ADSORPTION OF METHANE ON ACTIVATED CARBON BY VOLUMETRIC METHOD

A Project submitted to the
National Institute of Technology, Rourkela
In partial fulfillment of the requirements

Of

Master of Technology (Chemical Engineering)

By

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UNDER THE GUIDANCE

OF

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MAY- 2011

CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled "*Adsorption of methane on activated carbon by volumetric method*" in the fulfilment of the requirements of the award of the degree of **Master of Technology** in **Chemical Engineering,** submitted in the Department of Chemical Engineering, National Institute of Technology, Rourkela, Orissa, is an authentic record of my own work carried out during the period of July 2010 to April 2011 under the supervision of **Dr. S.Mishra**, Associate Professor, Department of Chemical Engineering, National Institute of Technology, Rourkela, Orissa.

I have not submitted the matter, embodied in this dissertation for the award of any other degree.

Date: May   2011   **(ABHISHANKAR KUMAR)**

Place: Rourkela

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

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ACKNOWLEDGEMENT

I would like to express my sincere gratitude to Prof. (Dr) S.Mishra for her guidance and assistance in this project. The technical discussions with Prof S .Mishra. were always been very insightful, and I will always be indebted to her for all the knowledge she shared with me. Her prompt responses and availability despite his constantly busy schedule were truly appreciated. The reality is that S.Mishra was much more than an advisor for me. She always helped me in all the technical and non-technical issues during the production of this work. Her encouragement and efforts led this project to successful completion in a timely fashion.

I would also like to thanks Prof (Dr) B.Munshi and Prof (Dr) M.Kundu for their insightful suggestions, which have been greatly helpful for the advance of my research and further study.

I would also like to thank Prof. (Dr) A.Sahoo. for being a uniformly excellent advisor. She was always open minded, helpful and provided us with a strong broad idea. I would also like to thank Prof. (Dr). K C Biswal our head of department to provide a good research environment.

In addition, I would like to express my heartfelt gratitude to my best friend Mrs.Debalxmi Pradhan ,Prateek Khare,Gaurav Chandrakar and Vamsi Krisnan for his constant encouragement and help throughout my whole study journey.
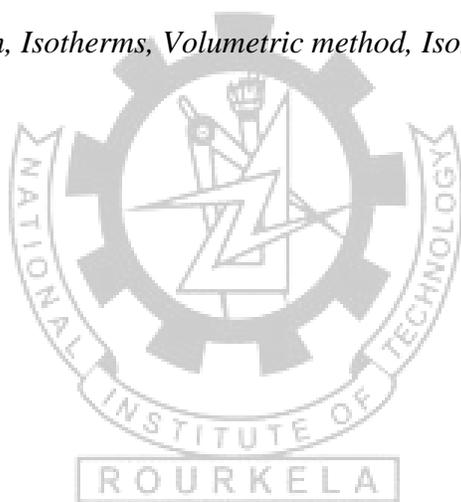
Last but not least, I take this opportunity to extend my deepest gratitude to my Parents and my brothers and sisters for their unfailingly love, unconditional sacrifice and moral support, which are far more than I could express in words.

ABHISHANKAR KUMAR

ABSTRACT:

The adsorption characteristics of methane on granular activated carbon were measured over the temperature range of (293 to 323) K and at pressures up to 900 psi using a volumetric measurement system. The surface of activated carbon has been modified with copper oxides and sliver in order to improve the adsorption capacity of methane. The results indicate that the adsorption capacity can be marginally improved by doping small amount of metal oxides The adsorption data were fitted to different isotherm models and the result shows that DA are able to predict data correctly at all temperature . The isosteric heat of adsorption, which is concentration- and temperature-dependent, is extracted from the data.

Key word: Adsorption, Isotherms, Volumetric method, Isosteric heat of adsorption.

CONTENTS

carbon by metel oxide or metel (impregmnation method) .

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ABBREVIATION

SC	Sample cell
FV	Reference cell
V1	Valve 1
V2	Valve 2
^{o}C	Degree Celsius
V_o	Void volume
	Initial pressure of reference cell
	Equilibrium pressure of reference cell
	Initial pressure of sample cell
	Equilibrium pressure of sample cell
Z	Compressibility factor
V_R	Volume of reference cell
T	Temperature
He	Helium
n_{ads}	mole adsorbed
g	Volume per unit mole
P_o	Vapor pressure
P_c	Critical pressure
T_c	Critical temperature
C_μ	Amount adsorbed
C_{max}	Maximum amount adsorbed
n	Structural heterogeneity parameter
E	Characteristic energy
A	Adsorption potential

AC	Activated carbon
ACR	Raw activated carbon
ACC	Activated carbon surface modified with copper oxide
ACA	Activated carbon surface modified with silver
R	Gas constant
b	Langmuir constant

Chapter1

Introduction

1. INTRODUCTION

Increased in environmental pollution by fossil fuel and instability in oil market has attracted great attention around the globe; consequently, kinds of alternate source of energies are put forward now. Natural gas is a promising one due to its abundance it creates less pollution, especially as transportation fuel allowing such less exhaustion than commercial gasoline or diesel. It is mostly composed of methane (87-96 mole percent) and has the highest heating value per unit mass (50.1 MJ.kg $^{-1}$) of the hydrocarbon fuels (e.g., diesel fuel, butane, gasoline, etc.). Russia and Persian Gulf is the major producer of conventional natural gas and it produces nearly 50 % of the world production.

1.1. Transportation and storage methods of natural gas.

The transportation and storage of natural gas or methane has been one of the barriers to natural gas utilization. Transportation of gas by pipeline requires large upfront capital, long pay-back periods and inflexibility once constructed. Another option for natural gas transport/storage is in the form of compressed natural gas (CNG), liquefied natural gas (LNG) and adsorbed natural gas (ANG).

1.1.1. Compressed natural gas (CNG): Which can be obtained by compressing natural gas to less than 1% of the volume it occupies at standard atmospheric pressure. It is stored and distributed in hard containers at a pressure of 200-248 bar, usually in cylindrical or spherical shape.CNG is used in traditional gasoline internal combustion engine that have been converted into bi-fuel vehicles (gasoline/CNG).Due to rising gasoline prices natural gas vehicles are increasingly used in Asia-Pacific, Latin America and Europe.

Advantages of compressed natural gas.

   I.   Lead fouling of spark plug is eliminated because absence of any lead or benzene content.
  II.   Low maintenance cost compare to other fuel-powered vehicles.
 III.   CNG fuel system are sealed, which prevents any spill or evaporation losses.
  IV.   Due to its high auto ignition temperature (540 ^{o}C) and narrow range (5-15 %) of flammability it is less likely to auto-ignite on hot surface.

V.   Compare to other commercial fuel like gasoline, diesel it emits significantly less pollutant such as carbon dioxide (CO_2), hydrocarbon, carbon monoxide (CO), nitrogen oxide (NO_x), sulfur oxide and particulate matter.

Drawbacks of compressed natural gas.

I.   Compare to conventional gasoline powered vehicles compressed natural gas vehicles require greater amount of space.

1.1.2   Liquefied natural gas (LNG)

In this method natural gas is liquefied under pressure of 10-20 bar at minus 161.5 ^{o}C. LNG requires the use of complex and expensive liquefactions equipment, thermos- like tanks and significant energy consumption (25-35 percent of original energy gas content) for the liquefaction and degasification.LNG storage tanks should have cylindrical or spherical shape. Due to a very distinctive advantage of scale it is applied mainly in marine transportation of very big quantity of gas. This technology is not yet mature for massive use in vehicles.

1.1.3 Adsorbed natural gas (ANG)

Alternative to the CNG for energy storage a new technology have been developed which give revolution for the storage of natural gas known as ANG technology.ANG is a technology in which natural gas is adsorbed by a porous adsorbent such as activated carbon at relatively low pressure (7-40 bar) and room temperature.

Applications of ANG technology.

The application of adsorbed natural gas (ANG) can be divided into three main categories.

a) **On –board fuel storage** for natural gas vehicles ranging from motorbikes, cars, buses, trains to ships.

b) **Mobile tanker supply.** Mobile ANG tankers supply natural gas by road, to transport natural gas from a pipeline or standard gas source for downstream utilization. It could also be used for the development of satellite natural gas city before it is connected to a pipeline network.

c) **Large-scale natural gas storage.** This statics strategic network storage can be used for diurnal peak shaving and tariff management. It could be implemented as a new installation as an alternative to linepack ,or retrofitted at the sites of existing gas holder and pressurized storage vessels by filling the vessels with activated carbon to gain from the enhanced storage capacity.

Advantage of adsorbed natural gas (ANG).

I. Storage distributed close to point of use, removing dependence on transmission system.
II. Lower safety hazards than CNG (7-40 bar).
III. No extensive inlet and outlet compression (like CNG) is required.
IV. High volumetric capacity.
V. Potential for removable fuel tanks for filling outside the vehicles.

Disadvantage of adsorbed natural gas (ANG)

I. Poor specific mass (ratio of useful gas stored to total parasitic mass of activated carbon and the container).

Yet, it can be construed as an alternative for the transport sector and remote area gas storage provided that higher than 160 (v/v) in volumetric storage capacity can be realized. The most promising adsorbents for ANG storage are the highly micro porous activated carbons with relatively high packing densities and higher specific surface areas.

The growth of natural gas operated vehicle worldwide is shown in fig 1
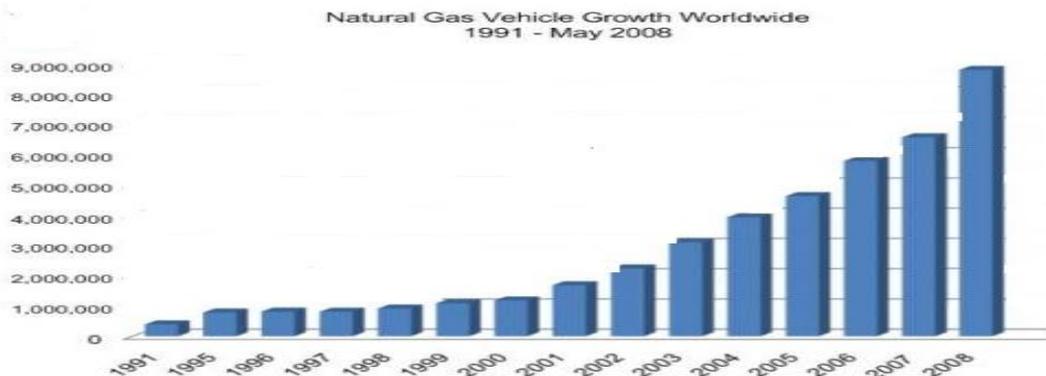
Figure 1: Growth of natural gas operated vehicle worldwide.

1.2 OBJECTIVE OF PROJECT:

a. Study the surface characterization of raw and modified activated carbon.

b. To Study the adsorption and desorption of methane on activated carbon above the critical temperature of gas and at high pressure.

c. To study the effect of increase in pressure step size on adsorption capacities.

d. To verify the theoretical models for methane adsorption on activated carbon.

e. To study the adsorption capacity of methane on the surface modified activated carbon.

f. To study the isosteric heat of adsorption at different temperature.

Chapter 2

Literature Review

2. LITERATURE REVIEW

This chapter firstly reviews fundamental of adsorption, adsorption methodology and measurement including isosteric heat of adsorption. In later section of the chapter a brief review of work by the different researcher is presented.

2.1 Adsorption Equilibrium.

When an adsorbent comes in contact with adsorbate (surrounding fluid) adsorption takes place. After a long time, the adsorbent and adsorbate reaches at equilibrium i.e. $W = f(P, T)$ where T is the temperature, P is the pressure and W is the equilibrium uptake of adsorbed adsorbate in unit of g/g or mole/gm. If the temperature is kept constant, the change in equilibrium uptake against the pressure is called the adsorption isotherm, $W = f(P)$. When the gas pressure is kept constant and the adsorbent temperature varies, the change in amount of adsorbate against the temperature is called the adsorption isobar, i.e. $W = f(T)$. Moreover, if the amount of adsorbate is kept constant, the change of pressure against the temperature is called the adsorption isosteric, i.e.

$P = f(T)$.

In an adsorption study, the adsorption isotherm is more likely to be used to express the result of adsorption rather than adsorption isobar or isostere. For the designing of any adsorption process equilibrium isotherm is one of the more important parameter. The amount of adsorbent needed in the absorber is determined by the equilibrium data, which in turn determines the key dimension and operation time for the process.

The adsorption isotherm can have different shape which is based on the adsorbent, adsorbate and the adsorbent adsorbate interaction. According to IUPAC adsorption isotherm is classified into six types. The adsorption types are shown in figure 2.

2.1.1 Type I isotherm

When an adsorbent contain very fine micropores which pore dimension is only few molecular diameters, the potential field of force from the neighboring walls of the pores will overlap causing an increase in the interaction energy between the adsorbent surface and gas molecules.

This will result in an increase in adsorption and may cause complete filling of pores at low pressure.

2.1.2 Type II isotherms

These isotherms correspond to multilayer physical adsorption. It is concave at low relative pressure, and then linear for a small pressure range where monolayer coverage is complete, and subsequently become convex to the relative pressure axis, indicating formation of multilayer whose thickness increases progressively with increase in relative pressure.
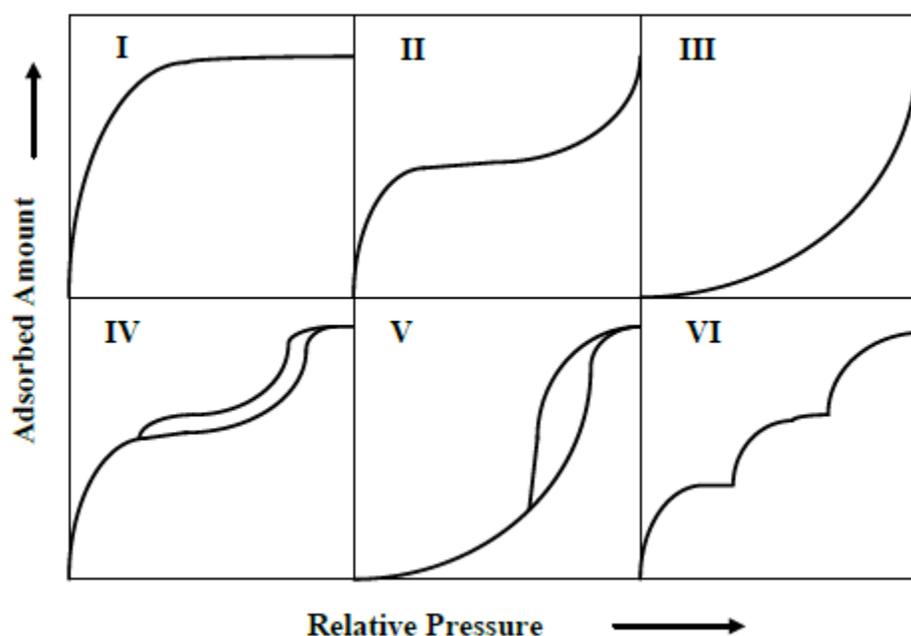
Figure 2: The IUPAC classification of isotherms

2.1.3 Type III and Type V isotherms.

Type III and Type V isotherms are characterized by being convex to the relative pressure axis. In type III isotherms the convexity continues throughout the isotherm but in type V the isotherm reaches a plateau at high relative pressure. The convexity of the isotherm is the indication of cooperative adsorption, which means that the already adsorbed molecules tend to enhance the adsorption of other molecules. In other words we can say that it support the adsorbate-adsorbate interaction.

Type III isotherms are generally observed in the case of nonporous or highly miacroporous adsorbents, and type V on mesoporous or microporous adsorbents for the adsorption of both polar and non polar adsorbent.

2.1.4 Type IV isotherms.

Type IV isotherms are obtained for adsorbent containing pores in the mesopore range. The shape of the type IV isotherm follows the same path as type II at lower relative pressure and the slope start decreasing at higher pressure. At saturation vapor pressure the isotherm levels off to constant value of adsorption. The portion of isotherm which is parallel to the pressure axis is attributed to pore filling by the capillary condensation.

2.1.5 Type VI isotherms.

Type VI isotherms shows discrete steps which may be caused by multilayer formation in different ranges of micropores.

2.2 Theoretical modeling of adsorption isotherms.

Theoretical modeling refers to fit the experimental data with the model which is based on the theoretical concept (equation of state, empirical).

2.2.1 Langmuir isotherm

However, the most commonly used model is Langmuir model that describes Type I isotherm and has been extensively used for adsorption of methane and CO_2 on coal. Langmuir model is based on the assumption that there exists a fixed adsorption sites on the surface of the solid and only one gas molecule is adsorbed at a single adsorption site. Moreover the adsorbent surface is energetically homogeneous and that the energy of adsorption is constant for all sites with no interaction between the adjacent adsorbate molecules.

The equation for the Langmuir isotherm is given as:

$$C_\mu = C_{max} \frac{bP}{1+bP} \qquad (1)$$

C_μ is the amount adsorbed in mole per unit mass or volume and $C_{\mu s}$ represents the maximum adsorbed concentration. The parameter b is called the affinity constant or Langmuir constant. It is a measure of how strong an adsorbate molecule is attracted onto a surface.

2.2.2 Freundlich isotherm

The Freundlich isotherm (1932) is one of the earliest empirical equations used to describe equilibrium data.

This equation is in the form of

$$C_\mu = KP^{1/n} \tag{2}$$

Where C_μ is the concentration of adsorbed species in mole/gm or vol/gm and K and n are generally temperature dependent. The parameter n is usually greater than unity .The larger the value, the adsorption isotherm become more nonlinear and its behavior deviates from linearity.

2.2.3 Polanyi's potential theory of adsorption isotherms

Polanyi potential theory of adsorption assumes the existence of a potential field around the surface of the solid into which the adsorbed gas molecule falls. The adsorption potential is the work done per mole of adsorbate needed in transferring molecules from the gaseous state to adsorbed state. It implicates the work done by temperature-independent dispersion forces. Therefore the potential curve is independent of temperature, and is typical of the particular gas-solid system alone. It is a function of the enclosed volume surrounding the adsorbent surface. Hence, the adsorbed volume is a function of adsorption potential (A) alone given as:

$$C=f\ (A) \tag{3}$$

The above relation is typical of a gas-solid system, and is called the characteristic curve (Yang, 1987). The characteristic curve generated from one experimental isotherm thus helps to predict the isotherms at different temperatures .Considering the adsorbate behaves as an ideal gas, the adsorption potential is given as:

$$A = RT\left(\frac{P_0}{P}\right) \tag{4}$$

where, R is the Universal Gas Constant, A is the adsorption potential, T is the adsorption temperature in absolute units, P is the adsorption pressure and Po is the saturated vapor pressure of the adsorbate at definite temperature T.

In 1967, Dubinin described adsorption on microporous adsorbents and proposed a new theory known as the theory of volume filling of micropore (TVFM). Theory of Volume Filling of Micropore postulates that, in micropores, the adsorbate occupies the pore volume by the mechanism of volume filling, and does not form discrete layers in the pores. In 1995, Dubinin and Astakhov proposed an equation based on this theory that represented the isotherms that obeyed the TVFM. The Dubinin- Astakhov (D-A) equation, it is expressed as follows:

$$C_\mu = C_{max} * \exp\left[-E\left\{\ln\left(\frac{P_0}{P}\right)\right\}^n\right] \tag{5}$$

where, C_μ is the amount adsorbed, C_{max} is the micropore volume, n is the structural heterogeneity parameter ,E is the characteristic energy of the adsorption system, Po is the saturation vapor pressure of the adsorbate at temperature T, and P is the equilibrium free gas pressure. Dubinin and Radushkevich restricted n = 2 for some cases, and modified the equation to Dubbin and Radushkevich equation (D-R) as below.

$$C_\mu = C_{max} * \exp\left[-E\left\{\ln\left(\frac{P_0}{P}\right)\right\}^2\right] \tag{6}$$

The vapor pressure at any temperature above T_c (critical temperature) is determined by using the following Dubinin equation:

$$P_0 = P_C\left(\frac{T}{T_C}\right)^2 \tag{7}$$

This approach not renders some experimental data to fall onto one characteristics curve. A generalized equation is given by Amankwah and Schwarz (1995) which is shown in equation 8

$$P_0 = P_C\left(\frac{T}{T_C}\right)^k \tag{8}$$

Where k is a parameter specific to the adsorbate -adsorbent system.

2.3 Isosteric heat of adsorption

Isosteric heat of adsorption is one of the basic quantities in the adsorption studies, which is define as the ratio of the infinitesimal change in the adsorbate enthalpy to the infinitesimal change in the amount adsorbed. The information regarding the heat released is important in the kinetic studies because when heat is released due to adsorption the released energy is partly absorbed by the solid adsorbent and partly released to surrounding. The portion absorbed by the solid increases the particle temperature and it is this rise in temperature that slow down the adsorption kinetics because the mass uptake controlled by the rate of cooling of the particle in the later course of adsorption (Duong D.D 1998).

The isosteric heat may or may not vary with loading. It is calculated from the following thermodynamic equation

$$\frac{\Delta H}{R_g T^2} = -\left(\frac{\partial \ln P}{\partial T}\right)_{c_\mu}$$ (9)

This equation is applied with the assumption that the volume of the adsorbed phase is negligible which is not true at high pressure so the equation is further modified by Chakrabarty et al., which is given in equation 10.

$$H_{ads} = RT^2 \left[\left(\frac{\partial \ln P}{\partial T}\right)_{c_\mu}\right] + T\upsilon_g \frac{dP}{dT}$$ (10)

Hear the first term of the right hand side is derived from Clausius-Clayperon equation and the second term comes due to non ideality of the gas.

2.4 Adsorption Measurement Technique

Adsorption measurement is to determine the adsorption characteristics of adsorbent-adsorbate pair, including isotherm, kinetics and heat of adsorption data. All these parameters are key variables for simulation and modeling of any adsorption process. Currently available adsorption measurement techniques or facilities can be basically classified into three types, i.e. volumetric gravimetric and gas flow (He Jing Ming., 2009)

2.4.1 Gas Flow Technique

This approach, firstly proposed by Nelsen and Eggertsen, and it was an alternative of gas chromatography. It used helium as carrier gas and partial pressure of adsorbate is determined by the gas flow meter. The volume adsorbed by the adsorbent was determined from the peak area in the adsorption/desorption chart recorded by a potentiometer over a period. This apparatus is simple, inexpensive and straightforward to handle, and no vacuum is required, and available gas chromatographers can be also modified for this approach. However, the measurement of the adsorbed amount is indirect and the method does not claim high precision. The method is usually applied for fast single point determinations of the specific surface area. Multipoint measurements of isotherms become complicated.

2.4.2 Gas Adsorption Volumetric Technique: In this technique a given amount of sorptive gas is expanded into a vessel which includes a sorbent sample and which initially has been evacuated Upon expansion the sorptive gas is partly adsorbed on the (external and internal) surface of the sorbent material, partly remaining as gas phase around the sorbent. By a mass balance, the amount of gas being adsorbed can be calculated if the void volume of the sorbent, i.e. the volume which cannot be penetrated by the sorptive gas molecules is known at least approximately. The line diagram of volumetric setup is shown in figure 3
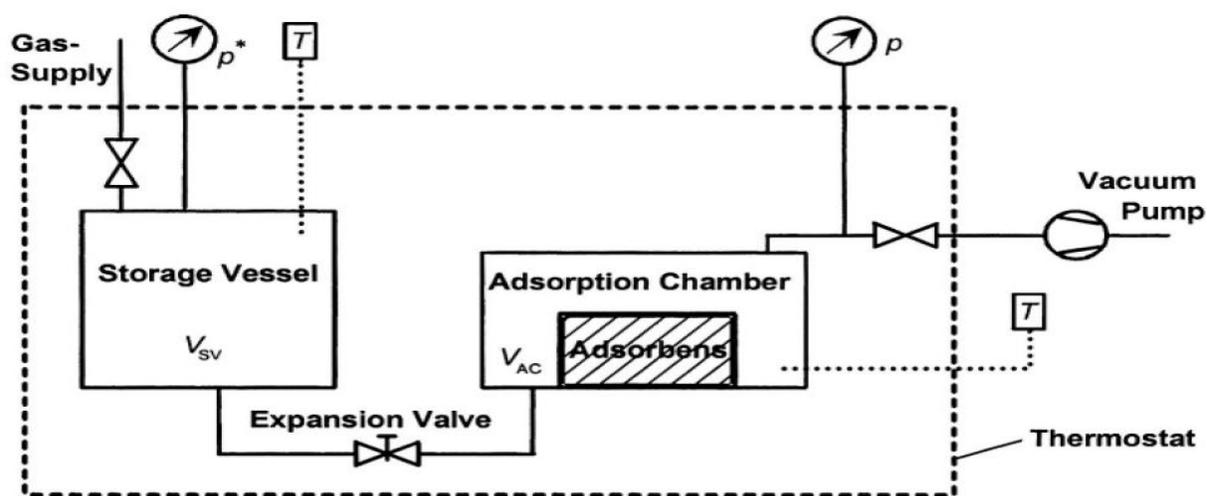

Figure 3: Experimental setup for (static) volumetric measurement of pure gas adsorption equilibria.

2.4.3 Gravimetric method: In gravimetric method, the weight change of the adsorbent sample in the gravity field due to adsorption from the gas phase is recorded. Various types of sensitive microbalance have been developed for this purpose. A continuous-flow gravimetric technique coupled with wavelet rectification allows for higher precision, especially in the near-critical region.
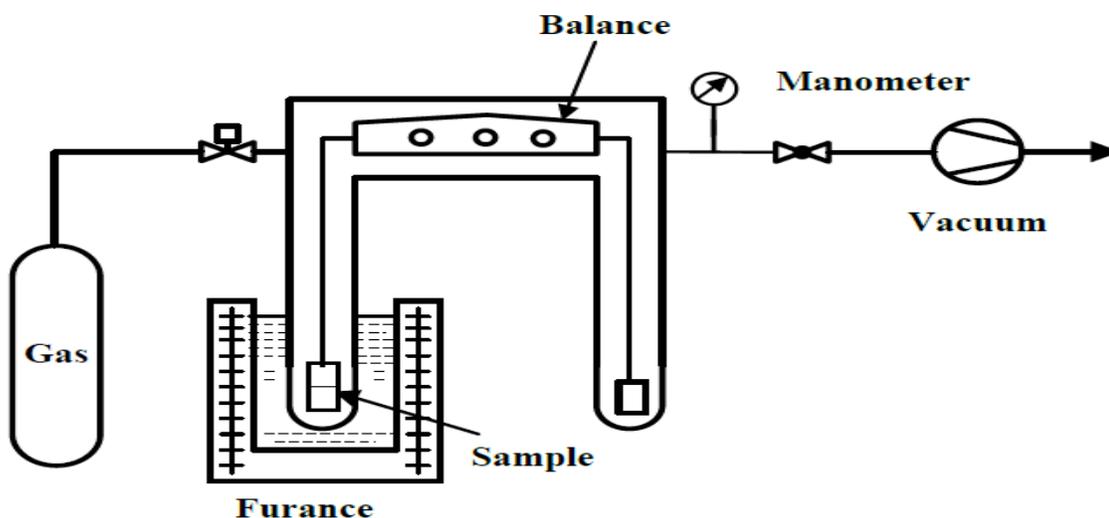
Figure 4: Schematic diagram of gravimetric apparatus.

2.5 Adsorption characteristic of gas

For the designing of any storage vessel or any absorption column for methane adsorption the adsorption characteristic of methane on the activated carbon such as isotherms, and heat of adsorption are fundamentally design parameter. However, even through the absorbed natural gas (ANG) technology is using from last 10 year for storage of natural on suitable adsorbent but yet it is in developing stage.

Several researchers have studied and changes different parameter to improve the adsorption capacity. Kazi Afzalur Rahman et al.(2010) have measured the adsorption isotherm of methane onto the pitch-based activated carbon type Maxorbe III for temperature ranging from 120 to 220 k and pressure up to 1.4MPa, for the application of adsorbed natural gas (ANG) storage systems when the low temperature natural gas regasified from the liquid phase is considered to charge in the storage chamber. Toth and Dubinin-Astakhov models are used to determine the adsorption

parameter and the isosteric heat of adsorption is extracted from these data. E. Salehi et al. (2007) has studied adsorption and desorption of methane on different granular activated carbon by volumetric method, up to pressure 500psi and at constant temperature 25 ^{o}C. The result reveal that BET surface area, micro pore volume, packing density and pore size distribution play an important role in the amount of methane to be adsorbed or desorbed. Xiaolin Wang et al. (2010) studied the adsorption characteristics of methane on a Maxsorbe II specimen of activated carbon were measured over the range of (281 to 343)K and at pressure up to 1.2 MPa using new volumetric measurement system.BET surface area, pore size distribution and skeletal density are used to characterized the adsorbent. The adsorption parameter is obtained by the equation proposed by Toth and Dubinin-Astakhov. The present data could complement efforts in designing adsorbed natural gas storage systems. Bidyut B. Saha et al. (2009) study the adsorption isotherms of R-134a (HFC134a) on highly porous pitch based activated carbon in the temperature range of 5-70 ^{o}C and pressure up to 12 bar using desorption method.Dubinin-Astakhov (D-A) isotherm model is used to fit the experimental data. The isosteric heat of adsorption of assorted adsorbent-refrigerant pair has also obtained from the preset experimental data.

S. Farzad et al. (2008) studied the adsorption and desorption of methane by activated carbon at constant temperature and various pressure .They also studied the effect of moisture on adsorption capacity and found that the moisture fill the pores which cause decrease in adsorption and desorption capacity.

Afsaneh Somy et al. (2009) have studied the effect of impregnation of activated carbon with Cr_2O and Fe_2O_3 and promotion by Zn^{+2} on its adsorptive properties of carbon dioxide by volumetric adsorption. To compare CO_2 capture capacity of the impregnated activated carbon promoted by Zinc slurry and solution impregnation methods were used. The result showed that amount of CO_2 adsorbed on the samples impregnated by Cr_2O was increased about 20% in compare to raw activated carbon and Fe_2O_3 was not an effective impregnating species for activated carbon modification Moreover slurry impregnation method showed higher CO_2 adsorption capacity in comparison with solution impregnation method. Co-impregnation of two metal species showed more adsorption capacity than samples impregnated by just one metal species individually. The result also shows 15% increase in CO_2 adsorption capacities when

washing the impregnated samples by metal oxide. Decreasing impregnation temperature from 95 to 25 ^{o}C in solution method showed a significant increase in CO_2 adsorption capacity. Sips equation was used to fit the adsorption data in this range. Jinghong Ma et al. (2010) have prepared Cu-based adsorbents for CO adsorption by impregnation activated carbon (AC) with aqueous solution of copper (II) chloride and copper (II) carboxalate. The characterization of adsorbent by N_2 adsorption at 77 k and XRD showed that cupric salts were completely converted to highly dispersed CuCl on activated carbon after pre-activation, resulting in the stochiometric adsorption by the coordination of CO with Cu (I).The result shows that adsorbent have high selectivity and good adsorption -desorption reversibility for CO with small heat of adsorption. Chen-Chia Huang et al. (2010) has investigated hydrogen adsorption on prepared super activated carbon using litchi trunk as precursor .Litchi trunk was activated by potassium hydroxide under N_2 or CO_2 atmosphere. Nanoparticles of palladium were impregnated to investigate the adsorption change. The result revel that the hydrogen adsorption capacity at 303 K and 6 MPa on 10 wt. % Pd-AC was obtained as 0.53 wt. %. This amount is higher than that on the pristine AC (0.41 wt. %) under the same condition.

Anutosh Chakraborty et al. (2009) has derived and developed thermodynamic properties surfaces for a single adsorbent +adsorbate system from the viewpoint of classical thermodynamics. They derive the enthalpy of the adsorbed phase, the isosteric heat of adsorption, specific heat capacity, and the adsorbed phase volume thoroughly. For calculating the energetic performance of any adsorption system use of this equation are very easy to handle. The result is able to fill up the information gap with respect to the state of an adsorbed phase to dispel the confusion as to what is the actual state of adsorbed phase. They also discussed and established the temperature-entropy diagram of (1) $CaCl_2$- in silica gel+water system for cooling application and (ii) activated carbon (Maxsorb III) +methane system for gas storage. D.D. Do et al. (2009) has tried to find Henry constant and the isosteric heat of adsorption at zero loading which are commonly used as indicators of the strength of the affinity of an adsorbate for a solid adsorbent with the assumption that (i) they are observable in practice (ii) the Van Hoff's plot of the logarithm of the Henry constant versus the inverse of temperature is always linear and the slope is equal to the heat of adsorption, and (iii) the isosteric heat of adsorption at zero loading is either constant or weakly dependent on temperature. They observed that these variable might not be observable since they are outside the range of measurability; second that the linearity of the Van Hoff plot

break down at very high temperature, and third that isosteric heat of adsorption verses loading is a strong function of temperature. They demonstrate these points using Monte Carlo simulation of adsorption of various gases on graphite surface.

Chapter 3
Material and methods

3. MATERIALS AND METHODS.

3.1 Activated carbon.

Granular activated carbon is used for the studies of methane adsorption which are obtained from Silicon P associate Mumbai. The moisture content of the samples was estimated using the standard test method for equilibrium [ASTM D 1424 – 93]. Then the activated carbon samples ACR (Raw activated carbon), ACC (activated carbon modified with copper) and ACA (activated carbon modified with silver) were evaluated for the proximate analysis using laboratory furnace as per the standard method [ASTM D 3172 – 07a] and ultimate analysis of AC samples were estimated using CHNS Analyzer [Perkin-Elmer], as per the standard methods [ASTM D 3176 – 09].

Figure 5: Granular activated carbon.

3.2 High purity helium and methane.

The high purity helium and methane of 99.999% is used in this study and were purchased from S.K.P Rourkela and Gujarat respectively.

3.3 Surface characterization of activated carbon

The surface characterization of raw activated carbon (ACR) and surface modified activated carbon is done by thermo gravimetric analysis (TGA), Fourier Transform Infrared spectroscopy (FTIR) and scanning electron microscope (SAM) images.

3.3.1 Thermo gravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of raw (ACR) and surface modified activated carbon activated (ACC & ACA) was carried out using TGA/DTG (DTG-60/60H of SHIMADZU) at a rate of heating 20 ^{o}C/min in the nitrogen atmosphere from room temperature to up to 600 ^{o}C to know the decomposition temperature or to find out the range of maximum degradation temperature.

3.3.2 Fourier Transform Infrared spectroscopy (FTIR) of activated carbon:

Fourier Transform Infrared spectroscopy is an important analysis technique which detects various characteristic functional groups presents on surface of activated carbon. On interaction of an infrared light with activated carbon surface, chemical bond will stretch, contract or bend, and as a result each functional group tends to absorb infrared radiation in a specific wave length range regardless of the structure of the rest of the molecules. The FTIR spectra were collected in the range of 400-4000 cm^{-1} region with 8cm^{-1} resolution. The FTIR imaging is carried out using Perkin Elmer RX.

3.3.3 Surface topography

A JEOL JESM -6480LV scanning electron microscope (SEM) was used in the study. The structural feature of the raw and surface modified activated carbons was observed at the accelerated voltage of 15 kV. Before observation, the samples were coated with platinum in Ion sputter.

3.4 Experimental set up of volumetric equipment.

A schematic diagram of the self fabricated experimental setup consisting of cylindrical stainless steel sample cell (SC), reference cell (FV), a set of valves and a high precision pressure transducer (10MPa, with a precision of 0.05%) shown in Fig.6. The volume between valve V1

and V2 including the dead volume of the pressure transducer, is used as reference volume and determined by helium expansion procedure. The granular activated carbon sample is placed into the sample cell. A micro filter (not visible in figure) was placed just above the sample chamber to prevent sample particles from entering the valve. The reference cell and the sample cell are kept in a water bath to maintain constant temperature with $+ 0.2^{\circ}C$ accuracy of the set point.
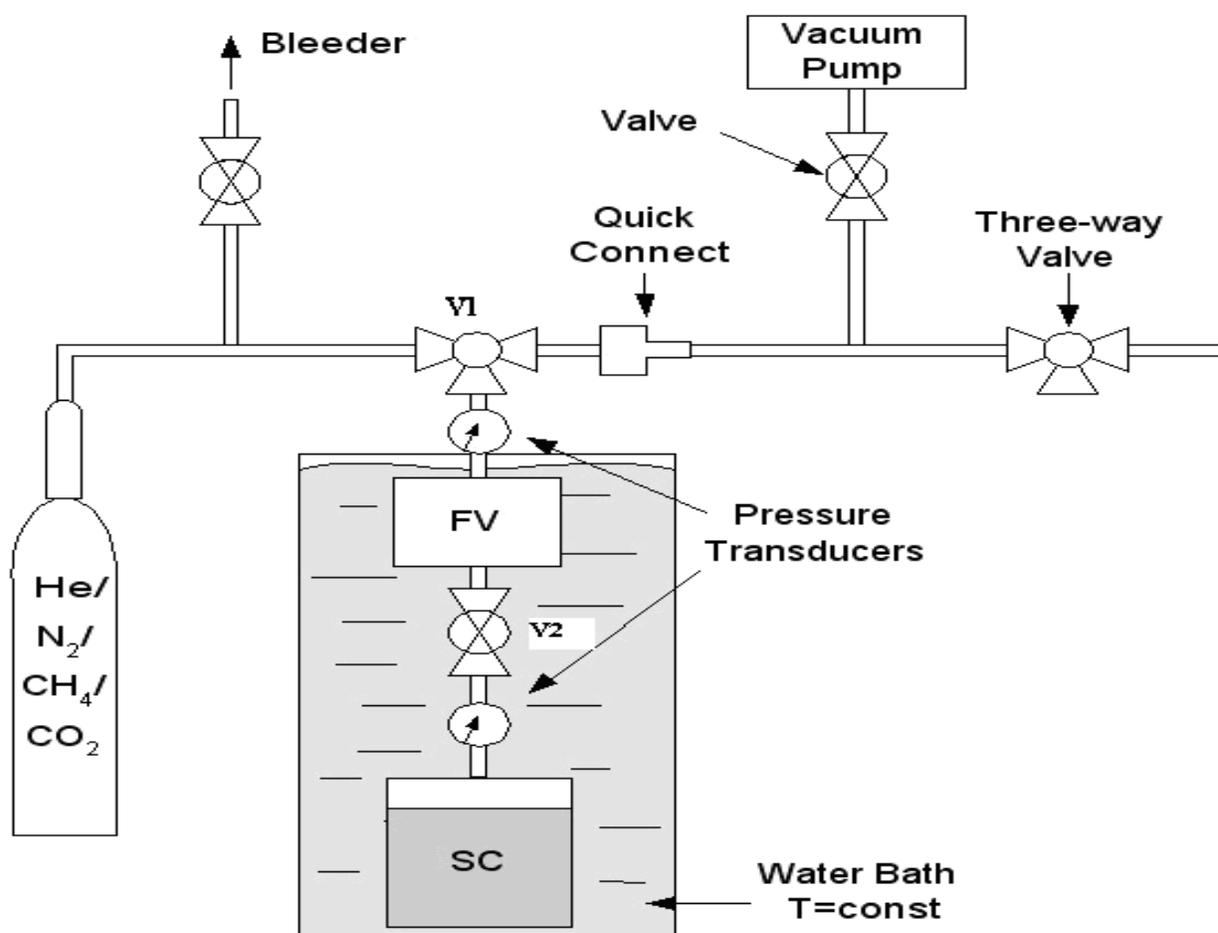

Figure 6: Schematic diagram of experimental set up for methane adsorption on activated carbon by volumetric method.

3.5 Volumetric method for methane sorption measurement on activated carbon.

The experimental method used for adsorption is based on mass balance principle,which employs precise measurment of pressure, volume and temperature. The entire apparatus is maintained in a constant tepperature water bath. The sample cell (SC) is filled with the adsorbent to be studied, and placed under vacuum prior to gas injection. The void volume (V_O) of the cell at equilibrium

was determined from measured values of temperature, pressure and amount of helium injected into the cell using the following equation 11.

$$V_O = \frac{\left(\frac{P_{R_1}}{Z_{1R}} - \frac{P_{R_2}}{Z_{2R}}\right)}{\left(\frac{P_{S_2}}{Z_{S_2}} - \frac{P_{S_1}}{Z_{S_1}}\right)} V_R$$

11

where Z is the compressibility factor of helium, T is the temperature, P is the pressure, subscripts 1 and 2 refer to the initial and equlibrium conditions and R and S represent reference and sample cells, respectively. V_R represents the volume of the reference cell. A picture of fabricated vollumetric set up is shown in fig 7.

Figure 7 : Photograph of fabiricated volumetric setup (Top view)

Several injections made into the cell at different pressures show consistancy in the calculated void volume. The helium void volume includes all of the volume of the cell section exclusive of the adsorbent volume that is impenetrable to helium gas.

The amount of adsorbed methane was calculated from the mass balance in the form of measurable quantities according to Ozdemir et al. (2002)

$$\Delta n_{ads} = \frac{1}{w}\left[\left(\frac{P_{R_1}}{Z_{R_1}} - \frac{P_{R_2}}{Z_{R_2}}\right)\frac{V_R}{RT} - \left(\frac{P_{S_2}}{Z_{S_2}} - \frac{P_{S_1}}{Z_{S_1}}\right)\frac{V_O}{RT}\right] \qquad\qquad 12$$

Where w is the weight of the sample ,V_R is the reference volume ,and V_O is the void volume of the sample cell .

The above procedure was repeated for incrementally increasing pressure of methane .Finally the estimate of the total amount of gas adsorbed ,n_{ads} at the ith step was determined from

$$n_{ads} = \Delta n_{ads1} + \Delta n_{ads2} + \ldots\ldots \qquad + \Delta n_{adsi} \qquad\qquad 13$$
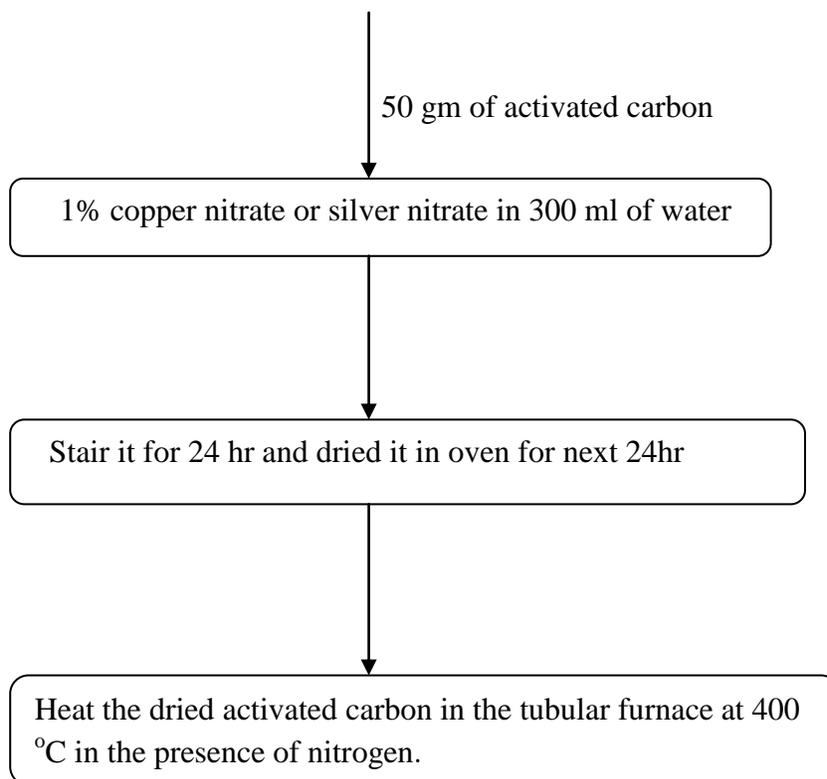
3.6. Gas Compressibility Factors

The accurate compressibility factors are required for pure methane and helium for proper adsorption data analysis.National institute of standards and Technology (NIST) version 9.09 is used for find out the compressiblity factor of methane.

The compressibility factor of helium is determine by the equation Sudibandriyo et al. (2003)

$$Z_{He} = 1 + (0.00147 - 0.000004779T + 0.00000000492T^2)/P \qquad\qquad 14$$

where T is the operating temperature

3.7.Experimental procedure for surface modification of activated carbon by metal oxide or metal (impregmnation method) .

50 gm of activated carbon

1% copper nitrate or silver nitrate in 300 ml of water

Stair it for 24 hr and dried it in oven for next 24hr

Heat the dried activated carbon in the tubular furnace at 400 ^{o}C in the presence of nitrogen.

The following decomposition reaction takes place

$$2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2 \hspace{3cm} 15$$

$$2AgNO_3 \rightarrow 2Ag + O_2 + 2NO_2 \hspace{3cm} 16$$

Chapter 4

Result and discussion

4. RESULT AND DISCUSSION

4.1 Characterization of raw and modified activated carbon

4.1.1 Study of Proximate and ultimate analysis of raw and modified activated carbon

The proximate and ultimate analysis of the raw and modified activated carbon have been performed which are shown in table 1.The result reveal that the percentage of fixed carbon is increased after modification and it is maximum 89.2 percent in the case of silver modified activated carbon followed by copper modified activated carbon(86.44 percent).The moisture content of the modified activated carbon is less compare to the raw activated carbon which may be the cause of blockage of the pore by the metal during impregnation.

The percentage of carbon hydrogen nitrogen sulphur and oxygen present in raw and surface modified activated carbon is shown by the ultimate analysis .The result shows that silver modified activated carbon content maximum percentage of carbon(89.08563 percent) followed by copper modified activated carbon (78.125 percent) .

Table 4.1: Proximate and ultimate analysis of raw and modified activated carbon

Proximate analysis			
Specification	Silver modified activated carbon	Copper modified activated carbon	Raw activated carbon
Moisture content	3.1	2.9	3.2
Fixed carbon	89.2	86.44	79.7
Volatile content	8.7	10.96	17.6
Ash content	2.1	2.6	2.7
Ultimate analysis			
Elements	Silver modified activated carbon	Copper modified activated carbon	Raw activated carbon
Carbon	89.0856	78.1250	78.014
Hydrogen	0.0771	0.06510	0.0442
Nitrogen	.69954	0.5873	0.4871
sulphur	0.08091	0.0701	0.0451
Oxygen	10.0568	21.1523	21.411

4.1.2 Surface topography of raw and modified activated carbon

The scanning electron microscope images of the raw and surface modified activated carbon is taken to see the pores developed on the surface before and after the modification which are shown in the figure 8.

The Elemental diffraction x-ray (EDX) of the raw and surface modified activated carbon by silver is also performed to see the presence of the metal on the surfaces which are shown in figure 9.The fig 9(a) shows the presence of silver metal on the surface of the activated carbon.
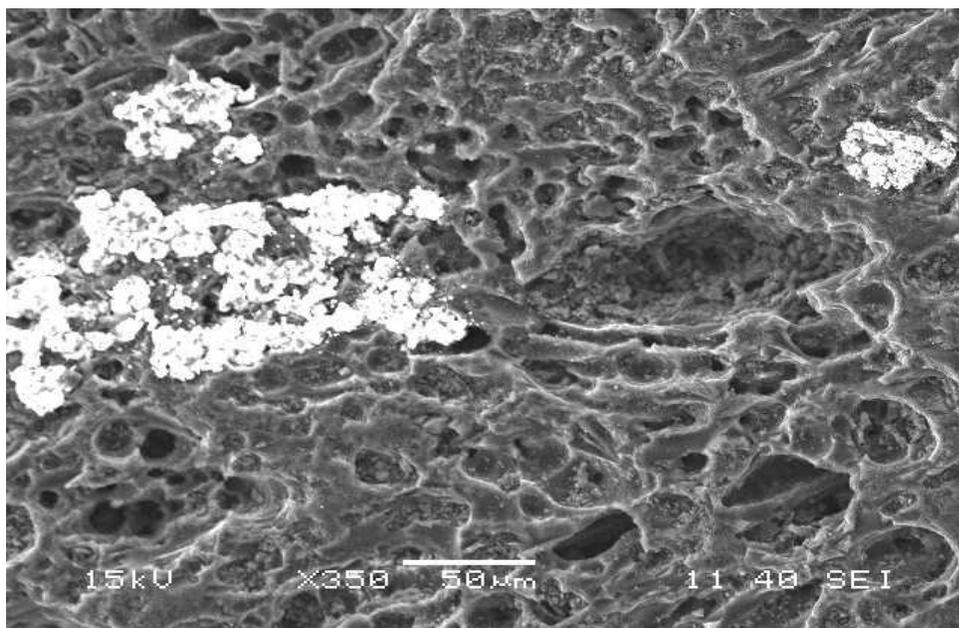
Figure 8(a): SEM image of silver modified activated carbon
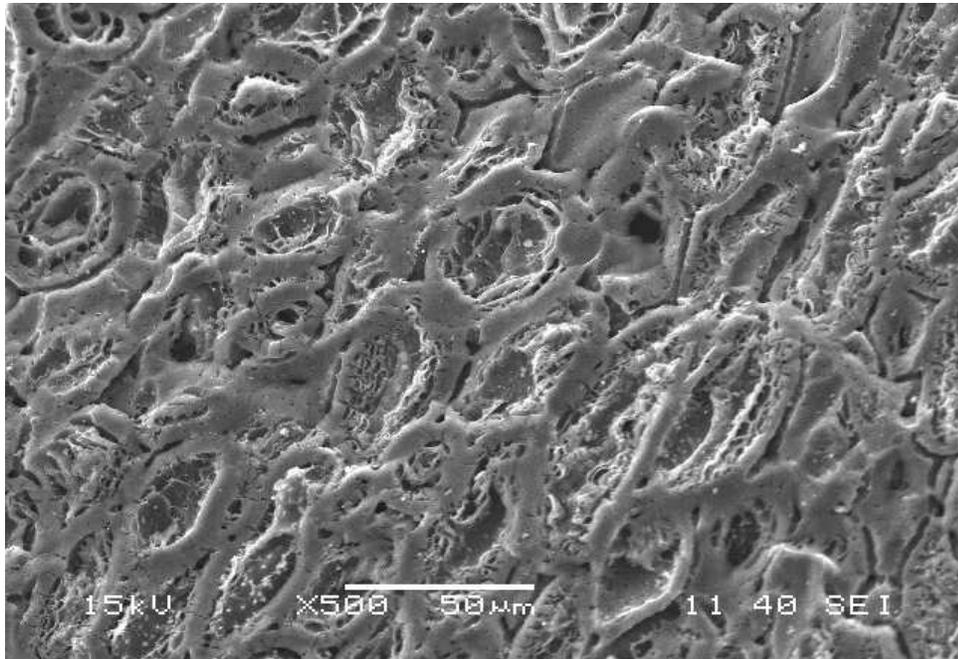
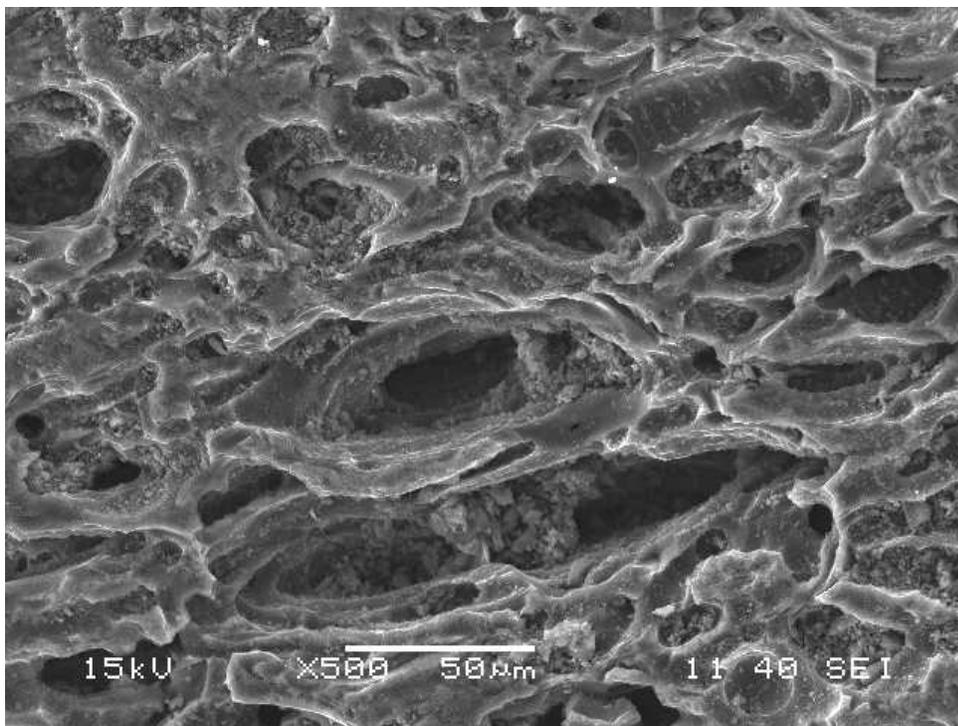Figure 8(b): SEM image of cupper modified activated carbon

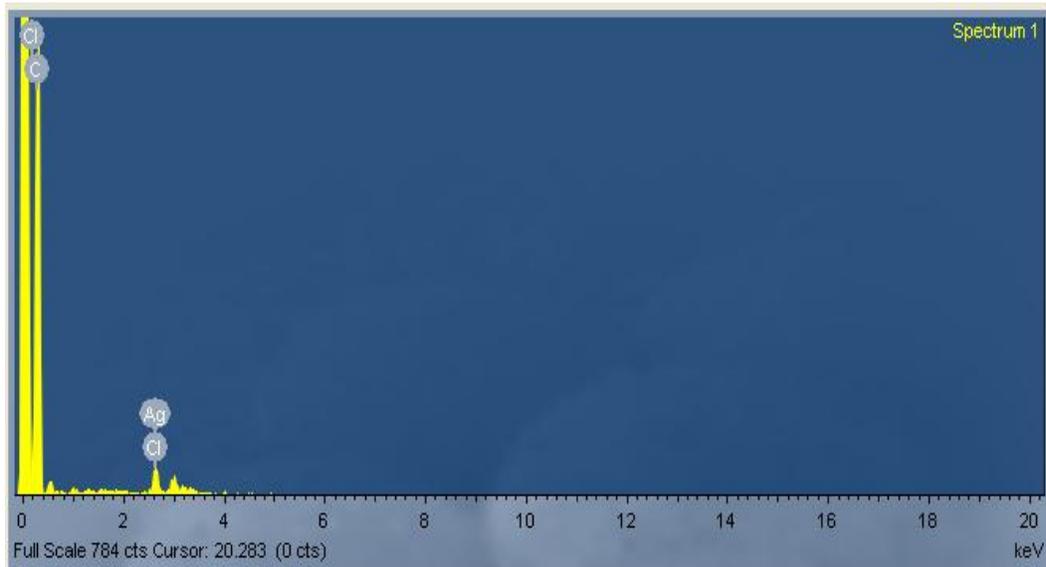Figure 8(c): SEM image of raw activated carbon

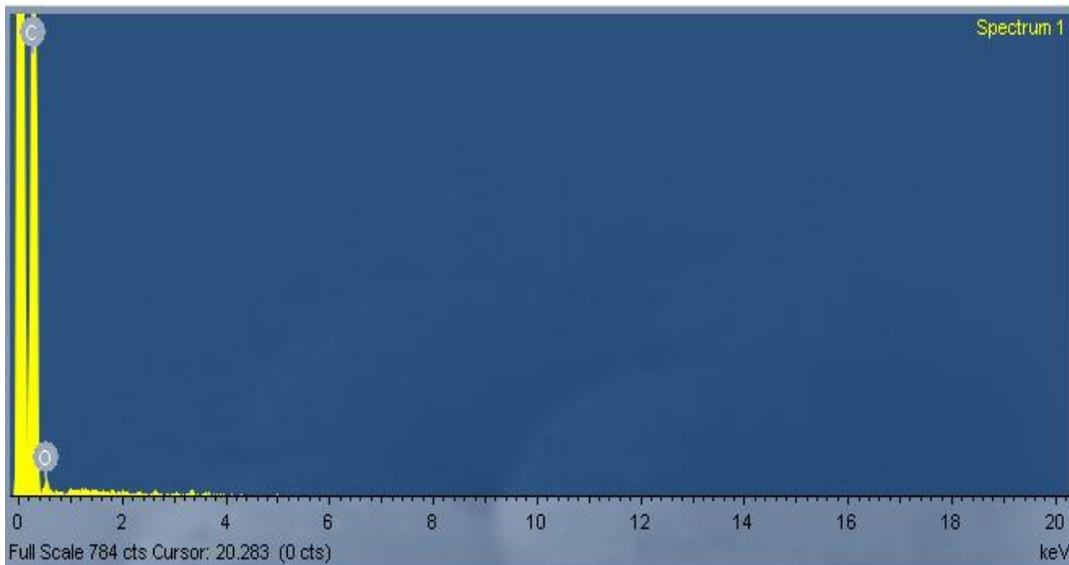Fig 9(a): EDX of silver modified activated carbon

Fig 9(b): EDX of raw activated carbon

4.1.3Thermogravemetric analysis (TGA) of activated carbon

Thermogravimetric analysis of raw and modified activated carbon is shown in figure 10.Three stage of decomposition occurs, at the first stage from temperature 39.24 to 249^{0}C total moisture has evaporated, in the 2ndstage of decomposition from 249 to 495^{0}C temperature devolatisation occurs. After 495^{0}C weight loss was stable. It indicates that all the activated carbons have shown similar trend to temperature increase. Thus it can be suggested that each of the activated carbons have activation between 249°C and 495°C. Hence activation was done in this range.
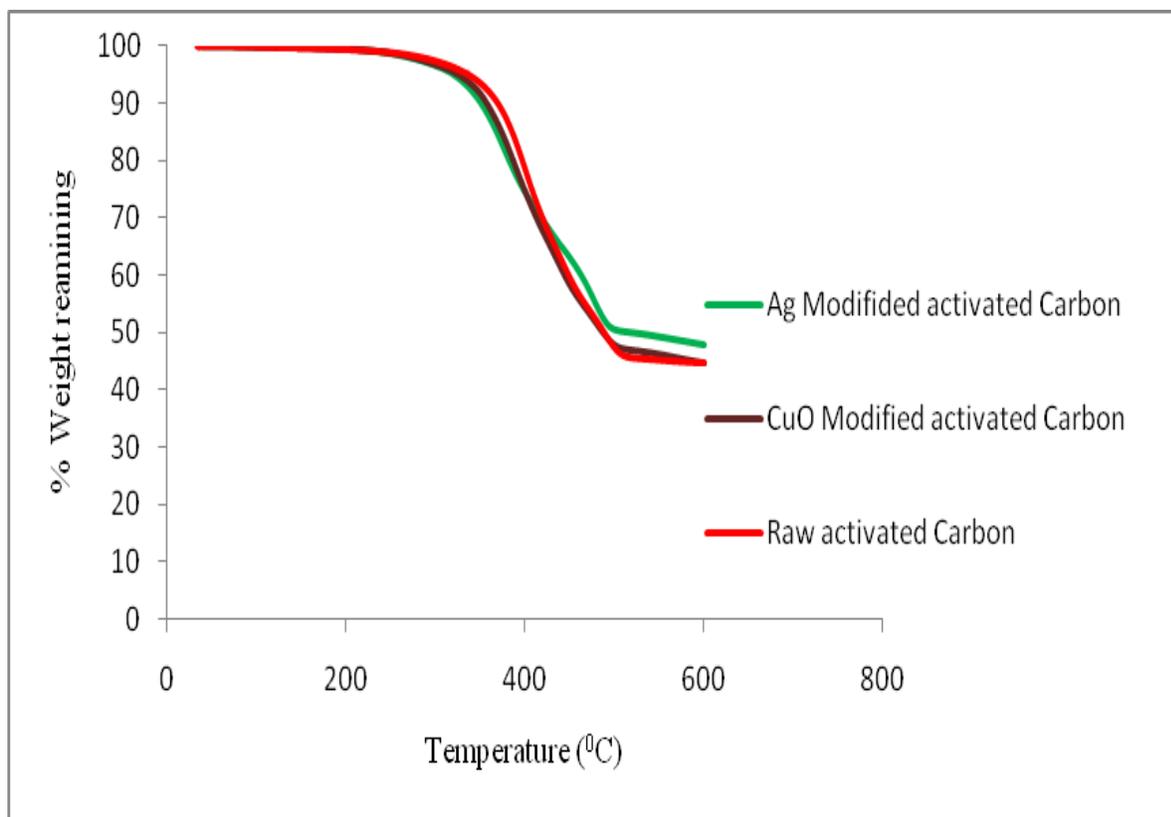

Figure 10: Thermogravimetric analysis of activated carbon.

4.2 Study the effect of adsorption capacity of methane on activated carbon above critical temperature.

The adsorption of methane on granular activated carbon have been studied at different temperature (293 k, 303k, 313k and 323k) and equilibrium pressure up to 7 Mpa which is shown in fig 11.The result shows that the increase in pressure increase the adsorption capacity of methane at a particular temperature but at the same time the adsorption capacity decrease with increase in temperature because the high temperature more heat is released due to adsorption the released energy is partly absorbed by the solid adsorbent and partly released to surrounding. The portion absorbed by the solid increases the particle temperature and it is this rise in temperature that slow down the adsorption kinetics and capacity because the mass uptake controlled by the rate of cooling of the particle in the later course of adsorption. The isotherm also shows the characteristic of type1 isotherms, indicating that the activated carbon is mainly microporous materials
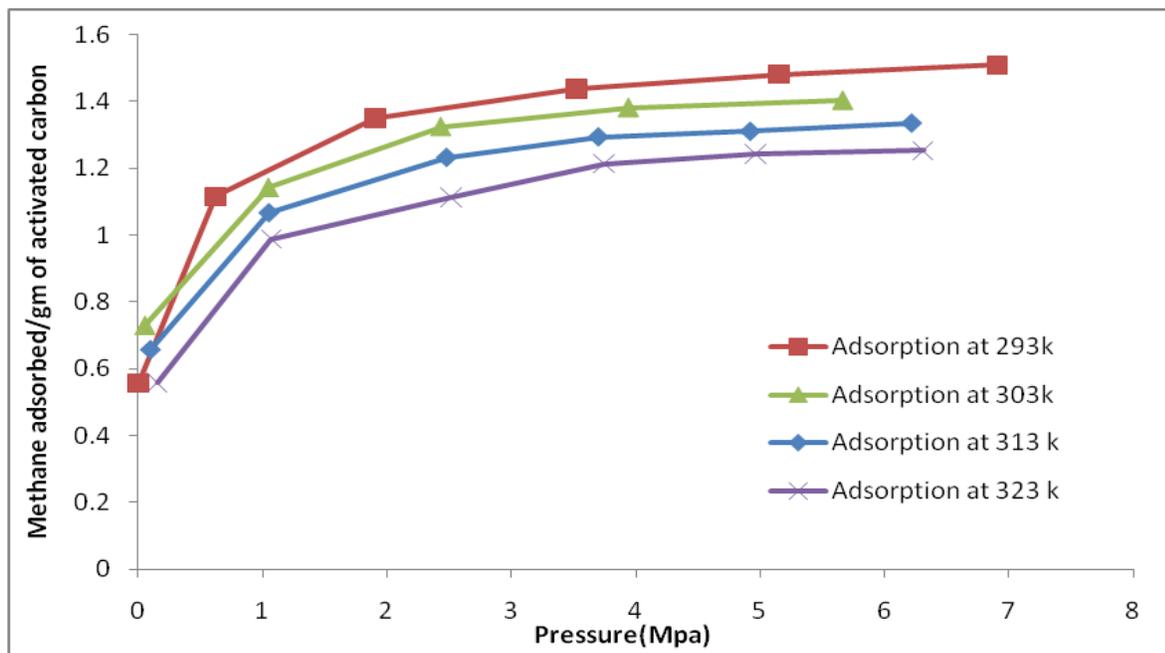

Figure 11: Effect of adsorption capacity of methane at different temperature and equilibrium pressure.

4.3 Study of adsorption desorption of methane on activated carbon at above critical temperature.

The adsorption and desorption capacity of methane have been studied at different temperature (293k,303k,313k and 323k) which are shown in figure 12.The fig 12 (a) shows the formation of hysteresis because at high pressure it desorbed less amount of gas compare to adsorption at the same pressure at particular temperature . The formation of the hysteresis may be the cause of gas condensation at low temperature. The figure 12 (a) to (c) shows no formation of hysteresis because at high temperature the gas evaporate from the pores of the activated carbon.
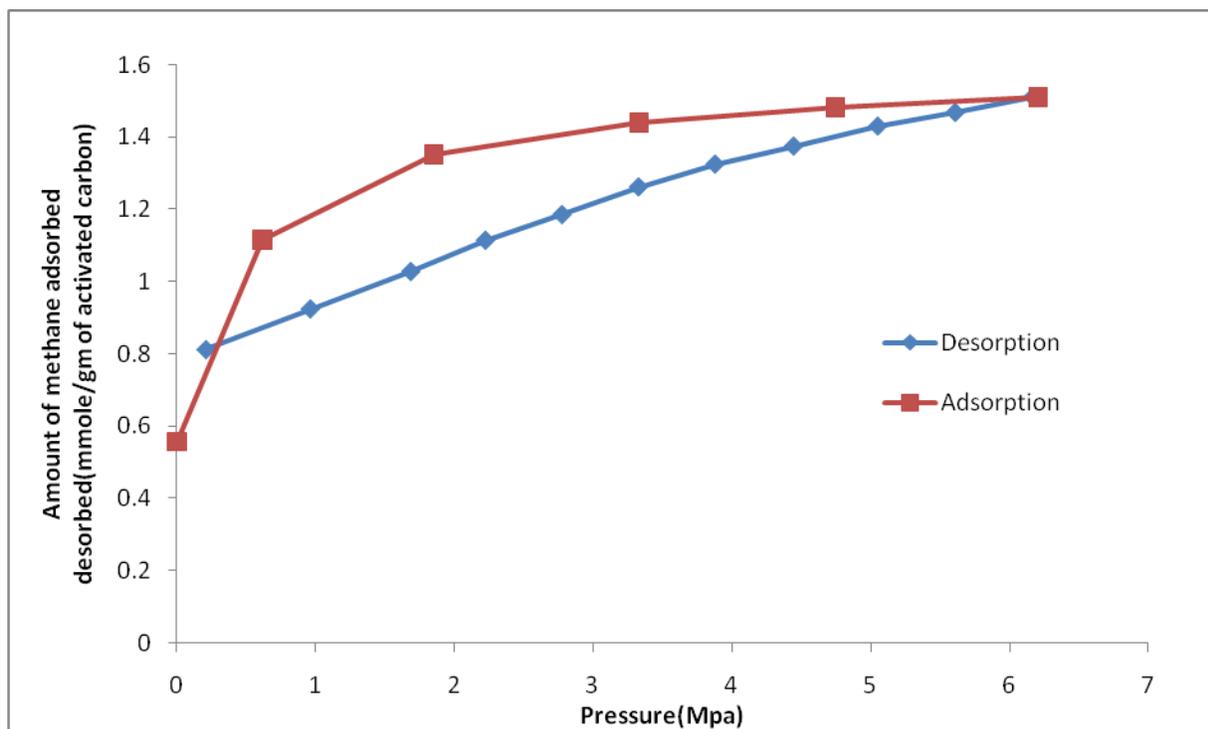

Figure 12(a): Adsorption desorption study of methane on activated carbon at 293K
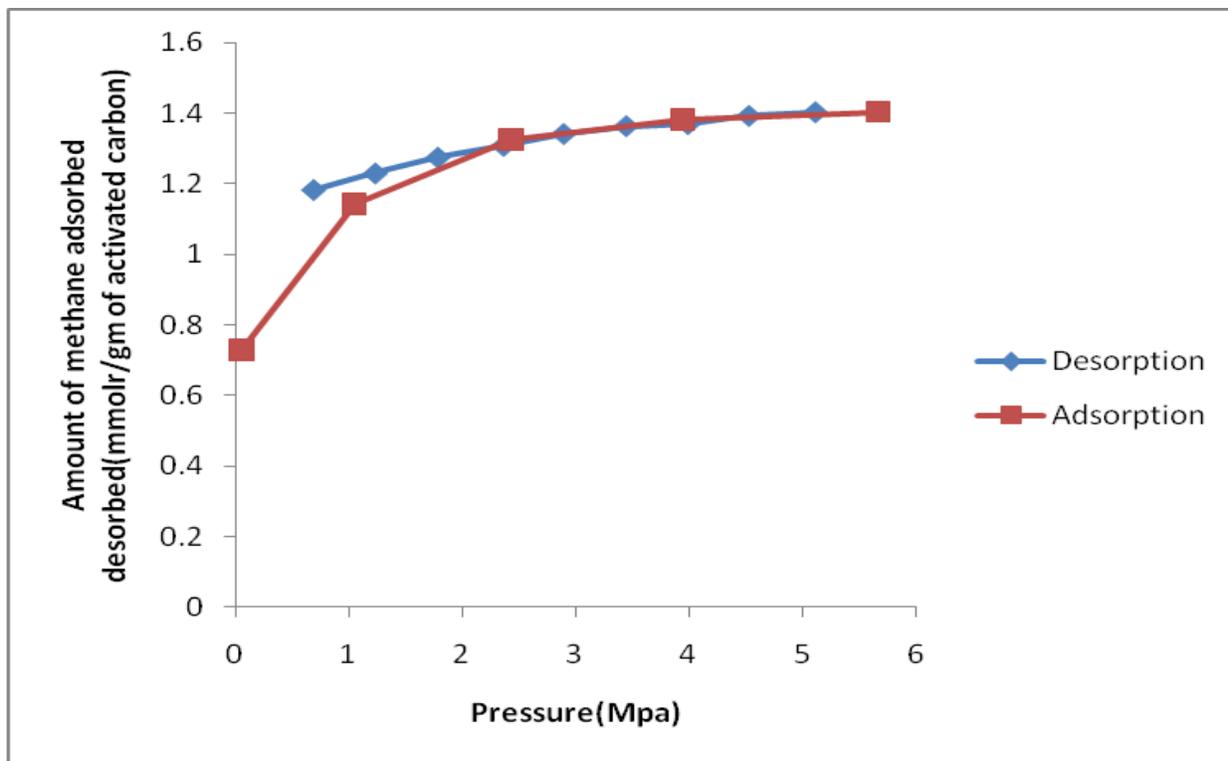
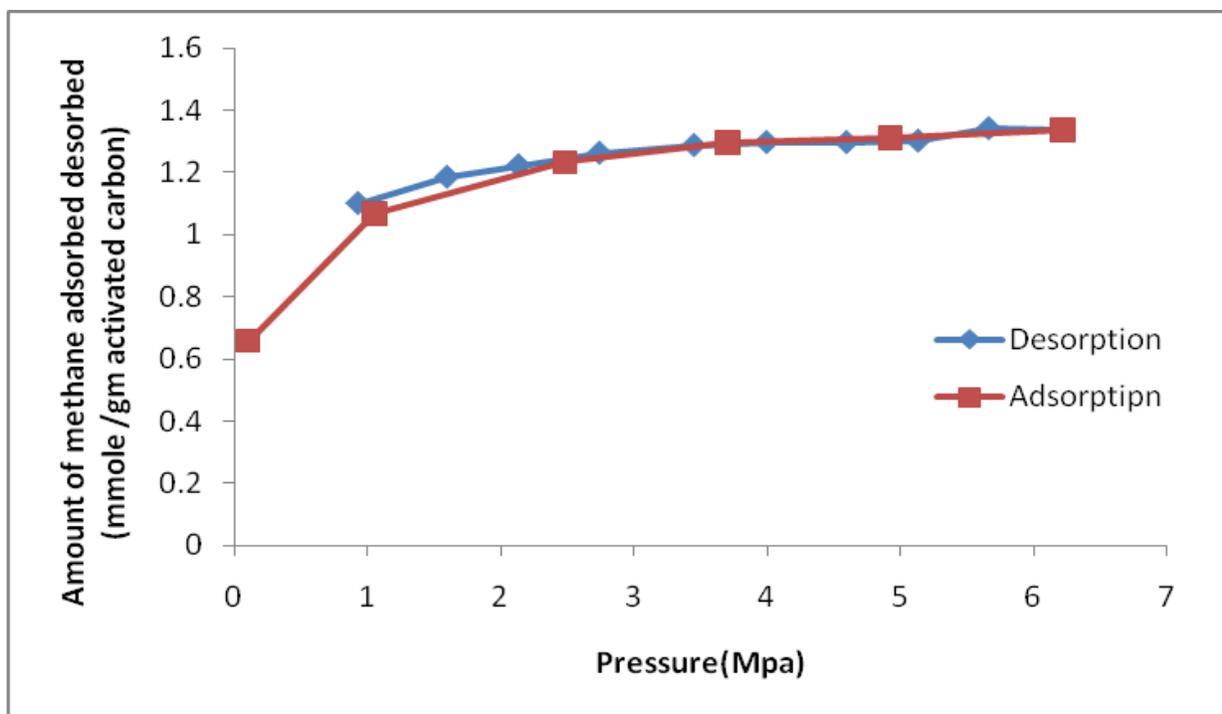Figure 12(b): Adsorption desorption study of methane on activated carbon at 303K

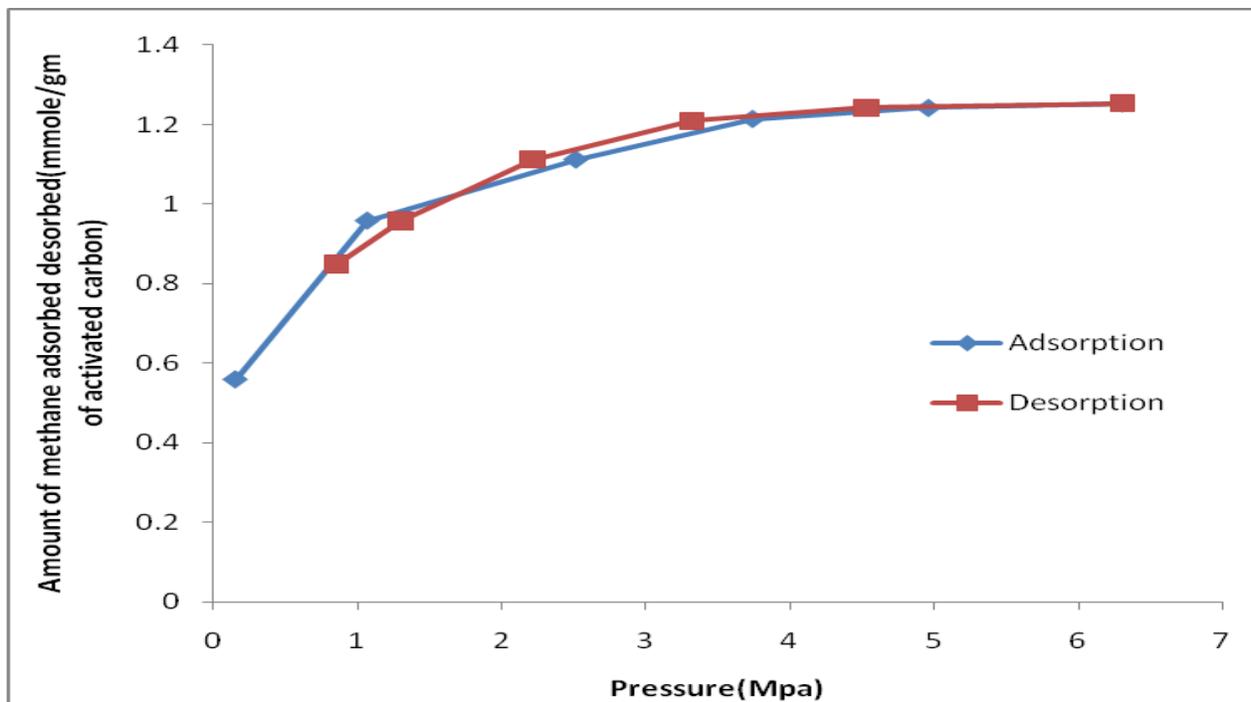Figure 12(c): Adsorption desorption study of methane on activated carbon at 313K

Figure 12(d): Adsorption desorption study of methane on activated carbon at 323K

4.4. Study the effect of pressure step size on the adsorption capacity.
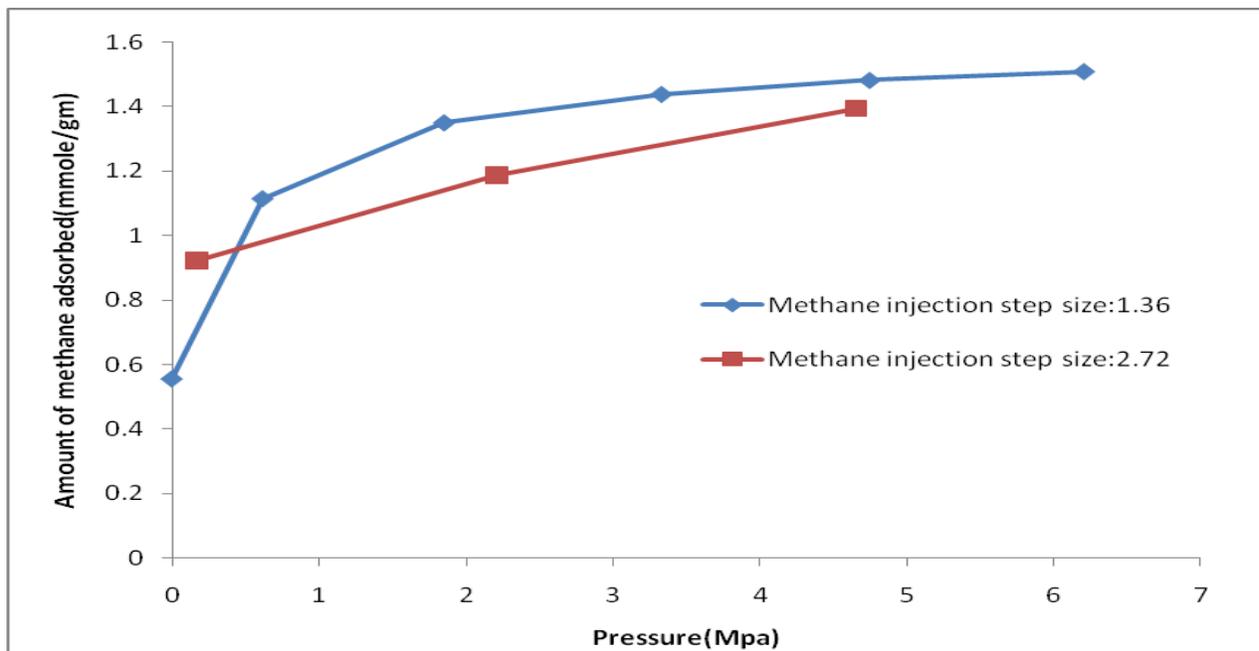

Figure 13: Effect of pressure step size on adsorption capacity.

The effect of pressure step size (1.36 and 2.76 Mpa) on adsorption capacity of methane on activated carbon is shown in fig 13.The fig shows that the adsorption capacity decreases with increase in the pressure step size.

4.5 Theoretical modeling of gas adsorption at different temperature.

The different isotherm model like Langmuir, Freundlich, Dubinin-Astakhov(DA) and Dubinin-Radushkevich (DR) are used to fit the experimental data which are shown in figure 14.The result reveal that at low temperature (293K) Langmuir and DR show good fit with the experimental data but DA and Freundlich fail to predict data correctly. At high temperature (303K, 313K and 323K) DR and DA shows good agreement with the experimental data but Langmuir predict high adsorption capacity at low pressure and low adsorption capacity at high pressure and Freundlich predict high adsorption at high pressure and low adsorption capacity at low pressure.
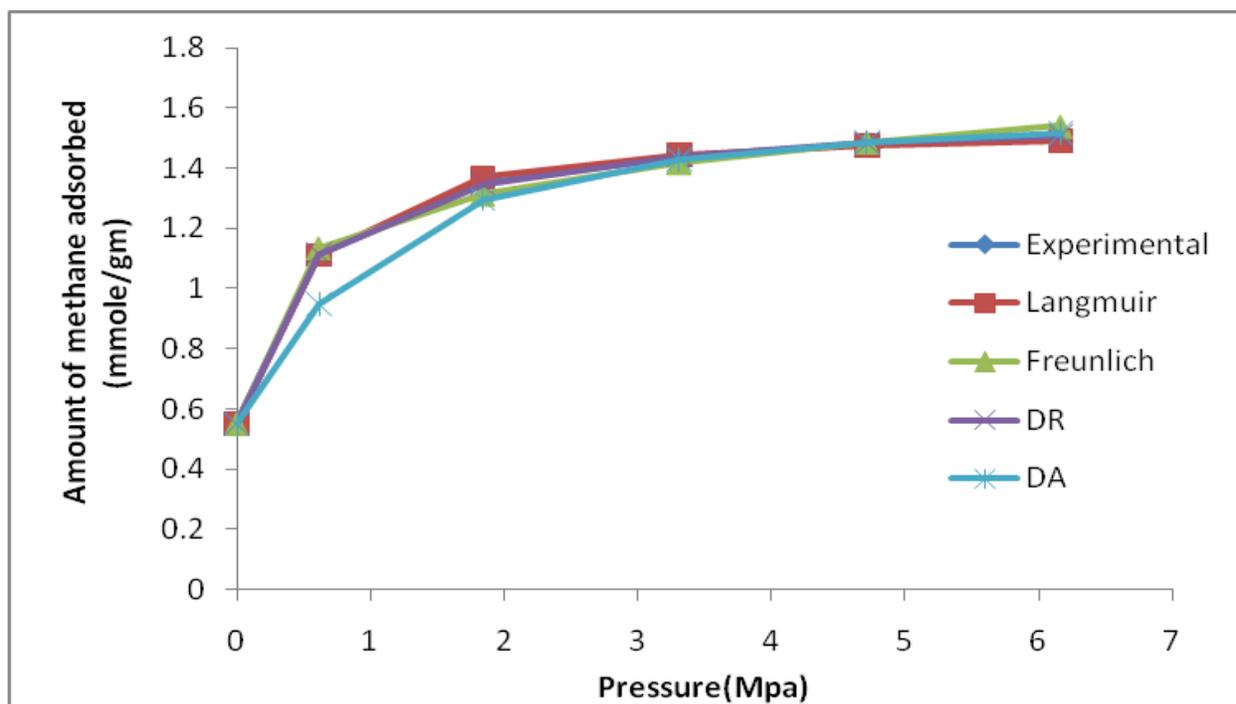

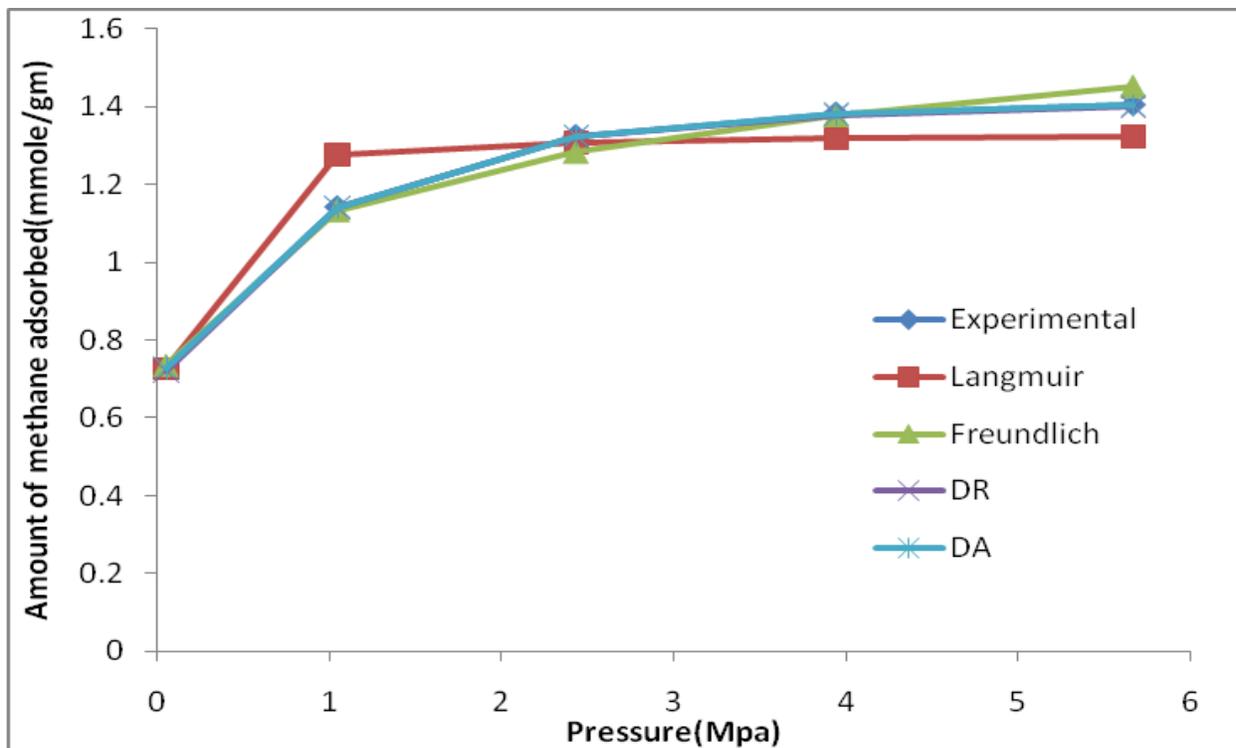Figure 14(a). Theoretical modeling of gas adsorption at temperature 293K

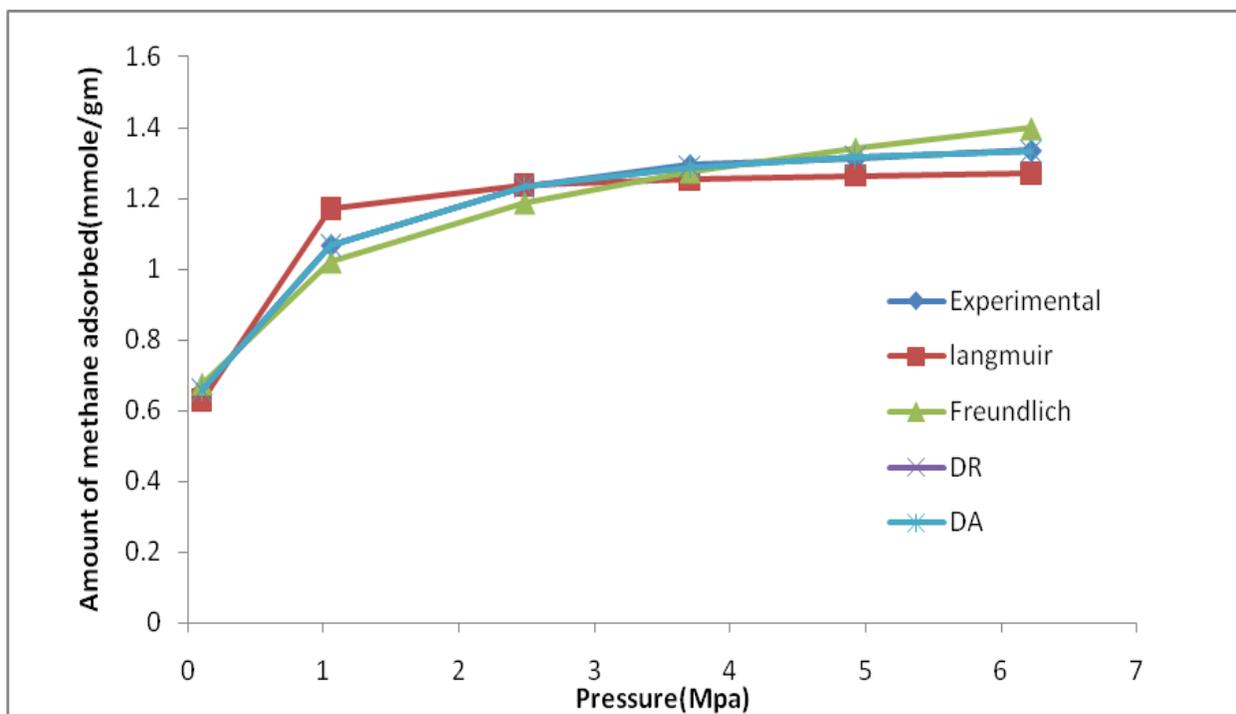Figure 14(b): Theoretical modeling of gas adsorption at temperature 303K

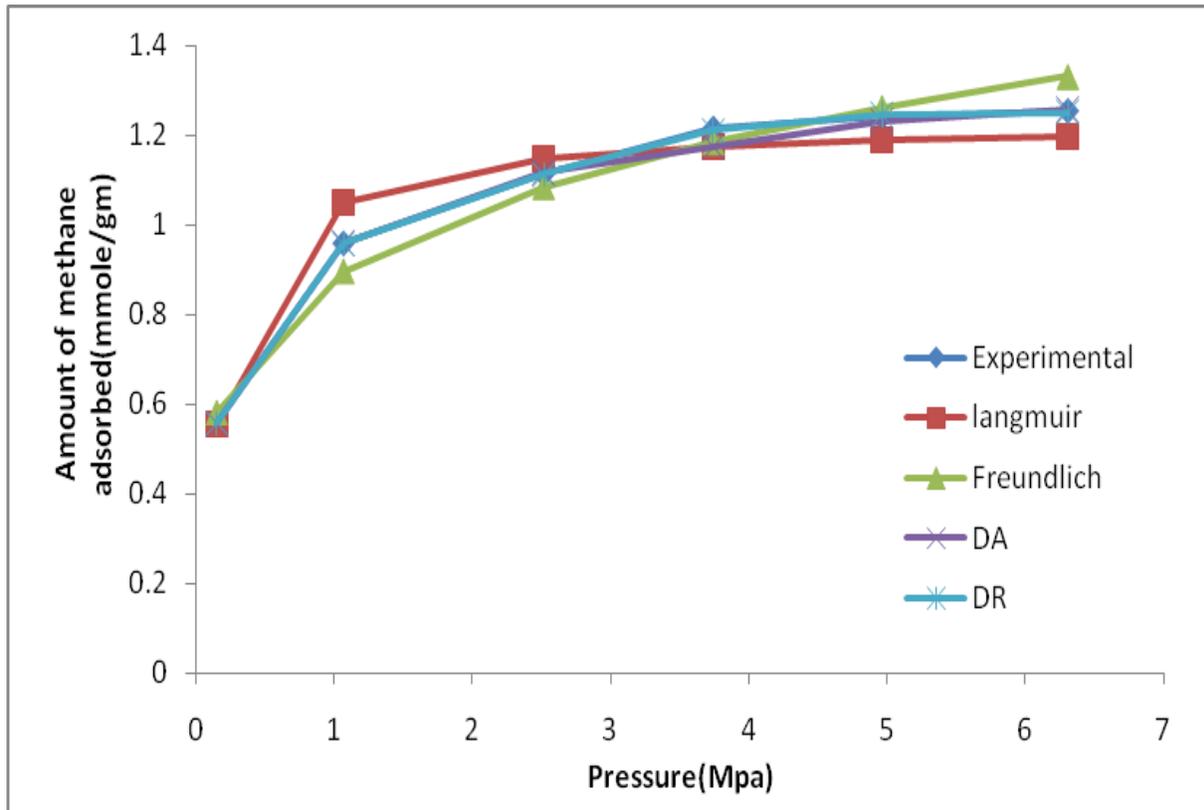Figure 14(c): Theoretical modeling of gas adsorption at temperature 313K

Figure 14(d): Theoretical modeling of gas adsorption at temperature 323K

Table 4.2: Isotherm parameter of different model

Temperature (K)	Isotherm Parameter			
	Langmuir	Freundlich	DR	DA
293	C_{max}=1.5509 b=4.1229	k=1.2111 n=7.564	E=13091.182 C_{max}=1.535 k=2.373	E=10310 C_{max}=1.579 n=1.948 k=2.534
303	C_{max}=1.3329 b=21.746	k=1.1258 n=6.81198	E=10046.093 C_{max}=1.404 k=0.719	E=10300.722 C_{max}=1.411 n=2.474 k=1.515
313	C_{max}=1.2921 b=9.2146	k=1.01136 n=5.6433	E=11829.525 C_{max}=1.344 k=1.426	E=12204.055 C_{max}=1.352 n=2.267 k=2.031
323	C_{max}=1.2394 b=5.405	k=0.8836 n=4.5372	E=6653.563 C_{max}=1.252 k=0.472	E=7522.885 C_{max}=1.275 n=3.871 k=2.384

E is in joule/mole , C_{max} is in mmoles/gm of activated carbon

4.6 Study the effect of adsorption capacity on surface modified activated carbon.

The adsorption capacity of methane on unmodified and surface modified activated carbon with copper oxide and silver are shown in figure 15. The result shows that the presence of metal on the surface increases the adsorption capacity of methane due to formation of complex with the metal. The adsorption capacity increases 54 percent in the case of copper oxide and 74 percent in the case of silver with increasing trend i.e. further increase in adsorption with the increase in pressure.
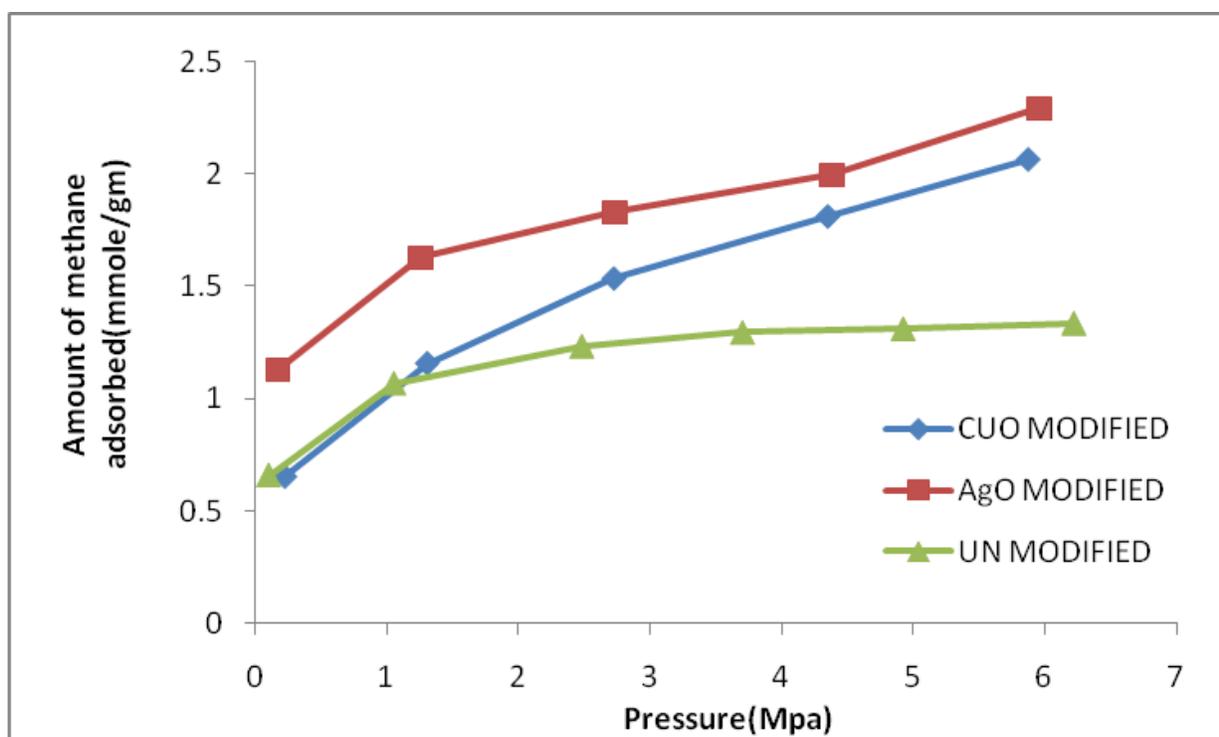
Figure 15: Study of adsorption capacity of methane on surface modified activated carbon.

4.7 Study the isosteric heat of adsorption at different temperature.

The study of isosteric heat of adsorption at different temperature is shown in figure 16.The result shows that heat of adsorption is more at high temperature for a fixed loading. The result also reveals that the heat of adsorption is high at low loading and start decreasing with the increase in loading.

Figure 16: Isosteric heat of adsorption at different temperature.

4.8 Absolute residual error of different theoretical adsorption isotherm.

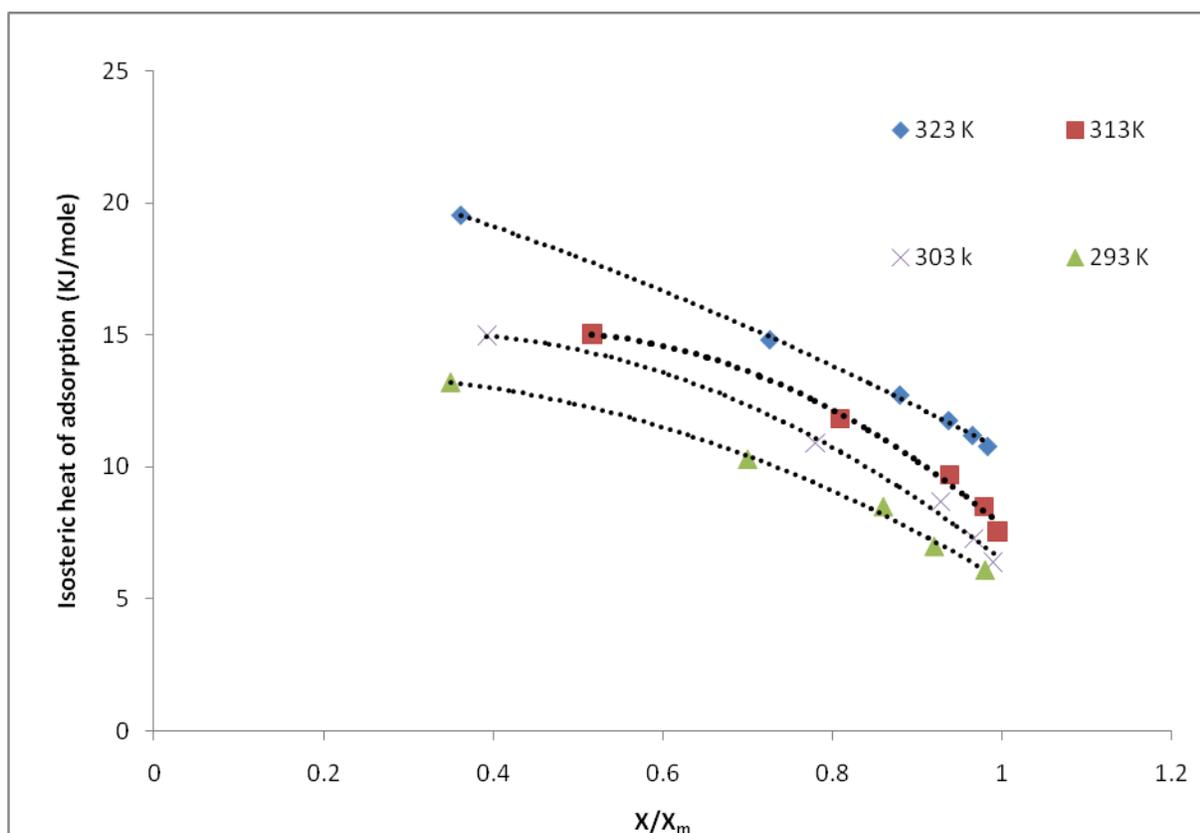The percentage of Absolute Residual Error (ARE) was used to calculate the percentage deviation of the experimental results from the theoretical models discussed above. The percentage error was calculated using the following equation.

$$\%\,ARE = \frac{\sum\limits_{i=1}^{j} abs\left(r_i\right)}{j}$$

Where r_i is the residual error calculated with the experimental value as the basis and j is the number of data points available for every sample. The percentage ARE values are shown in Table 2. From the ARE results it can be observed that the Langmuir model has highest residual error and D-A has lowest possible error. This justifies the fact that has been presented above as graphical comparison between experimental data and theoretical models.

Table 4.3: Calculation of percentage of absolute residual error

Temperature is in K	Percentage of Absolute Residual Error(ARE)			
	Langmuir	Freundlich	DR	DA
293	0.76748	1.6690	0.0722	0.023
303	5.8785	1.9426	0.22701	0.01885
313	4.45179	3.29431	0.2427	0.2327
323	4.8854	3.6544	0.97393	0.1684

Chapter 5

Conclusion

5. CONCLUSION

- The adsorption characteristics of methane on granular activated carbon were measured up to 7 Mpa and at fixed temperature using a volumetric measurement technique

- The isotherm at different temperature shows the characteristic of type 1 isotherms, indicating that the activated carbon is mainly microporous materials.

- Effect of pressure steps indicated that increasing pressure steps reduced adsorption capacity of activated carbon.

- Desorption isotherm illustrated the hysteresis at low pressures.

- Experimental data verified using different adsorption models showed best fit for DA model which are also supported by ARE calculation.

- Surface modification of activated carbon was accomplished using Copper oxide and Silver oxide.

- Adsorption capacity of activated carbon increased by 54% and 74% using CuO and Ag modified activated carbon respectively.

- The heat of adsorption is high at high temperature and decreased when the loading increased.

Chapter 6

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