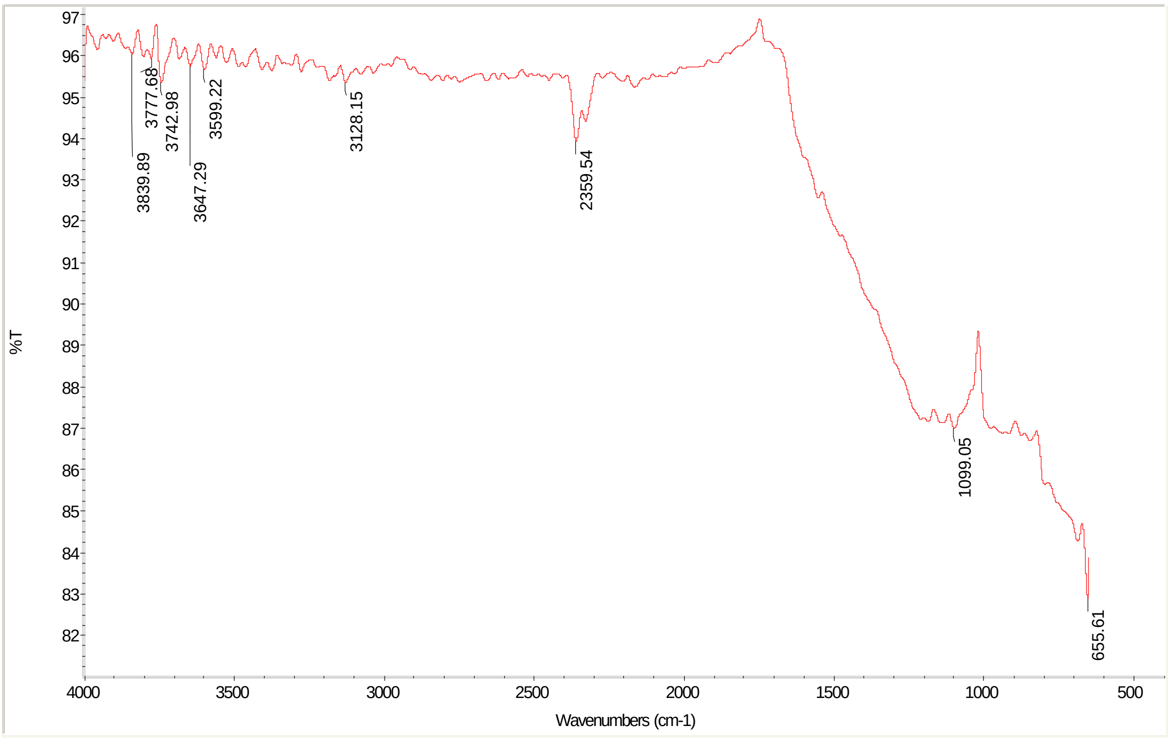


Figure 4.15 FTIR spectrum of synthesized adsorbent having template to precursor ratio of 1:4

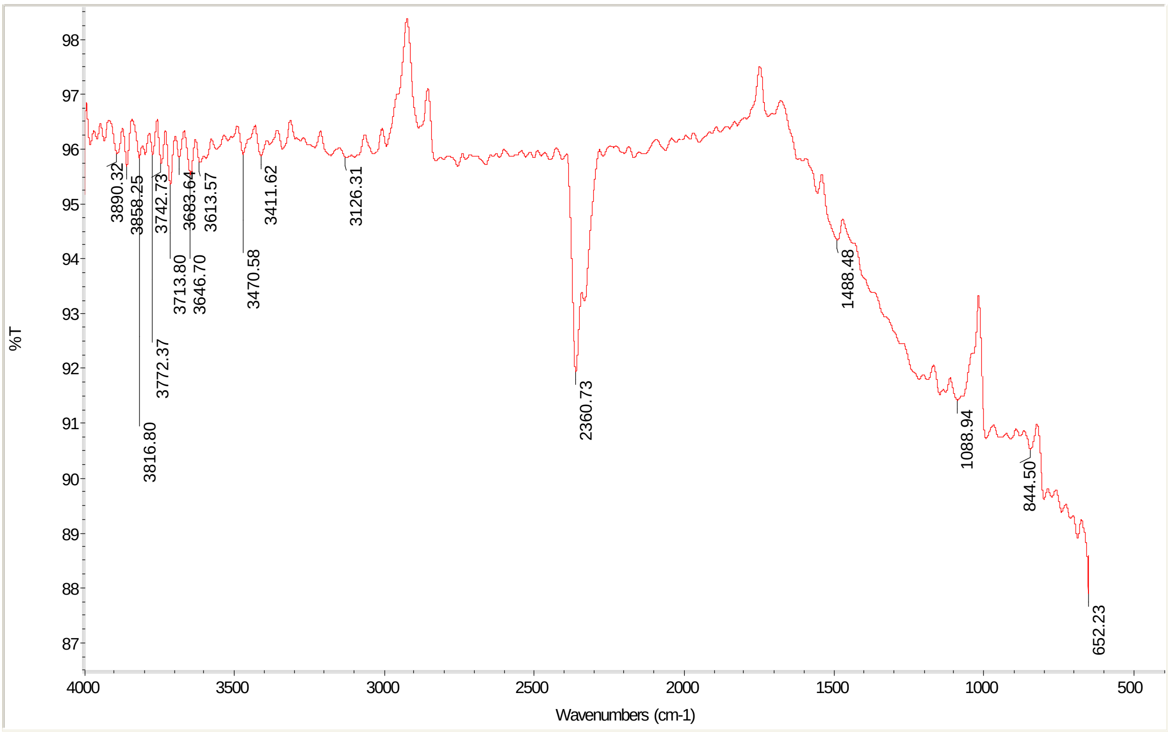


Figure 4.16 FTIR spectrum of synthesized adsorbent having template to precursor ratio of 1:3

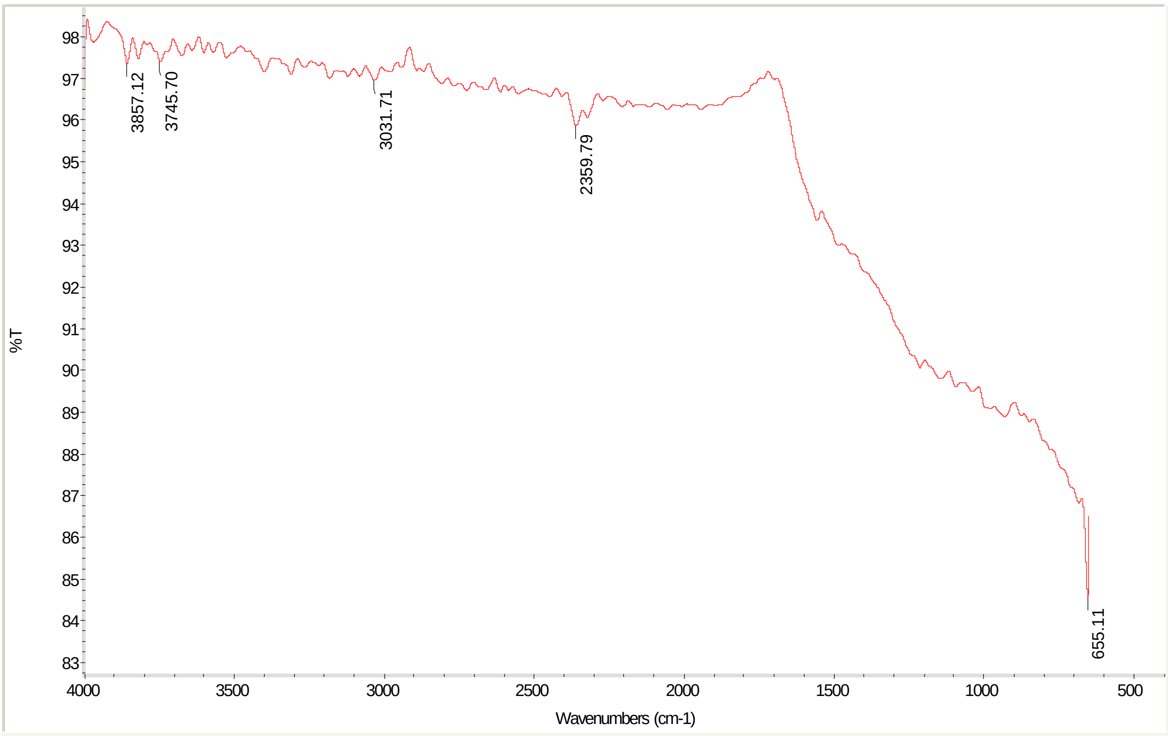


Figure 4.17 FTIR spectrum of synthesized adsorbent having template to precursor ratio of 1:2.4

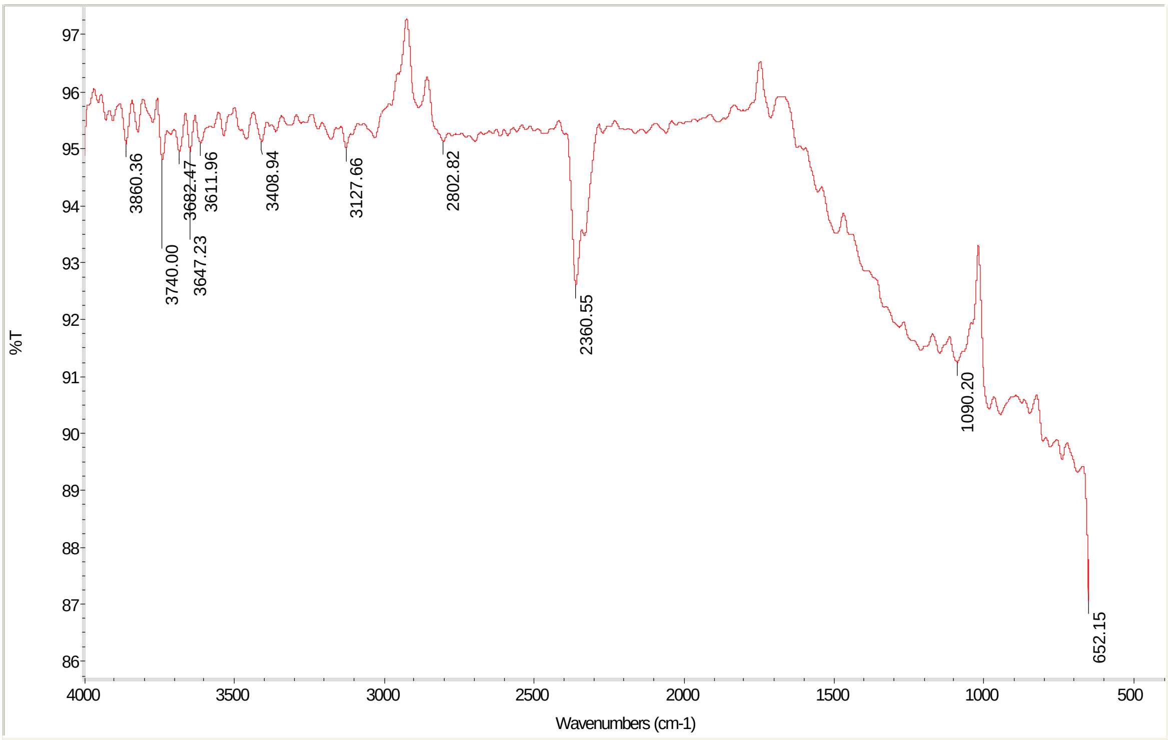


Figure 4.18 FTIR spectrum of synthesized adsorbent having template to precursor ratio of 1:2

The peak around 1090–1250 cm^{-1} corresponds to the stretching vibration of C–O bond, indicating the presence of ether group. Peaks in the range of 3200–3600 cm^{-1} are attributed to the stretching vibration of O–H bond and the small peaks in the range of 3000–3200 cm^{-1} correspond to the stretching vibration of C–H bond. But no peak is observed in the range of 1500–1650 cm^{-1}, attributing to the absence of C–N bond. Reason of absence of nitrogen in the synthesized adsorbents could be carbonization process conditions. It may have resulted in the loss of nitrogen. Also, to confirm the absence of nitrogen in the synthesized adsorbents, nitrogen content of the adsorbents has been estimated using Kjeldahl method.

4.2.4 Nitrogen content determination by Kjeldahl method

Kjeldahl method is used to determine the nitrogen content of the synthesized samples. In the FTIR spectra, no peaks for C–N bond were observed, showing the absence of nitrogen in the samples. Hence, Kjeldahl test was carried out to check the presence of nitrogen in the synthesized adsorbents. The digestion of the synthesized adsorbents was done for around 3 hours, followed by distillation for 2-3 hours. During the titration step, when mixed indicator was added to the collected sample, its color change was observed. The colorless solution became green for few seconds and then it changed to purple, which is the end point of the titration. This shows that no nitrogen is present in the samples. This was observed for all the samples.

Absence of nitrogen can be attributed to the loss of nitrogen during carbonization process. The carbonization process conditions i.e. carbonization temperature and rate of heating may have to be optimized to avoid the loss of nitrogen in the samples.

4.2.5 Surface area and pore volume determination

Surface area and pore volume are two important parameters that need to be estimated for an adsorbent. But the synthesized adsorbents could not be characterized for these two parameters because of non-availability of the facility in the University. Attempts need to be made to get the samples characterized for these parameters from outside organizations having the requisite facility.

4.3 CO_2 Adsorption Study

Due to the loss of nitrogen from the synthesized adsorbents, they did not adsorb carbon dioxide when a mixture of CO_2 and N_2 was passed over them at room temperature. As CO_2 is acidic in nature, carbon adsorbent has to be alkaline in nature for CO_2 adsorption. After the loss of nitrogen from the same, it might have become acidic / neutral and therefore, did not adsorb carbon dioxide. To confirm the same and check the integrity of the new adsorption study step, a conventional adsorbent zeolite 13X was used for carbon dioxide adsorption study. 1.8 g of zeolite 13X was used. A gas mixture with flow of 15.4% by volume of CO_2 and balance N_2 was passed through the adsorption bed. Total feed rate was maintained at 26 ml/min (CO_2 = 4 ml/min and N_2 = 22 ml/min). Temperature maintained was at 30 °C. The exit gas stream from the adsorption bed was analysed by gas chromatograph. Initially there was a drop in the CO_2 concentration in the exit stream. Analysis was continued till the concentration of CO_2 in the product was found to be equal to that in the feed, i.e. up to saturation of adsorbent bed.

CO_2 adsorption was studied using breakthrough adsorption curve method. Let 'C_O' be the initial concentration of CO_2 i.e. in the inlet gas stream and 'C' be the CO_2 concentration at any time 't'. Initial concentration of CO_2 (C_O) in the gas stream is known. CO_2 concentration (C) at any time is obtained from the gas chromatograph. A graph was plotted between C/C_O vs time (figure 4.19). This breakthrough curve is used to calculate the adsorption capacity of zeolite 13X at room temperature. Adsorption capacity of zeolite 13X at 30 °C is estimated to be 4.08 mmol CO_2/g of adsorbent.

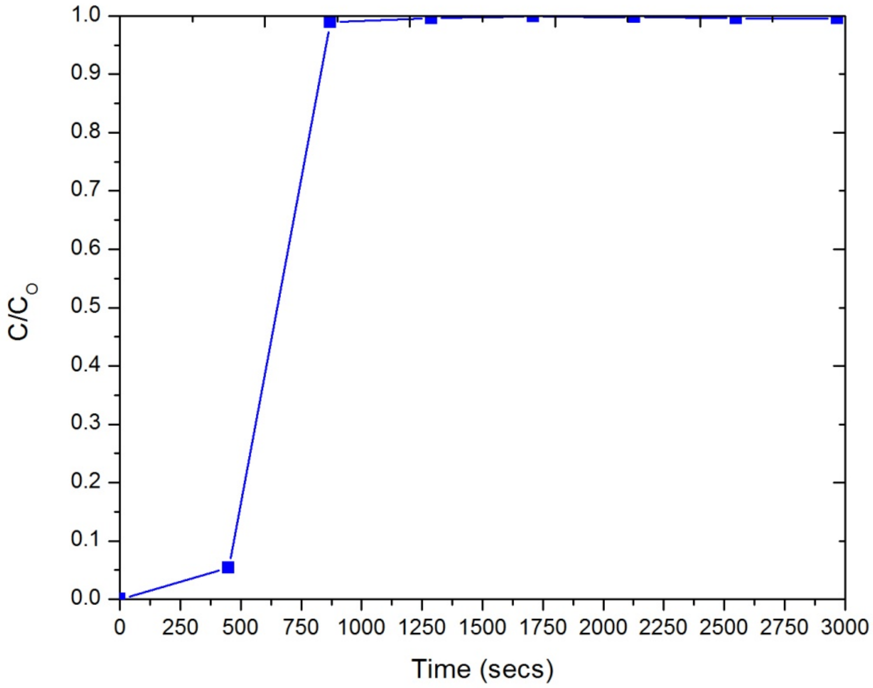


Figure 4.19 Breakthrough curve of CO_2 on zeolite 13X at 30° C

Same procedure was followed for the synthesized adsorbents but there no CO_2 adsorption was observed. This is because of the loss of nitrogen from the synthesized adsorbents during carbonization process. Hence this process needs to be optimized to avoid this loss of nitrogen from the adsorbent.

CHAPTER 5

CONCLUSIONS

Adsorption of CO_2 using basic adsorbents requires high pressure operation, hence modified adsorption routes need to be developed with higher adsorption capacity, less energy and cost intensive. This can be achieved by two ways, namely (i) modification of adsorbents and (ii) development/modification of nano-structured adsorbents.

The nano-structured adsorbents are synthesized by using melamine-formaldehyde resin as the precursor. Mesoporous silica is used as the template for the development of tailor-made adsorbents. Preparation of adsorbent includes two steps: synthesis of resin (precursor) and carbonization of the templated resin samples. Process conditions for the resin synthesis are optimized. During condensation reaction, there is a drastic change in pH with temperature and it has to be maintained above 7 to avoid solidification. The next step is carbonization, which results in the thermal degradation of the precursor. It is done at 500 °C for 1 hour. This process results in the formation of pores in the material. Material obtained from this process is expected to be nitrogen enriched carbon adsorbent. But from the characterization of the synthesized adsorbents (FTIR and Kjeldahl test), it is found that nitrogen is not present in the synthesized adsorbents. This is attributed to the loss of nitrogen during carbonization process. Hence carbonization process conditions i.e. carbonization temperature and rate of heating have to be optimized to avoid the loss of nitrogen in the samples.

The XRD patterns of the synthesized adsorbents show that the material is carbon in nature with hexagonal structure. Also the line broadening of XRD peaks predict that the material is nano-structured. The SEM images also show the formation of the pores in the synthesized adsorbents. Surface area and pore volume are two important parameters that need to be estimated for an adsorbent. But the synthesized adsorbents could not be characterized for these two parameters because of non-availability of the facility in the University. Porous and nano-structured adsorbents are obtained but due to the loss of nitrogen, they do not adsorb carbon dioxide when a mixture of CO_2 and N_2 is passed over them at room temperature. As CO_2 is acidic in nature, carbon adsorbent has to be alkaline in nature for CO_2 adsorption. After the loss of nitrogen from the same, it might have become acidic / neutral and therefore, did not adsorb carbon dioxide. CO_2 adsorption study is carried out for zeolite 13X to check the integrity of the new adsorption study set up.

Recommendations for Future Work

- Melamine-formaldehyde resin was used as the precursor. Other polymeric materials can also be used as precursor like urea-formaldehyde resin etc. The synthesis process of other polymeric materials has to be optimized.

- Nitrogen plays an important role in the tailor-made adsorbents, as it enhances the CO_2 adsorption capacity of the adsorbent via chemisorption. Hence the process conditions for the carbonization are to be optimized to avoid the loss of nitrogen from the synthesized adsorbents.

- CO_2 adsorption study of these carbon adsorbents has to be carried out at various temperatures. The ultimate aim is to capture CO_2 from the flue gases. These flues gases are at higher temperatures. Hence the need is develop the adsorbents with high CO_2 adsorption capacity at higher temperatures.

- Regeneration of the adsorbent is an important factor. Regeneration strategy will influence adsorbent lifetime and replacement rate. The regeneration process conditions are to be optimized for minimum temperature differential between adsorption–desorption cycles.

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