Carbon adsorbents synthesized from plastic waste for CO_2 capture

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of

Masters of technology

By

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Certificate

This is to certify that the dissertation work entitled "**Carbon adsorbents synthesized from plastic waste for CO_2 capture"** being submitted by **Simarjot Kaur (Roll. No. 601611004)** to Department of chemical Engineering for the partial fulfillment for the award of degree of **Master of Technology** in Chemical Engineering from Thapar Institute of Engineering & Technology (Deemed to be University), Patiala, Punjab, has been carried out by her under our supervision.

This work has not been submitted partially or wholly to any other university or institute for the award of this or any other degree or diploma.

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Declaration

I hereby declare that the work being presented in the dissertation report entitled **"Carbon adsorbents synthesized from plastic waste for CO_2 capture"** by me in the partial fulfillment of the requirements for the award of degree of Master of Technology in Chemical Engineering from Thapar Institute of Engineering & Technology (Deemed to be University), Patiala, Punjab, is an authentic record of my work carried under the supervision of Dr. Haripada Bhunia, Professor & Head and Dr. Raj Kumar Gupta, Professor, Department of Chemical Engineering, Thapar Institute of Engineering & Technology (Deemed to be University), Patiala. The matter presented in this dissertation has not been submitted in any other University/ Institute for the award of any degree/ diploma.

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Abstract

PET waste has been used to develop carbon adsorbents by direct carbonization followed by chemical activation using KOH. The textural properties of the adsorbents were studied using N_2 adsorption-desorption isotherms and presence of functional groups were analyzed using XPS analysis. With chemical activated conditions it was observed that optimum sample (PET-3-700) showed highest surface area of 1428.7 m^2 g^{-1} and total pore volume of 0.47cm^3 g^{-1}. Presence of oxygen functionalities in the sample was confirmed by XPS analysis. Fixed bed adsorption setup was used for estimating CO_2 uptake capacity for adsorbents under dynamic conditions, with varying concentrations of CO_2 (5-12.5%) and adsorption temperatures (30-100 °C), these conditions are relevant to flue gas conditions at industrial level. PET-3-700 under pure CO_2 flow and at temperature of 30 °C produced maximum CO_2 uptake capacity of 1.3 mmol g^{-1}. Adsorbent produced was found to be completely regenerable, tested by multiple adsorptions-desorption cycles. There was decrease in adsorption capacity with increase in adsorption temperature indicating pysiosorption behavior of the adsorbent. Freundlich isotherms best described the adsorption process at different adsorption temperatures and CO_2 concentrations. Further, in order to save experimentation time a model was developed and simulated, which estimated the breakthrough profiles at different experimental conditions. Hence, combining all above discussions makes the adsorbent potential material for CO_2 capture for industrial and other relevant applications. Fig.1 shows schematic of overall dissertation work

Keywords: PET waste; KOH activation; CO_2 adsorption; Adsorption kinetics; Adsorption isotherm; Modelling & simulation

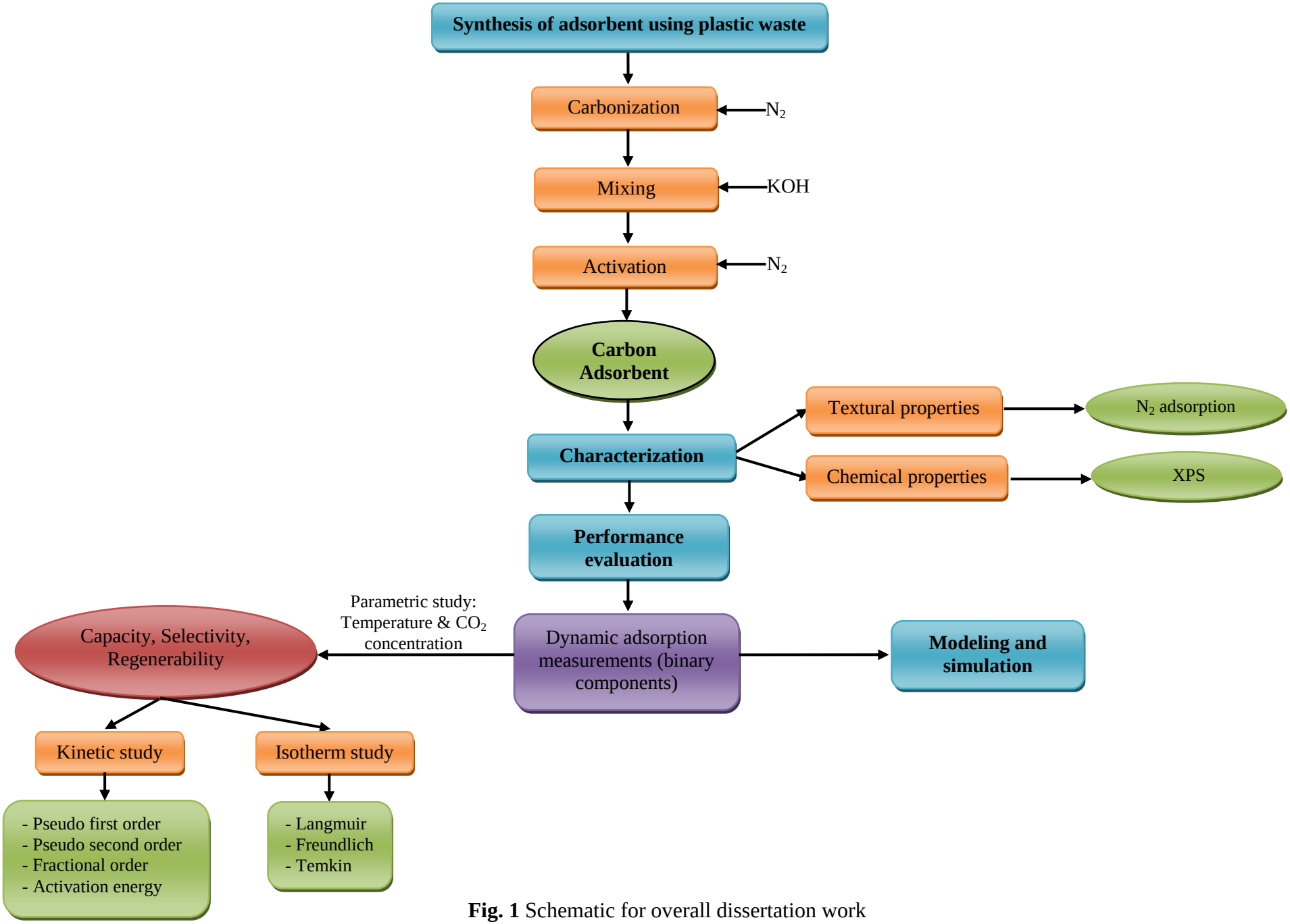

Fig. 1 Schematic for overall dissertation work

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List of Symbols

C	Effluent CO_2 concentration, volume%
C_{in}	Inlet CO_2 concentration in simulated feed gas, volume%
Error (%)	Error function
k_1	Pseudo-first order rate constant, min^{-1}
k_2	Pseudo-second order rate constant, g $mmol^{-1}$ min^{-1}
k_n	Fractional order rate constant
m	Fractional order model constant related to adsorption time
M	Mass of the adsorbent, g
n	Fractional order model constant related to driving force
N	Total number of experimental points
q_e	Dynamic adsorption capacity at equilibrium, mmol g^{-1}
$q_{e,i}$	Equilibrium adsorption capacity of component *i* in the mixture, mmol g^{-1}
$q_{e,exp}$	Amount of adsorbate adsorbed at equilibrium determined experimentally, mmol g^{-1}
$q_{e,pred}$	Amount of adsorbate adsorbed at equilibrium as predicted by model, mmol g^{-1}
q_i	Adsorbed amount of component *i* in mixture, mmol g^{-1}
q_m	Maximum monolayer capacity, mmol g^{-1}
q_t	CO_2 adsorption capacity at time t, mmol g^{-1}
q_T	Total adsorbed amount in mixture, mmol g^{-1}
$q_{t,exp}$	Amounts of CO_2 adsorbed at a given time determined experimentally, mmol g^{-1}
$q_{t,pred}$	Amounts of CO_2 adsorbed at a given time predicted by model, mmol g^{-1}
Q	Gas flow rate, cm^3 min^{-1}
R	Universal gas constant, kJ mol^{-1} K^{-1}
R^2	Regression coefficient
S_{BET}	BET surface area, m^2 g^{-1}
S_{CO_2}	Selectivity of CO_2 over N_2

t	Time, min
t_b	Breakthrough time, min
t_e	Equilibrium time, min
T	Temperature, K
V_P	Total pore volume obtained at a relative pressure of 0.99, $cm^3\ g^{-1}$
C_b	Concentration of component i in the gas phase, mol m^{-3}
d_p	Diameter of the particle, m
d_b	Diameter of bed, m
D_{ax}	Axial dispersion coefficient, $m^2\ s^{-1}$
u	Interstitial velocity, m s^{-1}
u_s	Superficial velocity, m s^{-1}
k_{fi}	Film mass transfer coefficient, m s^{-1}
y_i	Molar fraction of component i
P_t	Total pressure, atm
q_i	Adsorbed phase concentration of component i, mmol g^{-1}
T	Temperature, K
x	Axial distance along the column, m
M_i , M_j	Molecular weight of component i and j, g mol^{-1}
R_g	Universal gas constant
r_p	Radius of the pore, m
R_p	Radius of the particle, m
q_o	Value of q (adsorption capacity) at equilibrium (mmol g^{-1})
T_i	Feed temperature, K

Dimensionless numbers

Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number

φ_{ij}

Greek letters

ε_b	bed porosity
ε_p	particle porosity
ε_M	macropore prosity
$\varepsilon_{\square}$	micropore porosity
$\frac{\varepsilon_i}{\kappa}, \frac{\varepsilon_j}{\kappa}$	Lennard Jones parameter for pure gases, K
$\frac{\varepsilon_{ij}}{\kappa}$	Lennard Jones parameter for gas mixture, K

List of Abbreviations

A%	Relative area contribution
APTS	aminopropyltrietoxysilane
B. E.	Binding energy
BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
BMC	Basic magnesium carbonate
CNT	Carbon nanotubes
DEA	Diethanol amine
DOE	Department of Energy
ED	Ethylenediamine
FTIR	Fourier transform infrared
FWHM	Full width at half maximum
GHG	Greenhouse gases
$GtCO_2eq$	Gigatonnes CO_2-equivalents
HFC	Hydrofluorocarbons
HMMM	Hexamethoxymethyl-melamine
IPA	Isopropanol amine
IPCC	Intergovernmental panel on climate change
MDEA	Methyldiethanol amine
MEA	Monoethanol amine
MWCNT	Multi-walled carbon nanotubes
PET	Poly (ethylene terephtalate)
PFC	Perfluorocarbons
ppm	Parts per million
PET	Poly(ethylene terepthalate)

PSA	Pressure swing adsorption
PSD	Pore size distribution
PTSA	Pressure temperature swing adsorption
SSE	Sum of the squared relative error
SWCNT	Single-walled carbon nanotubes
TEM	Transmission electron microscopy
TEPA	Tetraethylenepenta amine
TEPAN	Tetraethylenepenta amine acrylonitrile
TSA	Temperature swing adsorption
VSA	Vacuum swing adsorption
wt%	weight%
XPS	X-ray photoelectron spectroscopy

Chapter 1 – Introduction

1.1 Climate changes due to CO_2 emissions

Excessive burning of fossil fuels and industrial development has led to increase in the concentration of greenhouse gases (GHGs). This in is result has highly affected our environment by increasing global temperature and sea level [1]. Among all major GHGs (CO_2, CH_4, N_2O, O_3, PFCs, HFCs and SF_6) [2]. CO_2 is the considered to be major GHG which is effecting our environment in a withering manner.

Report of Intergovernmental Panel on Climate Change (IPCC), 2018 states that there is 44% increase in carbon dioxide concentration. Initially, in pre-industrial age, CO_2 concentration was approximately 275–285 ppm which is now recorded to be 410 ppm in 2018. If the trend continues, it is expected that it may reach upto 570 ppm by 2100 [1, 3].The major contributor for this uncontrolled growth of CO_2 concentration from pre-industrial stage is fossil fuels. In 2010, about 38±3.8 Gt CO_2 eq (~76%) CO_2 emissions from burning of fossil fuels was found which increased in the year 2010-2011 and 2011-2012 at a rate of 3% and 1-2% respectively [3]. Further this excess fossil fuel burning is depleting our environment by raising the global temperature, sea level, melting of glaciers and surface ice [4]. This can even be observed from the fact that there is decrease in thickness of ice by nearly 40% of arctic from last few decades even during 1901-2010; the sea levels have risen by 0.19 m. This increasing CO_2 concentration have even lead to acid rains which has affected the pH of sea and turned sea water acidic and hence causing harm to marine life. In recent times, frequency of the weather pattern change is increasing like larger storms, heat waves, droughts, heavy rainfall and wild fires. By the end of 21st century, this increasing rate of CO_2 levels will cause rise of average global temperature by 2-6°C by the year 2100, CO_2 concentration stabilization to a level of 450 ppm is considered [5]. Fig. 1.1 shows global greenhouse gas emissions during in the year between 1980 and 2017.

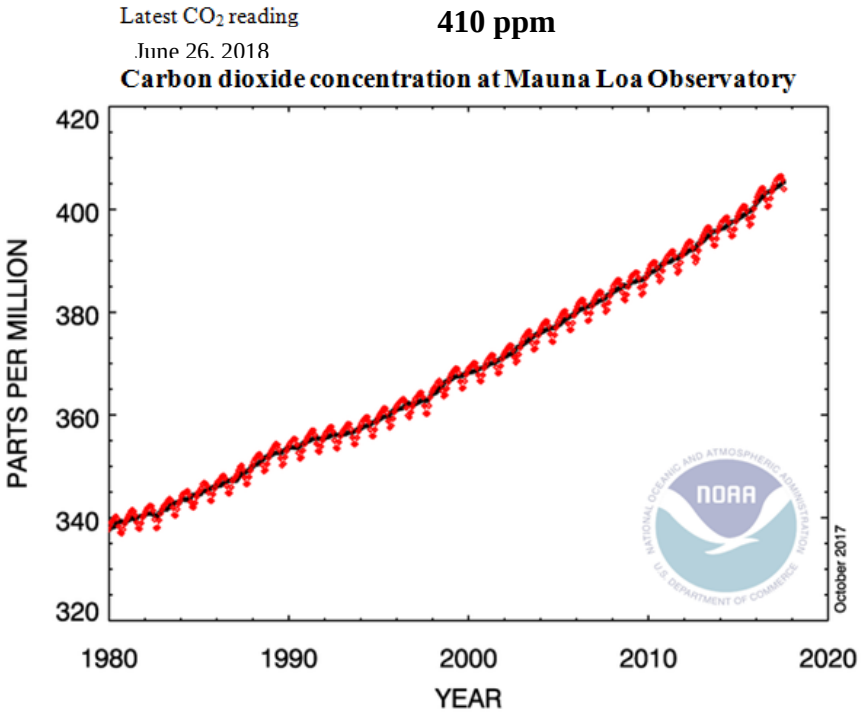


Fig. 1.1 Global greenhouse gas emissions during 1980-2018[6]

1.2 CO_2Mitigation pathways

Increase in CO_2 concentration can be controlled in many ways. Some of these are mentioned below:

i. developing efficient technologies so that demand for energy can be reduced and hence reducing CO_2 emissions,
ii. laying emphasis on renewable energy resources and developing technologies for using then, rather than depending on conventional energy resources,
iii. introducing multiple approaches like afforestation and reforestation which are related to geo-engineering,
iv. capturing and sequestrating of carbon dioxide.

Among all approaches mentioned above CCS can be considered as the best way to control GHGs emissions since these can be effectively implemented within short time and hence can be considered as promising approach. Since this technology will not stop the usage of fossil flues as energy resource and will provide enough time for other technologies to develop [7, 8].

1.3 Carbon dioxide capture and sequestration

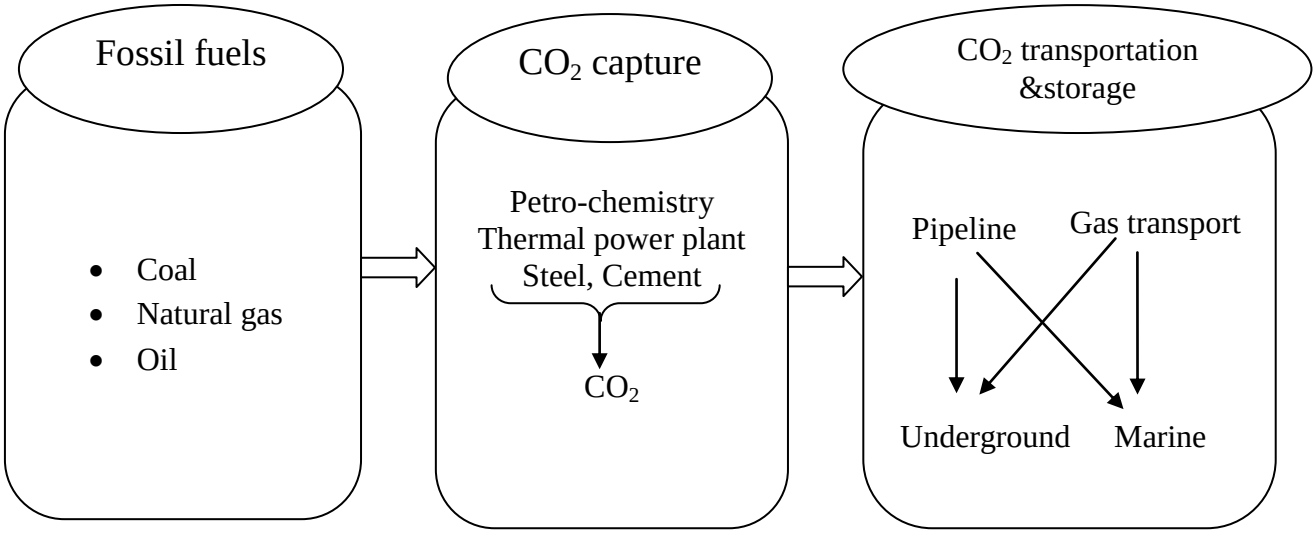


Fig. 1.2 Summary for CO_2capture and storage (CCS) [9]

Fig. 1.2 shows overall CCS technology which is generally capturing CO_2 without discharging into atmosphere and sequestration/storage. There are several important factors (such as plants scale, fuel cost, distance between capture location and storage site, characteristic of power plants technology, etc.) which need to be considered related to cost involved for application of CCS on fossil fuels. CO_2 storage sites include geological formation like oil and gas fields which is estimated to sequester around 1120–3400 Gt CO_2. Sequestration requires high pressure and concentrated CO_2 stream considering the economics involved in its transportation and injection into storage site. CO_2 transportation through pipeline are marginal portion of overall cost [10, 11]. Well known technologies available for CO_2 transportation were developed for enhanced oil recovery.

1.3.1 CO_2 capture technologies

Among many technologies available, three main approaches for capturing CO_2 are; post-combustion, pre-combustion and oxyfuel combustion.

1.3.1.1 Pre-combustion

In this process capturing of CO_2 is performed earlier to fossil fuel combustion. This is done by either partial oxidation/gasification of fuel (coal or natural gas) carried out in a gasifier under low oxygen level to produce synthesis gas which considers CO and H_2 as

shown in Fig. 1.3. This is free from other pollutants gas. Further syngas under water-shift reaction with steam need to be developed to produce CO_2 and H_2. This process has several advantages like due to CO_2 pressure and density in gases leads to easy removal and small equipment sizes. This is also having disadvantages as conversion of fuel is expensive and process is complex. This process is used mainly in integrated gasification combined cycle (IGCC) plant using fuel like coal but with disadvantage of efficiency loss of 7-8%. Also, in fertilizer industry and hydrogen generation, this process is used.

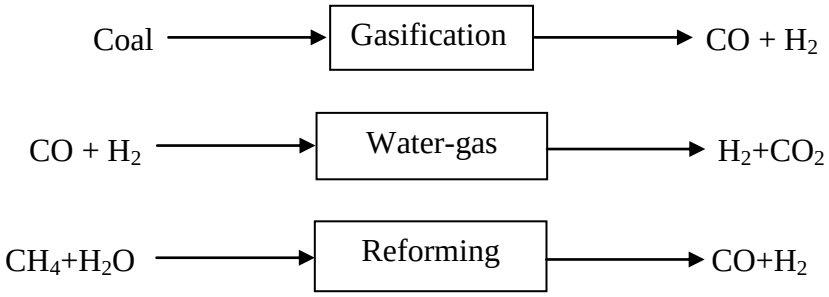


Fig. 1.3 Schematic representation of pre-combustion process

1.3.1.2Oxyfuel-combustion

This combustion capture technology, instead of air, uses pure oxygen (95% purity) for fossil fuel combustion and this is in trial phase. As oxygen is used for combustion, main components of flue gas are CO_2, H_2O, SO_2 and particulates. Removal of $SO_2$and particulates is carried out using conventional electrostatic precipitator and flue gas desulphurization methods. Left out gas containing higher concentration of CO_2 is compressed, transported and stored according to Fig. 1.4. The disadvantage of this process is that it consumes huge amount of oxygen which is generated using an energy intensive air separating unit which results in energy penalty of over 7% in comparison to without CCS. Corrosion problem occurs due to high concentration of SO_2 in flue gases [12-14].

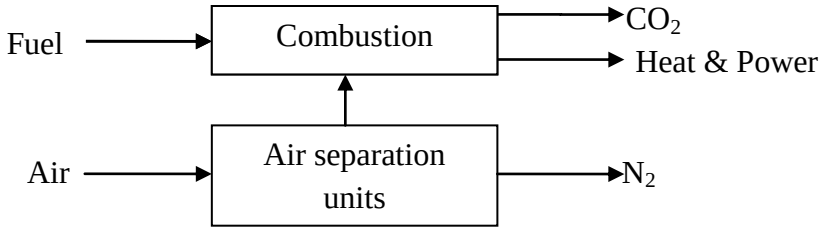


Fig. 1.4 Schematic representation of oxyfuel-combustion process

1.3.1.3 Post-combustion

This type of capture technology is the most preferable because it gets retrofitted to existing power plants. It is used to separate CO_2 after combustion. At small scale, this technology with CO_2 recovery rate of 800 t day^{-1} has proved to be the best among these technologies. The challenge for this technology is high energy penalties and cost of CO_2 capturing units for reaching CO_2 concentration of above 95.5% needed for transportation and storage. This is because the CO_2 level in flue gases is only 7-14%. It is estimated by National Energy Technology and Laboratory that 32 and 65% electricity cost would increase in gas and coal fired plants [15-17].

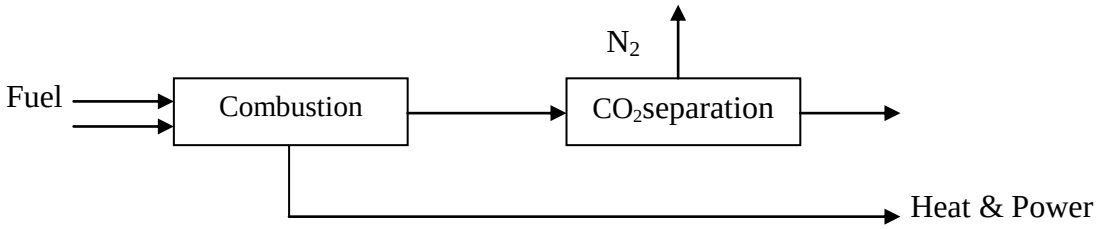


Fig. 1.5 Schematic representation of post-combustion process

Post-combustion carbon capture technologies are; (a) absorption, (b) membrane separation, (c) cryogenic distillation, (d) microalgal bio-fixation and (e) adsorption. Fig. 1.6 shows complete technology options

1.3.1.3.1 Absorption

This process is the most matured and established technology in petroleum and chemical industries for CO_2 separation. Fig. 1.7 shows absorption carbon capture process. Typical liquid sorbents are monoethanol amine (MEA), diethanol amine (DEA), methyldiethanol amine (MDEA) etc., ammonia solution, rectisol (chilled methanol) [18].

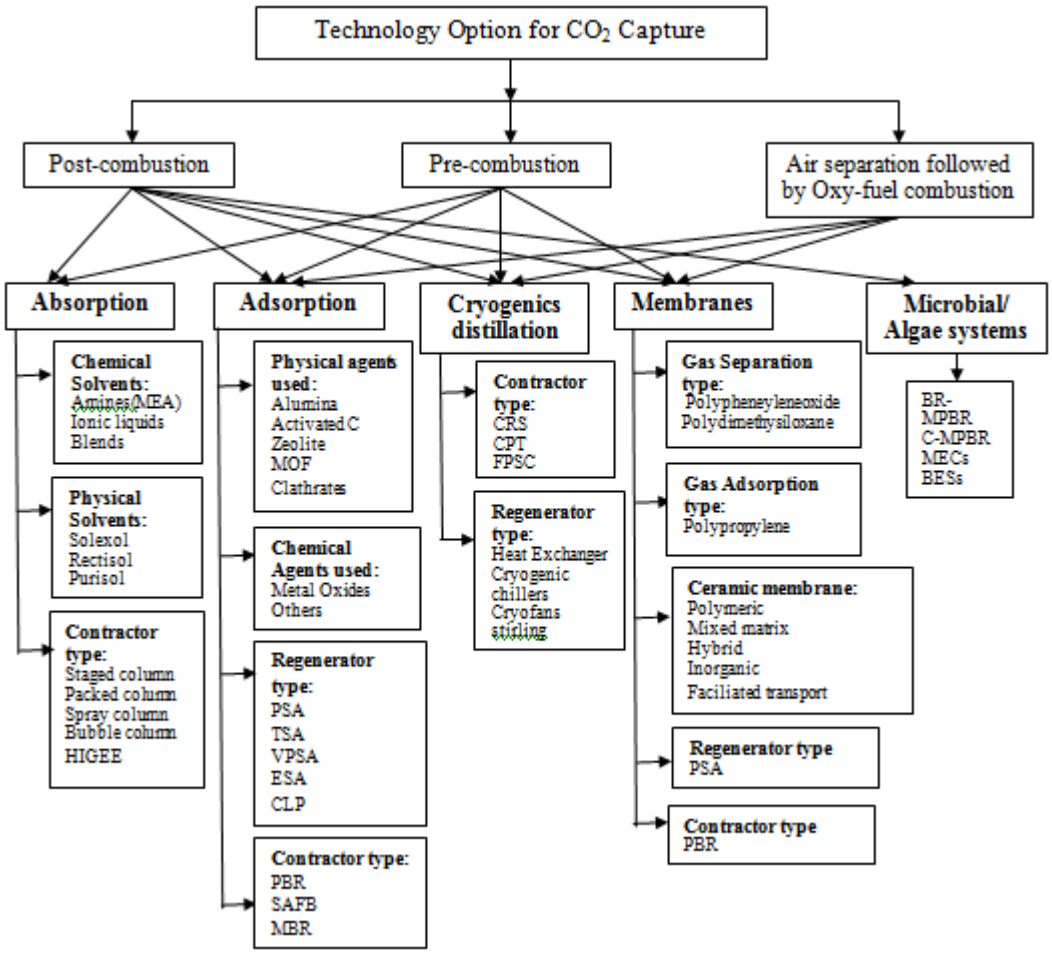


Fig. 1.6 Technology options for CO_2 separation and capture [19]

Veawab *et al.* [20] and Aaron *et al.* [21] in their studies for CO_2 separation, used MEA which is considered highly efficient (about 90%) for CO_2 absorption. At present capacity of 1t CO_2 h^{-1} pilot plant was tested successfully for coal fired power plant which is using 30% MEA solution. Other sorbents like piperazine and anion-functionalized ionic liquid have attracted consideration because piperazine reacts much faster than MEA but having problem of larger volatility than MEA. This technology suffers from problem like amine degradation. Degradation causes solvent loss, equipment loss, generation of volatile harmful compounds and high energy requirement for regeneration which impede its implementation.

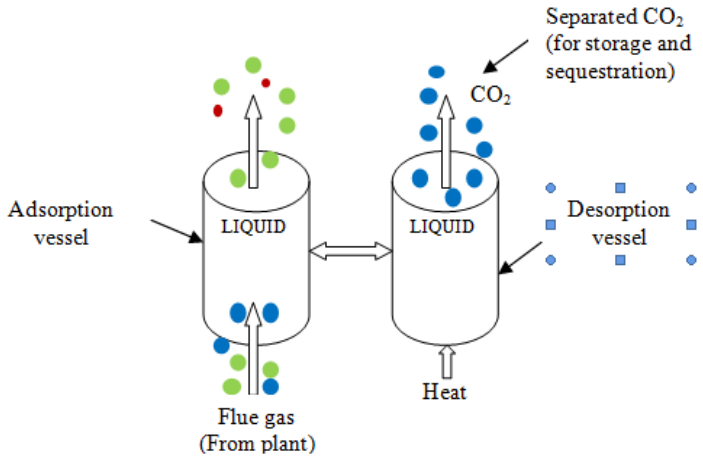


Fig. 1.7 Schematic of absorption carbon capture process usingamine [22]

1.3.1.3.2 Membrane separation

In this process, a membrane is used to which allows only CO_2 to pass through it among all flue gas components (Fig.1.8). Membrane, which is the essential part of this process, made up of composite polymers having a layer which is lean discriminatory is attached to thick cheap non-selective layer, which supports the membrane [23]. The major hurdle of this process is low CO_2 concentration and pressure. This process is used to separate O_2 from N_2 and CO_2 from natural gas.

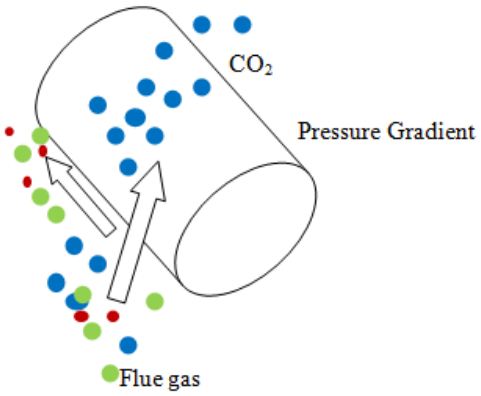


Fig.1.8 Schematic of membrane carbon capture process

1.3.1.3.3 Cryogenic distillation

This process is performed at high pressures and low temperatures and is analogous to other conventional distillation process. The only difference is that it is used for separating gaseous mixtures by their boiling point difference while other processes are used separating

the liquids. In this process CO_2 separation is done by cooling flue gas from 100 to 135 °C which is de-sublimation temperature. After this, the separation of solidified carbon dioxide is done from light gas followed by compression to 100-200 atmospheric pressure. In this process upto 90-95% CO_2 is recovered but as it is performed at lower temperatures and higher pressure conditions and energy intensive. Also, this practice is applicable for only higher carbon dioxide concentration which makes its application unsuitable for practical applications [21].

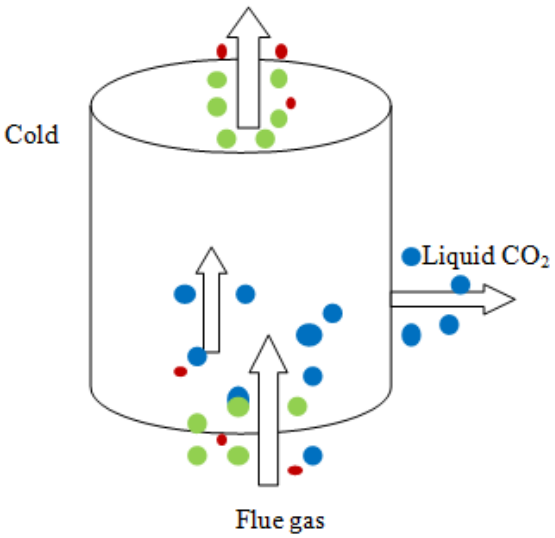


Fig. 1.9 Schematic of cryogenic carbon capture process

1.3.1.3.4 Adsorption

Capture of CO_2using adsorption process is gaining attention since it is afeasibleand practical alternative in comparison to current energy-demanding aqueous amines absorption technologies because of ease of application, less energy requirements and lower equipment costs. This technology uses a solid adsorbent with porous structure which selectively removes CO_2 gas based on gas-solid interactions. A huge amount of solid adsorbents like zeolites, activated carbons, silica, amine modified adsorbents etc. have been reported for capturing carbon dioxide. But these conventional adsorbents suffer from large pressure or temperature gradient between adsorption and desorption steps and low selectivity towards CO_2. Thus, synthesis of an efficient and selective adsorbent will make adsorption the most promising technology.

1.4Thesis motivation and objectives

It has been found that conventional adsorbents exhibit low selectivity and poor performance under humid conditions. Extensive work has been carried out on amine modified adsorbents for CO_2 capture. But impregnation of amines or high thermal treatments with various chemical agents is sometimes considered less favorable because this leads to blocking of pores of the adsorbent. Hence, many efforts have been made to fabricate materials with well-developed pore structure and enhanced selectivity towards CO_2. Among the available adsorbents, carbon-based adsorbents have been selected for the present study, as their preparation can be carried out using variety of raw materials and their porous structure can be tailored based on the application. Most of the carbon adsorbent development has been carried out using direct carbonization and activation (physical or chemical) of different starting materials. The objective of dissertation study is to prepare carbon adsorbents having specific pore structure; we have selected the development of carbons using PET waste. Research groups have carried out development of carbon adsorbents from PET waste for capturing CO_2 from flue gas. Moreover, most of the adsorbents developed have been evaluated at static conditions, generally at room temperature or 0 °C, which is not pertinent to flue gas application. Hence, we aim to develop carbon adsorbents which remove CO_2 continuously under dynamic flow conditions.

The overall objective of the research is to develop effective sorption process for the continuous removal of CO_2 from point source. The specific objectives are:

- Synthesis of carbon adsorbents from PET waste.
- Characterization of synthesized adsorbents for their relevant properties.
- Study the adsorption performance of adsorbent using a fixed bed adsorption setup operated at variable flow rates, temperatures, and feed concentrations of CO_2.
- To fit the kinetic and isotherm models for the experimental data.
- To model the fixed bed adsorption process using MATLAB software in order to predict breakthrough curves.

1.5 Thesis overview

This thesis has been divided into **six chapters**. PET waste was used for producing oxygen enriched carbon adsorbent by initially direct carbonizing and then by chemically activating for adsorbing CO_2 under simulated flue gas conditions. Thorough characterization of was carried out for investigating textural, surface and chemical properties of the prepared carbons. Dynamic adsorption-desorption experiments were conducted in the fixed-bed system to evaluate their CO_2 adsorption capacities, selectivity and regeneration under simulated flue gas conditions. Adsorption of CO_2 on these adsorbents was also evaluated from kinetics, isotherm and thermodynamic point of view. Energy required for CO_2 desorption was also calculated.

Chapter one (Introduction) presents issues which are effecting our environment and briefly describes the different process involved for CO_2 capture. It slightly discusses about different greenhouse gases especially CO_2 and its impact on global climate. Approaches for mitigating these issues have also been addressed in this chapter and provides the problem objectives of this dissertation study.

Chapter two (literature review) discusses different types of adsorbents and their adsorption performances were compared. More emphasis has been given to carbon based adsorbents as the current work focuses on them.

Chapter three (Materials and methods) briefs about the experimental works carried out in current studies. The materials, chemicals and experimental methods used for the characterization and performance evaluation used for carrying out the adsorption-desorption experiments are listed in the first and second part. The experimental setup for fixed-bed adsorption study is also presented in this chapter. In the third part, various adsorption kinetic, isotherm models and thermodynamic parameters are discussed.

Chapter four (Modeling of fixed bed setup) mathematical model of fixed bed adsorption set up has been designed in order to understand dynamics of the bed. This model development helps in reducing the experimentation time. The equation developed has been substituted in MATLAB software and simulated in order to obtain breakthrough curves.

Chapter five (Results and discussions) covers the preparation of carbon adsorbents using PET waste and chemical activation with KOH followed by their characterization. CO_2

adsorption-desorption studies on these carbons were performed under dynamic conditions and the optimized sample was investigated comprehensively. Static adsorption capacities of the optimized sample were evaluated at varying temperatures under 100% CO_2 and N_2 conditions. Kinetic models and isotherms were fitted on experimental data. The breakthrough curves predicted by modeled equation along with experimental data has been also shown which discusses about variation in actual data and predicted data.

Finally, chapter six (Conclusions) summarizes the important finding of the work.

After this, the references cited are listed. At the end, publications are listed.

Chapter 2 – Literature Review

2.1 Adsorption technology

In this technology, the adsorbate (CO_2) molecules are adsorbed onto a surface of solid sorbent. The process can be physical adsorption (physiosorption) and chemical adsorption (chemisorption) depending on interaction between adsorbent and adsorbate molecules. Physical adsorption involves weak Van der Waal forces while chemisorption involves chemical bond between adsorbent and adsorbate molecules. Moreover, physical adsorption requires lesser energy as there is no chemical bonding between adsorbent and adsorbate. We need to develop adsorbent which requires less energy since during regeneration of the captured CO_2, process consumes a huge amount of power in CCS.

There are several problems associated with CO_2 capture process like lower CO_2 loading, low efficiency due to presence of moisture, poor CO_2/N_2 selectivity, additional required energy, which needs to overcome for a good potential for energy saving.

In adsorption process CO_2capturing is carried out by using several approaches like (i) isothermal regeneration means, like pressure swing adsorption (PSA), including vacuum (VSA) or (ii) non-isothermal regeneration means, like temperature swing adsorption (TSA) [24-26]. In PSA, CO_2 adsorption is performed at higher pressure while depressurization is done by swing to low pressure (usually atmospheric pressure). In TSA, desorption is done by raising the temperature. TSA requires large amount of time than PSA but it provides higher purity of CO_2i.e more than 95% and 80% of recovery can be achieved [27, 28].

2.2 Types of adsorbents

Several available adsorbents are zeolites, silica, metal organic frameworks and polymers, activated alumina, carbon based adsorbents, carbon nanotubes (CNTs), activated carbon fibers, and graphene [29, 30]. For effective capture of CO_2 by adsorption process, strengths and limitations of each adsorbent should be considered. Even the adsorbents developed should posses high surface area, high CO_2 uptake capacity, regenerative property, less energy requirements and should be less expensive. But, it is very difficult by a single technology to fulfill all criteria of National Energy Technology Laboratory (NETL) and

Department of Energy (DOE) [31, 32]. Eventually, adsorbents that can work effectively within the practical CO_2 capture process will be the winners.

2.2.1 Silica based adsorbents

Mesoporous silica materials due to their higher surface areas, tunable porous structures provide faster diffusion for gases. Therefore, this has gained much attention for the purpose of capturing CO_2 applications. Hydroxyl groups are present in large amount on the surface of mesoporous silica which facilitates grafting of amine groups by which the adsorption capacity gets enhanced.

First study was carried out by Xu *et al.* [33] on CO_2 adsorption (determined by thermogravimetric analysis) using amine-impregnated mesoporous silica. Using wet impregnation method, they impregnated polyethyleneimine (PEI) at different loadings on MCM-41 silica which was termed as "molecular basket" [34-37]. With 75 wt.% PEI loading at adsorptiontemperature of 75 °C with 10% concentration of CO_2, they reported the CO_2 uptake capacity of ~2.1 mmol g^{-1} [33]. On rising the adsorption temperature from 25 °C to 75 °C, subsequent increase in adsorption capacity was also observed. They compared two other methods, one was two-step impregnation and second was mechanical mixing; and it was observed that one-step wet impregnation method was better [37].

In another study by Belmabkhout *et al.* [38] on MCM-41 type mesoporous silicas in which CO_2 capture at adsorption temperatures from 60 °C to 120 °C was evaluated. At 1 bar pressure and at 100 °C, the adsorbent illustrated CO_2 uptake of 0.66 mmol g^{-1} whereas for 45 bar and at 25 °C, it increased to value of14.7 mmol g^{-1}. Using MCM-41-100 and hydrothermal treatment, the adsorbent developed was pore-expanded mesoporous silica (PE-MCM-41) grafted with triamine, CO_2 hold up studies on this adsorbent were performed thermogravimetrically at four adsorption temperatures and with low pressure conditions. TRI-PE-MCM-41 at 25 °C and 1 bar exhibit CO_2 uptake of 2.8 mmol g^{-1} and when moisture was introduced, the adsorption capacity increased since bicarbonate partial bicarbonates formation took place[39, 40].

Chen *et al.* [41] impregnated PEI and tetraethylene penta amine (TEPA) on monolithic silica and observed that for 5% CO_2 feed stream, 65% PEI loaded monolith silica at 75 °C, maximum gravimetric uptake capacity was 3.75 mmol g^{-1}. On the other hand, TEPA modified monolith silica at 75 °C under 100% CO_2 flow showed CO_2holdup of 5.91 mmol g^{-1}. Main

disadvantage of using TEPA is that it showed decrease in uptake capacity after but 5 runs of adsorption–desorption cycle.

2.2.2 Zeolites based adsorbents

Zeolites are highly crystalline & ordered microporous alumino silicates with having distinct internal specific surface areas and volumes [42-44]. They are generally used at high pressures (> 2 bar) and it is reported that their adsorption capacity is highly effected bymoisture existing in gas stream. This is as of hydrophilic nature in which polar water molecules adsorbs on the surface of zeolite and causes blockage in hence making unavailable for CO_2 by which CO_2 capacity get reduced. This is the main reason for very high temperature (>300 °C) requirement for regeneration of zeolites and therefore large energy are required for regeneration [45-47].

Bertsch *et al.*[48-50] using zeolite X and Y confirmed that physiosorption was the dominating process for these zeolites. A littleholdup of 0.15 mmol g^{-1} was found. They studied changes in CO_2 uptake capacities of zeolite on introducing aluminium into it.

Barthomeuf *et al.*[51] showed the strength of basic site on different zeolites X, Y, mordenite (MOR), and ZSM-5 (MFI). They showed that with the increase of aluminium content, basic strength of zeolites increased due to lower electro-negativity of aluminium. In other study, same authors showed different types of exchangeable cations. They found that basicity increases with decrease in electro-negativity and base strength of Cs-exchanged zeolite X is highest among all. It was also suggested that porous characteristics are also having effect on CO_2 adsorption capacities on commercially available zeolites and synthesized zeolites.

Siriwardane *et al.*[52] carried out adsorption/desorption study on zeolite 13X at 295 K and 17 bar under 15% CO_2 concentrations. Under humid conditions, they found that after carrying out two cycles of sorption, CO_2 holdup decreased from 6 to 4 mmol g^{-1}.

Chatti*et al.* [53] using different amines like MEA, ethylenediamine (ED) and isopropanol amine (IPA) modified CO_2uptake capacity of zeolite 13X. Dynamic CO_2 adsorption capacity of IPA modified zeolite under 15% CO_2 (remaining He) flow was 0.52 mmol g^{-1}> MEA modified zeolite (0.45 mmol g^{-1}) > bare zeolite (0.36 mmol g^{-1}). With 100%

flow of CO_2 at adsorption temperature of 75 °C, equilibrium adsorption capacity of MEA modified zeolite and bare zeolite was 1.1 and 0.85 mmol g^{-1}, respectively.

2.2.3 Carbon based adsorbents

Carbon based adsorbents have been considered as potential CO_2 adsorbents because they are completely regenerable over several adsorption-desorption cycles, possess high surface area, are thermally/mechanically stable, and are hydrophobic. Furthermore, their prepared can be carried out using many easily available of low cost sources [54-56]. Different carbon-based adsorbents are activated carbons, carbon molecular sieves and carbon nanotubes (CNT). Many different material have been used for development of different adsorbents (activated carbons) and on these adsorbents CO_2 adsorption studies have been carried [57, 58].

2.2.3.1 Commercial activated carbons

. For high pressure CO_2 capture application, activated carbon, charcoal and coal all being carbon-based materials have been used because of low cost, their insensitivity to moisture and high surface areas.

Na *et al.* [59] in his study carried out on commercial activated carbon. Using pressure swing adsorption process, he evaluated CO_2 uptake of developed adsorbents at 1 bar and different adsorption temperatures of 15 °C and 55 °C. They obtained equilibrium CO_2 holdup of 3.2 and 1.6 mmol g^{-1} respectively under 100% CO_2 flow.

Himeno *et al.* [60] using MAXSORB activated carbon showed static equilibrium carbon holdup of 25.7 mmol g^{-1} at 25 °C and 30 bar.

2.2.3.2 Carbon adsorbents from renewable resources

In the recent time, porous carbons have been produced by carbonizing different carbon containing resins, fly ash, or biomass and it is amorphous porous forms of carbon. Due to large number of availability of raw materials, tailoring of these materials in terms of PSDs, active surface structures, pore structures and other factors like adsorption properties can be done.

Using raw materials, these materials can be prepared by using two steps: carbonization and/followed by activation. Direct carbonization was performed by placing precursors in inert atmosphere and heating it and pyrolysing it to produce carbonaceous materials (char) [58].

During this process, release non-carbon elements (hydrogen, oxygen, and nitrogen) form precursor took place. This developed the materials having a inflexible carbon skeletons known as chars which possess poor surface and structural properties [61]. To improve the surface areas, porosity and active sites, activation was performed using chemical treatment. Chemical activation is performed at lower temperature by using chemicals such as KOH, $ZnCl_2$, NaOH, H_3PO_4 etc. [62]. In chemical activation, the yield of carbon is much higher with well-developed porosity and surface areas [62, 63].

Adsorbents are obtained using fly ash via. impregnation of organic bases like polyethyleneimine (PEI) aided by polyethylene glycol, tetraethylene-pentaamineacrylonitrile (TEPAN) and diethanolamine (DEA). The obtained materials exhibited CO_2 holdup of approx. ranging between 0.91–1.3 mmol $g^{-1}$with pure CO_2 flow at 75 °C [64]. In another study carried out on fly ash derived carbons, obtained by impregnation of different kind of amines (MEA, DEA, and MDEA) to improve the textural properties, were evaluated the CO_2 adsorption performance at different temperatures. CO_2 uptake of 1.56 mmol g^{-1} is observed for MEA impregnated carbon at 30 °C which was higher than parent activated fly ash carbon (0.95 mmol g^{-1}). It was also observed that due to impregnation, specific surface area of the carbons decreased because of blocking of the pores [65].

Plaza *et al.* [66] in his study using biomass residue (olive stones) by CO_2 activation and treatment with ammonia (NH_3) developed activated carbons. The obtained carbon activated by CO_2 at temperatures 25 °C and 100 °C under complete CO_2flows showed CO_2 holdup capacities of 2.4 mmol g^{-1} and 0.7 mmol g^{-1} respectively. On the other hand, at same condition but NH_3 treated carbons showed CO_2 capacities of 1.9 mmol g^{-1} and 0.6 mmol g^{-1}, respectively.

In another study on almond shell based activated carbons, obtained from CO_2 activation exhibited CO_2 holdup of 1.2 mmol g^{-1} in a mixture containing 15% CO_2 in N_2 and 2.6 mmol g^{-1} under pure CO_2 atmosphere at adsorption temperature of 25 °C while aminated almond shells based carbons, (with 4.5% nitrogen), at 25 °C under 15% and complete CO_2 flow demonstrates CO_2 holdup of 1.1 and 2.2 mmol g^{-1} [67].

Olivares-Martin *et al.* [68] developed carbon adsorbents from waste carpet materials using carbonization and then activating the adsorbent with KOH. The obtained adsorbent under complete CO_2 and with 30 °C of adsorption temperature gave CO_2 uptake of 3.13 mmol

g^{-1}. On raising the temperature of adsorption upto 100 °C, the uptake capacity reduced to 0.7 mmol g^{-1}. Less than 15% CO_2 concentration, at 25 °C and 100 °C, CO_2 uptake of 0.89 mmol g^{-1} and 0.16 mmol g^{-1} was attained. This study shows the effect of activation conditions and type of precursor used.

In another work, Sevilla *et al.* [69] developed porous carbons from polysaccharides (starch and cellulose) and biomass (sawdust) using hydrothermal carbonization and chemical activation with KOH. The obtained material (at 25 °C, 1 bar pressure) showed static CO_2uptake of 4.8 mmol g^{-1} and at 50 °C showed 3.6 mmol g^{-1} CO_2 uptake.

2.2.3.3 Carbon adsorbents from synthetic polymers

Synthetic polymers have also gained popularity in present studies as polymeric precursor apart from conventional activated carbons and biomass derived carbons. Since the developed porous carbons contain refined pore structures, improved chemical properties and better surface chemistry. Different methods developed for the synthesis of porous carbons are direct carbonization, sol-gel process, chemical vapor deposition and hard-templating method (nanocasting method).

Goel *et al.* [70] took hexamethoxymethyl-melamine (HMMM) as precursor and nanocasted it using MCM-41 silica as template for developing nitrogen enriched carbon adsorbents. The optimum adsorbent which was developed at 700 °Chad CO_2capture capability of 0.80 mmol g^{-1}, which was evaluated at adsorption temperature of 30°C under complete CO_2 flow.

Deepak *et al.* [71]used nanocasting technique for developing mesoporous carbon adsorbent using epoxy resin as template and mesoporous zeolite as precursor. Dynamic CO_2studies were performed on developed adsorbents different temperatures (30 to 100 °C) by using fixed bed adsorption experimental setup and observed that carbon developed at carbonization temperature of 700 °C showed CO_2 adsorption of 0.65 mmol g^{-1} under 12.5% CO_2atmosphere at 30 °C. Other studies were carried out in which oxygen enriched carbon adsorbent were developed using nanocasting technique taking mesoporous zeolite as precursor and epoxy resin as template. CO_2 uptake was determined thermogravimetrically at different adsorption temperature ranging between 30 to 100 °C and maximum CO_2 uptake of 0.91 mmol g^{-1} at adsorption temperature of 30 °C was achieved with 100% CO_2 flow [72].

Balsamo *et al.* [73] used coal tar pitch and furfural and carbonized them and then activated the product using steam to develop activated carbon (F50) which showed dynamic CO_2 uptake capacity (using breakthrough column study) of 0.61 mmol g^{-1} at condition of 30 °C under 15% CO_2 concentration. The CO_2 holdup decreased on increasing temperature from 50 °C to 75 °C from ca. 0.30 mmol g^{-1} to 0.15 mmol g^{-1}. In this study, oxygen functionalities on the surface and microporous structure play a major role.

Tseng *et al.* [74] using melamine modified phenol-formaldehyde resin and steam activation developed highly porous carbons. The obtained material at 0 °C and 1 bar showed CO_2 uptake of 6.71 mmol g^{-1} which decreased from 2.2 mmol $g^{-1}$to 0.4 mmol g^{-1} with increasing the adsorption temperature from 25 °C to 50 °C.

One of the commonly generated plastic wastes that is affecting our environment is **PET** poly(ethylene terephthalate). It can act as a potential carbon precursor for CO_2 capture.

Przepio´rski *et al*. [75] prepared porous adsorbents using PETin combination with basic magnesium carbonate (BMC) which mere heated in argon atmosphere, and then washed the sample prepared with acid. Then the effects of this mixture of BMC on PET adsorbent surface at different carbonization temperatures were studies. Firstly, the initial sample prepared using simple heating method in argon atmosphere developed some amount of mesopores and higher amount of micropores. And after carbonization using magnesium salt developed a highly porous carbon having BET surface area c. a. 2000 m^2g^{-1}.

Kartel *et al*. [76] prepared adsorbents from PET waste using H_2SO_4 at the time of carbonization and then activating it using steam activation. But this process required two steps i.e. carbonization and activation which made this process a tough practice for synthesizing adsorbents, besides the developed carbons were having both micropores and mesopores.

Przepio´rski *et al.* [77] used PET waste and dolomite and simple heated this mixture. This resulted in formation of nanoporous carbons which contained MgO and CaO. They prepared carbons at different temperatures of 850 upto 1000 °C. Investigations revealed that at time of heating the minerals inside the mixture went under the thermal degradation and produced MgO and CaO and alsoCO_2. The resultant material developed mesoporous and microporous structures within them which can behave as a carbon adsorbent. Hence this can be observed that dolomite can act as a good activating agent for PET which developed carbon adsorbent having porous structures from simple raw waste of polymers.

Parra *et al*. [78, 79] pyrolysed PET waste in quartz tube under inert atmosphere of N_2 at 400 ^{0}C and then activated it with CO_2 at 925 ^{0}C . The investigations resulted in highly microporous materials with noticeable BET surface area of 2500 $m^2 g^{-1}$.

Adibfar *et al.* [80] performed a comparative study on various adsorbents prepared from PET wastes by using different activating agents like KOH, H_3PO_4, $ZnCl_2$ and H_2SO_4 at static conditions. Maximum CO_2 adsorption capacity was observed c.a. 8.0 $mmolg^{-1}$ for PET activated with KOH and least value c. a.4.0 mmol g^{-1} for PET activated with H_2SO_4.

Mishra *et al.* [81] used PET waste as precursor and made changes on in reaction time, reaction temperature, concentration of H_2SO_4, and carbonization time on PET and studied is effect on the adsorbents formed. Mechanism of PET carbonization was explained by modified shrinking-core model.

Esfandiari *et al.* [82] produced activated carbon from PET wastes by physically activating it under carbon dioxide (CO_2) flow at the time of pyrolysis. It was observed that mesoporous carbon produced had 360 mg I_2 gm^{-1} C and 780 m^2 gm^{-1} surface areas. Activated carbon possessed high density, good conductivity, low ash content and the carbon has amphoteric surface nature.

Czepirski *et al.* [83] studied the effects of varying mass ratio of pitch/polymer, carbonization temperature changes, as well as the activation agents used (steam, carbon dioxide, potassium hydroxide) on the characteristics of the PET, poly(methylene methacrylate), phenol/formaldehyde resin and coal-tar pitch was studied. Results provided method for preparing activated carbon possessing porous structures and additionally perceiving of the formation technique of carbon adsorbents.

Mendoza *et al.* [84] used PET bottle waste for preparing activated carbons by using steam activation and chemical activation by KOH. They obtained adsorbents with commercial activated carbons for CO_2 capture and observed 10% more amount of CO_2 was absorbed by steam activated same and 32.07% by KOH activated samples. Maximum BET surface areas of developed carbons were obtained to be 1235m^2 g^{-1} for steam at 900 °C and 1002 m^2 g^{-1}at 850 °C for KOH activated samples.

Arenillas *et al.*[85] investigated, the CO_2 uptake capacity of chemically activated adsorbents obtained from recycled PET by KOH. The sequence of adsorbents containing

nitrogen components which were developed by carbonization of PET waste along with N compounds, showed a moderate affectivity for CO_2 holdup. CO_2 capturing capacity of 4.8 wt% at 25 °C and 1.2 wt% at 1000 °C were achieved.

2.2.3.4 Carbon nanotubes

Carbon nanotubes can be used for CO_2 capture due to their distinct pore structure, which allows them to achieve an ample series of surface functional groups when treated thermally or chemically. They comprise of single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) modified using amine solutions. CO_2 was adsorbed on purified SWCNTs with temperature ranging from 0 to 200 °C.

Cinke *et al.* [86] developed purified SWCNTs at different temperatures between 0 to 200 °C, which exhibited high specific surface area and total pore volume of 1587 $m^2\ g^{-1}$ and 1.55 $cm^3\ g^{-1}$. Higher uptake capacity (~4.1 mmol g^{-1}) compared to activated carbon (~2.2 mmol g^{-1}) at 35 °C and pressure of 1 bar was obtained.

Lu *et al*. [87] developed multi-walled carbon nanotubes (MWCNTs) impregnated with 3-aminopropyltriethoxysilane (APTS), which at 25 °C under 10% and 50% CO_2 flow, showed dynamic CO_2 adsorption of 0.93 and 2.2 mmol g^{-1} respectively.

It can be concluded from the literature that many adsorbent using PET waste have been synthesized using direct carbonization method or by physical activation method and further studies have been performed on them. Very few adsorbents synthesis has been carried out using chemical activation method. By activating adsorbent using chemical activation method the textural properties of adsorbent improves. Theoretically, CO_2 uptake estimation under static conditions mainly at 30 ˚C shows higher values in comparison to dynamic conditions. But for CCS the CO_2 uptake evaluation should be performed at higher temperature range with dynamic conditions. Therefore, there is a need to develop material using chemical activation. Also, there is a need to work on direct carbonization and to evaluate these materials under flue gas conditions, i.e. low CO_2 partial pressure and high temperatures, by dynamic methods, to predict the applicability of these materials in real situation.

Chapter 3 – Experimental Methods, Kinetics and Isotherm Models

3.1 Materials

PET waste used in this study is obtained from post-consumer soft drink and water bottles from household.

Chemicals sulfuric acid, acetone (100% pure) and KOH used in were provided by M/s S. D. Fine Chemicals Ltd., India and is of analytical grade.

Nitrogen gas (99.995%), carbon dioxide gas (99.999%), and gas mixtures used in this study were supplied by M/s. Sigma Gases and Services, India.

3.2 Characterization methods

3.2.1 Surface area

For studying the structural properties of the adsorbent N_2sorption isotherms at -196 °C were obtained using a Micromeritics ASAP 2010 sorption analyzer. In order to ensure the complete removal of unwanted gases the samples were degassed at 200 °C for 12 h was performed initially before carrying out any analysis. The specific surface area was obtained using Brunauer-Emmet-Teller (BET) method (S_{BET}). The total amount of N_2 adsorbed at a $p/p_o = 0.99$ provided the total volume of the pore (V_{total}).

3.2.2 X-ray photoelectron spectroscopy (XPS)

To identify different elements and their specific function groups present in adsorbent, XPS was carried out. Measurements were carried out using Kratos axis ultra DLD system having Al-kα monochromatic source which was operated at potential of 15 kV. For analyzing survey spectra energy of 50 eV was used, whereas for analyzing individual components spectra pass energy of 20 eV and emission current of 10 mA was used. Pressure at the time of analysis in the chamber was maintained at 2×10^{-9} torr. The deconvulation of spectra was performed using the XPS peak 4.1 software and fitting of spectra was done using Gaussian-Lorentzian convoluted function (80/20) and Shirley function for subtracting the back ground.

3.3 Performance evaluation of adsorbents

3.3.1 Fixed-bed adsorption study setup

In order to study the performance of the adsorbent using a fixed bed under dynamic conditions a system was taken which included a stainless-steel column having length of 34 cm and inner diameter of 0.939 cm. This column was placed in an oven whose temperature can be varied. The feed before introducing inside the column was mixed in a mixer in which the flow of CO_2 and N_2 gases entering in it where controlled by MFCs (mass flow controllers) Bronkhorst, Netherlands. The outlet of the column was connected to an online GC as shown in Fig. 3.1. Pressure build up inside the bed was avoided and column could work at atmospheric pressure. At the time of packing bed, glass wool which is resistant to temperature changes was placed at the inlet and outlet of column to reduce the loss of adsorbent. K type thermocouple is positioned within bed for monitoring temperature of the adsorbent bed. The simulated flue gas mixture which is regulated using MFCs from which pure N_2 and CO_2 gases which is formed in gas mixing section acts as the inlet feed for the bed. This feed can also be bypassed to GC, for initializing inlet concentration of the gas mixture entering the bed. For controlling bed temperature, a temperature controller was used in order to carry out adsorption and desorption. CO_2 and N_2 concentrations at outlet of adsorption column is monitored periodically using GC (GC 7890A, Agilent Technologies, US) outfitted with thermal conductivity detector. Helium gas was used as carrier gas and operating conditions of GC were injection temperature of 180°C, oven temperature of 60°C and detector temperature of 200°C.

Fused silica capillary column of 30 m length and with diameter of 0.32 mm having film thickness 20 μm which is made of polystyrene divinyl-benzene (HP Plot Q, Agilent Technologies, USA) was used in analysis.

3.3.2 Dynamic CO_2 adsorption measurements

Before carrying our any analysis on adsorbent, the adsorbent synthesized was placed in oven at 200 °C for minimum 12 h so that any moisture trapped inside the pores of the adsorbent gets removed and pore becomes completely vacant. Then the packing of bed was done using 2 g of adsorbent which was kept in oven. Then the bed was introduced to N_2 atmosphere with 50 ml min^{-1} of flow rate and temperature of 200 °C for 2 h in order to ensure the removal of any adsorbed gas. After this condition the temperature of the bed was reduced

to adsorption temperature at which analysis has to be carried out (30 to 100 °C). Then the flow rates of N_2 and CO_2 were set according to concentration of (5-12.5%) as per the requirement with same combined flow rate of 80 ml min^{-1} for each concentration of CO_2. At desired conditions the adsorption analysis was carried out. Then after adsorption desorption of CO_2 was performed by raising the temperature of bed to 200 °C and switching from CO_2 to N_2 with 50 ml min^{-1} flow rate. In order to carry out regenerability studies four cycles were repeated in same pattern.

The below mentioned equation (3.1) was used for evaluating CO_2 uptake of developed adsorbent, expressed as q_t (mmol g^{-1}),

$$q_t = \frac{1}{m}\int_0^t Q\left(C_0 - C\right)dt \tag{3.1}$$

where,

m (g) is weight of adsorbent located in column, Q (ml min^{-1}) is rate of flow of gas, C_0 and C are CO_2 inlet and outlet concentrations in (vol. %) and t (min) is time.

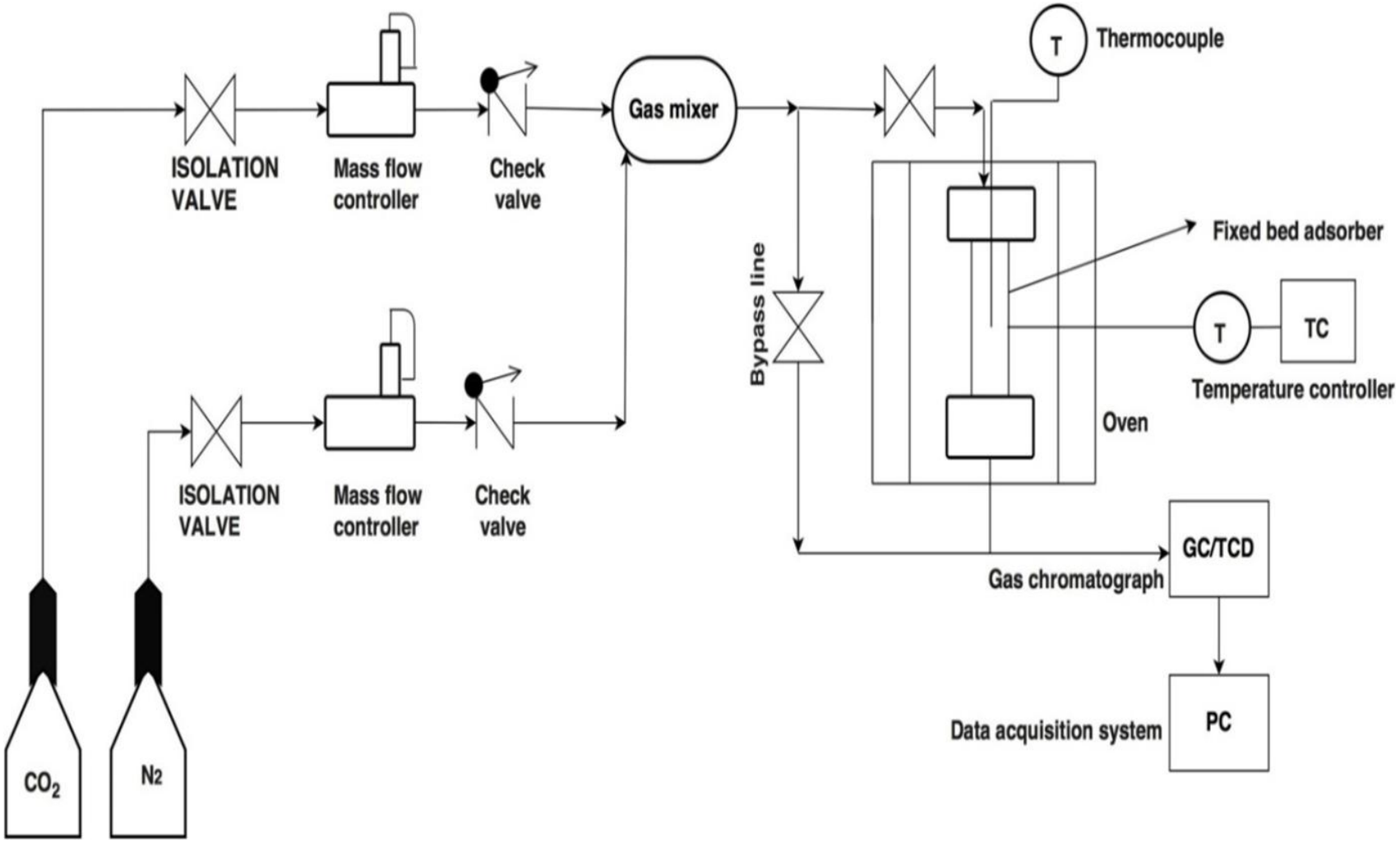


Fig. 3.1 Schematic diagram of the experimental setup [1]

3.4 Kinetic study

Adsorption kinetics which gives important information for predicting adsorption rates such as diffusion control and modeling of adsorption operation can be useful for designing adsorber. This study was carried out by fitting the experimental data with three different kinetic models as mentioned below which provided its performance in real scenarios. They also determine rate controlling mechanisms for adsorption process for instance mass transfer and diffusion control.

3.4.1 Pseudo-first order model

This kinetic model [88] considers that adsorption rate varies directly according to the driving force. This model depends on the adsorption capacity value and driving force here directly related to vacant sites in the adsorbent. It is written as:

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

where,

k_1 is rate constant of pseudo-first order (min^{-1}). Integrating eq. (3.2) with boundary conditions: $q_t|_{t=0}=0$ and $q_t|_{t=t}=q_t$, yields

$$q_t = q_e\left(1-\exp\left(-k_1 t\right)\right) \tag{3.3}$$

where,

q_e and q_t are uptake capacities (mmol g^{-1}) at equilibrium and at various times t (min).

3.4.2 Pseudo-second order

This kinetic model considers that adsorption rate is varies as the square of driving force of the adsorbent. It was given by Ho *et al.* [89] and is written as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3.4}$$

Integrating eq. (3.4) with initial conditions, yields

$$q_t = \frac{k_2 q_e^2 t}{1+k_2 q_e t} \tag{3.5}$$

where,

k_2(g mmol^{-1} min^{-1}) is the rate constant of pseudo–second-order.

3.4.3 Fractional – order model

This kinetic model considers that adsorption rate is influenced by n^{th} power of driving force and m^{th} power of the adsorption time and is expressed as:

$$\frac{dq_t}{dt} = k_n\left(q_e - q_t\right)^n t^{m-1} \tag{3.6}$$

where,

k_n is rate constant of the fractional-order model. Integrating eq^n - (3.6) yields

$$q_t = q_e - \frac{1}{[((n-1)k_n/m)t^m + (1/q_e^{n-1})]^{1/n-1}} \tag{3.7}$$

where n is driving force effect and m is diffusion resistance [90].

3.4.4 Error calculation

The variation of experimental values to that of predicted values of the fitted model is determined in order to confirm the exact behavior of the system. For this Error (%) was evaluated using eqn:

$$Error(\%) = \frac{\sqrt{\sum\left[\left(q_{t(e)} - q_{t(p)}\right)/q_{t(e)}\right]^2}}{N-1} \times 100 \tag{3.8}$$

where,

$q_{t(e)}$ and $q_{t(p)}$ are experimental and predicted CO_2loading and N is the number of measurements, respectively.

3.5Adsorption isotherm models

Adsorption isotherm describes the adsorption mechanism on adsorbent surface and indicates relationship between adsorption capacity at equilibrium and equilibrium concentration at constant temperature. Several equilibrium isotherm equations, namely, Langmuir, Freundlich and Temkin were analyzed to represent the experimental sorption isotherm data.

3.5.1 Langmuir isotherm model

This model, considers that there exists monolayer coverage on the surface of adsorbent of the adsorbate. In this after equilibrium, no adsorption takes place further. This model is relevant for homogeneous adsorption; adsorption where same activation energy is possessed by each molecule. It can be expressed as:

$$q_e = \frac{q_m K_L P}{1 + K_L P} \tag{3.9}$$

where,

q_m (mmol g^{-1}): maximum adsorption capacity and q_e (mmol g^{-1}): equilibrium adsorption capacity, P (atm): partial pressure of gas and K_L (atm^{-1}): Langmuir constant.

3.5.2 Freundlich isotherm model

Freundlich isotherm model is an practical equation and predicts sorption of sorbate molecules on heterogeneous surfaces without considering saturation of sorbate binding sites, expressed as:

$$q_e = K_F P^{1/n} \tag{3.10}$$

where,

K_F is Freundlich constants, and n is Freundlich coefficients indicates intensity for adsorption. Its value lies between ranges of 1 to 10. Nearer the value of n to 0, more heterogeneity will exist.

3.5.3 Temkin isotherm model

This model considers that there is linear decrease in heat of adsorption of molecules in comparison to logarithmic with coverage of molecules because of interactions that exists between adsorbent and adsorbate. It is expressed as:

$$q_e = B \ln(K_T P) \tag{3.11}$$

where,

K_T (atm^{-1}) and $B = RT/b$ with $B$is Temkin constant, b is heat of adsorption (J mol^{-1}),T (K) is temperature and R is gas constant (8.314 J mol^{-1} K^{-1}).

3.6 Selectivity

Selectivity the desirable characteristic property of the adsorbent can also be calculated for CO_2 over $N_2(S_{CO_2})$ and collated with the experimental data achieved from breakthrough curve. It can be expressed as:

$$S_{CO_2} = \frac{x_{CO_2} / x_{N_2}}{y_{CO_2} / y_{N_2}} \tag{3.12}$$

where,

x_{CO_2} and x_{N_2} are adsorbed molar fractions of CO_2 and N_2whereas y_{CO_2} and y_{N_2} aregaseous molar fractions of CO_2 and N_2, respectively.

3.7 Software used

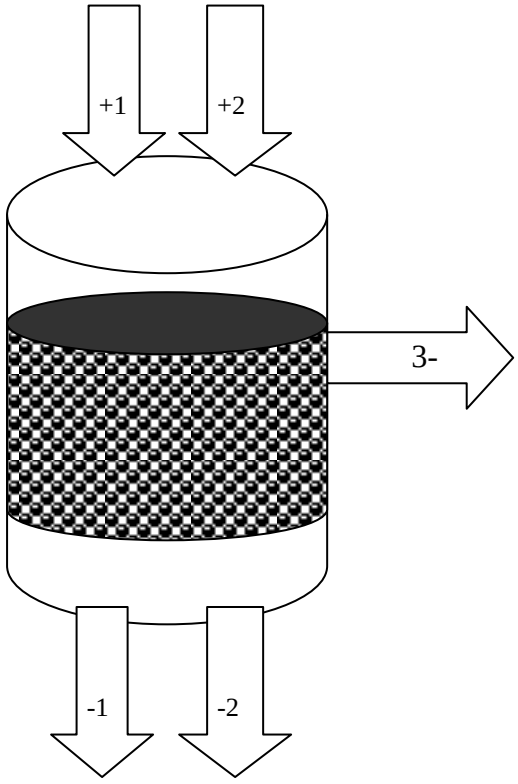
Here, fitting of various kinetic and adsorption models with the experimental data was done using Origin Pro 8 software, for predicting breakthrough plots from mathematical model MATLAB 2015.a software was used.

Chapter 4 – Modeling & Simulation of Fixed Bed Adsorption

4.1 Model development

4.1.1 Mathematical equation

In order to model and simulate the fixed bed adsorption process, there is requirement of model development, which describes the dynamics taking place inside the bed loaded with the specific adsorbent [91]. The mass transport of solute in the fluid phase is governed by convection and axial dispersion mechanisms. Intraparticle diffusion takes place inside the particle, in which the molecules move inside the different pores existing within the particle. The mass conservation equation for CO_2 flow through a porous packed-bed shown in Fig. 4.1 with simultaneous adsorption process can be written as follows:



1: Convective mass transfer
2: axial dispersion
3: mass of adsorbate adsorbed by adsorbent
4: accumulation of adsorbate

(1+)- (1-) $-u\frac{\partial C_b}{\partial Z}$

(2+)- (2-) $-D_{ax}\frac{\partial^2 C_b}{\partial x^2}$

(3-) $\frac{1-\varepsilon_b}{\varepsilon_b}\frac{\partial q_t}{\partial t}$

(4) $\frac{\partial C_b}{\partial t}$

Fig. 4.1 Schematic representation of a mass conservation of a control volume

Hence, the final equation after combining all transports can be represented as:

$$D_{ax}\frac{\partial^2 C_b(x,t)}{\partial x^2}+\frac{\partial\left(uC_b(x,t)\right)}{\partial x}+\frac{\partial C_b(x,t)}{\partial t}+\frac{1-\varepsilon_b}{\varepsilon_b}\frac{\partial q_t(x,t)}{\partial t}=0 \quad (4.1)$$

where,

D_{ax} is axial dispersion coefficient ($m^2\ s^{-1}$), u velocity in the bed ($m\ s^{-1}$), x is variable distance, t is time (s), ε_b is bed porosity, C_{in} is inlet concentration ($molm^{-3}$) and q_t is total sorbed phase concentration of all the particles ($mmol\ g^{-1}$) [91].
Concentration C_b is given by:

$$C_b=\frac{y_i P}{RT_g} \quad (4.2)$$

where

y_i is molar fraction in gaseous phase, P (atm) is total pressure, Tg (K) is temperature of gas and R is gas constant.

Concerning the diffusion within particle, four models have been proposed namely HSDM model (homogeneous surface diffusion model), PSDM (pore/surface diffusion model), Pore diffusion model(PDM) [92] and linear driving force (LDF) model [93]. LDF model is a lumped model in which rate of mass transfer is given below:

4.1.2 Linear driving force model

The Linear Driving Force model provides an sufficient estimation by using a simple form which replaces all tough and time consuming diffusing models [94]. Considering LDF approximation, mass balance equation within the particle is given by Eqn. (4.3).

$$\rho_s\frac{\partial q_p}{\partial t}=\frac{3k_f}{a_p}\left(C_b-C_s\right) \quad (4.3)$$

where,

k_f ($m\ s^{-1}$) is film mass transfer coefficient and C_b ($mol\ m^{-3}$) is bulk phase concentration, and C_s ($mol\ m^{-3}$) concentration at equilibrium.

D_{ax} (axial dispersion coefficient) can be calculated using equations mentioned in Table 4.1 summarized orderly.

4.2Simulation of fixed bed adsorption

Simulation of the mass balance equation can be done using various mathematical tools and software. Since the equation varies with time and distance simultaneously, so we need mathematical tools to solve it. Now we look at how and what can be done to solve the equation. For predicting properties of particles adsorbed in porous material molecular simulation is considered to be most feasible method. Simulations of this type assume that force field completely explains about the interaction that exists between atoms. For computing the transport properties molecular dynamic simulations uses both force fields and crystal structure [95]. A basic simulation process including all parameters calculated can be performed in scheme as shown in Fig. 4.2. Among all different techniques available MATLAB software is selected for current studies.

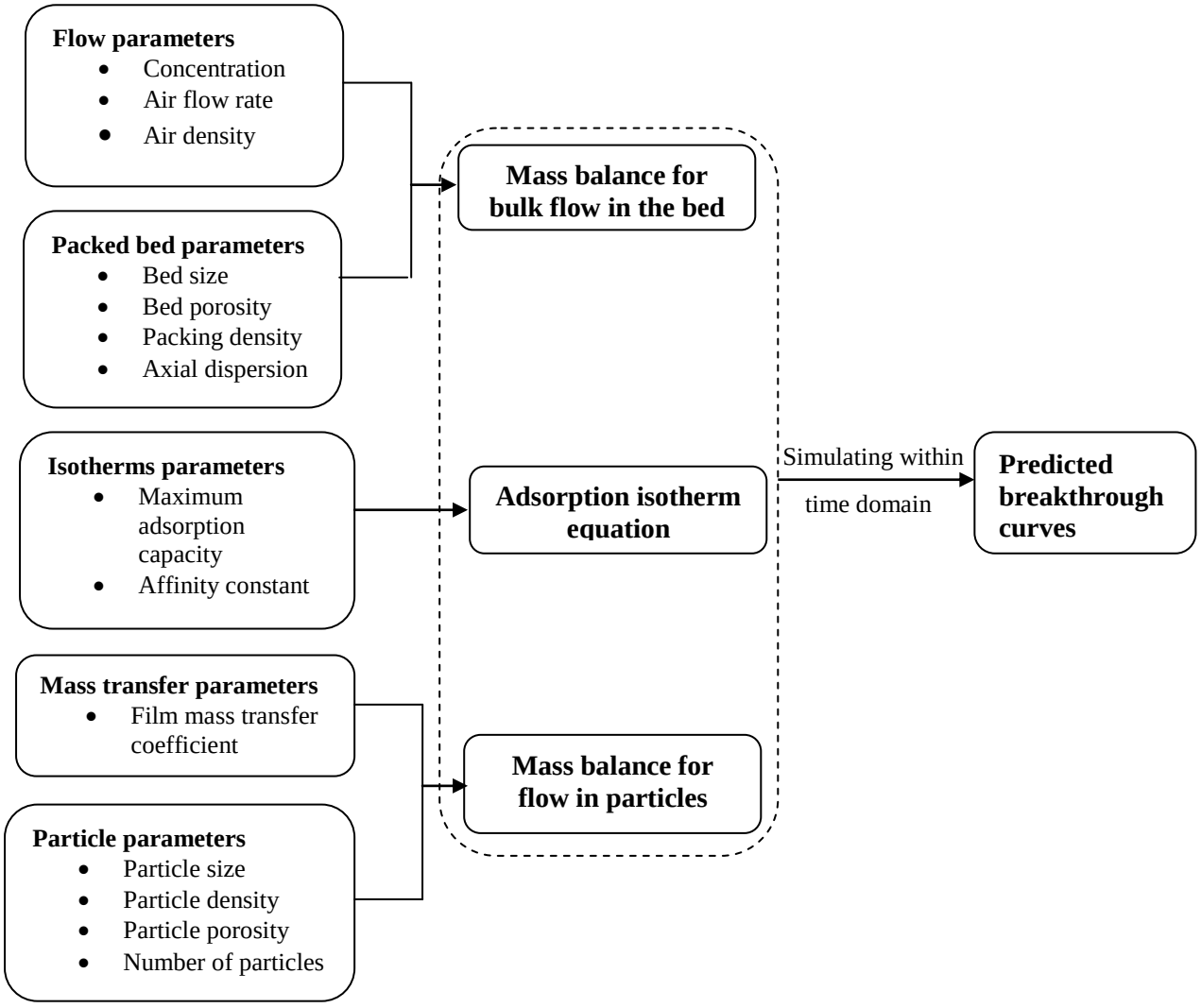


Fig. 4.2 Structure for simulating a modeled equation

4.2.1 MATLAB

MATLAB has various inbuilt solvers for different types of equations and we can use them to solve our PDE in the simplest way to obtain results and plot them. There many ways to solve the equation in MATLAB. Since the equation is a PDE, so we need to write the equation in a way because MATLAB understands a single pattern only. Or the other way is to convert this Partial Differential Equation into a simple Ordinary Differential equation and then write it into MATLAB and use the boundary and initial conditions to solve the equation using various methods like, Method of Lines, Finite Element methods and many more. Method of lines has been used in current model for Discretization of PDE's of current model.

4.2.1.1Method of lines

The method of lines (MOL) is a universal practice for the solution of time dependent partial differential equations (PDEs).

MOL is the technique which helps in predicting the values of system containing boundary conditions using algebraic equations which replaces the partial differential equations (PDEs). After replacing the partial differential equation with algebraic equation, the independent variables no more remains in the independent form since no boundary conditions exists. The algebraic equation is given an initial value on which completely solution of the equation depends which is basically the independent variable in the system now. This can also be said that method of lines converts the set of PDEs to ordinary differential equations (ODEs) which provides the values for PDEs as such. The approximate initial value is what which on which complete solution depends. After the initial values are determined then any technique available for solving ODEs can be used for obtaining the approximate value of partial differential equations.

Table 4.1 Equations for estimation of mass transport and physical parameters

Corresponding Equations	**Correlations Required**	**References**	**Data Required**
			Fixed Bed Characteristics
$D_{ax}\frac{\partial^2 C_b(x,t)}{\partial x^2}+\frac{\partial\left(uC_b(x,t)\right)}{\partial x}+\frac{\partial C_b(x,t)}{\partial t}+\frac{1-\varepsilon_b}{\varepsilon_b}\frac{\partial q_t(x,t)}{\partial t}=0$	1. $\frac{\varepsilon_b D_{ax}}{D_m}=20+0.5Sc.Re$	[96]	Bed diameter, d_b; Bed length, L; Bed void fraction, ε_b;
	2. $Re=\frac{u_s d_p \rho_g}{\mu_g}$, $Sc=\frac{\mu_g}{\rho_g D_m}$	[96]	
	3. $u=\frac{u_s}{\varepsilon_b}$, $u_s=\frac{v}{A_s}$	[97]	
	4. $C_{in}=\frac{y_i P_t}{RT_g}$	[93]	
	5. $D_{m,i}=\frac{1-y_i}{\sum_{j=1}^{n}\frac{y_j}{D_{ij}}}$, $D_m=\sum_{i=1}^{n} y_i D_{m,i}$	[98]	Adsorbent Properties
	6. $D_{ij}=\frac{0.0018583\sqrt{T^3\left(\frac{1}{M_i}+\frac{1}{M_j}\right)}}{P_t\sigma_{ij}^2\Omega_{ij}}$ (Chapman Enskog Eq.)	[99]	Particle diameter, d_p; Particle porosity, ε_p; Particle density, ρ_g; Particle tortuosity, τ_p;
	7. $\sigma_{ij}=\frac{\sigma_i+\sigma_j}{2}$	[99]	

where ,

D_{ax} is the axial dispersion coefficient (m^2s^{-1}),

u is the interstitial velocity in the bed ($m\ s^{-1}$),

x is the axial distance variable,

t is the time (s),

ε_b is the bed porosity,

C_{in} is the inlet concentration ($mol\ m^{-3}$) and

q_t is the total sorbed phase concentration of all the particles (mmol g^{-1}).	8. $\Omega_{ij} = 1.06036\left(\frac{\varepsilon_{ij}}{\kappa T}\right)^{0.15610} + 0.19300e^{-0.47635\frac{\kappa T}{\varepsilon_{ij}}} + 1.03587e^{-1.52996\frac{\kappa T}{\varepsilon_{ij}}} + 1.76474e^{-3.89411\frac{\kappa T}{\varepsilon_{ij}}}$	[99]	
	9. $\varepsilon_{ij}/\kappa = \sqrt{\varepsilon_i}\varepsilon_j/\kappa$	[99]	
	10. $\mu_g = \sum_{i=1}^{n} \frac{y_i \mu_i}{\sum_{j=1}^{n} y_i \Phi_{ij}}$	[99]	
	11. $\Phi_{ij} = \frac{1}{\sqrt{8}}\left[1 + \left(1 + \frac{M_i}{M_j}\right)\right]^{-1/2}\left[1 + \sqrt{\frac{\mu_i}{\mu_j}}\left(\frac{M_i}{M_j}\right)^{-1/4}\right]^2$	[99]	
	12. $\mu_i = 2.6693 \times 10^{-5} \frac{(M_i T)^{0.5}}{{\sigma_i}^2 \Omega_\mu}$	[99]	
	13. $\Omega_\mu = 1.16145\left(\frac{\varepsilon_i}{KT}\right)^{0.14874} + 0.52487e^{-0.7732\frac{KT}{\varepsilon_i}} + 0.16178e^{-2.43787\frac{KT}{\varepsilon_i}}$		
	14. $\rho_g = \frac{P}{R_g T}\sum_{i=1}^{n} y_i M_i$	[99]	
	15. $D_{ax} = (0.45+0.55\,\varepsilon)D_{m,i} + 0.35\, r_p u$		
	16. $k_f = \frac{Sh.Dm}{dp}$	[97]	

Chapter 5 – Results and Discussion

5.1Development of adsorbents

5.1.1 Carbonization of PET waste

Plastic waste bottles were cut into small pieces and were placed in sample holder. Then the sample holder was kept in quartz tubular furnace and left for heating at temperature of 700 ºC in N_2 atmosphere (with flow rate = 60 ml min^{-1}) at heating rate of 10 ºC min^{-1}. After attaining required temperature, the system was kept isothermal for 2 h. Then the system was left for cooling at room temperature with N_2 atmosphere. Sample obtained post carbonization was assigned PET-700. This sample obtained was considered as reference sample for performing further studies on this adsorbent.

Schematic for preparation of PET-700 can be seen in Fig. 5.1.

5.1.2 Chemical activation of direct carbonized PET at different PET: KOH ratio

KOH (potassium hydroxide) was used as the activating agent for chemically activating all samples. PET-700 was thoroughly mixed with different ratios of KOH varying from 1 to 4. Four different samples with KOH: PET (mass ratio) of 1-4 was obtained. Then the samples were dried in over for 12 h at 105 ºC temperature.

5.1.3 Carbonization of chemically activated adsorbents

After chemical activation of samples, carbonization was done by placing the samples in tubular furnace at different carbonization temperatures varying from 500 ºC to 800 ºC with N_2 atmosphere and flow of N_2 maintained at 60 ml min^{-1}. After attaining required temperature, the system was kept isothermal for 2 h. Afterwards the system was left to cool at room temperature, and this was followed by the washing of samples using 1 M HCl in order to remove KOH and then by distilled water for removing excess chloride ions and neutralizes the sample. Obtained samples were dried at 120 ºC in oven and resultant samples obtained were the adsorbent for this study. Schematic for chemical activation of PET-700 can be seen in Fig. 5.2. Table 5.1 lists the obtained carbon adsorbent with their specifications and the conditions at which they prepared. Naming of samples was doneas PET-x-y where x is the ratio of KOH added to PET and y is temperature at which activated samples were carbonized.

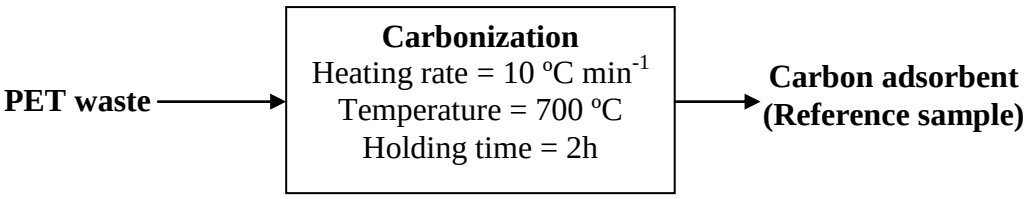


Fig. 5.1 Schematic for preparing adsorbent using direct carbonization technique

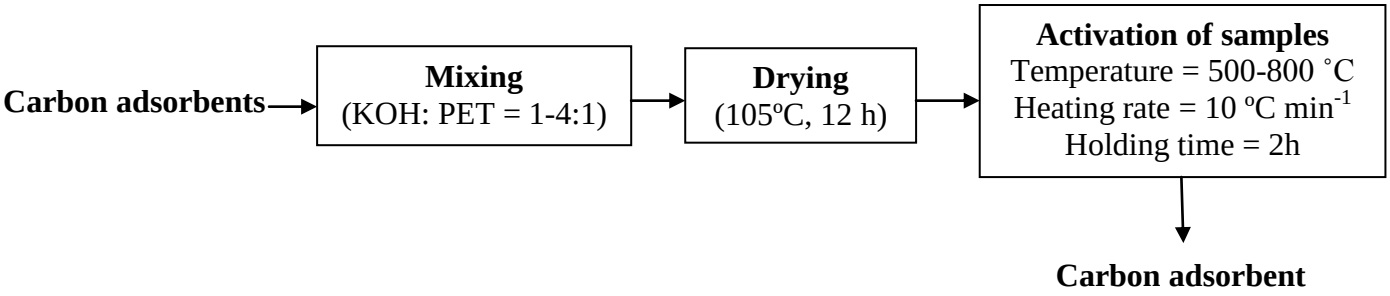


Fig. 5.2 Schematic for preparing adsorbent using chemical activation process

Table 5.1 Conditions at which samples are prepared

Sample	Direct carbonization temperature (ºC)	Chemical activation temperature (ºC)	KOH: PET (mass ratio)
PET-700	700	-	-
PET-1-700	700	700	1
PET-2-700	700	700	2
PET-3-700	700	700	3
PET-4-700	700	700	4

5.2 Characterization of adsorbents

5.2.1 Surface area and pore size distribution

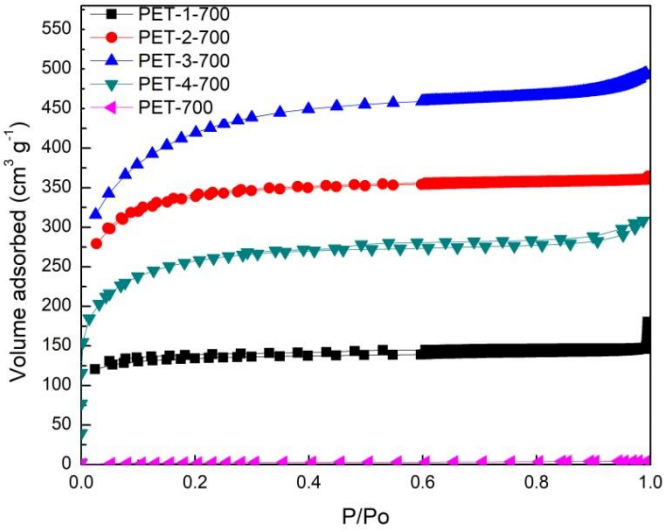


Fig. 5.3N_2 adsorption-desorption isotherms

For sample which was directly carbonized has shown a little amount of N_2 adsorption/desorption which indicates that negligible number of pores are present in the adsorbent as shown in Fig. 5.3. Whereas, activated carbons N_2 adsorption/desorption follows type 1 isotherm as per IUPAC classifications with H4 hysteresis loop, which implies that the adsorption process is dominated by micropores indicating their presence. PET-3-700 has shown maximum N_2 adsorption which means that PET-3-700 is highly porous among all samples.

From literature it was inferred that KOH behaves as a catalyst for accelerating the gasification reaction (Eqn. 2 and 3). The intermediates like K_2CO_3 and K_2O, released in the reaction at 700 °C activation temperature which reacted at active sites present in carbon (Eqn. 5 and 6) and abundant micropores were developed in carbon framework [100]. Same was seen in sample synthesized in current studies.

$$2KOH \rightarrow K_2O + H_2O \quad (4.1)$$

$$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3 \quad (4.2)$$

$$K_2CO_3 \rightarrow K_2O + CO_2 \quad (4.3)$$

$$K_2CO_3 + 2C \rightarrow 2K + CO \quad (4.4)$$

$$K_2O + C \rightarrow 2K + CO \quad (4.5)$$

Parameters calculated using N_2 adsorption are shown in Table 2 and this can be observed that there is increase in BET surface area with increase in KOH: PET mass ratio till 3 and its highest value is observed for PET-3-700 (1478.28 m^2 g^{-1}). This sample shows total volume of 0.47 cm^3 g^{-1}, respectively. There was further decrease in surface area on increasing KOH: PET mass ratio to 4 which may be resulted due to collapsing of pore which caused blockage. Further, observation was made that till KOH: PET mass ratio of 2 the micropores increased in comparison to mesopores whereas, at mass ratio of 3 mesopores were in comparison to micropores. Over activation may affect microporous structure of the adsorbent by partially cracking them. Hence, this conclusion can be made that activation affects the micropores structures along with development of highly porous adsorbents. Similar trends were also observed by Liu *et al.* [101].

Table 5.2 BET surface area values along with pore values

Carbon sample	BET surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})
PET-700	9.86	0.009
PET-1-700	481.51	0.24
PET-2-700	951.29	0.30
PET-3-700	1,478.28	0.47
PET-4-700	943.89	0.41

5.2.2XPS (X-ray photoelectron spectroscopy)

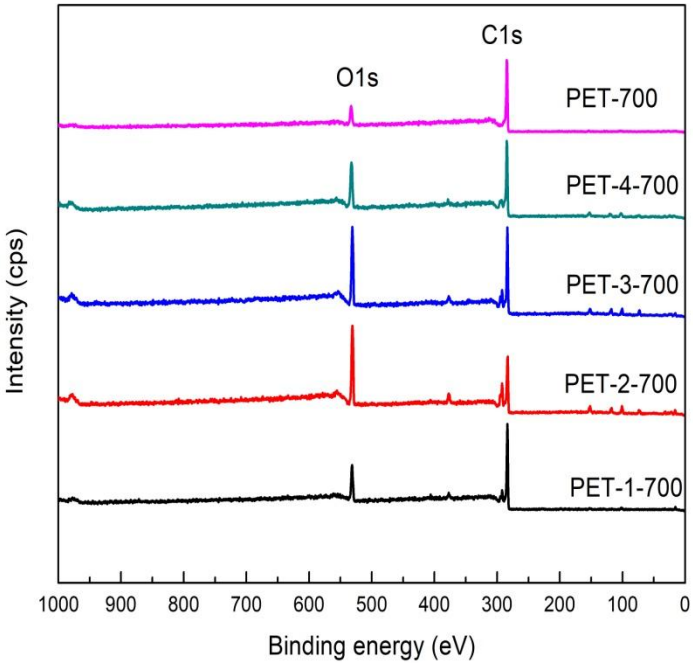


Fig. 5.4XPS survey scan spectra of carbon adsorbents

Survey spectra for different carbon adsorbents can be seen in Fig 5.4.Two distinct peaks at 285and 532 eV can be observed which attributes to carbon (C1s), and oxygen (O1s) respectively.

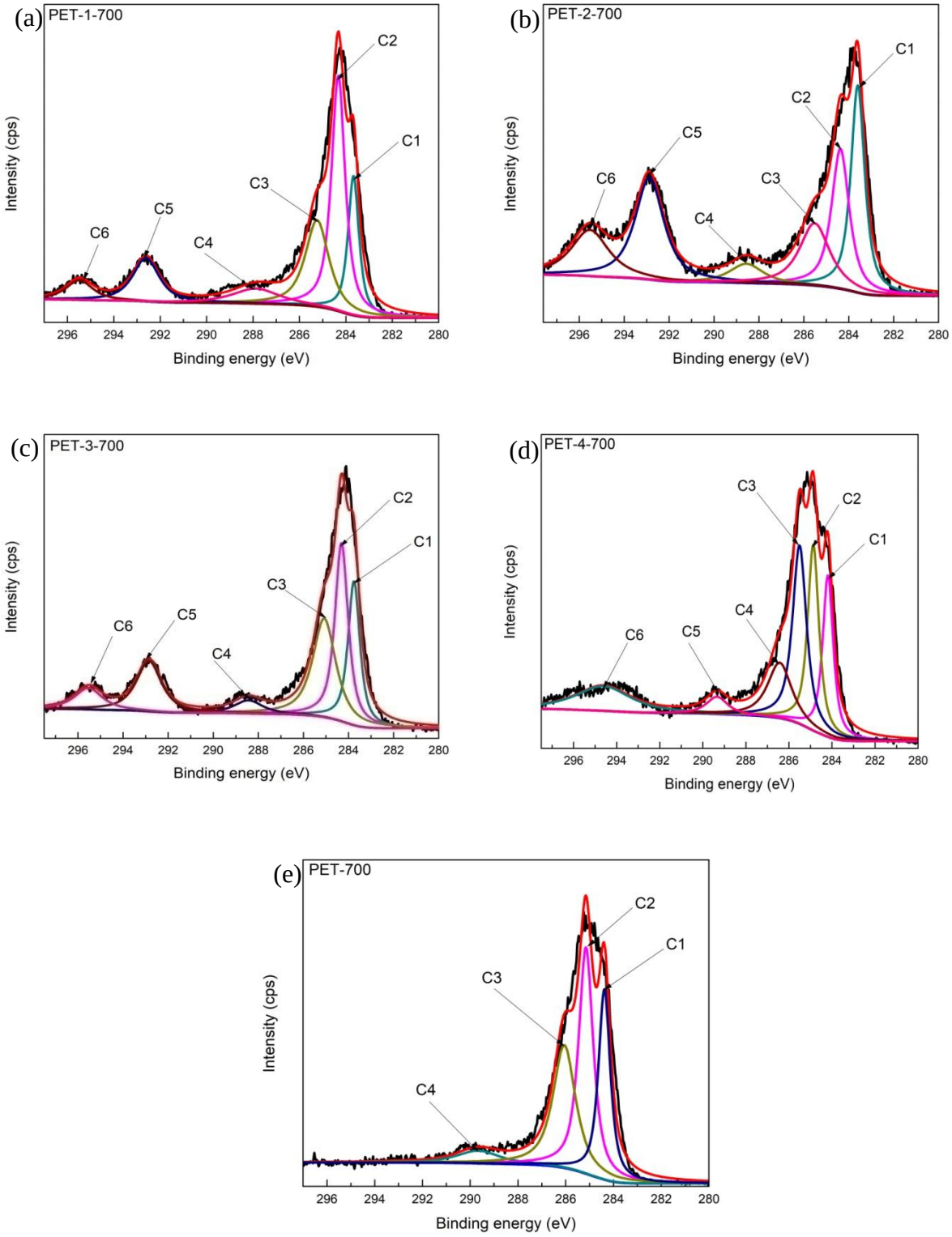


Fig. 5.5 Deconvoluted C1s XPS spectra of carbon adsorbents (a) PET-1-700, (b) PET-2-700, (c) PET-3-700, (d) PET-4-700, (e) PET-700

Table 5.3 Assignment of different deconvoluted C1s peaks

Peak	Position (eV)	Assignment	Relative area percentage				
			PET-700	PET-1-700	PET-2-700	PET-3-700	PET-4-700
C1	284.19	Graphite structure	-	16.6	22.9	26.34	18.26
C2	284.8	sp^2& sp^3	25.31	35.21	19.77	24.23	22.44
C3	285.52	Phenol & alcohol	7.41	17.18	14.84	25.04	26.61
C4	286.43	Carbonyl group	31.11	17.68	9.16	5.07	14.17
C5	289.34	Carbonate group	6.09	12.48	23.4	22.02	3.9
C6	294.61	Formaldehyde group	-	5.8	13.78	7.27	14.57

C1s spectra for all samples has been deconvoluted into four different peaks as shown in Fig. 5.5 which are 284.19 eV (C1), 284.8 eV (C2), 285.52 eV (C3) and 286.43 eV (C4), 289.34 eV (C5), 294.61 eV (C6). Here, peak C1 peak is known to exhibit graphite structure and have C=C bonding in structure [102], C2 represents sp^2 and sp^3 carbon atoms[103], C3 represents phenol & alcohol, C4 represents carbonyl groups, C5 represents carbonate group, C6 represents formaldehyde group [104] as shown in Table 5.3. Here, increase in A% of C1 can be observed at higher KOH: PET ratios indicating formation of higher graphite type structures. C1, C6 is completely absent in PET-700 indicating its less stable structure and also it can be observed that C2 is present highly in other samples, indicating there more stability. PET-3-700 has shown higher graphite structure presence as observed from higher value of A%.

Table 5.4 XPS data of C1s core level spectra of carbon adsorbents

Sample		C1	C2	C3	C4	C5	C6
PET-700	BE	-	284.38	285.15	286.06	289.67	-
	FWHM	-	0.59	0.73	1.12	2.11	-
	A %	-	25.31	17.41	31.11	6.09	-
PET-1-700	BE	283.67	284.32	285.23	287.87	292.60	295.47
	FWHM	0.56	0.71	1.21	2.39	1.35	1.38
	A %	16.6	35.21	17.18	7.68	12.48	5.8
PET-2-700	BE	283.6	284.37	285.52	288.56	292.87	295.52
	FWHM	0.73	0.93	1.58	1.77	1.53	1.98
	A %	22.9	19.77	14.84	9.16	23.4	13.78
PET-3-700	BE	284.36	285.13	288.4	292.86	293.76	295.54
	FWHM	0.71	1.22	1.68	1.36	0.65	1.41
	A %	26.34	24.23	25.04	5.07	22.02	7.27
PET-4-700	BE	284.19	284.87	285.51	286.43	289.34	294.61
	FWHM	0.59	0.63	0.77	1.32	1.17	3.05
	A %	18.26	22.44	26.61	14.17	3.9	14.57

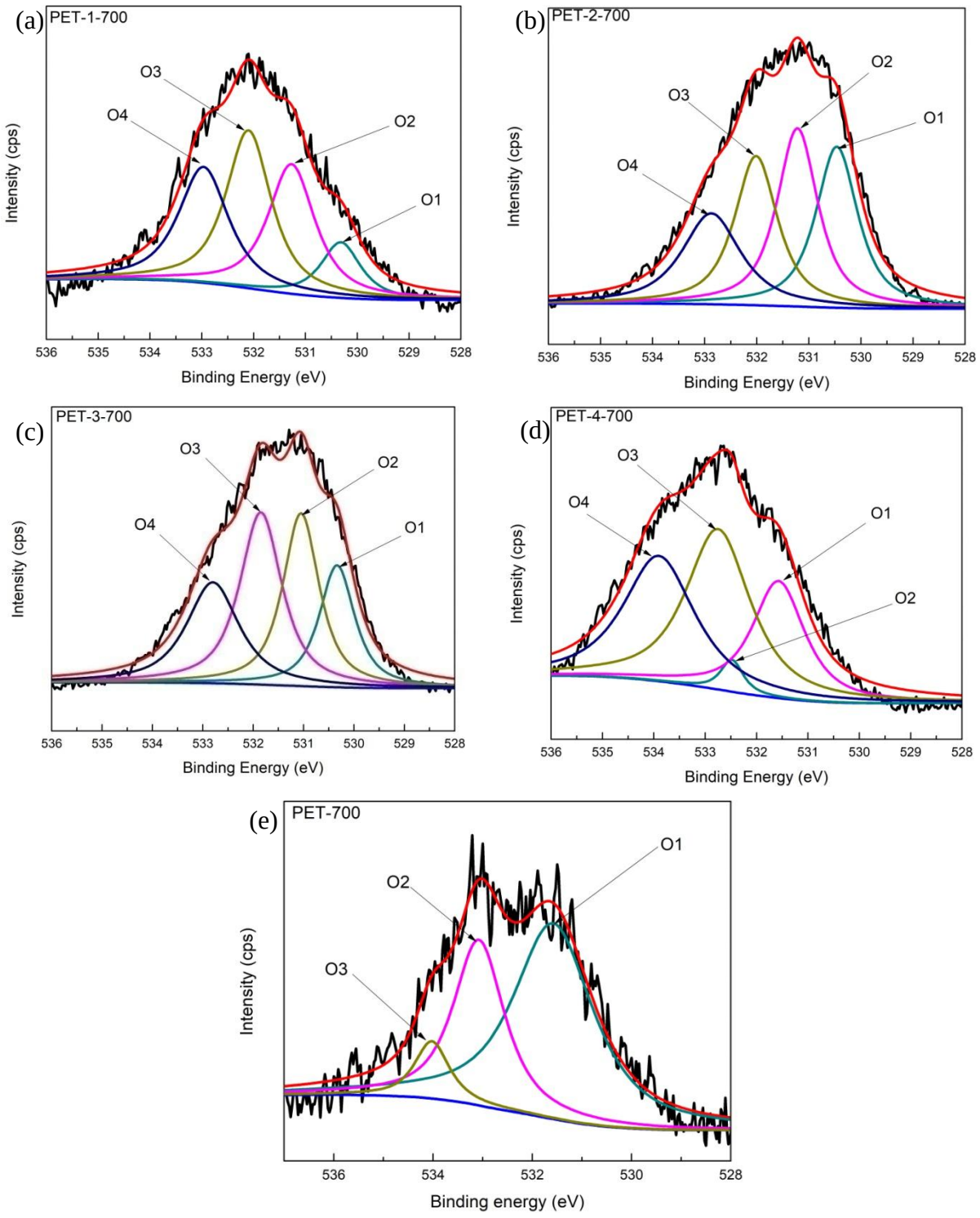


Fig. 5.6 Deconvoluted O1s XPS spectra of carbon adsorbents (a) PET-1-700, (b) PET-2-700, (c) PET-3-700, (d) PET-4-700, (e) PET-700

Table 5.5 Assignment of different deconvoluted O1s peaks

Peak	Position (eV)	Assignment	Relative area percentage				
			PET-700	PET-1-700	PET-2-700	PET-3-700	PET-4-700
O1	530.34	Carboxylate group	-	10.43	26.3	18.69	2.7
O2	531.05	Carbonyl group	32.30	28.62	28.3	31.3	23.7
O3	531.85	Hydroxyl group	7.61	33.6	24.8	27.2	39.6
O4	532.8	Carboxylic group	60.11	27.27	22.4	20.7	34.0

O1s spectra for all samples has been deconvoluted into four different peaks as shown in Fig. 5.6 which are 530.34 eV (O1), 531.05 eV (O2), 531.85 eV (O3) and 532.8 eV (O4). Here, peak O1 corresponds to carboxylate groups [105], O2 corresponds to carbonyl [106], O3 corresponds to hydroxyl group [107] and O4 corresponds to carbonyl and carboxylic group [108] as shown in Table 5.5. There increase in O1, O2, O3 peaks up to KOH: PET mass ratio of 3 but on further increasing mass ratio to 4 there is sudden increase in O4 group which makes it more acidic. Observation can be made that O1, O2, O3 which attributes to presence of more basicity in sample [109] are present highest in PET-3-700 as confirmed from highest A% from Table 3. This makes sample most basic and increases its affinity towards CO_2 by generating Lewis basic sites.

Table 5.6 XPS data of O1s core level spectra of carbon adsorbents

Sample		O1	O2	O3	O4
PET-700	BE	-	533.076	534.02	531.58
	FWHM	-	1.21	0.83	1.92
	A %	-	32.30	7.61	60.11
PET-1-700	BE	530.32	531.27	532.1	532.97
	FWHM	0.91	1.07	1.03	1.14
	A %	10.43	28.62	33.6	27.27
PET-2-700	BE	530.46	531.22	532.01	532.88
	FWHM	0.96	0.93	0.96	1.32
	A %	26.3	28.3	24.8	22.4
PET-3-700	BE	530.34	531.05	531.85	532.8
	FWHM	0.84	0.86	0.99	1.23
	A %	18.69	31.3	27.2	20.7
PET-4-700	BE	532.48	531.57	532.75	533.9
	FWHM	0.52	1.21	1.49	1.63
	A %	2.7	23.7	39.6	34.0

5.3 CO_2adsorption performance

5.3.1 Activation parameters optimization for CO_2 adsorption

Activation time, KOH: PET ratio and activation temperature are the parameters which effects CO_2 uptake capacity. They were optimized to obtain the most favorable conditions for adsorbent preparation.

5.3.1.1Activation time

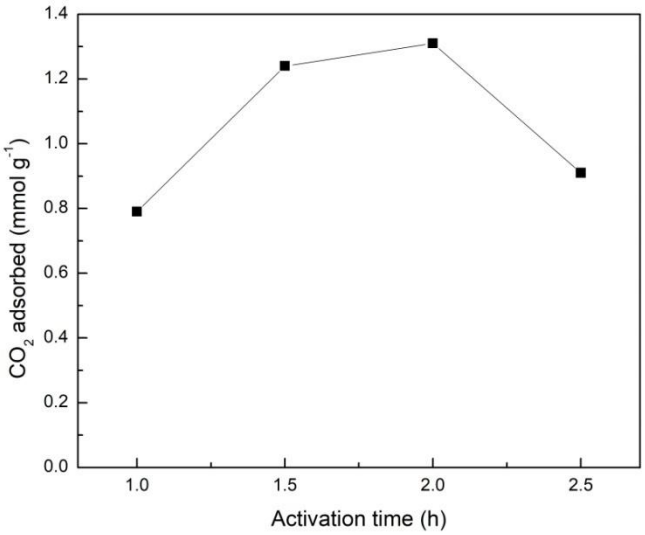


Fig. 5.7 Effect of activation time on CO_2 adsorption capacity of prepared adsorbents at 12.5% CO_2 and 30 °C

Adsorbent preparation at different activation time was performed. Different CO_2 uptake capacities of sample were obtained for different activation times as shown in Fig. 5.7. Observation was made that there was increase in adsorption capacity till the activation time of 1-1.5 h but when activation time was increased to 2 h there was no relevant change, further after 2 h the adsorption capacity decreased. Hence, 2 h is considered as optimum activation time for preparation of adsorbent.

5.3.1.2KOH: PET mass ratio

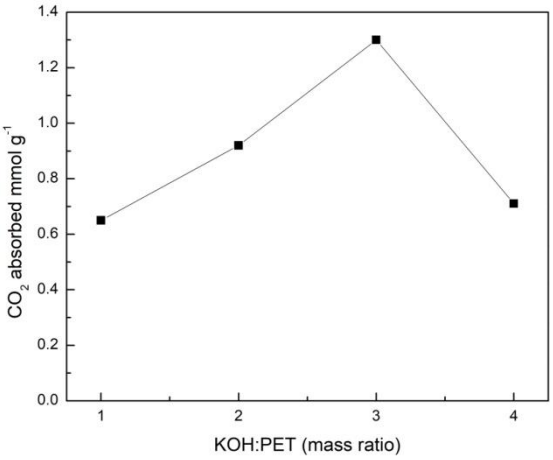


Fig. 5.8 Variation of adsorption capacity due different KOH: PET mass ratio on prepared adsorbents (700°C and 2 h activation time) at 12.5% CO_2 and 30 °C

For carbonization temperature of 700 °C and activation time of 2 h, four different carbons were prepared using different KOH: PET ratios (1-4). It was observed that there was increase in CO_2 uptake till KOH: PET mass ratio of 3 but when ratio was increased to 4 there was substantial decrease in CO_2 uptake as shown in figure Fig. 5.8. As a result, for further study KOH: PET mass ratio of 3 was selected.

5.3.1.3 Activation temperature

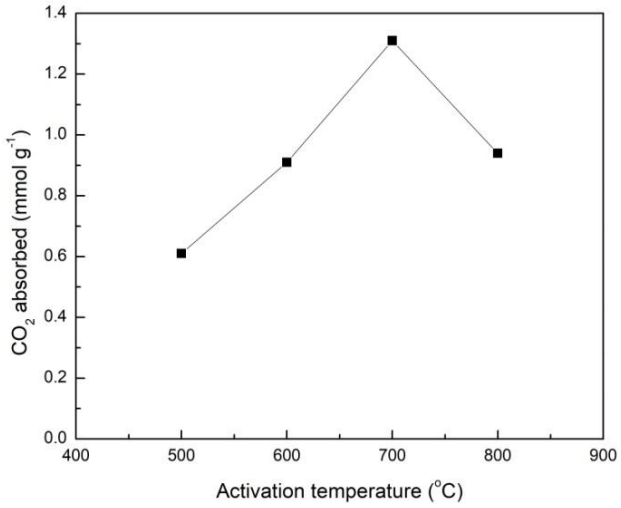


Fig. 5.9 Variationdue activation temperature on CO_2uptake at 12.5% CO_2 and 30 °C

For KOH: PET mass ratio 3 adsorbents were synthesized at different activation temperatures (500 to 800 °C) and their uptake capacities were evaluated as shown in Fig. 5.9. There was significant increase in CO_2 uptake capacities till 700 °C temperature and on further

increase of temperature to 800 °C the CO_2 uptake capacity decreased. The lower value of adsorption was obtained at lower activation temperature due to less amount of reaction of KOH with carbon molecules which resulted in formation of lesser number of micropores, while the higher activation temperature was sufficient enough for KOH to completely react with carbon molecules resulting in development of micro and mesopores. N_2 adsorption-desorption isotherms has shown analogous trends, as there is removal of alkali metals with increasing activation temperature which makes sample highly porous and develops an good surface area with superior value of pore volume as well. The decrease in CO_2 uptake capacity was observed for 800 °C due to collapsing of pore because of overheating which caused blockage in developed pores. Therefore, 700 °C as activation temperature was considered as the optimum temperature for activation, along with KOH: PET mass ratio of 3 and 2 h as activation time. Thus, for further study PET-3-700 was considered.

5.3.2 Dynamic CO_2 adsorption performance

5.3.2.1 Effect of KOH: PET mass ratio

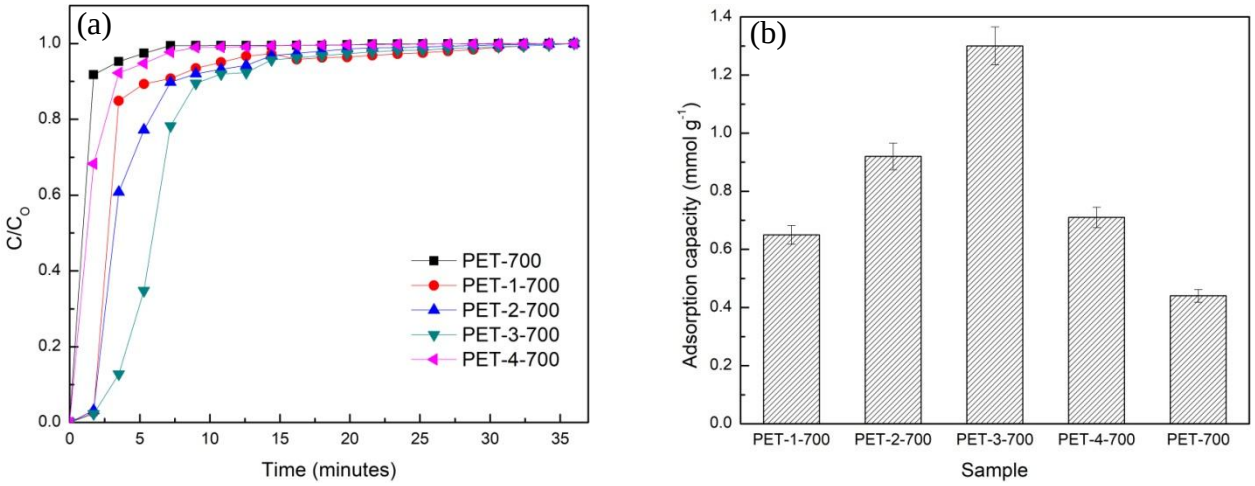


Fig. 5.10(a) CO_2 breakthrough curves for different adsorbents, and (b) CO_2 adsorption capacities for different adsorbents under 12.5% CO_2at 30 °C

For different synthesized adsorbent, breakthrough curves and their corresponding equilibrium CO_2 uptake capacities at adsorption temperature of 30 °C and CO_2 concentration of 12.5% are shown in Fig. 5.10. Initially for 1 min no CO_2 can be detected at the outlet of the bed which indicates mass transfer zone exits inside the bed. But, after 1 min some amount of CO_2 appeared at the outlet stream indicating shift of mass transfer zone towards the outlet of bed. Breakthrough curve for PET-3-700 is broader in comparison to the other adsorbents

breakthrough curves with PET-700 having the steepest one and even the adsorption capacity of PET-3-700 is highest in comparison to other adsorbents. This can also be observed that CO_2 uptake of adsorbents increased till KOH: PET mass ratio of 3 but on further increasing a decrease in CO_2 uptake was noticed.

PET-3-700 showed highest CO_2 uptake due to its well-developed porous structure confirmed by BET analysis and due to presence of oxygen functionalities as confirmed by XPS analysis which make adsorbent basic and increases its affinity toward acidic CO_2 gas. Since acidic character was detected in PET-700 with poor textural properties therefore it showed lowest adsorption capacity. Therefore, this can be concluded that surface properties and basicity of adsorbent highly affects its CO_2 capture capability.

5.3.2.2 Effect of adsorption temperature and CO_2feed concentration

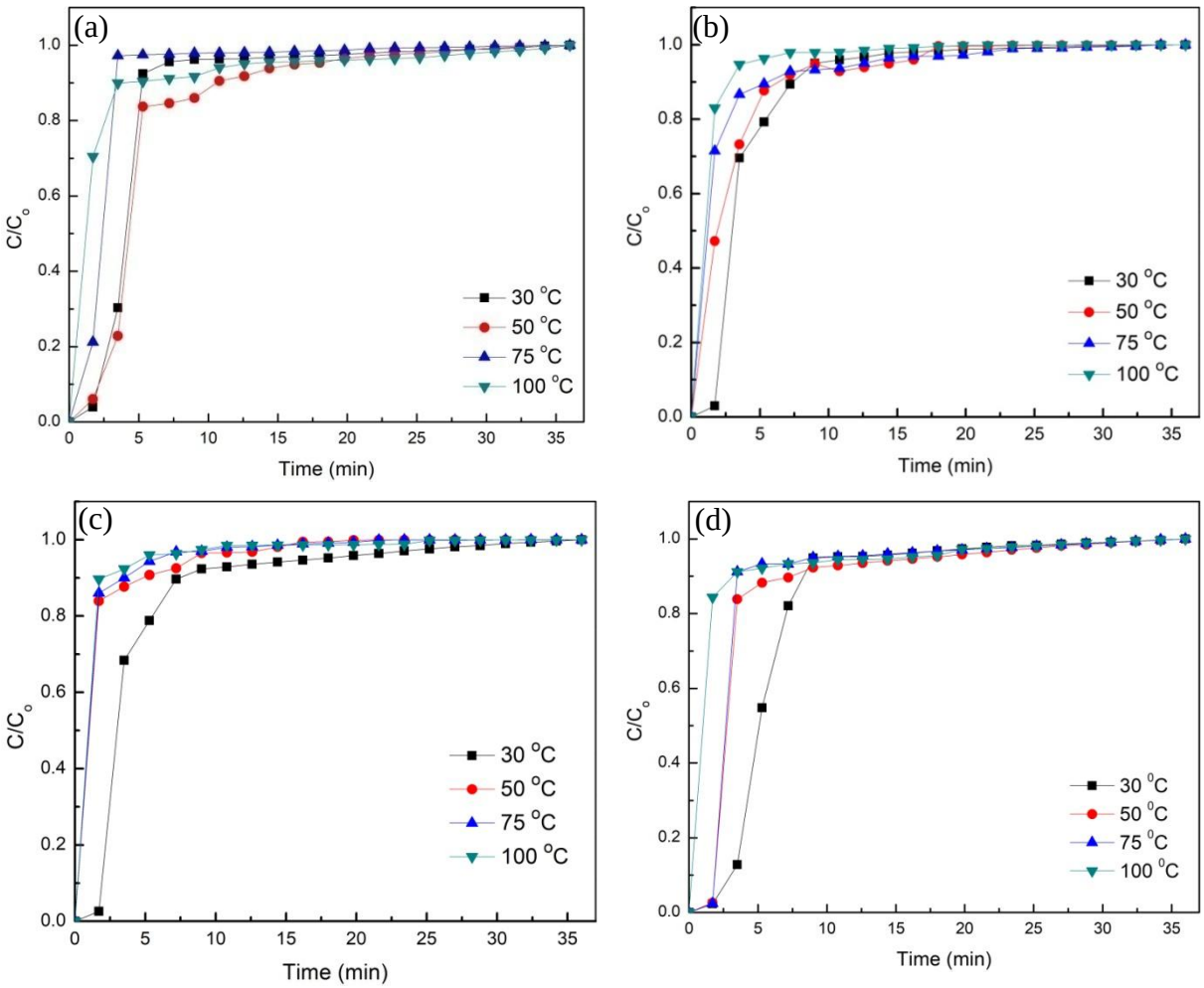


Fig. 5.11CO_2 breakthrough curves for (a) 5%, (b) 7.5%, (c) 10%, and (d) 12.5% of CO_2 at different temperatures

Different experimental breakthrough curves of PET-3-700 obtained at various adsorption temperatures (30, 50, 75, 100 °C) and CO_2 concentration are shown in Fig. 5.11. Initially it can be seen that there is absence of CO_2since the molecules of CO_2 gets adsorbed on active pore sites available in the bed. Further, it can be observed for every CO_2 concentration the bed gets saturated earlier, this implies that there is decrease in adsorption capacity with increasing adsorption temperature also the breakpoint gets shifter towards lower times at higher temperatures. From this, it can be concluded that physiosorption nature is exhibited by the adsorbent since CO_2 uptake decreased with increasing adsorption temperature.

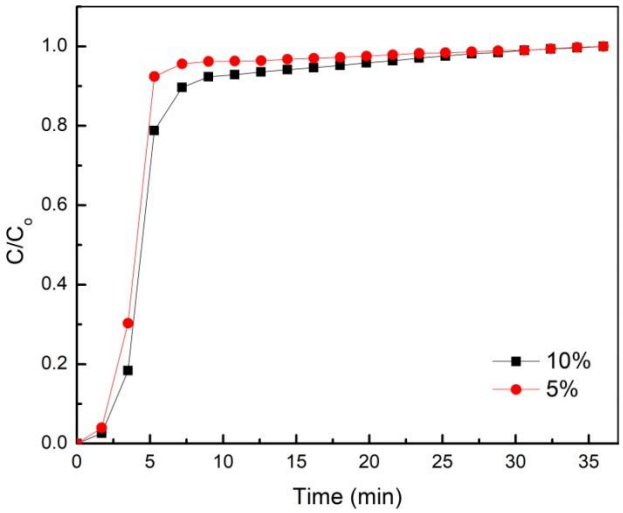


Fig. 5.12 CO_2breakthrough curves for 5% and 10% CO_2 at 30 °C

Effect of the variation of feed concentration (5 and 10%) on CO_2 uptake of PET-3-700 at adsorption temperature of 30 °C was studied as shown in Fig. 5.12. Observation can be made that, on increasing feed concentration there was shift in breakpoint to lesser time which means that the bed attains saturation earlier for higher CO_2 concentrations. Breakpoint for 5%, appeared at 1.40 min, and for 10% it appeared at 0.37 minutes.

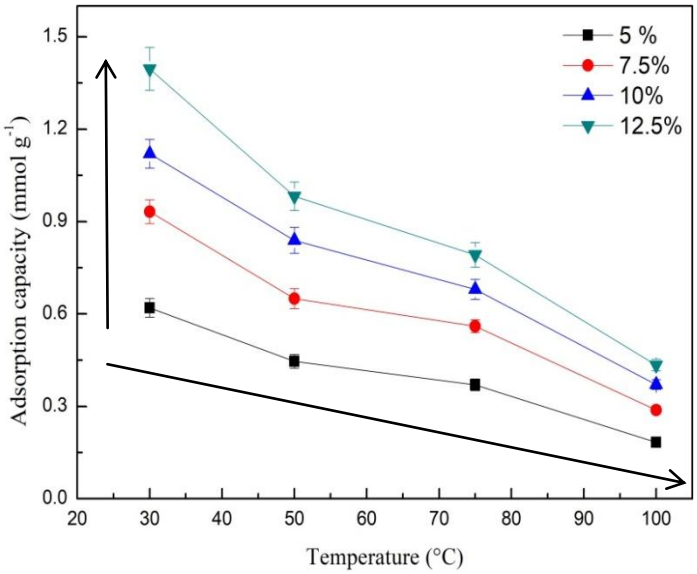


Fig. 5.13 CO_2 adsorption capacity of PET-3-700 at different adsorption temperatures and CO_2 concentrations

Effects of variation of adsorption temperature along with concentration of CO_2 on adsorption capacity can be seen in Fig. 5.13. Observation can be made that on increasing adsorption temperature (30 to 100 °C) adsorption capacity tends to decrease. And on increasing concentration of CO_2 (5% to 12.5%) at a fixed adsorption temperature the adsorption capacity increases from 0.55 to 1.3 mmol g^{-1} which is resultant of more amount of CO_2 available to active sites for adsorption with increasing CO_2 concentration.

5.3.3 CO_2 selectivity studies

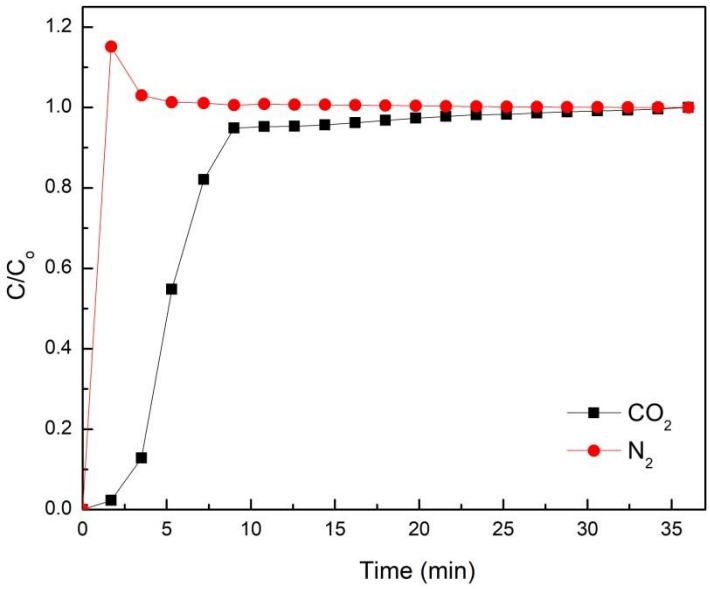


Fig. 5.14 Selectivity of PET-3-700 at 12.5% $CO_2$and 30 °C

CO_2/N_2 breakthrough curves at 12.5% CO_2at adsorption temperature of 30 °C are shown in Fig. 5.14. Since in the breakthrough curve it can be observed that N_2 gets detected earlier at the outlet in comparison to CO_2, this means that adsorbent selectively adsorbed CO_2. Further, the initial (C/C_0) values for N_2 being greater than 1 indicates that initially vacant sites are occupied by N_2 but later on CO_2 replaces N_2 from those sites, indicating adsorbent having higher affinity towards capturing CO_2.

5.3.4Adsorption/desorption studies of CO_2 at 30 °C

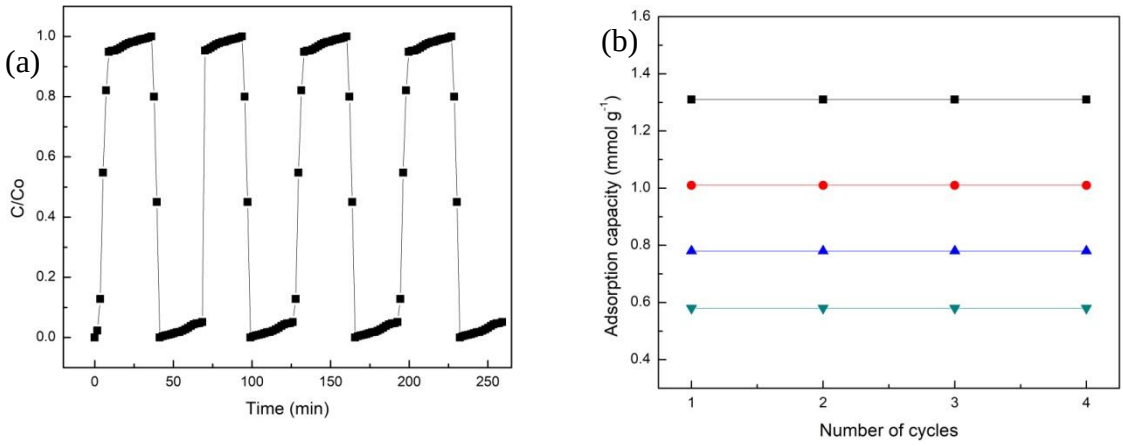


Fig.5.15(a) Breakthrough curves for PET-3-700 of fresh and adsorbent after multiple regeneration(b)adsorption-desorption cycle for PET-3-700 under 12.5% flow at different temperatures

In order to confirm regenerability of PET-3-700 adsorption-desorption studies were performed. After the adsorption step, the temperature of system was raised to 200 °C with 100% N_2 flow (50 ml min^{-1}) and same was repeated over four cycles. It was observed that adsorbent was completely regenerable after fourth cycle. Also, CO_2 desorbed easily as shown in Fig. 5.15(a). It was also observed that adsorbent remained stable over four adsorption-desorption cycles since same amount of adsorbent was regenerated along with this same adsorption capacity after every cycle.

5.4 Kinetic study

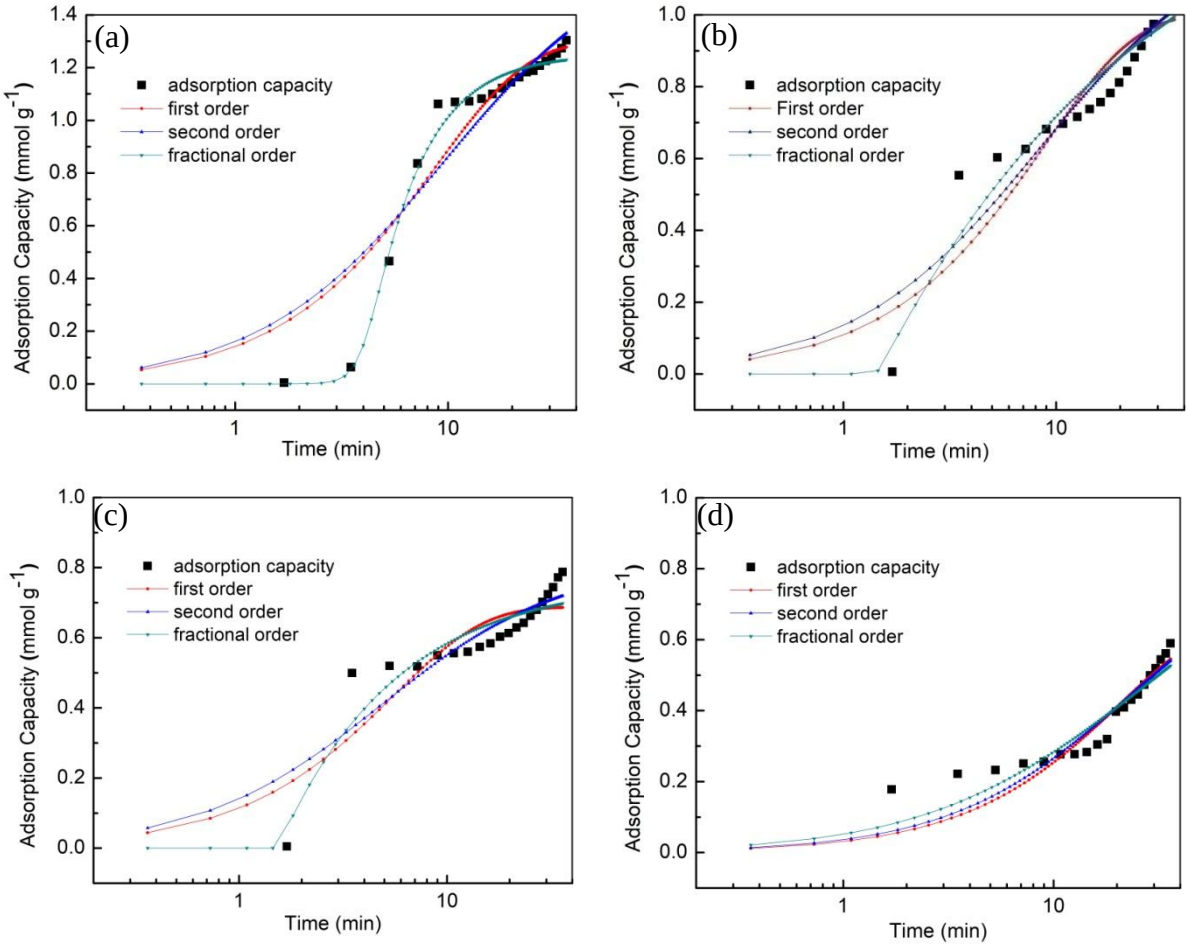


Fig. 5.16CO_2 uptake kinetics: Experimental and model predicted capacities at 12.5% CO_2at (a) 30 °C, (b) 50 °C, (c) 75 °C and (d) 100 °C

Kinetic fitting for PET-3-700 is shown in Fig. 5.16. Three different type of kinetics predicted model values along with the experimental values of samples at different adsorption temperatures under 12.5% CO_2 flow are fitted. And it can seen that pseudo first order and pseudo second order kinetic model under has shown large variations in comparison to experimental data. And it can seen that pseudo first order and pseudo second order kinetic model over-estimated the initial regions for all samples. This indicates that both kinetic models are not correctly fitting and not describing kinetics for all samples. But fractional order kinetic fitted best. And it predicted most suitable values at all adsorption temperatures with higher values of R^2. All parameters calculated using fractional-order kinetic model are shown in Table 5.7. Fraction-order kinetic model has fitted well along with complete data of

initial and final regions. The adsorption process slows down as it reaches equilibrium due to less availability of unoccupied sites for CO_2 capture.

Table 5.7 Kinetic model parameter values for PET-3-700 at 12.5% CO_2 concentration and 30^oC

Model	Parameters	Temperature (°C)			
		30	50	75	100
Fractional –order	k_n	0.75	0.27	0.53	0.06
	q_e	1.25	1.05	0.76	0.57
	n	6.25	3.33	1.56	4.68
	m	9.67	4.36	1.18	0.91
	R^2	0.98	0.93	0.91	0.98
	Error %	1.09	1.65	0.96	0.94

5.5 Adsorption isotherm study

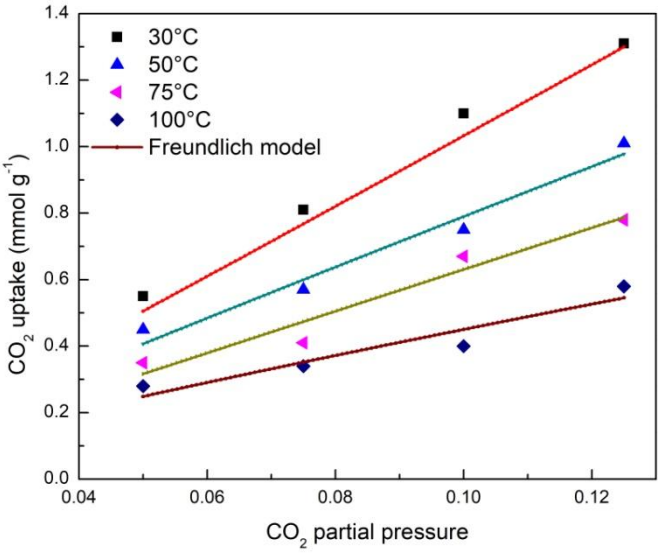


Fig. 5.17CO_2 uptake isotherm on PET-3-700: Experimental and model predicted values

Three different isotherm models fitting on experimental data was carried out and it was observed that Freundlich model best fitted on all experimental data of PET-3-700 as shown in Fig. 5.17. This observation can also be made from comparative lager values of R^2 as shown in Table 5.8. From the decreasing values of K_f with increasing temperature this can be

conclude that the adsorbent follows physiosorption behavior and is heterogeneous in nature. With value of n being greater than 1 it indicates adsorption process being favorable [110]. Also decreasing constant values also indicates adsorption process being favorable at lower temperature i.e. maximum CO_2 uptake can be observed at 30 °C.

Table 5.8 Isotherm parameters values

Langmuir			
T (°C)	K_L (atm^{-1})	q_m (mmol g^{-1})	R^2
30	0.015	6.53	0.97
50	0.18	4.38	0.95
75	0.23	2.06	0.96
100	1.37	3.74	0.95
Freundlich			
	K_F (mmol $g^{-1}atm^{-1/n}$)	N	R^2
30	11.09	1.96	0.98
50	7.14	1.04	0.96
75	6.23	1.00	0.97
100	3.24	1.16	0.98
Temkin			
	K_T(atm^{-1})	b (kJ mol^{-1})	R^2
30	35.75	3.02	0.90
50	39.40	4.63	0.91
75	36.94	5.90	0.90
100	45.9	10.37	0.94

5.7Simulation of adsorption process

Table 5.9 Model parameters obtained for simulation

Parameters	**Value**
ρ_b, Bulk density of solids (kg m^{-3})	980
ρ_b, Particle density (kg m^{-3})	1860
ε_b, Bed porosity	0.23
k_f, External film mass transfer coefficient (m s^{-1})	$3x10^{-6}$
D_{ax}, Gas phase axial dispersion (m^2 s^{-1})	$1.35x10^{-4}$
a_p, Size of the particle (m)	0.001
l, Bed length (m)	0.085
d_b, Diameter of the bed (m)	0.0093
C_0, Inlet concentration (mol m^{-3})	5.02

Parameters used for simulating the model equation mentioned in chapter four are written in Table 5.8. These parameters were calculated using the experimental conditions and equations mentioned in chapter four available. It was observed that clustering phenomenon exists in the bed due to which the particle size in bed was large in comparison to the actual size of the particle. For simulating the model 12.5% concentration of CO_2 at inlet with 30 °C as adsorption temperature was considered. Fig 5.19 shows the simulated breakthrough curve predicted by modeled equation along with experimental data obtained at 12.5% inlet concentration CO_2 with adsorption temperature of 30 °C. It can be seen that results obtained are completely in accordance with experimental breakthrough curve. This indicated that using LDF model for mass transport in adsorption process and simulating model using MATLAB software predict good results for concentration profile inside the bed and this model can be further used for carrying out simulation at different adsorption conditions and at different setup for fixed bed absorbers as well. These results further completely justify the theoretical scenarios by validating the mass balance and parameters values predicted using different set of equations.

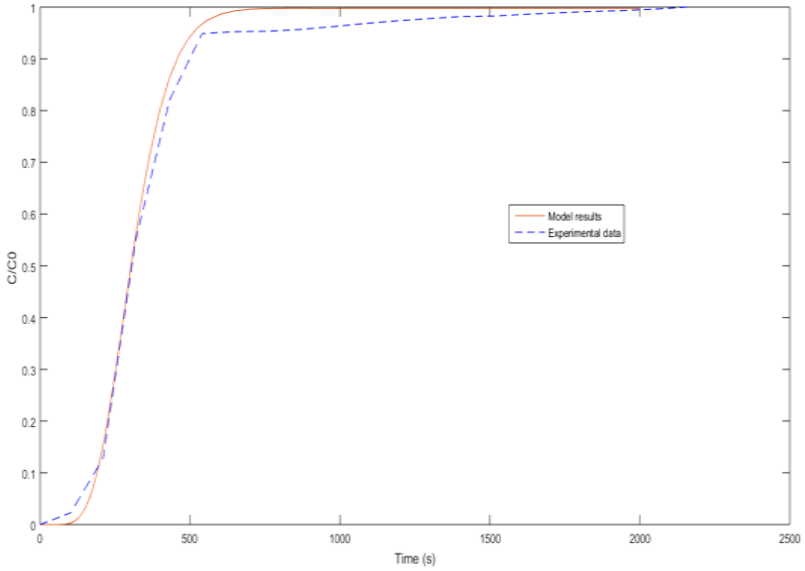


Fig. 5.19 Experimental results v/s simulated breakthrough plot

Chapter 6 - Conclusions

Study of the development of adsorbent with high surface area using PET waste has been carried out. Presence of oxygen functionalities which enhanced the adsorption capacity of absorbent in comparison to the adsorbent developed using direct carbonization technique was confirmed by XPS analysis. PET-3-700 has shown maximum CO_2 uptake capacity of 1.30 mmol g^{-1}. The adsorbent was found to be completely regenerable and stable even after multiple adsorption/desorption cycles and was selective for CO_2in comparison to N_2 for adsorption. Kinetics of adsorption was best explained by fractional order kinetic model. Adsorbent surface was heterogeneous in nature dominated with physiosorption behavior confirmed from Freundlich model fitting. Further, the fixed bed adsorption simulation showed very good match with the experimental data obtained for breakthrough studies.

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