

**STUDY OF ADSORPTION OF METHANOL IN AN ACTIVATED CARBON
AND CARBON NANOTUBE MATRIX FOR USE IN A SOLAR BASED
REFRIGERATION CYCLE**

A Thesis

by

SRIVATHS SAMBATH

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

May 2011

Major Subject: Mechanical Engineering

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for Use in a Solar Based Refrigeration Cycle

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Approved by:

Chair of Committee,	Jorge Alvarado
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ABSTRACT

Study of Adsorption of Methanol in an Activated Carbon and Carbon Nanotube Matrix
for Use in a Solar Based Refrigeration Cycle.

(May 2011)

Srivaths Sambath, B.E., Anna University

Chair of Advisory Committee: Dr. Jorge Alvarado

This thesis seeks to investigate the adsorption capabilities of activated carbon and carbon nanotubes. The adsorption of methanol on both of these substances was tested for their application in a solar based refrigeration cycle. Research on carbon nanotubes and their growth has been carried out for applications in the semiconductor industry. Enough focus has not been given to the use of nanotubes for refrigeration purposes.

Adsorption refrigerators have been designed with the energy source being solar energy. Various adsorbent/adsorbate pairs have been tested in literature. The present work focuses on carbon nanotubes because theoretically, nanotubes should be able to adsorb better than activated carbon due to their high surface to volume ratios and hence a higher number of adsorption sites available for methanol to adsorb.

The amount of adsorption of methanol on nanotubes depends on whether the end caps of the nanotubes are open or closed and also on the hydrophilic nature of the nanotubes. Nanotubes with ends closed are supposed to adsorb less than the nanotubes with their ends opened. The ends of carbon nanotubes can be blocked because of iron and other impurities. In this project, nanotubes are annealed under high vacuum to open

the end caps. The hydrophobic nature of the nanotubes is corrected by treating them with concentrated nitric acid. The hydrophobic nature of the nanotubes is corrected by treating them with concentrated nitric acid. The acid treated nanotubes are used to obtain adsorption data at different temperatures.

The adsorption of methanol on activated carbon, pristine and treated carbon nanotubes is measured at different temperatures. Electron microscopy is used to validate that annealing the nanotubes at high temperature under vacuum opens the end caps of the nanotubes. Finally, a matrix of nanotubes and carbon powder is prepared with different concentrations. The mixture is tested for adsorption of methanol.

It is observed that the carbon nanotubes, pristine or treated, do not perform better than activated carbon. However, performance seems to increase when mixtures of activated carbon and carbon nanotubes are used as adsorbent. Also, it is found that mixtures containing annealed nanotubes perform better than mixtures with pristine nanotubes. Kinetics of the adsorption process is calculated for the different adsorbents used, which is used to explain the increase in the amount of methanol adsorbed for the activated carbon-carbon nanotube mixture.

To my mother

ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Jorge Alvarado, for his inspiration, guidance and the personal care he took in making my project a success. His constant support and insightful suggestions were instrumental in completing my thesis. I would like to thank my committee members, Dr. Jaime Grunlan and Dr. Alex Fang for their support and helping me whenever I needed guidance.

I would like to thank Clifford Aigbotsua, graduate student in Mechanical Engineering, who helped me in the initial stages of my project. I am grateful to Adam Farmer who helped in the manufacturing part of my project. I would like to thank Rodney Inman in aerospace engineering for his support and advice which helped me overcome major problems I encountered in my experiments.

I would like to mention the contribution of Dr. Bhuvanesh Nattamai, Dr. Yordanos Bisrat and Dr. Hansoo Kim for helping me perform XRD, SEM and TEM analysis on my samples. I also want to thank Dr. Angie Hill Price and Mahesh Nair for their help in the acid treatment experiments.

NOMENCLATURE

AC	Activated Carbon
CNT	Carbon Nanotube
MWCNT	Multi Walled Carbon Nanotube
SEM	Scanning Electron Microscopy
SWCNT	Single Walled Carbon Nanotube
TEM	Transmission Electron Microscopy
XRD	X Ray Diffraction

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CHAPTER I

INTRODUCTION

Renewable energy has been gaining more importance over the past few decades with the increasing shortage and high demand for fossil fuels. A lot of research is being done in the renewable energy technologies like solar, wind and tidal energy. Solar energy has been used for a variety of purposes including heating, refrigeration and photovoltaics. One of the major problems facing the advent of solar energy is its discontinuity due to the cycle of day and night. Hence focus is concentrated on designing solar based systems which take advantage of the natural diurnal cycle. Solar based refrigerators fall under this category.

Adsorption refrigerators use the phenomenon of adsorption to induce the refrigeration cycle. Adsorption is the adhesion of molecules of a liquid, gas or dissolved solids to a surface. The liquid or gas is called as the adsorbate and the surface on which it adsorbs is called as adsorbent. Adsorption is a surface phenomenon where the adsorbate molecules adhere to the micropores on the surface of the adsorbent material. Adsorption is classified into Physisorption, which takes place due to weak van der Waal's forces between the adsorbent and adsorbate, and Chemisorption, which takes places due to chemical reaction taking place at the surface of the material.

In an adsorption refrigerator, an adsorbate with a low boiling point is usually adsorbate liquid take in heat from outside and change phase to gaseous phase which are

This thesis follows the style of Carbon.

chosen to be able to store energy as latent heat of the adsorbate. Molecules of the adsorbate are then transported by a difference in pressure between two containers. The molecules then give away the heat to condense into a liquid phase, thereby completing the cycle. This phase change is caused by heat from the sun in a solar adsorption refrigerator. No other energy source is required for this cycle.

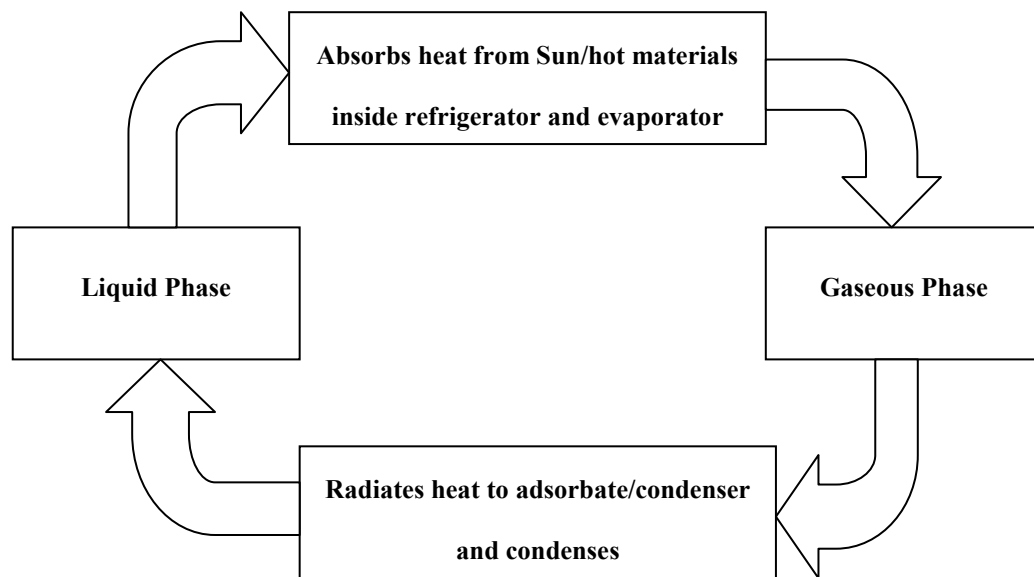
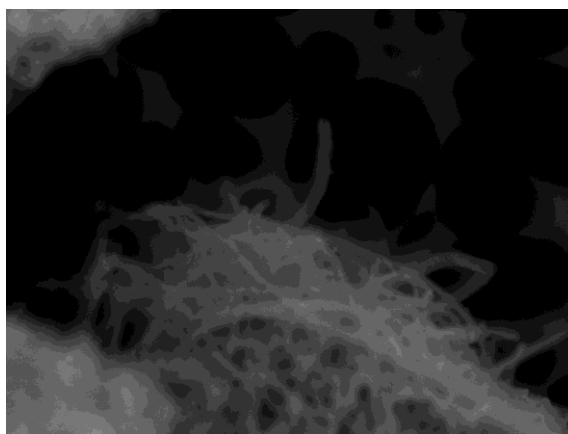


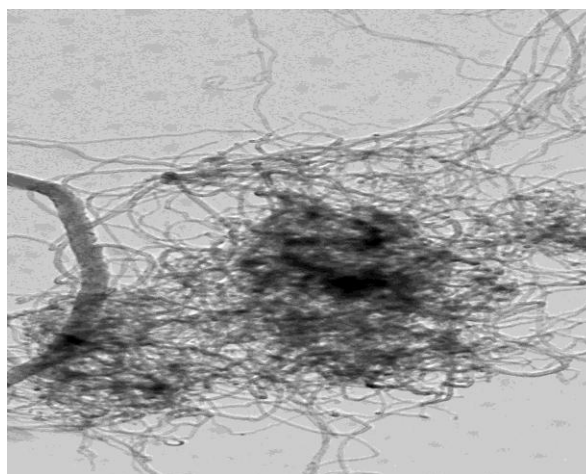
Figure 1: Adsorbate two phase cycle in solar based adsorption refrigerator

Experiments have been carried out using a variety of adsorbent/adsorbate pairs. Some of the pairs are Zeolite + Water, Ammonia + Water, Calcium Chloride + Ammonia and Charcoal + Methanol [1]. Li et. al used a solid adsorption pair of Activated carbon + Methanol for ice making. Methanol is a preferable adsorbate because of its low boiling point and low latent heat of vaporization. At low pressures, methanol

boils even at room temperatures, making it a very effective adsorbate. Researchers have been working on finding newer adsorbent/adsorbate pairs which could lead to a better amount of adsorption. One of the materials which is expected to play a big role in gas adsorption is Carbon Nanotubes.



(a)



(b)

Figure 2: (a) SEM and (b) TEM images of a carbon nanotube bundle

Adsorption of gases on the surface of nanotubes is expected to be dependent on whether the ends of the nanotubes are open or closed. Acid treatment, annealing and sonication are some of the techniques used to open the ends of close ended carbon nanotubes. The effect of annealing to open the ends of the carbon nanotubes can be verified through a variety of validation techniques including X Ray Diffraction, Transmission or Scanning Electron Microscopy, Thermo-gravimetric Analysis or other methods.

In this thesis, XRD, TEM and SEM are used to validate whether the carbon nanotubes are opened or closed. Raman Spectra was also used to analyze the effect of annealing and acid treatment on the carbon nanotubes. This thesis combines the field of adsorption refrigerators and field of nanotube adsorption. Current and previous research in the aforementioned two fields will be discussed in the next chapter. Work done by researchers from various parts of the world on the topic is reviewed.

CHAPTER II

LITERATURE REVIEW

Research in the area of solar refrigerators has only considered activated carbon as adsorbent. No studies have been reported that consider the use of carbon nanotubes as adsorbents in solar refrigerators.

Developments in the field of adsorption refrigeration

The earliest known adsorption refrigerators date back to 1980 where a group of scientists in China used the adsorption pair of ammonia and water. In 1981, Pons and Grenier[1] used the adsorption pair of Zeolite and Water. The same group used activated carbon and methanol for adsorption in 1987.

E.E. Anyanwu, C.Z. Ezekwe [2], researchers from Nigeria built a Solar Refrigerator using the same adsorption pair in 1995 to produce ice. The researchers however purged the activated carbon with methanol initially to enable maximum adsorption for an overnight adsorption period of 12 hours. They also used a selective surface to allow and prevent heat transfer as and when required, and valves were used to control the flow of methanol through the system. During daytime, the selective surface was removed, thereby allowed the heat from sunlight to evaporate the methanol adsorbed inside the activated carbon. This cycle was a diurnal cycle. Though cold water at 1^o C was produced, ice could not be made using this method.

In 1999, Z. F. Li used the same adsorption pair to design an ice maker which is powered by solar energy. However, this method prevented desorption at temperatures

higher than 150 °C as the methanol reacts with carbon at temperatures higher than 150 °C [1].

A complete adsorption apparatus was built to determine the best adsorbent material from a set of three different types of activated carbon by Li et. al. The setup was used to test the adsorption of methanol at different temperatures from 80° C to 135° C. The change in pressure was obtained as a function of time for each temperature. The Dubinin-Radushkevitch equation is used to calculate the amount of methanol adsorbed as a function of the change in pressure. A graph depicting the adsorption isotherm for that specific temperature can be found in Li et. al.[1]. The Dubinin-Radushkevitch equation is given below.

$$\ln W = \ln W_o - D \left[T \cdot \ln \left(\frac{P}{P_o} \right) \right]^2 \quad \text{Equation (1)}$$

where W is the amount of methanol adsorbed corresponding to pressure P, W₀ is the maximum amount of methanol adsorbed for temperature T and D is the structural constant of the adsorbent.

Z.F. Li and K. Sumathy [1] created an adsorption ice maker modeled on their laboratory apparatus. The ice maker used solar energy instead of a heated oil bath to induce desorption of methanol in the system. The ice maker produced 4-5 kg of ice per day depending on the amount of sunlight incident on the system. The experimental setup presented in this thesis is based on the laboratory setup used by this research group.

In 2000, Catherine Hildbrand et al.[3] designed a solar refrigerator which used the adsorption pair of Silica Gel and water in Yverdon les Bains, Switzerland.

The refrigerator was tested for a total period of 68 days to see how it responded to the weather changes of the diurnal cycle. The corresponding coefficients of performance of the refrigerator over the 2 month were published.

In 2003, a novel ice maker was designed where the collector area was covered with selective surface and the evaporator was kept near the refrigerator and the ice produced was removed regularly. In this refrigerator, a single heat exchanger was used as both condenser and evaporator alternatively. This eliminated the need for a valve between the condenser and the evaporator [4]. Using this technology, the condenser is cooled through natural convection by means of fins. Overall, the collector-condenser equipment reduces manufacturing costs considerably and also a performance improvement of more than 10%.

Despite the progress in the design and use of solar-based refrigerators, most of them still exhibit a low coefficient of performance. Therefore a better adsorbent-adsorbate pairs and experimental conditions need to be identified to enhance performance.

Developments in the field of nanotube adsorption

Carbon nanotubes are members of the fullerene family. They are also called as buckytubes. They consist of one or more sheets of graphene rolled into a cylindrical structures. The diameters of nanotubes are in nanometers, but their length can be a lot longer, ranging to a few micrometers. Nanotubes have received a lot of focus since their discovery in 1991 by Sumio Iijima [5]. Because of their unique structure and properties,

nanotubes have a variety of applications including nanotechnology, medicine, optics and material science. One of their potential applications is gas adsorption.

Carbon nanotubes can be classified into two categories based on their structure.

1. Single walled carbon nanotubes – consist of a single layer of graphene rolled into a cylinder
2. Multi-wall carbon nanotubes – consist of two or more layers of graphene rolled into cylindrical structure. These cylinders are concentric to each other.

Multi-wall carbon nanotubes are not as expensive as single walled nanotubes, but it is difficult to explain the internal mechanism of these nanotubes. The single and multi-walled carbon nanotubes are depicted in fig. 2.

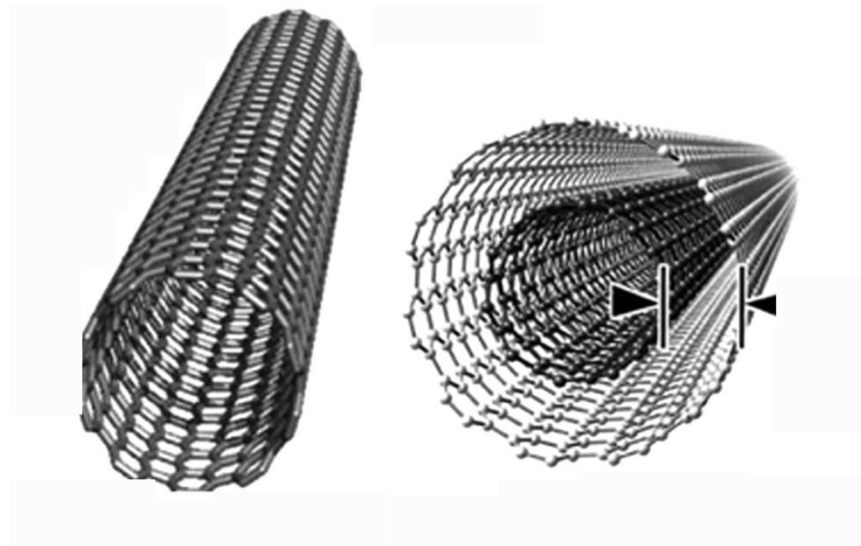


Figure 3: Single wall and multi-wall carbon nanotubes

Due to their unique properties, these cylindrically shaped nano structures have been researched widely. More emphasis has been placed on their electrical properties, but not enough focus has been on the adsorption capabilities of carbon nanotubes. It is predicted that there is a higher chance of adsorption in opened carbon nanotubes than in nanotubes with closed ends.

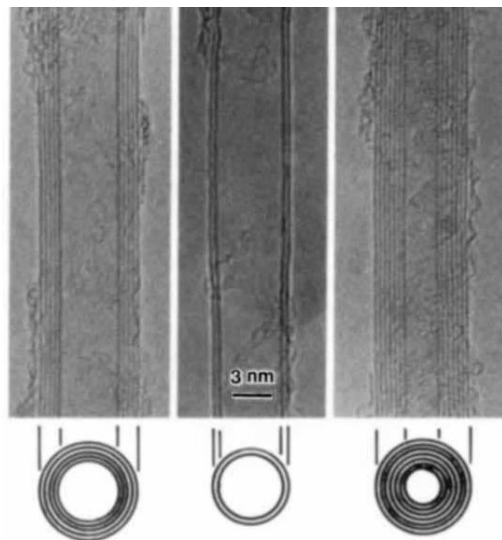


Figure 4: Carbon nanotubes of varying diameters discovered by Iijima[5]

Carbon nanotubes were first discovered by Sumio Iijima in 1991[5]. He produced the carbon nanotubes using an arc-discharge evaporation method which is used for fullerene synthesis. Iijima referred to the new type of carbon structure he discovered as ‘needle-like tubes’. Electron microscopy was used to understand the structure of these

tubes better and it was found that each needle comprised of co-axial tubes of graphitic sheets.

Nanotubes which are produced by chemical cutting have their ends closed. Closing of the ends could be because of the metallic impurities blocking the edges of the tubes. This would mean that adsorption of the gas molecules on the nanotubes is restricted to the exohedral layers (the outer surface) of the nanotubes.

Adsorption of gases on nanotubes takes place in 3 zones, namely the endohedral, exohedral and the interstitial zones [6].

Carbon nanotubes are of great interest to the field of adsorption because of their unique structure. Carbon nanotubes are expected to play a big role because theoretically, nanotubes have more adsorption sites on which the adsorbate molecules can attach themselves. There are three different sites on carbon nanotubes where the gas molecules can attach themselves.

1. Endohedral sites – Found on the inner layers of the nanotubes
2. Exohedral sites – Found on the outer layers of the nanotubes
3. Interstitial sites – Refer to the locations between two adjacent nanotubes on which the gas molecules can adsorb

Researchers have performed various experiments and molecular simulations which help us better understand gas adsorption in the above specified layers of carbon nanotubes. Some of these experiments and their results will be discussed briefly in this dissertation.

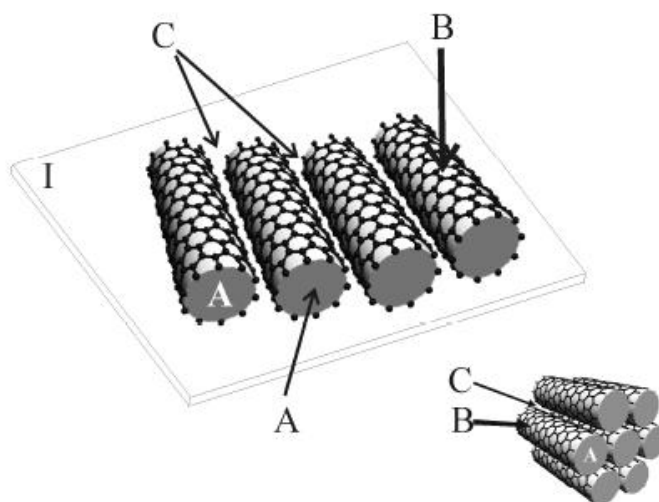


Figure 5: Endohedral(A), exohedral(B) and interstitial(C) layers of CNTs [6]

Another important physical property of nanotubes is whether the ends of the nanotubes are opened or closed. Ends of the nanotubes are often closed when they are produced due to chemical cutting of the nanotubes. Nanotube ends could also be closed due to the presence of metal impurities blocking the ends of the nanotubes. Various techniques have been utilized to open the ends of the nanotubes, namely:

1. High temperature annealing of the nanotubes under vacuum
2. Oxidation of nanotubes in air at high temperatures
3. Oxidation of nanotubes in concentrated acids

Oxidation of nanotubes in atmosphere at high temperatures is considered the most effective way to purify the metallic impurities of carbon nanotubes [7]. But the weight loss due to oxidation is the highest in this method because of the formation of metallic oxides. Also, when annealing in the presence of air, annealing temperature must

be high enough for the metallic impurities to form oxides, but the carbon in the nanotubes should not react with the atmosphere. In order to counter this problem, the nanotubes can be annealed to very high temperatures under vacuum. It is found that most of the impurities are removed using this method [8].

Acid treatment of carbon nanotubes is also considered as an effective method to remove the impurities from the carbon nanotubes. Acid treatment is usually carried out in the presence of air under reflux. A condenser with cold water running through the system helps in refluxing the acid and preventing it from vaporizing. The acid is usually heated to its boiling point during acid treatment. Some of the important parameters to be considered during acid treatment are

1. Type of acid used
2. Concentration of acid used
3. Amount of nanotubes mixed in acid
4. Duration for which acid treatment is carried out
5. Temperature at which acid treatment is carried out
6. Drying conditions

The acid is neutralized at the end of the acid treatment using de-ionized water and the nanotubes are filtered using a filtration system. The filtered nanotubes are then dried using a laboratory oven and hence the drying conditions play an important role because all the moisture must be removed to obtain a pure sample of carbon nanotubes through acid treatment.

All the above methods have been tested for opening the ends of the carbon nanotubes and found to have been effective in removing impurities and etching the ends of the nanotubes thereby opening them. Opening the ends of the nanotubes is essential if adsorption has to take place on the inside of the nanotubes. Otherwise, adsorption on the nanotubes will be restricted to the outer surface and the interstitial spaces of the nanotubes.

Hence in order to test if the carbon nanotubes were conducive and effective for gas adsorption in nanotubes, various methods have been considered to open the ends of the nanotubes. Carbon nanotubes can be opened either by annealing under vacuum, oxidation in the presence of air or by oxidation in concentrated acids.

Experiments have shown that Carbon nanotubes tend to open at temperatures higher than the reaction temperature of Carbon C60 atoms, but lower than the temperature where the carbon is consumed for oxidation when heated in the presence of air [7]. This paper also reports that when nanotubes are opened with liquid lead, the metal forms a decorative layer on the outside, but does not get filled. Also, it is found that presence of some metal oxides catalyze the opening of the nanotubes, causing them to open at lower temperatures.

In 1999, a group of scientists from India [8] ran experiments to see the effect of carbon nanotubes after acid treatment. They treated the single walled carbon nanotubes with nitric acid and another batch of the same with sulphuric acid and compared the adsorption of nitrogen, benzene and methanol.

They compared the amount of adsorption of the gases on these two samples and compared it with the as-prepared samples. It was observed that the adsorption level was higher for the treated carbon nanotubes than the pristine nanotubes.

A research group, led by S. Talapatra [9], from the Southern Illinois University observed the binding energies of xenon, methane and neon on the surface of single walled carbon nanotubes. This was compared with the binding energy of the gases on planar graphite. It was found that the ratio of the increase in binding energy of the gases on nanotubes over planar graphite was found to be the same for all three gases. This meant that the gases adsorb on the same sites for all the gases. These carbon nanotubes had closed ends. This proved that the gases do not adsorb on the interstitial channels of carbon nanotube bundles. This was an important discovery as it meant that the adsorption can only take place in the grooves of the close ended carbon nanotubes.

In 2001, researchers from the University of Kentucky purified multi-walled carbon nanotubes by high temperature annealing. R. Andrews et. al. [10] reported that graphitization of the carbon nanotubes occurred at high temperatures. The carbon nanotubes were purged in nitrogen to 1000 °C. The annealing temperature was slowly increased to 3000 °C. X-Ray diffraction was used to test the effect of annealing, and the sharp peaks with higher intensities shows the graphitization of the sample at higher temperatures. Scanning and Transmission Electron Microscopy was used to look at the structure of the carbon nanotubes after annealing.

Scientists from the Tsinghua University[11], Beijing tested the effect of annealing carbon nanotubes to aid in hydrogen storage. Tests were run with single

walled carbon nanotubes as prepared and after annealing them from 1700-2200 °C for 2 hours in flowing argon. The annealed nanotubes adsorbed almost thrice as much of hydrogen as was adsorbed by the pristine nanotubes.

X-Ray Diffraction was used to test the effect of annealing on the carbon nanotubes [11] The samples used were single walled carbon nanotubes. A sharp increase in the intensity of the reflected X rays was found. Also, the peaks for the annealed carbon nanotubes were sharper than the as prepared carbon nanotubes.

In the same year, Wei Huang [12] from the same university obtained 99.9% pure multiwall carbon nanotubes by annealing them in vacuum at very high temperatures from 1500-2150 °C for 2-5 hours. He also confirmed that vacuum annealing rid the nanotubes of impurities and opened the ends of the nanotubes.

Raman Spectra was used to analyse the specimens obtained as-prepared, after annealing and after acid treatment. The I_{1360}/I_{1580} ratio was a reflection of the graphitization of the material, where the I_{1360} peak corresponds to the defects present in the material and the I_{1580} peak corresponds to carbon nanotubes. Removal of the metallic defects was observed as the I_{1360}/I_{1580} ratio decreased for the annealed samples. In case of the acid treated samples, addition of oxygenated groups resulted in an increased reactivity to oxygen. This resulted in lowering of the decomposition temperature though the purity of the nanotubes was increased.

The effect of annealing on disordered multi-wall carbon nanotubes has also been studied. Y.A. Kim et. al.[13] studied the multiwall carbon nanotubes which were heated to 2800 °C in a high argon environment. The paper concluded that heating above 1800

$^{\circ}\text{C}$ was an efficient way to remove metallic particles from the tips of the carbon nanotubes [13].

M.R. Babaa et. al. [14] obtained conclusive proof that annealing opened the tips of carbon nanotubes by the use of Transmission Electron Microscopy (TEM) images. Carbon nanotubes were subjected to CO_2 oxidation for 1 hour at 525°C , and it was found that their ends were opened. The adsorption isotherm of Krypton shows that adsorption is higher in the oxidized samples. The paper also shows that opening of the ends increases the amount of adsorption.

Acid treatment was another method used to open the ends of carbon nanotubes. Acid treatment is carried out on carbon nanotubes to increase the solubility of the nanotubes. Acid treatment is also used to add functional groups to the surface of the carbon nanotubes.

One important thing which must be noted is that when open ended carbon nanotubes are treated with acid under refluxing, the hydroxyl groups are added to the surface of carbon nanotubes. However there is a chance that the hydroxyl groups get attached to the ends of the carbon nanotubes thereby blocking endohedral adsorption in the carbon nanotubes. Anya Kuznetsova et. al. [15] discussed this possibility.

In order to rectify this and allow adsorption on the inside of the carbon nanotubes, the acid treated nanotubes are heated to 600 K under vacuum thereby removing the functional groups which blocked the ends of the nanotubes. However, this might be working against gas adsorption sometimes because functionalization of surface nanotubes helps in increasing adsorption.

In 2001, scientists from Tohoku University in Japan [16] chemically modified nanotubes by nitric acid oxidation to change the properties of the nanotubes. The carbon nanotubes were coated on a cylindrical film of aluminum oxide templates and treated with nitric acid. The temperature programmed desorption profiles for desorption of carbon monoxide and carbon di-oxide are obtained for the pristine and the acid treated samples. The adsorption of the gases is a lot higher for the oxidized acid treated samples than for the pristine samples.

The carbon nanotubes which were coated with aluminum oxide were treated with 20% nitric acid for 6 hours under refluxing conditions. After the refluxing process, the solution was washed with de-ionized water to neutralize the acid solution and dried at 100 °C. The nanotubes were separated from the aluminum oxide film by dissolving in sodium hydroxide at 150 °C. The nanotubes which were obtained were found to be hydrophilic on the inner surface, allowing them to adsorb gases. However, the outer surface which was protected by the aluminum oxide film during acid treatment remained hydrophobic after the oxide film was removed. This proved that the interior of the carbon nanotubes can be modified by chemical treatment without affecting the outer surface.

In the same year, Jeong Mi Moon et. al [17] obtained high purity carbon nanotubes using a two step process. In the first step, the carbon nanotubes were annealed in atmosphere at 470 °C. The annealed nanotubes were treated with hydrochloric acid for 24 hours. After the second step, the nanotubes were treated in 30% nitric acid for 4 - 6 hours. The acid treated sample was washed with deionized water and filtered using a

poly tetra fluoro ethylene (PTFE) membrane. After drying, a thin mat of carbon nanotubes was obtained.

It was found, by analysis of the Raman Spectra, that the acid treated carbon nanotubes reflect a higher intensity beam than the annealed and pristine carbon nanotubes. The acid treated nanotubes were found to be more than 96% pure with less than 1% metallic impurities. Longer treatment should result in a higher purity but could result in a low yield of carbon nanotubes and hence a proper balance needs to be struck between the two parameters.

I.D. Rosca et. al. in 2005 [18] conducted extensive research on the acid treatment on carbon nanotubes. The nanotubes were treated in nitric acid and the weight loss due to oxidation in nanotubes was obtained. The concentration of the acid used and the amount of nanotubes treated in acid was also varied and the weight loss was calculated. The different parameters which were varied are listed in Table 1.

Table 1: Parameters varied during acid treatment for MWCNTs

Concentration of Nitric Acid	Concentration of MWCNT
70%	10 mg/ml
60%	5 mg/ml
48%	2.5 mg/ml
35%	1 mg/ml

Graphs were plotted which compared the weight loss for the different parameters for the treatment time varying from 0-48 hours. High solubility of the carbon nanotubes was obtained after prolonged exposure but the small diameter carbon nanotubes were lost after 24 hours of treatment, which led to a weight loss of the sample.

Dengsong Zhang et. al. [19], modified the carbon nanotubes by acid treatment. The raw multiwall carbon nanotubes were treated with 20% nitric acid for 2 hours and washed several times with distilled water to neutralize the acid. Then they were heated in an oven at 100 °C for 24 hours to remove the moisture. Also the CNTs were refluxed in a solution of concentrated nitric acid and concentrated sulphuric acid for 0.5 hours. After the acid treatment, the nanotubes were then washed with deionized water to remove any acidity in the solution. In order to remove the moisture in the solution, the nanotubes were heated in an oven at 100 °C for 24 hours to dry and obtain a pure acid treated nanotubes sample. The sample which was dried in the oven after acid treatment was then annealed in air at 600 °C for 0.5 hours and later milled for 2 hours at 1200 rpm using a ball mill.

It was found that the surface area and amount of adsorption of the samples increases with each step. It was found that the metallic impurities at the tips of the nanotubes were etched away. Also, it was found that the nanotubes were reduced in length. However, the cylindrical structure of the nanotubes was maintained.

Reyhani et. al.[20] tested the effects of various acids on the purification of multi-walled carbon nanotubes. The acids which were tested were hydrochloric acid, nitric acid, sulphuric acid and hydrofluoric acids. The adsorption of nitrogen at 77k was tested

and it was found that most of the samples were mesoporous. Nitrogen adsorption was found to be highest for carbon nanotubes treated with hydrofluoric acid. This could be confirmed by the Raman Spectra and the intensity of the reflected rays was found to be highest for hydrofluoric acid.

It is expected that the above specified treatments used to enhance adsorption also helps change the kinetics of the adsorption process. B.B. Saha et. al from Kyushu University, Japan [21] conducted experiments to observe the kinetics of adsorption on activated carbon fibers. A thermo gravimetric analyzer was used to obtain the mass uptake of ethanol at different points of time. The readings were taken under a controlled pressure and temperature environment. The experiment was repeated for various adsorption temperatures ranging from 27 °C to 60 °C and readings were taken for a time interval of 0.5 seconds. Kinetic constants of the adsorption processes were obtained using the adsorption isotherm of each sample. It was found that the kinetics of the adsorption processes was higher during the initial phases of the transient curve.

Adsorption of gas molecules on the surface of a solid depended on four important parameters including the type of solid, the type of gas, the temperature of the system and the pressure of the gas. For a particular solid adsorbing a particular gas, the amount of adsorption is related to the temperature of the system and the pressure of the gas. If the system is kept at constant temperature, then the volume of adsorption is proportional to the pressure of the gas. The curve obtained is called as an Adsorption Isotherm. For micro porous solids like carbon powder and carbon nanotubes, a Type I adsorption isotherm is obtained.

The importance of the isotherm is that, since temperature is constant, the rate of adsorption depends only upon the pressure inside the system, the pore structure of the adsorbent material and the distribution of the adsorbent sites [22]

The different types of isotherms are listed in Table 2 which is listed below. Most of the materials which are used as adsorbent materials fall under one of these categories.

Table 2: Types of isotherms

Type	Description	Example Material
I	Microporous materials	Activated carbon
II	Non-porous materials	Silica
III	Non-porous or macroporous	Carbon black at 30 ⁰ C
IV	Mesoporous materials	Alumina powder
V	Mesoporous or macroporous	Activated carbon at 100 ⁰ C

The flow of fluids through carbon nanotubes was discussed by Mainak Majumder et. al[2005] of the University of Kentucky. They discussed the rapid flow of water through nanotubes. The mechanism for transport of water in a nanotube was attributed to the hydrophobic nature of the nanotubes which caused ordered hydrogen bonds to be formed within the water molecules yielding almost frictionless flow through the nanotubes.

Sony Joseph et. al.[23] from University of Illinois, Urbana Champaign attributed the higher flow rates of water in CNTs to the smooth surface of the carbon nanotubes. They stated that the orientation of the OH groups on the nanotubes and the hydrogen bonding has an impact on the velocity of water through these nanotube channels. It was proposed that since the OH groups face the wall of the carbon nanotubes, the formation of hydrogen bonds are less, thereby increasing flow of water through them. Joseph et. al. [2008] also suggested that adsorbents with rough surfaces had a higher tendency for hydrogen bonding which could impede water flow through such surfaces.

The experimental setup which was used for the experiments conducted as part of this thesis, the problems faced during the experiments, the adsorption isotherms and the results that were obtained will be discussed in the following chapters.

CHAPTER III

EXPERIMENTAL SETUP

The adsorption test setup was designed to run adsorption experiments for different adsorbent materials to find the amount of evaporated liquid that can be adsorbed in the adsorbents. The adsorption test setup consists of the following important parts, namely the adsorption cell, connections to the vacuum pump, connections to the evaporator, a vacuum pump and the evaporator.

The experimental setup was constructed to test the adsorption of methanol on activated carbon and carbon nanotubes. It consists of a 4-in by 4-in by 4-in aluminum block on which a square 2-in by 2-in hole was drilled 3 inches deep. This acted as the cell which housed the activated carbon and carbon nanotubes (Fig. 6).



Figure 6: Adsorption cell

The aluminum block had two grooves machined on the top surface to fit rubber gaskets to help seal an acrylic lid on top of the cell. The acrylic lid measured 4-in by 4-in

and was $\frac{1}{2}$ -in thick. Latches were machined on the aluminum block which sealed the acrylic against the gaskets tightly preventing any leaks.

The aluminum block was connected through two L shaped $\frac{1}{4}$ " 316 stainless steel tubing to a pressure gauge in one end and a rubber stopper on the other end. A vacuum pump was connected in series to the pressure gauge and aluminum cell to help pull a vacuum. Pressure inside the cell was maintained by closing a valve which was placed before the vacuum pump. Due to pressure leaks on the rubber stopper side, reinforcements were designed, as shown in Fig. 7, to help maintain the low pressure inside the system.

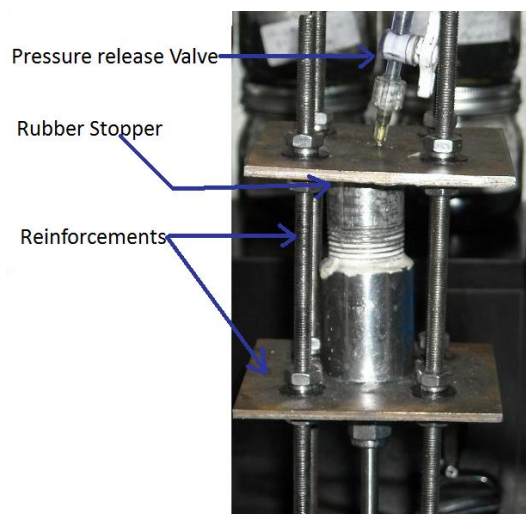


Figure 7: Reinforcements for rubber stopper to prevent leaks

The system was connected to a reservoir containing methanol. The reservoir, a graduated burette made of acrylic, was connected to a copper pipe sealed at the other

end. The copper pipe and burette contained methanol. A copper pipe was used to enhance heat transfer between the methanol and the surroundings as the acrylic burette is not a good conductor of heat (Fig. 8).

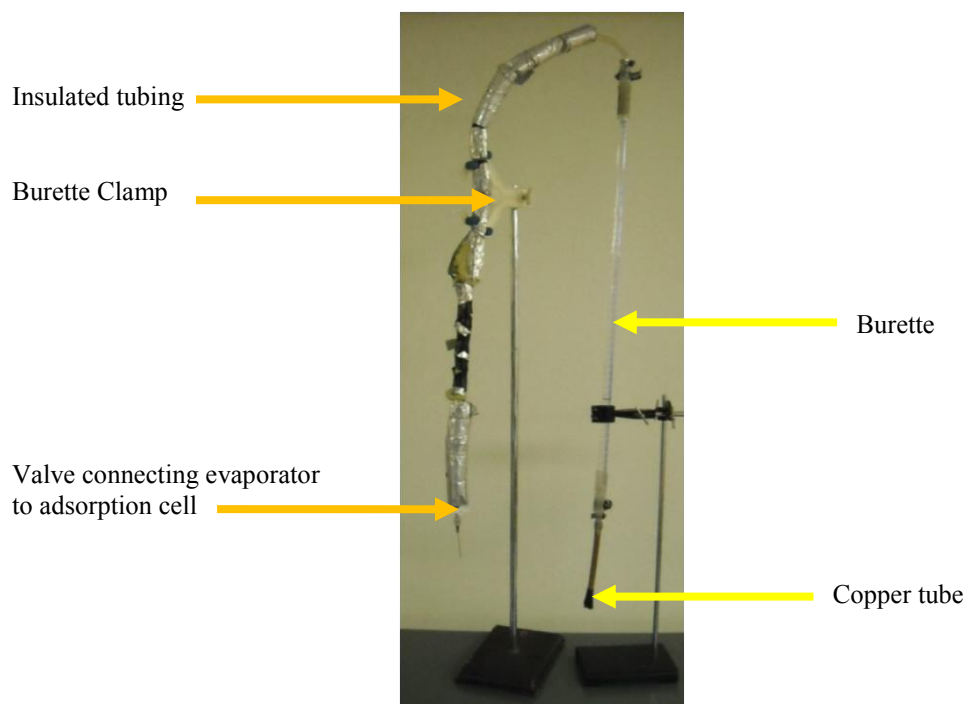


Figure 8: Evaporator (methanol reservoir)

The burette was connected to the system by means of a syringe needle which was opened or closed by means of a valve. The tygon tubing connecting the burette to the syringe was covered with thermal insulation to prevent any heat transfer. In order to maintain the temperature of the system a constant, and to keep the system at the required

temperature, a water chiller was used. It was connected to a plate heat exchanger and placed inside a water bath. The cell was placed inside the water bath during the adsorption tests. Thus, system temperature was maintained a constant during each experiment.

The pressure gauge used for the adsorption test was a DPG7000 from Omega. The gauge was a digital test gauge. It operated between temperatures of 0 to 150 °C and can measure vacuum upto -30 inHg(-1 MPa) with a resolution of 0.001 inHg (3.386 Pa) .



Figure 9: Pressure gauge connected to vacuum pump

The adsorption test setup was designed to be a solar-based test setup, which uses the diurnal cycle of the sun to provide energy to the system. However, during the testing

phases, the required energy was supplied by a hot plate through heat conduction. The main purpose of the adsorption test setup, shown in Fig. 10, was to calculate the amount of adsorption of methanol on carbon nanotubes and activated carbon.

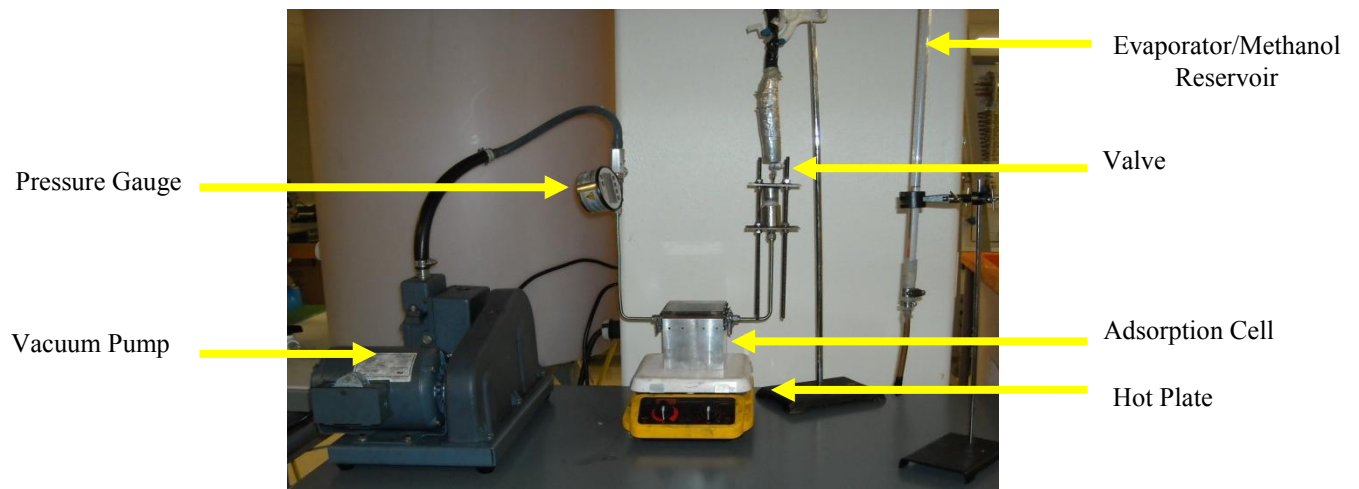


Figure 10: Complete setup of adsorption test unit

Methanol was used as the adsorbate fluid for the experiments because it has a latent heat of vaporization of 1165 kJ/kg at 25 °C. At low pressures, it boils even at room temperature. This was very useful as the methanol could absorb heat from the surroundings easily even at room temperature.

The adsorption cell was filled with the adsorbent material. Initially activated carbon was used as the adsorbent. Later, pristine and annealed carbon nanotubes were used as adsorbent material. Also, acid treated nanotubes were tested for their adsorption

capacity. Finally, a mixture of carbon nanotubes and activated carbon was used as the adsorbent material.

Many problems were faced during the design and execution of the experiment. The next chapter talks in detail about the challenges faced and the solutions that were carried out to ensure that accurate results could be obtained.

CHAPTER IV

EXPERIMENTAL PROCEDURE

The adsorption of methanol on activated carbon and carbon nanotubes was observed during the course of the project. This chapter details the selection of the adsorbent material. The preparation techniques and treatments that the adsorbent was subjected to are also explained. The characterization of the adsorbent after treatment and the procedure for the adsorption test also form a part of this chapter. The challenges which were encountered during the experiments and the solutions which were implemented are also listed.

Adsorbent selection

Choosing a proper adsorbent was very essential because it predetermines the number of adsorption sites available for methanol molecules to get attached to the material. From literature, it was observed that activated carbon was a very effective adsorbent. In this project, adsorption tests were first conducted using activated carbon.

Carbon nanotube was also considered as adsorbent material because of its unique properties. The structure of a nanotube and the high surface to volume ratio means that there was a high surface area available for the methanol to get adsorbed. It was this property which was primarily considered in choosing carbon nanotubes as adsorbent.

Three different sizes of carbon nanotubes were chosen. Average diameters ranging between 10-20 nm, 40-60 nm and 60-100 nm were chosen. The reason for choosing adsorbents with different diameters was to observe the effect of nanotube diameter on the adsorption of methanol on carbon nanotubes.

Preparation and treatment of adsorbent

For each adsorption test, the adsorbent was placed inside the adsorption cell and was activated as explained below.

Activation of adsorbent

Activating the adsorbent was important because activation removes all air caught between the micro-pores of the adsorbent. This was vital because if the sample was not activated, then the air trapped inside competes for adsorption sites with the adsorbate. This would result in a lower amount of adsorbate adsorbed during the process.

In order to activate the sample, the sample placed inside the cell was first heated to 100-110 °C for 15-20 minutes using the hot plate. This increases the kinetics of the air trapped and provides enough activation energy to release trapped air molecules (i.e N₂). A vacuum was pulled using the vacuum pump and air was removed out of the system. The system was then allowed to cool naturally. Once the cell had cooled to room temperature, it was heated again as before and the process was repeated. Vacuum was pulled more than once for each cycle, thereby removing all the air in the system, maximizing the available adsorption sites.

The activation process was repeated till we were able to reach the required vacuum pressure, observed through the reading on the pressure gauge. The actual vacuum inside the system was noted only after the system cooled down to room temperature. Activation process was carried out for both activated carbon and also carbon nanotubes before the adsorption test was performed on both these adsorbents.

Annealing of nanotubes

Adsorption of gases in the nanotubes takes place in three separate zones, namely the exohedral, the endohedral and the interstitial zones, as mentioned in the literature. However, due to chemical cutting of the nanotubes during production, the ends of the nanotubes could be closed and this could affect the adsorption of methanol on the carbon nanotubes. A TEM image of the nanotubes obtained from the website of the vendor is shown below.

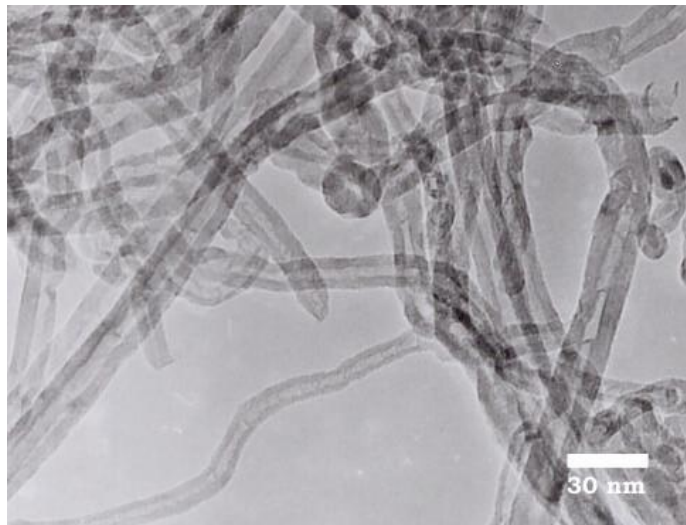


Figure 11: TEM image of as prepared carbon nanotube

The ends of the nanotubes were found to be closed when the nanotubes were purchased (as-prepared) from the vendor. This can be proved by looking at the

Transmission Electron Microscopy image of the as prepared nanotubes. This meant that there could be no gas adsorption on the inner surface of the nanotubes.

In order to rectify this problem and to enable adsorption of methanol on the inner surface of the carbon nanotubes, the nanotubes were annealed under vacuum at high temperatures. The carbon nanotubes were placed inside a cylindrical quartz tube closed at one end. The other end was connected to the vacuum pump. The vacuum pump was started and vacuum to the order of 10^{-4} Torr was obtained. During the process of pulling vacuum, heat was applied to the quartz tube to remove all the air inside the nanotubes. The glass tube was then sealed.

The quartz tube containing CNTs was then placed in a high temperature oven and heated up to 950 °C for 8 hours. The temperature of 950 °C was chosen because of restrictions of upper temperature limit of the lab oven. Also, the quartz tube used would have reached its softening point when heated above 1000 °C. The annealing of the carbon nanotubes was expected to open the ends of the carbon nanotubes. Adsorption tests were performed on the annealed carbon nanotubes.

Acid treatment of the carbon nanotubes

Carbon nanotubes were expected to be extremely hydrophobic by nature. Hence it was assumed that methanol would not have a high probability of getting adsorbed on the carbon nanotube surface, thereby resulting in a lower adsorption of methanol. In order to rectify the hydrophobic nature of nanotubes, the nanotubes were treated with concentrated acid, as motivated by the work done by Rosca et. al. [18]. This would result

in the addition of hydroxyl groups added to the surface of the nanotubes, thereby making the tubes less hydrophobic and slightly hydrophilic.

Based on the literature available for the acid treatment of nanotubes, a recipe was prepared for making nanotubes hydrophilic. The chemicals used, equipment required and steps for acid treatment are listed in Table 3.

Table 3: Equipment and chemicals required for acid treatment of nanotubes

Equipment required:	Chemicals required:
<ol style="list-style-type: none"> 1. Glass beaker(1 liter) 2. Reflux condenser(coil type preferred) 3. Stirring hot plate 4. Magnetic stirrer 5. Sonicator apparatus 6. Stand for holding the sonicator and reflux condenser 7. Rubber Stopper 8. Filtration system 9. Lab oven 10. Fume hood with running water available 11. Vacuum pump 	<ol style="list-style-type: none"> 1. Nitric acid(68% concentration) 2. De-ionized water 3. Carbon nanotubes(which need to be treated)

Procedure for acid treatment

Acid treatment of carbon nanotubes was carried out with the intent of increasing the level of methanol being adsorbed on the surface of the CNTs. The steps that were followed to acid-treat the carbon nanotubes are listed below.

1. Required safety equipment was worn and the ingredients were placed inside the fume hood.
2. The beaker was placed on top of the hot plate and was closed through a stopper
3. Reflux condenser was placed on top of beaker through a hole in the stopper. Condenser was held in place using the stand.
4. Hoses were connected to the condenser to allow water to flow through them. The hose connected to the entry of the reflux condenser was connected to the water tap and water was allowed to flow slowly. The other end of the condenser was connected to a hose which drains the water into the sink.



Figure 12: Sonicator probe inserted inside glass beaker, placed on hot plate

5. The condenser was lifted and the beaker was removed from top of the hot plate.
6. 250 ml of concentrated nitric acid was added to the beaker
7. 25 grams of carbon nanotubes were added to the beaker.
8. The sonicator was dipped in the beaker which contained the mixture of acid and nanotubes (Fig. 12). The mixture was sonicated for 5 minutes to allow dispersion. Then it was set aside for 20 minutes. After this time, it was again sonicated for 5 minutes.
9. The dispersed mixture was placed on top of the hot plate and was allowed to boil at 120 °C during the course of the experiment.
10. The reflux condenser was placed over the beaker with a variable diameter stopper (Fig. 13). The reflux process was allowed to take place for 4 hours.
11. After 4 hours, the reflux condenser was removed and the hot plate was turned off. The beaker was allowed to cool.
12. After cooling, the solution was diluted in de-ionized water to neutralize acid concentration
13. The dilute solution was passed through a filtration system (Fig. 14) to separate the nanotubes from the liquids. A vacuum pump was required to cause a pressure difference to enable flow of liquid through the filter.
14. The acid treated nanotubes were then placed inside the adsorption cell and were activated for the adsorption test.



Figure 13: a) Acid treatment process b) Reflux condenser with tubing

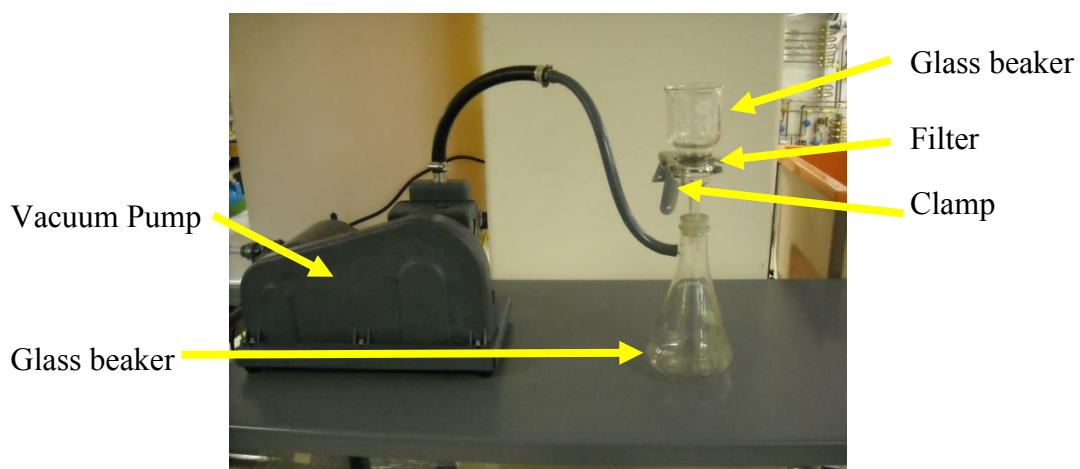


Figure 14: Filtration system to remove water from nanotubes

The wet nanotubes retained in the filter were heated in an oven (Fig. 15) at 100°C for 24 hours to remove all the moisture.



Figure 15: Oven used for drying carbon nanotubes

Acid treatment of the carbon nanotubes was expected to provide hydroxyl groups on the surface of the carbon nanotubes. This should help in the adsorption of methanol on the surface of nanotubes owing to the hydrogen bonding between the hydroxyl group in the carbon nanotube and methanol. This was expected to reduce the hydrophobic nature of carbon nanotubes. Adsorption tests were performed on the acid treated carbon nanotubes.

Characterization of carbon nanotubes

The treatment of carbon nanotubes was carried out in order to check if there was an increase in the adsorption of methanol on the nanotubes. But in order to verify if the treatment actually had any effect on the nanotubes, several validation techniques were

employed. The different techniques that were used to characterize the treatment of nanotubes were

1. Scanning Electron Microscopy
2. Transmission Electron Microscopy
3. X-Ray Diffraction
4. Raman Spectroscopy

Scanning Electron Microscopy

Scanning electron microscopy was used to test if the ends of the carbon nanotubes were opened due to annealing of nanotubes. A 3-dimensional image was the result of scanning electron microscopy. The following image shows the SEM image of annealed nanotubes.

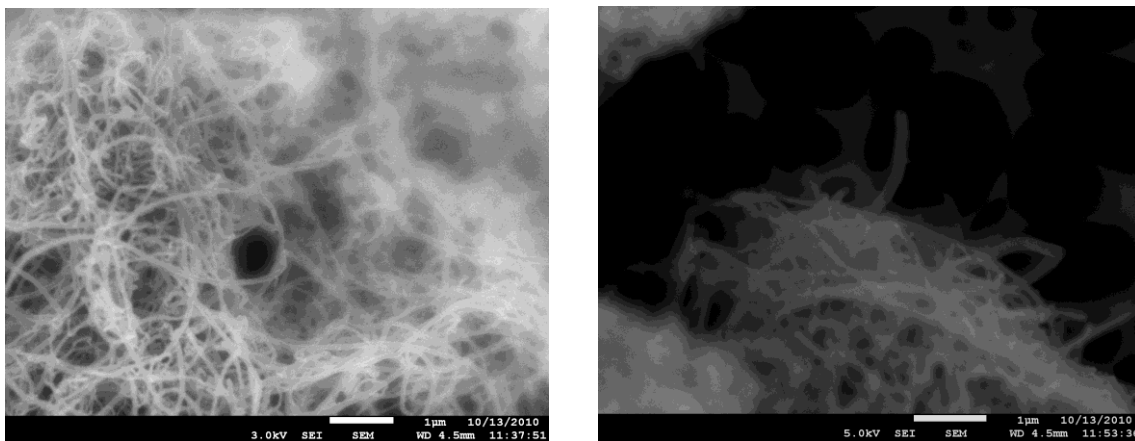


Figure 16: SEM image of annealed carbon nanotubes

There was a certain bit of difficulty associated with finding open nanotubes using SEM because of the resolution limits of SEM. It was difficult to find a single nanotube from the 3-dimensional images of nanotubes captured which were opened. This was because the nanotube end must be located and the end of the nanotube must be facing the SEM detector in order to judge if the nanotube was opened or closed.

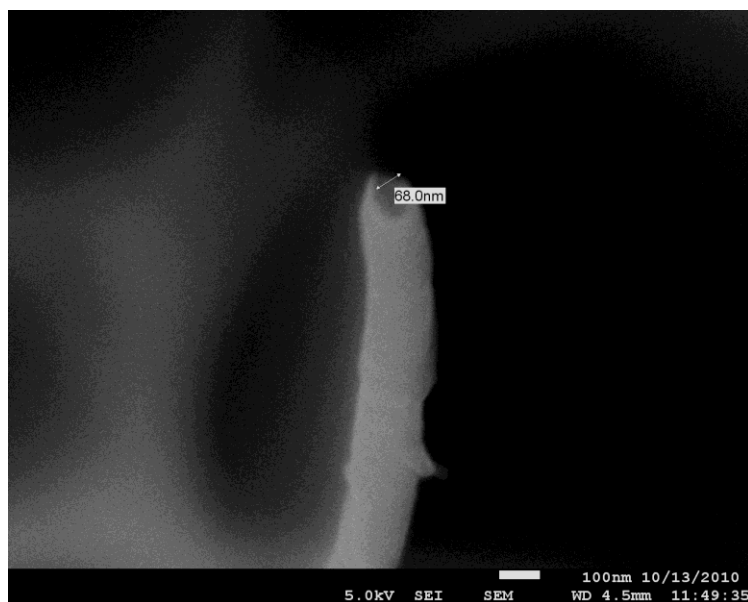


Figure 17: Opened nanotube end obtained through SEM

The image of a single nanotube with an open end is shown in Fig. 17. This proves that the vacuum annealing process helped open carbon nanotube ends. However, the SEM results were not too convincing to claim that vacuum annealing could open a

significant number of CNTs. Therefore, TEM was also used to verify the effectiveness of vacuum annealing.

Transmission Electron Microscopy

Since SEM does not conclusively prove that all the nanotubes were opened, TEM was used to validate the effect of high temperature annealing under vacuum. TEM was a better method for validation because in TEM, the images were formed by the electrons passing through the carbon nanotubes, which results in a better resolution of the images obtained.

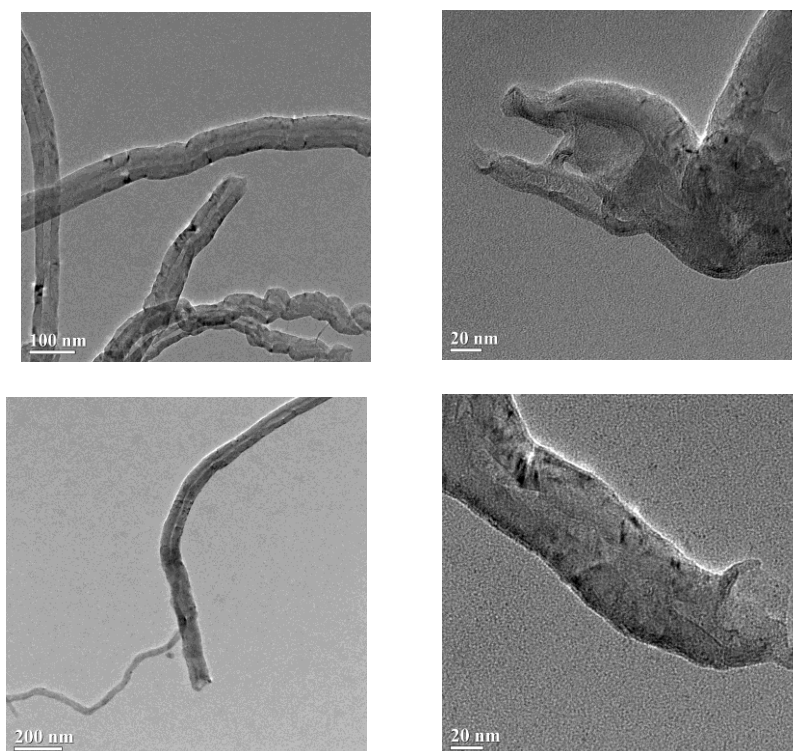
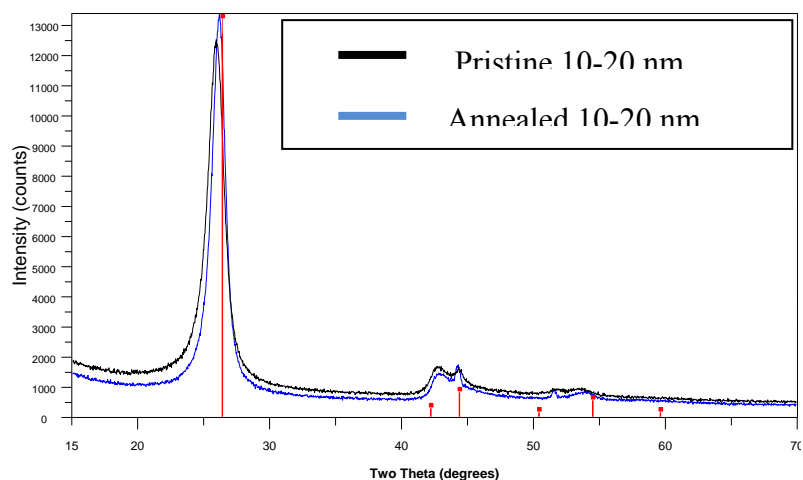


Figure 18: TEM images of various opened CNTs

Fig. 18 shows TEM images of opened carbon nanotubes found at different locations in the carbon nanotube sample. The carbon nanotube sample which is shown above is the sample which had been annealed at high temperatures under vacuum. The TEM images prove that opening of carbon nanotubes took place. The resolution of the images is higher than what is obtained through scanning electron microscopy.

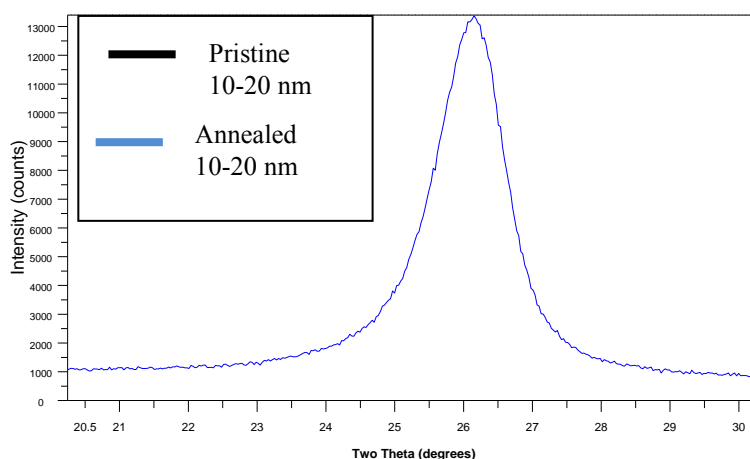
X-Ray Diffraction

X-Ray diffraction is a validation technique which uses the diffraction of X-Rays off the material to characterize the difference in the structure of the pristine as-prepared nanotubes and the annealed nanotubes. XRD curve exhibits the intensity of the diffracted X-rays and the material was characterized by noting the difference in the peaks as shown in Fig. 19.



(a)

Figure 19: (a) XRD curve for 10-20 nm pristine and annealed nanotubes (b) XRD image which shows the difference in peak intensity



(b)

Fig. 19(continued)

The XRD curves shown above (Fig. 19 (a), (b)) represent the X ray diffraction pattern for 10-20 nm nanotubes. The black curve represents the pristine nanotube and the blue curve represents the annealed nanotubes. A higher intensity of the peak at $2\Theta = 26^\circ$ represents a higher level of graphitization of the material [10]. It was found that the curve has a lower intensity at all other values of 2Θ , which implies a reduction in the other materials (impurities) present in the carbon nanotubes. This proved that annealing caused the nanotubes to become ordered and also removed some of the impurities in the nanotubes.

Similar XRD curves were obtained for 40-60 nm CNTs and 60-100 nm CNTs. The plots are shown below (Fig. 20, Fig. 21).

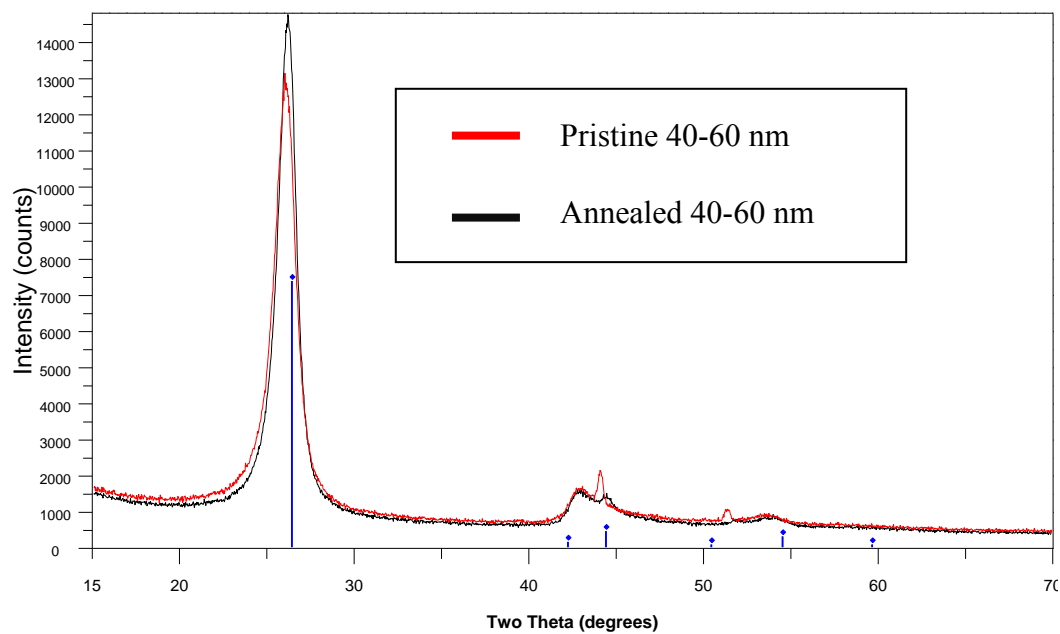


Figure 20: XRD patterns for 40-60 nm pristine and annealed CNTs

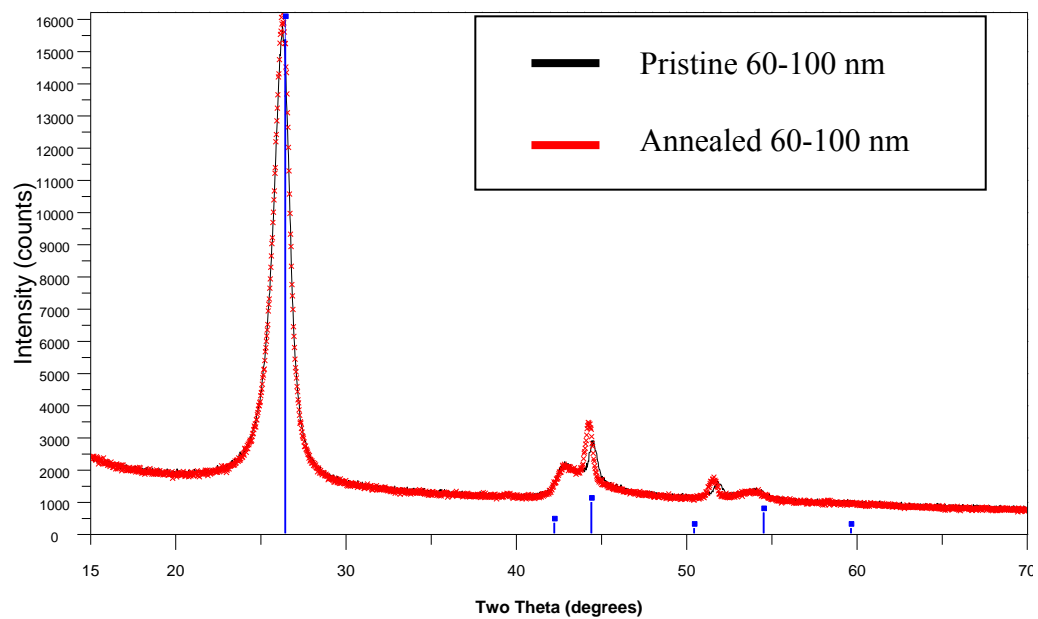


Figure 21: XRD patterns for 60-100 nm pristine and annealed CNTs

The straight lines in the curves represent characteristic materials. At $2\theta = 26$, the lines were indicative of the presence of graphite. The peaks found at $2\theta = 42$ and $2\theta = 44$ represent impurities present in the nanotubes.

Raman Spectra

Raman Spectra was the final validation technique used for the characterization of the nanotubes. Raman Spectra is similar to X ray diffraction, but it uses the excitation of atoms and the inelastic scattering of photons when a laser beam falls on them and based on the intensity of the reflected beam, the material was characterized. The Raman Spectra observed for the annealed and pristine carbon nanotubes of 10-20 nm diameter are shown below (Fig. 22).

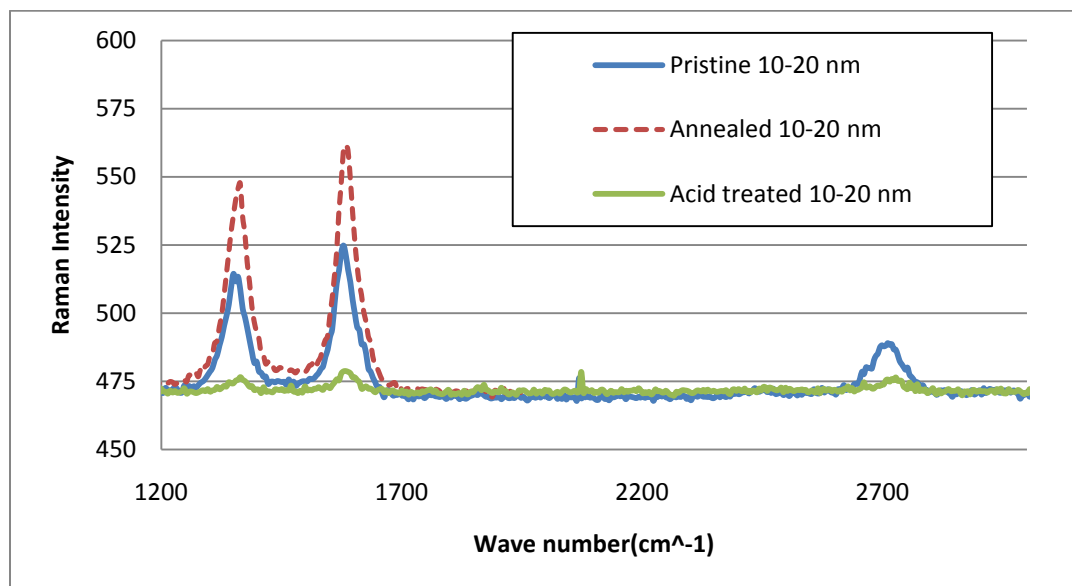


Figure 22: Raman Spectra of 10-20 nm CNTs

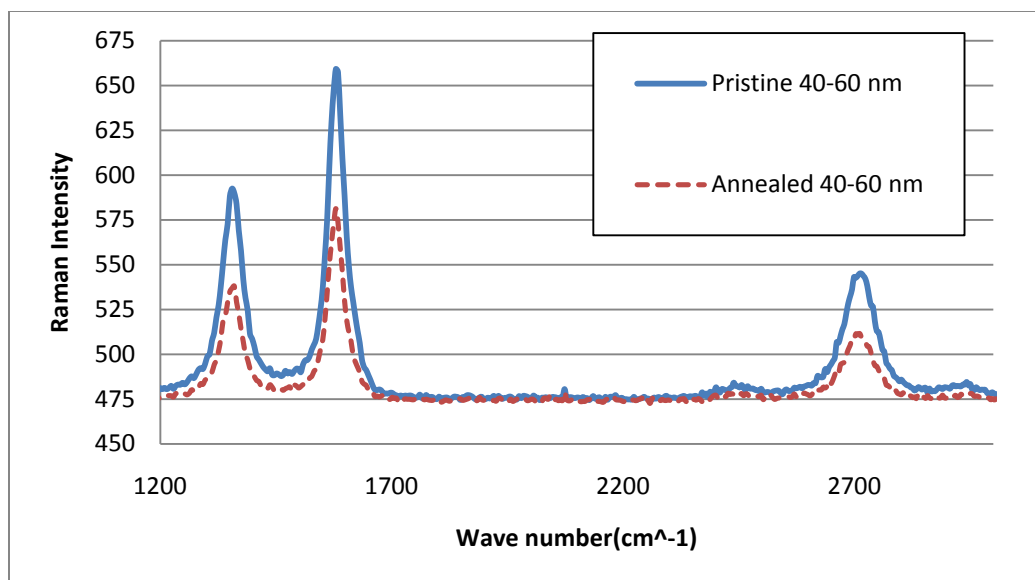


Figure 23: Raman Spectra of 40-60 nm CNTs

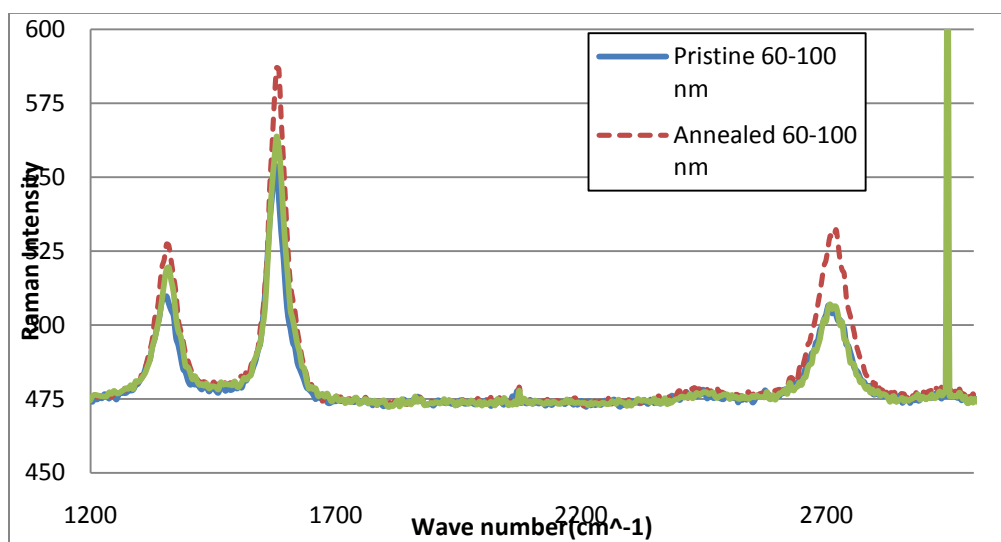


Figure 24: Raman Spectra of 60-100 nm CNTs

Similarly, the Raman Spectra were obtained for 40-60 nm and 60-100 nm carbon nanotubes (Fig. 23, 24 respectively).

The peak corresponding to the wavelength of 1580 cm^{-1} was referred to as I_G which represented the peak due to the characteristic material, which were carbon nanotubes. The peak corresponding to the wavelength of 1356 cm^{-1} was referred to as I_D , which represented the impurities or defects present in the substance. The I_{1356}/I_{1580} value was important as it is used to evaluate if impurities were removed due to annealing or any fictionalization of the carbon nanotubes had taken place due to acid treatment of carbon nanotubes. The implications of the Raman Spectra obtained for the different diameter tubes are explained in the Chapter V.

Adsorption test procedure

The amount of methanol adsorbed in the adsorption cell was observed through the adsorption test carried out for various adsorbents. The following were the various steps which constitute the adsorption test procedure.

1. A specific amount of adsorbent was placed inside the adsorption cell
2. The lid was placed on the nanotube and was clamped down
3. The pressure gauge was switched on and the valve was opened.
4. The vacuum pump was switched on and vacuum was pulled from inside the system
5. The adsorption cell was heated and cooled alternatively to eliminate all the air trapped inside the adsorbent material.

6. Vacuum was pulled many times during the activation process to remove all the air from the system. This step was required to create the maximum adsorption sites.
7. The adsorption cell was placed inside a water bath
8. A heat exchanger was placed in the water bath. The heat exchanger was connected to a water chiller to maintain a required temperature of the adsorption system.
9. The needle was inserted into the rubber stopper. This connected the evaporator to the adsorption cell
10. The initial volume of methanol was noted. The needle valve was opened allowing methanol in the evaporator to expand into gaseous phase
11. Once the vapor methanol reached the adsorbent, it got adsorbed on the pores of the adsorbent
12. The adsorption test was run for a total of 150 minutes
13. The needle was removed from the stopper and the valve was opened. The final value of methanol in the burette was noted.
14. The difference between the initial and final volume in the burette gives the total amount of methanol adsorbed in the adsorbent.
15. Pressure readings on the pressure gauge were noted every 5 minutes once for the total time period of the experiment.

The above given steps were carried out for different adsorbents. The various adsorbents used were

- a. Activated carbon
- b. As-prepared(Pristine) CNTs (10-20 nm, 40-60 nm, 60-100 nm)
- c. Annealed CNTs (10-20 nm, 40-60 nm, 60-100 nm)
- d. Acid Treated nanotubes (10-20 nm, 60-100 nm)
- e. Acid Treated + Sonicated nanotubes (10-20 nm, 60-100 nm)
- f. Mixture of activated carbon and carbon nanotubes

The different types of mixtures which were tested for adsorption of methanol are listed in Table 4.

The amount of methanol adsorbed was calculated for all the mixtures listed and the corresponding variation of pressure with time was noted. Time-dependent pressure curves were plotted to understand the kinetics of the adsorption process. The total amount of methanol adsorbed in each test was recorded. Except for the mixtures, all the other adsorption tests were carried out at three different temperatures, which were $T = 25$ °C, 30 °C and 35 °C.

Table 4: List of carbon nanotube-activated carbon mixtures tested

Mixture	% of Carbon nanotubes in mixture	% of activated carbon in mixture
Mixture 75% 60-100 nm P CNT - 25% AC T =25	75	25
Mixture 50% 60-100 nm P CNT - 50% AC T =25	50	50
Mixture 25% 60-100 nm P CNT - 75% AC T =25	25	75
Mixture 15% 60-100 nm P CNT - 85% AC T =25	15	85
Mixture 50% 40-60 nm P CNT - 50% AC T =25	50	50
Mixture 25% 40-60 nm P CNT - 75% AC T =25	25	75
Mixture 15% 40-60 nm P CNT - 85% AC T =25	15	85
Mixture 15% 10-20 nm P CNT - 85% AC T =25	15	85
Mixture 15% 60-100 nm A CNT - 85% AC T =25	15	85
Mixture 15% 40-60 nm A CNT - 85% AC T =25	15	85
Mixture 15% 40-60 nm A CNT - 85% AC T =30	15	85
Mixture 15% 40-60 nm A CNT - 85% AC T =35	15	85
Mixture 15% 10-20 nm A CNT - 85% AC T =25	15	85
Mixture 15% 60-100 nm AT CNT - 85% AC T =25	15	85
Mixture 10% 40-60 nm A CNT - 90% AC T =25	10	90

P – Pristine A - Annealed AT – Acid Treated + Sonicated

Challenges faced

The biggest challenge faced during the adsorption tests was the problem of leaks. Because the phase of methanol was dependent on the pressure inside the system, it was very important that the setup was leak free. However, when the lid was placed on top of the adsorption cell and sealed, and a vacuum was pulled inside the system using a vacuum pump, the pressure in the system kept increasing.

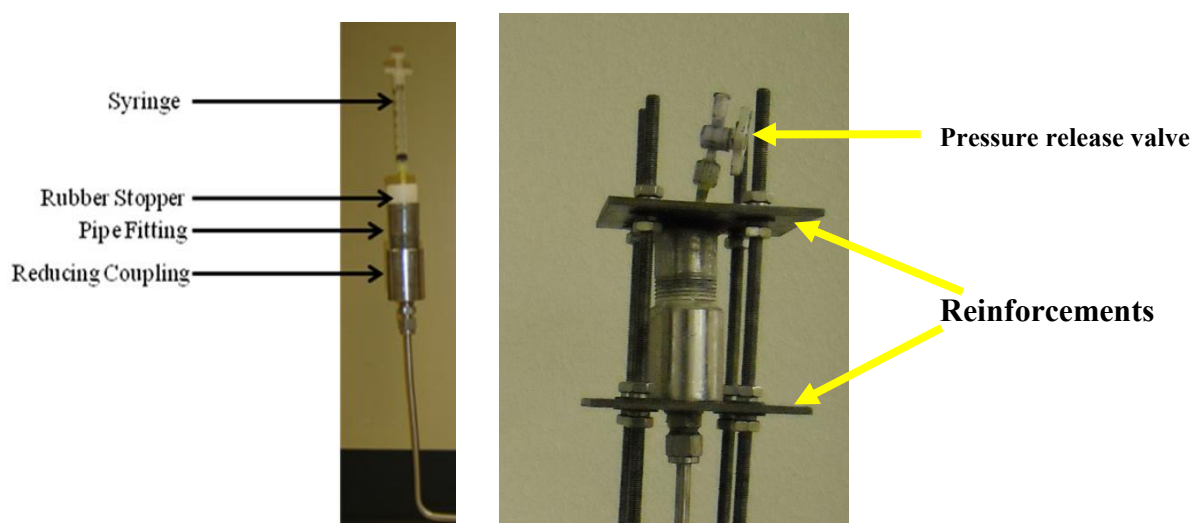


Figure 25: (a) Original stopper arrangement, (b) Reinforcements to hold pressure

Initially the setup was designed with a rubber stopper into which a syringe containing methanol was inserted (Fig. 25(a)). However, it was found out that the stopper was not able to hold the high vacuum. Hence, a new reinforcement design shown in Fig. 25(b) was adapted to the stopper side of the system in order to hold the stopper in its position. This reduced the leaks to a certain extent. Furthermore, DOW corning vacuum

grease was applied to the joints and top of the gaskets to prevent other leaks which might be present.

The adsorption of methanol was supposed to take place when methanol was in the gaseous phase. However, if the original syringe setup was used, then methanol will be flushed inside the nanotubes in the liquid phase. In order to avoid this, a burette was used as the methanol reservoir instead of the originally proposed syringe system.

CHAPTER V

RESULTS AND DISCUSSION

The amount of methanol adsorbed by each sample of adsorbent material was noted and the mass of methanol adsorbed per unit mass of adsorbent was calculated. This value was used to determine if the adsorbent material used performed better than activated carbon or not. The results obtained and the inferences that can be drawn out of the results are discussed in this chapter.

Methanol adsorption

The adsorption tests were carried out as explained above. The initial and final volume of methanol in the burette was used to determine the level of adsorption of each sample. Equation (2) was used to determine the adsorption levels.

$$\text{Amount of Methanol adsorbed in adsorbent} = m_{CH_3-OH} / m_{Adsorbent} \quad (2)$$

The volume of methanol adsorbed is calculated using equation (3)

$$m_{CH_3-OH} = (V_{initial} - V_{final}) * \rho_{CH_3OH} \quad (3)$$

where $V_{initial}$ is the initial volume of methanol in burette, V_{final} is the final volume of methanol in burette and ρ_{CH_3OH} is the density of methanol = 0.789 kg/l. Adsorption values were plotted which helped us compare the amount of methanol adsorbed for each adsorbent sample used. Histograms were used to compare the amount of methanol adsorbed.

Also, the variation of pressure with respect to time for 150 minutes of the adsorption test was noted for every single test. A graph depicting pressure vs. time was plotted. The different plots for each adsorption test can be found in Appendix 1.

In order to determine the level of adsorption by activated carbon and the carbon nanotube samples at different temperatures, experiments were carried out at 25 °C, 30 °C and 35 °C (Table 5)

It was found that the adsorption of methanol reduced as the temperature of the system was increased, regardless of the type of adsorbent used for the test. This result was expected and was similar to the results obtained by Li and Sumathy [1].

Table 5: Effect of temperature on methanol adsorption in CNTs

Mass of CH₃OH adsorbed/ Mass of Adsorbent W/V (g/kg)			
Adsorbent	T = 25 ° C	T = 30 ° C	T = 35 ° C
Activated carbon	161.43	126.61	98.12
CNT 10-20 nm Pristine	84.41	73.85	36.93
CNT 10-20 nm Annealed	73.85	73.85	73.85
CNT 40-60 nm Pristine	52.75	47.48	42.20
CNT 40-60 nm Annealed	63.30	63.30	63.30
CNT 60-100 nm Pristine	68.58	42.20	36.93
CNT 60-100 nm Annealed	58.03	52.75	36.93

The following figure (Fig. 26) shows the value of amount of methanol adsorbed as temperature of the system was increased. It was noted that the amount of methanol

adsorbed was reduced as temperature was increased for activated carbon. The same trend was observed for pristine carbon nanotubes for all diameters.

However, in case of annealed 10-20 nm and 40-60 nm carbon nanotubes, no difference in the amount of methanol adsorbed was observed as temperature increased. This was because after annealing of the carbon nanotubes, there was an increase in the graphitization of the material, as confirmed by the Raman Spectra. The nanotubes had become more ordered after high temperature annealing under vacuum. All this would mean that the amount of adsorption zones (sites) available remains constant and are not affected by slight changes in temperature.

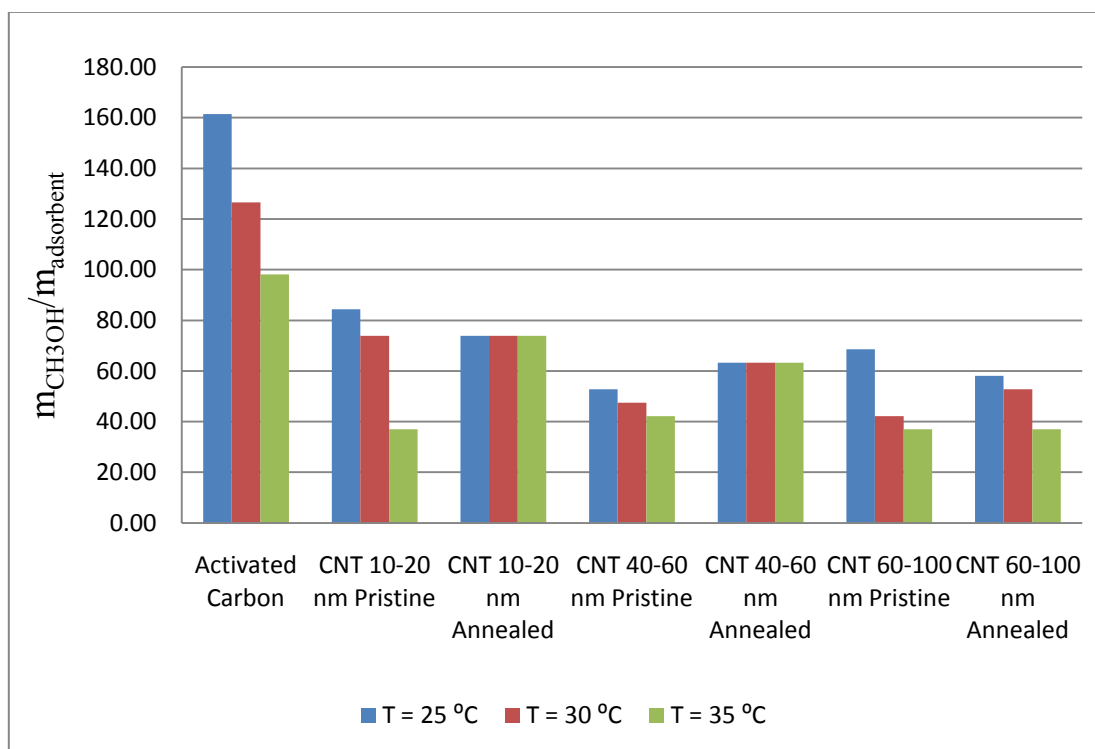


Figure 26: Effect of temperature on CNTs

It was observed that both pristine and annealed carbon nanotubes adsorbed lower than activated carbon, as seen in Fig. 26. A difference between the amount of methanol adsorbed by pristine and annealed nanotubes was found. It was found that annealing of the nanotubes does not increase the adsorption in the carbon nanotubes at 25 °C. In fact, the volume of methanol adsorbed was found to decrease for 10-20 nm and 60-100 nm. The amount of methanol adsorbed was higher for 40-60 nm for the annealed sample at 25 °C. At higher temperatures (30 °C, 35 °C), the level of methanol adsorbed on annealed carbon nanotubes was found to be same or higher than the amount of methanol adsorbed for pristine (as-prepared) carbon nanotubes.

Table 5 also shows that the nanotube diameter has an effect on the level of adsorption. It can be found that for pristine 10-20 nm CNTs, adsorption is the highest and is the lowest for 40-60 nm CNTs.

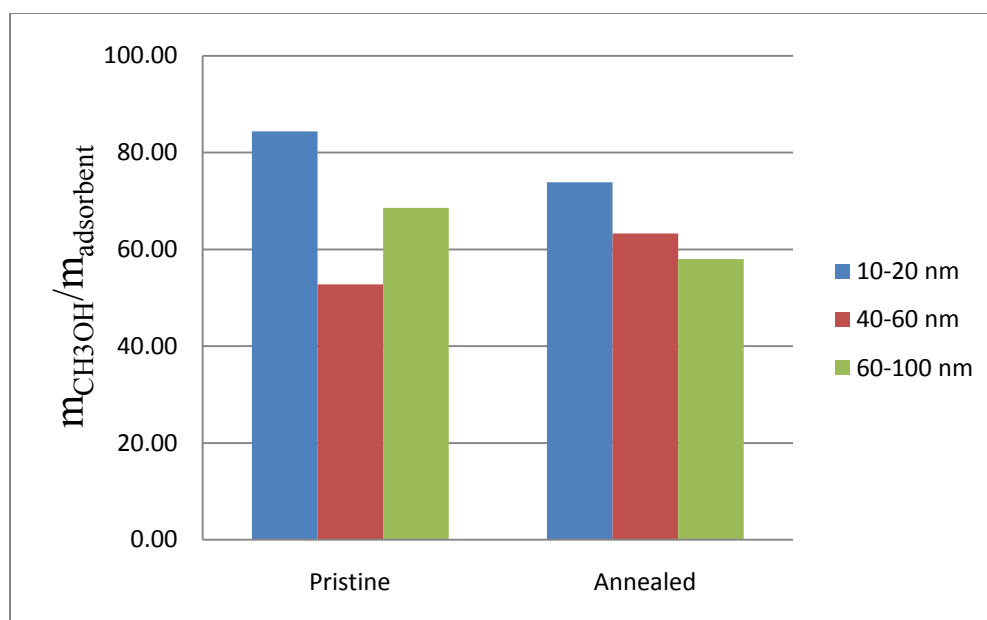


Figure 27: Effect of carbon nanotube diameter on methanol adsorption

For annealed nanotubes, the amount of adsorption was found to vary linearly with the carbon nanotube diameter. This information could be useful when deciding on the level of adsorption for specific adsorbents, which directly would reflect on the amount of heat adsorbed.

It has been mentioned that the carbon nanotubes are extremely hydrophobic in nature. Hence, to rectify this and make them less hydrophobic to enhance methanol adsorption, acid treatment was carried out. This was performed for the 10-20 nm and 60-100 nm CNTs. The results are shown in Table 6.

Table 6: Effect of acid treatment on CNTs

Adsorbent	Mass of CH₃OH adsorbed/ Mass of Adsorbent W/V (g/kg)			
	Pristine	Annealed	Acid Treated	Sonicated after Acid Treatment
CNT 10-20 nm	84.41	73.85	58.03	52.75
CNT 60-100 nm	68.58	58.03	52.75	52.75

Acid treatment of carbon nanotubes was expected to increase the level of adsorption by the addition of functional hydroxyl groups on the surface of the carbon nanotubes. Since this could potentially block the ends of the carbon nanotubes (Kuznetsova et. al. 2000), the nanotubes which were acid treated were sonicated for 10 minutes, in two 5 minute sonication periods separated by a 20 minute wait time in between, to break them and thus allowing adsorption on the inner surface of the nanotubes. The adsorption tests were carried out on these sonicated nanotubes as well. Fig. 28 exhibits the adsorption values for the acid treated nanotubes.

It was observed that the acid treatment did not produce an increase in the amount of methanol adsorbed. Sonication reduced the amount of methanol adsorbed even further.

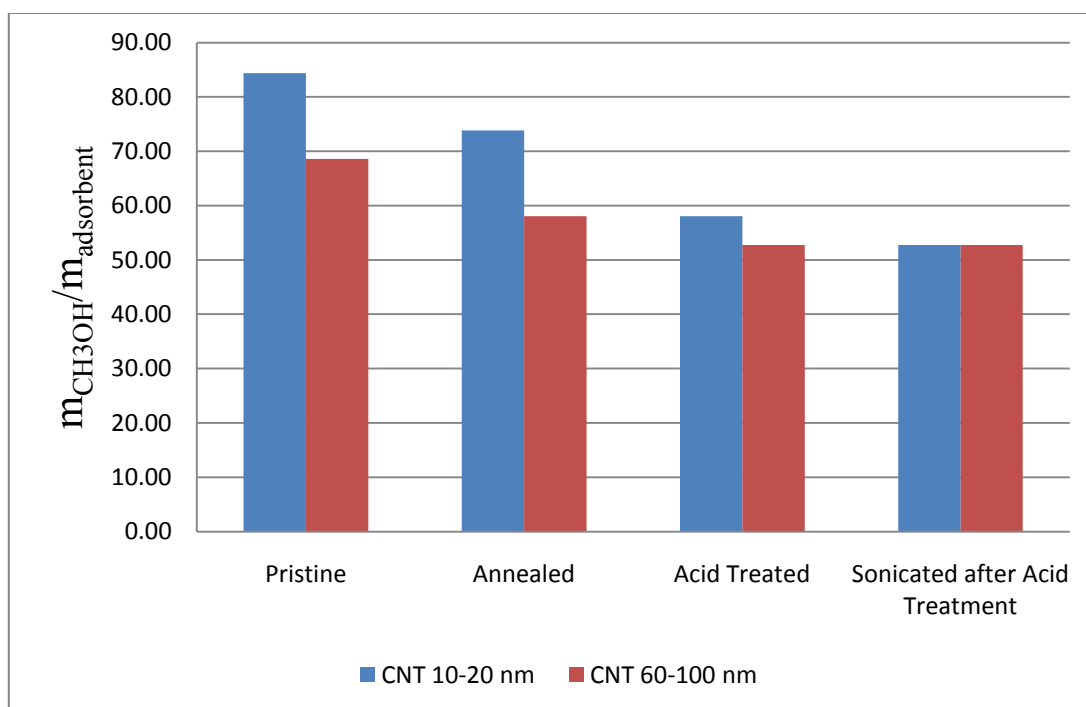


Figure 28: Effect of acid treatment on the adsorption of methanol on CNTs

Even though the challenges that were faced, like closed ends of nanotubes or hydrophobic nature of nanotubes were anticipated, the steps were taken to rectify them did not result in greater adsorption of methanol. To understand the effect of different treatments on CNTs, Raman spectroscopy was undertaken.

Raman Spectra analysis of treated carbon nanotubes

Raman Spectra data and Raman Spectra plots were obtained for pristine, annealed and acid treated carbon nanotubes. The plots can be found in Chapter IV. Based on literature, the I_D/I_G value (which is I_{1356}/I_{1580} , in our case) is useful in characterizing the material [12]. It could be used to analyze the graphitization of the

material, the presence or absence of impurities and the addition or removal of functional groups.

Raman spectroscopy measurements were made for the Pristine, Annealed and Acid Treated Samples for the 10-20 nm, 40-60 nm (no acid treated sample) and 60-100 nm as shown in Fig. 29. The Raman spectrum was obtained for the above stated 8 samples.

The I_D/I_G value was calculated for all the samples. The I_D/I_G ratios for the 10-20nm and 60-100 nm nanotubes show similar trends to previous Raman spectroscopy studies discussed in literature. However, 40-60 nm CNTs exhibit an increase in the I_D/I_G value after annealing.

It is interesting to see that the I_D/I_G value for pristine 40-60 nm is lower than the 10-20 nm and 60-100 nm CNTs, meaning there were less defects in the pristine 40-60 nm. However, an increase in the I_D/I_G value for the 40-60 nm annealed. Fig. 29 exhibits I_D/I_G ratios for all the 8 samples for which Raman Spectra data was obtained. Apart from the 40-60nm carbon nanotubes, annealing and acid treatment processes provided expected results.

Raman Spectra data also show a decrease in the I_D/I_G value after annealing all the other CNT samples, which implies that metallic impurities had been removed during the process. An increase in the I_D/I_G value after acid treatment implies that functional groups could have been added to the nanotubes during acid treatment [12]. However, the magnitude difference in the I_D/I_G value for each CNT batch (i.e. same size) suggests that optimal treatment conditions can still be pursued to achieve the treatment objectives.

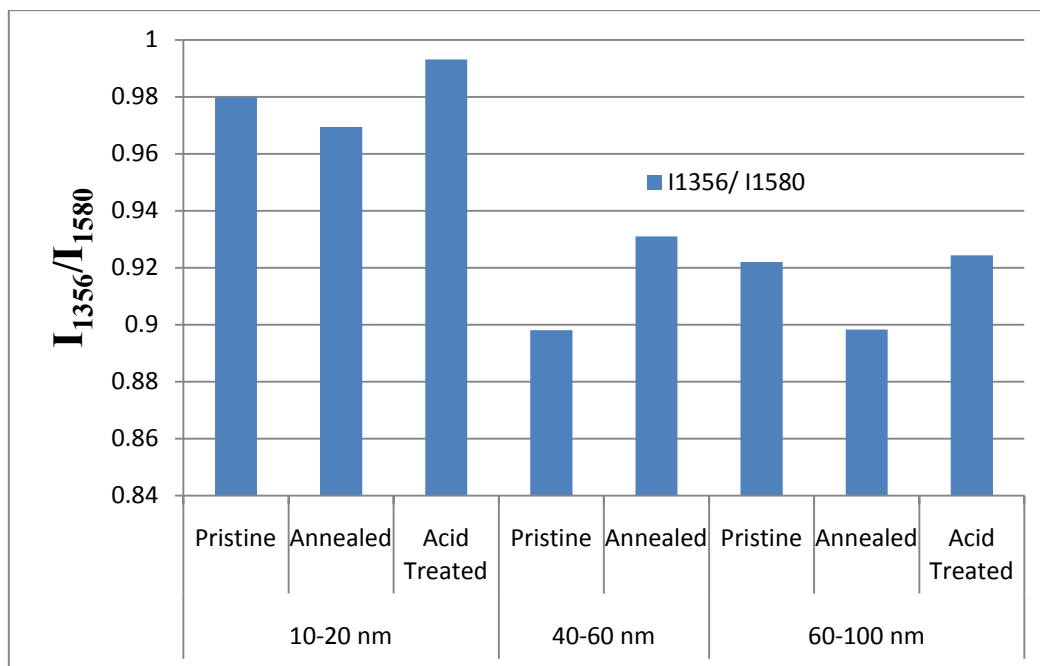


Figure 29: I_D/I_G (Y axis) values obtained through Raman Spectra

Based on the Raman Spectra analysis, we treatments undertaken did have an effect of all the carbon nanotube samples.

Activated carbon-carbon nanotube matrix

After measuring the level of adsorption of the untreated and treated CNT, it became clear that CNT did not exhibit better adsorption performance than activated carbon. However, the effects of adding CNT to an activated carbon matrix are still largely unknown. Therefore, several mixtures of CNT and activated carbon were prepared and tested to explore any possible effects on adsorption.

In order to test the effect of mixing of activated carbon with carbon nanotube matrices with different concentrations of activated carbon and carbon nanotubes were prepared. The mixture was blended well, but was not compacted. In other words, the mixtures were not tightly packed.

Table 7: Adsorption of methanol on mixtures using 10-20 nm CNT

CNT 10-20 nm	
Adsorbent	T = 25 °C
CNT 10-20 nm Pristine	84.41
Blend 15% 10-20 P CNT - 85% AC	200.46
Blend 15% 10-20 A CNT - 85% AC	242.67
Activated carbon	161.43

Table 8: Adsorption of methanol on mixtures using 40-60 nm CNT

CNT 40-60 nm	
Adsorbent	T = 25 °C
CNT 40-60 nm Pristine	52.75
Blend 50% 40-60 P CNT - 50% AC	158.26
Blend 25% 40-60 P CNT - 75% AC	189.91
Blend 15% 40-60 P CNT - 85% AC	221.56
Blend 15% 40-60 A CNT - 85% AC	253.22
Activated carbon	161.43

Table 9: Adsorption of methanol on mixtures using 60-100 nm CNT

CNT 60-100 nm	
Adsorbent	T = 25 °C
CNT 60-100 nm Pristine	84.41
Blend 75% 60-100 P CNT - 25% AC	116.06
Blend 50% 60-100 P CNT - 50% AC	147.71
Blend 25% 60-100 P CNT - 75% AC	200.46
Blend 15% 60-100 P CNT - 85% AC	211.01
Blend 15% 60-100 A CNT - 85% AC	226.84
Blend 15% 60-100 Acid CNT - 85% AC	237.39
Activated carbon	161.43

The previous chapter detailed the various matrices that were prepared by varying the concentrations of carbon nanotubes and activated carbon. The amount of methanol adsorbed by these matrices is listed in Tables 7-9.

Based on the results obtained, it is observed that using a mixture of activated carbon and carbon nanotubes increases the amount of methanol adsorbed when compared to plain activated carbon. The difference in the level of adsorption can be seen in figures 30-32.

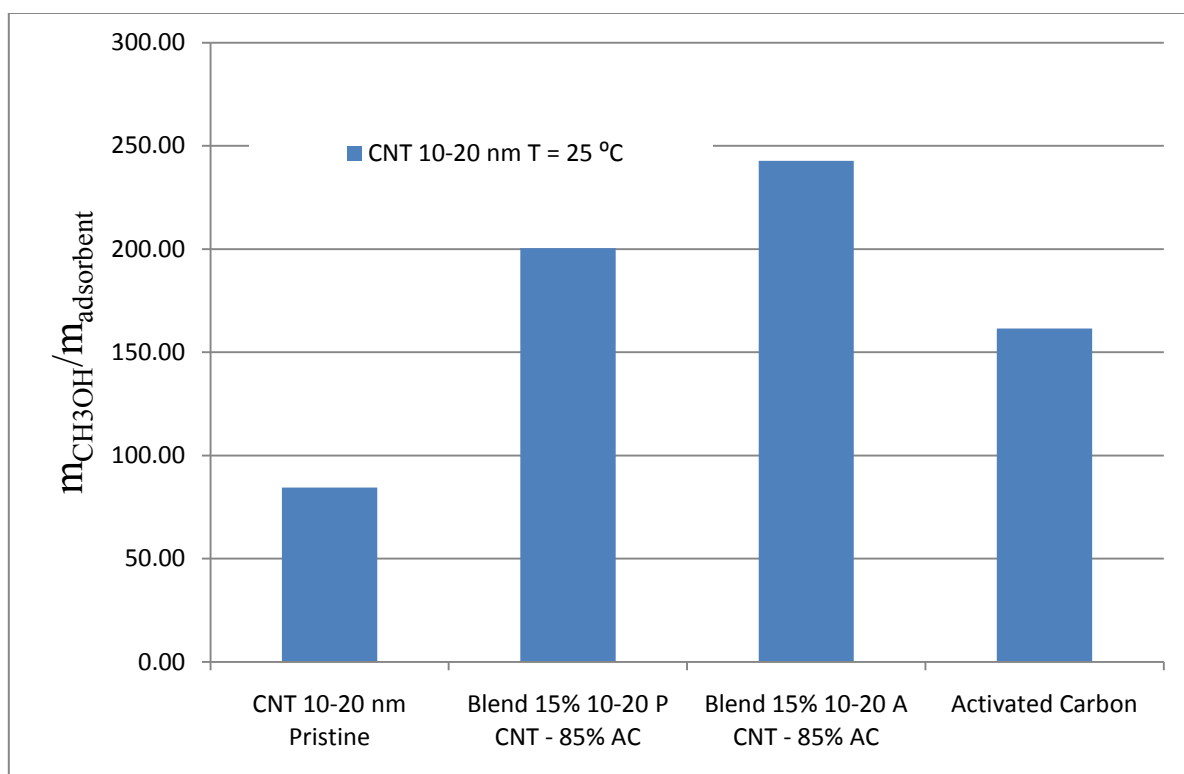


Figure 30: Mixture of 10-20 nm CNT with activated carbon

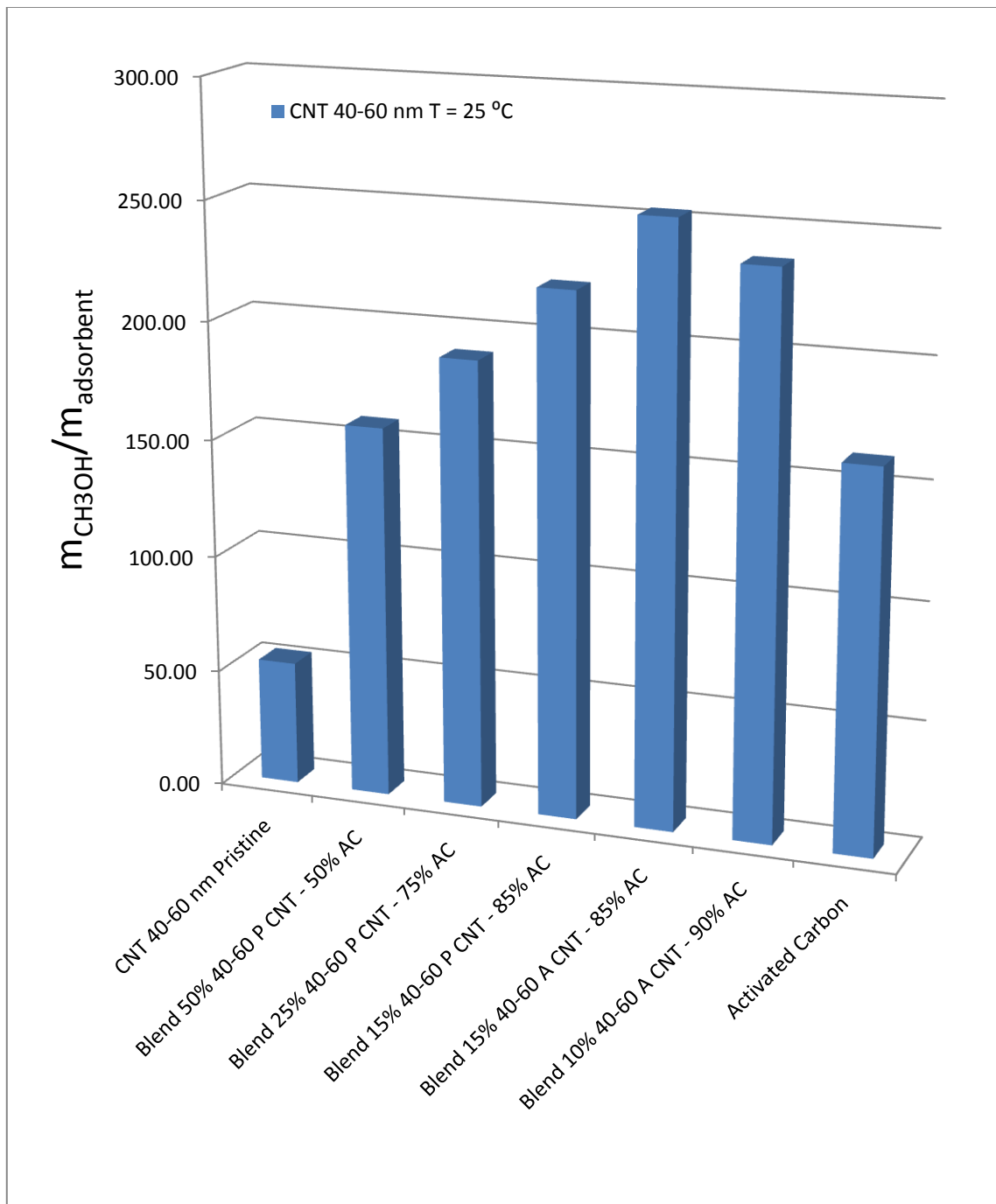


Figure 31: Mixture of 40-60 nm CNT with activated carbon

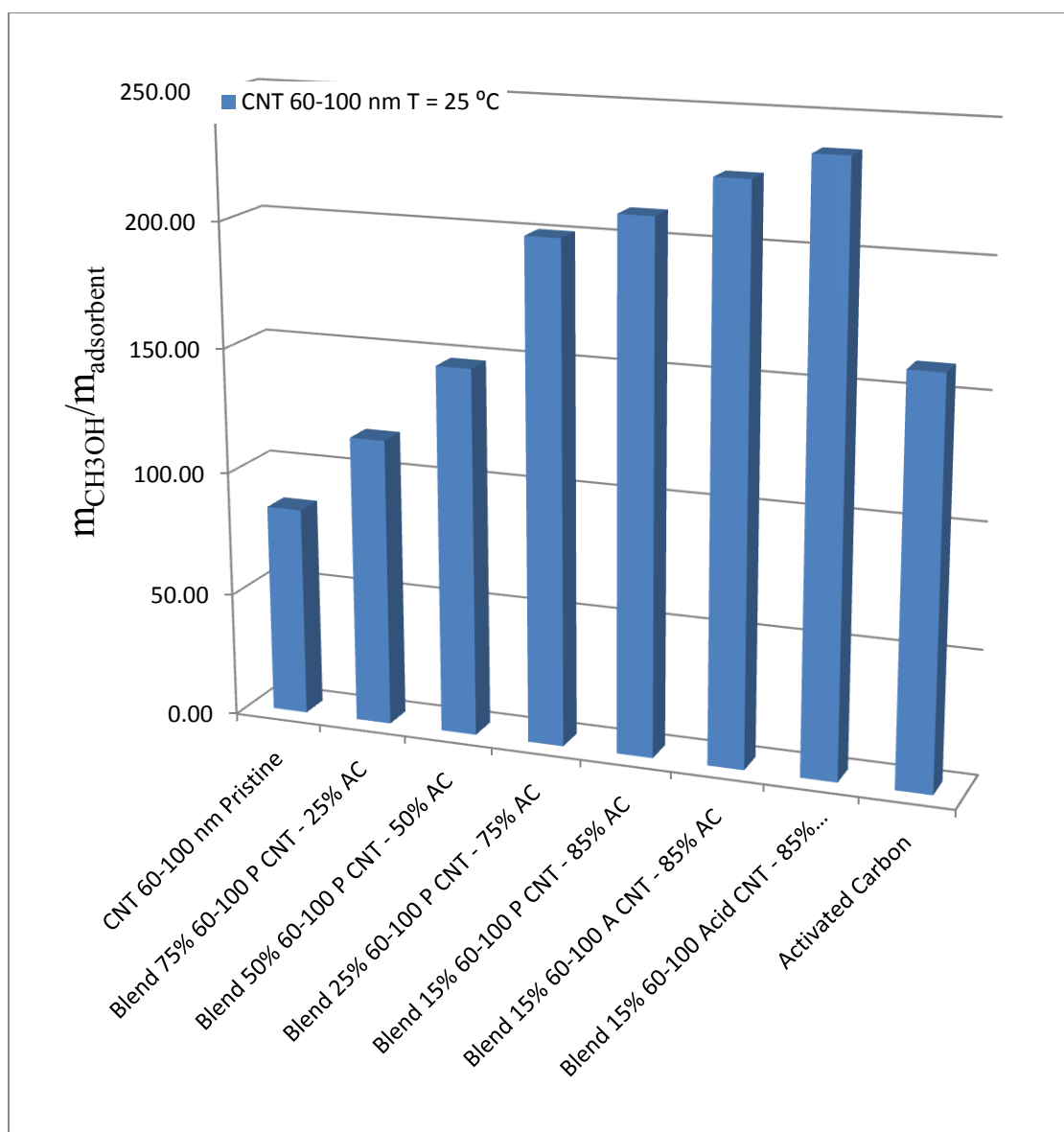


Figure 32: Mixture of 60-100 nm CNT with activated carbon

From the above figures, it is observed that mixing nanotubes with activated carbon does improve adsorption. It is found that the optimum blend consists of 85% of activated carbon with 15% of carbon nanotube which results in maximum adsorption. It

was confirmed that if more than 85% of activated carbon was present in the mixture, the adsorption decreases (Fig. 31).

Table 10: Adsorption of methanol in 85% AC – 15% CNT mixture

Adsorbent	85%AC-15%CNT: T = 25 ° C	
	Pristine	Annealed
10-20 nm	200.46	226.84
40-60nm	221.56	253.22
60-100 nm	211.01	242.67

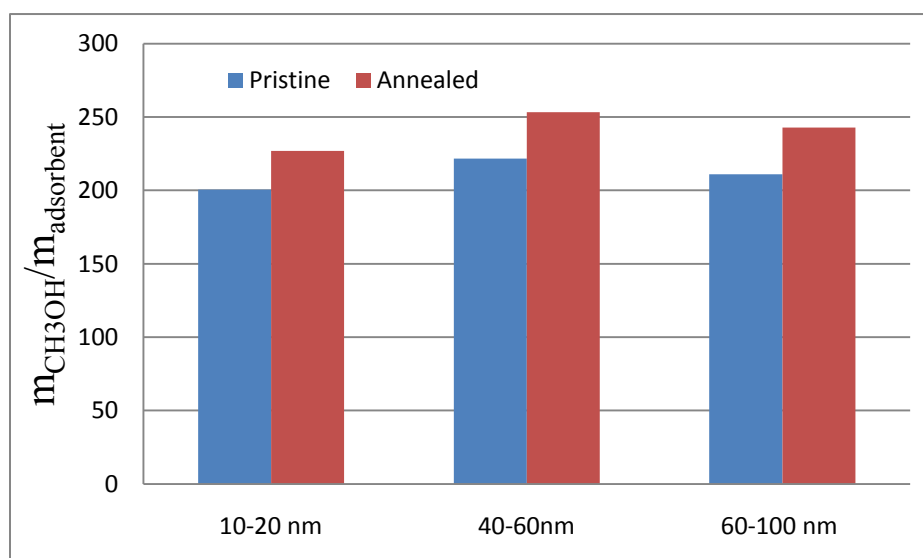


Figure 33: Adsorption of methanol in 85% activated carbon – 15% CNTs

In order to determine the best carbon nanotube size to be used for the mixture, several adsorption tests were performed using mixtures of 85% activated carbon – 15%

nanotube is plotted for different sizes and types (treatments) of CNTs (Fig. 33). The levels of adsorption in the mixtures of methanol are listed in Table 10.

From Fig. 33, it is observed that a mixture of annealed carbon nanotubes and activated carbon performs better and adsorbs a higher amount of methanol than a mixture of pristine nanotubes with activated carbon. This means that the structural changes which the carbon nanotubes underwent during the annealing process helps in increasing the rate of adsorption when used in the mixture. Furthermore, XRD results shown in chapter IV indicate the annealing improved the level of graphitization of 40-60 nm carbon nanotubes.

The level of methanol adsorption for all the samples tested is listed in Table 11. Also, the enhancement in the level of methanol adsorption for all the samples when compared to the level of adsorption of methanol in activated carbon can be found using the formula

$$\text{Percentage of Enhancement} = \frac{(m_{\text{activated-carbon}} - m_{\text{CNT sample}})}{m_{\text{activated-carbon}}} * 100 \%$$

The percentage of percentage of enhancement is also listed in Table 11. It was also found that the pristine and annealed CNT samples show a reduction in the amount of methanol adsorbed than activated carbon. However, when there is a mixture of carbon nanotubes and activated carbon, an increase in the amount of adsorption is observed. For mixtures with high percentage of activated carbon (especially the 85% activated carbon – 15% CNT mixture) a significant improvement in the amount of methanol adsorbed (56%) can be attained the mixture when using 40-60 nm annealed nanotubes.

Table 11: Mass of CH₃OH adsorbed/ Mass of adsorbent at T = 25 °C

Adsorbent		Methanol Adsorption g/kg	Enhancement Levels, %	Increase/ Decrease
Activated carbon		161.43		
CNT 60-100 nm	Pristine	84.41	-47.71	D
	Annealed	58.03	-64.05	D
	Acid Treated	52.75	-67.32	D
	Acid Treated+Sonicated	52.75	-67.32	D
	Mixture 75% 60-100 P CNT - 25% AC	116.06	-28.10	D
	Mixture 50% 60-100 P CNT - 50% AC	147.71	-8.50	D
	Mixture 25% 60-100 P CNT - 75% AC	200.46	24.18	I
	Mixture 15% 60-100 A CNT - 85% AC	226.84	40.52	I
Mixture 15% 60-100 Acid CNT - 85% AC		237.39	47.06	I
CNT 40-60 nm	CNT 40-60 nm Pristine	52.75	-67.32	D
	CNT 40-60 nm Annealed	63.30	-60.79	D
	Mixture 50% 40-60 P CNT - 50% AC	158.26	-1.96	D
	Mixture 25% 40-60 P CNT - 75% AC	189.91	17.65	I
	Mixture 15% 40-60 P CNT - 85% AC	221.56	37.25	I
	Mixture 15% 40-60 A CNT - 85% AC	253.22	56.86	I
CNT 10-20 nm	CNT 10-20 nm Pristine	84.41	-47.71	D
	CNT 10-20 nm Annealed	73.85	-54.25	D
	CNT 10-20 nm Acid Treated	58.03	-64.05	D
	CNT 10-20 nm Acid Treated+Sonicated	52.75	-67.32	D
	Mixture 15% 10-20 P CNT - 85% AC	200.46	24.18	I
	Mixture 15% 10-20 A CNT - 85% AC	242.67	50.33	I

D – Decrease, I – Increase P – Pristine, A – Annealed

A graph is plotted with the enhancement levels of the 85% activated carbon – 15 % carbon nanotube mixtures which uses pristine and annealed nanotubes of all three diameter ranges. The enhancement levels are shown in Fig. 34.

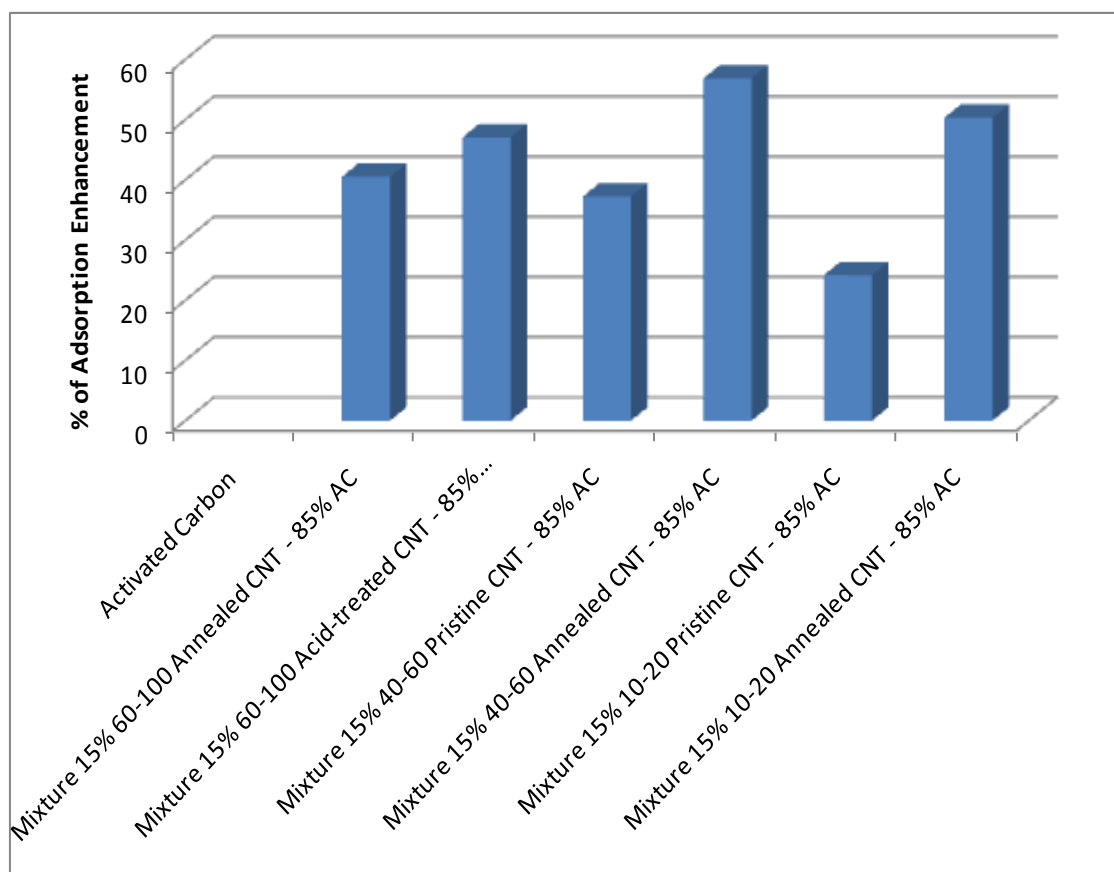


Figure 34: Enhancement levels of 85% activated carbon - 15% CNT mixtures

The reason for the increase in adsorption of methanol in the activated carbon-CNT matrix can be explained by one or both of the following proposed hypotheses:

- a. Increase in the interstitial space between CNT and activated carbon and availability of number of adsorption sites on the activated carbon surface
- b. Multi layer adsorption of methanol facilitated by fast diffusion transport of methanol through carbon nanotube network. The CNT network allows for better penetration of methanol into activated carbon, resulting in an increase of the kinetics of the adsorption process.

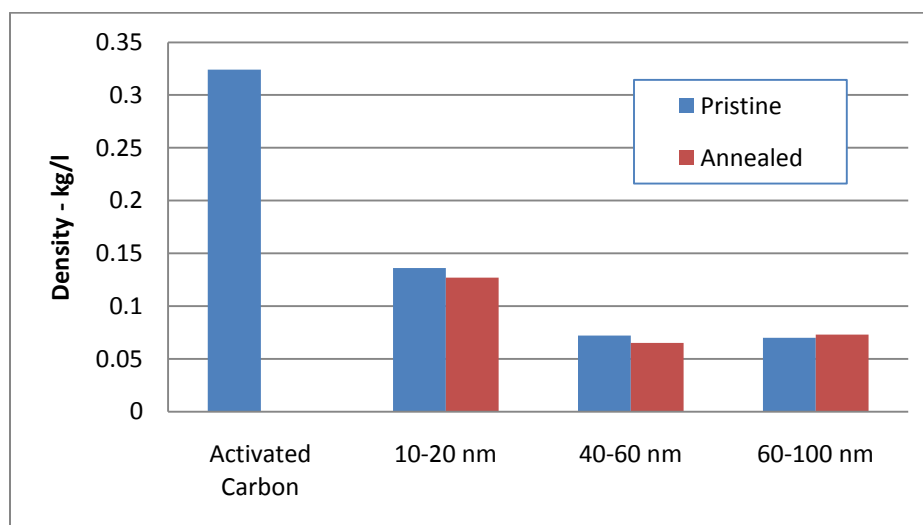
Increase in interstitial space

The increase in the amount of adsorption for the activated carbon - carbon nanotube mixture could be attributed to the increase in the interstitial space in the porous activated carbon due to the addition of nanotubes. In order to validate this hypothesis, density values of the different adsorbent samples were calculated. The density values of the adsorbents were calculated by measuring volume and mass for each sample. Based on the density values, the interstitial spaces can be approximately analyzed.

The calculation of the density values of the various samples is listed in Table 12. The change in density of the pristine and annealed nanotubes is shown in Fig. 35. Also annealed nanotubes exhibit a lower density than pristine (as-is) nanotubes.

Table 12: Density calculation of adsorbent samples

Sample	Volume(ml)	Mass(gms)	Density
Activated carbon	2	0.6486	0.324
Pristine 10-20 nm	2	0.2721	0.136
Pristine 40-60 nm	2	0.1435	0.072
Pristine 60-100 nm	2	0.1395	0.070
Annealed 10-20 nm	2	0.2541	0.127
Annealed 40-60 nm	2	0.1297	0.065
Annealed 60-100 nm	2	0.1465	0.073
Acid Treated 10-20 nm	2	0.375	0.188
Acid Treated 60-100 nm	2	0.2864	0.143
Pristine 10-20 nm 85%AC-15%CNT	2	0.692	0.346
Annealed 10-20 nm 85%AC-15%CNT	2	0.7203	0.360
Pristine 40-60 nm 85%AC-15%CNT	2	0.4942	0.247
Annealed 40-60 nm 85%AC-15%CNT	2	0.5332	0.267
Pristine 60-100 nm 85%AC-15%CNT	2	0.4668	0.233
Annealed 60-100 nm 85%AC-15%CNT	2	0.53	0.265
Acid Treated 60-100 nm 85%AC-15%CNT	2	0.6061	0.303

**Figure 35: Comparison of density values of pristine and annealed carbon nanotubes**

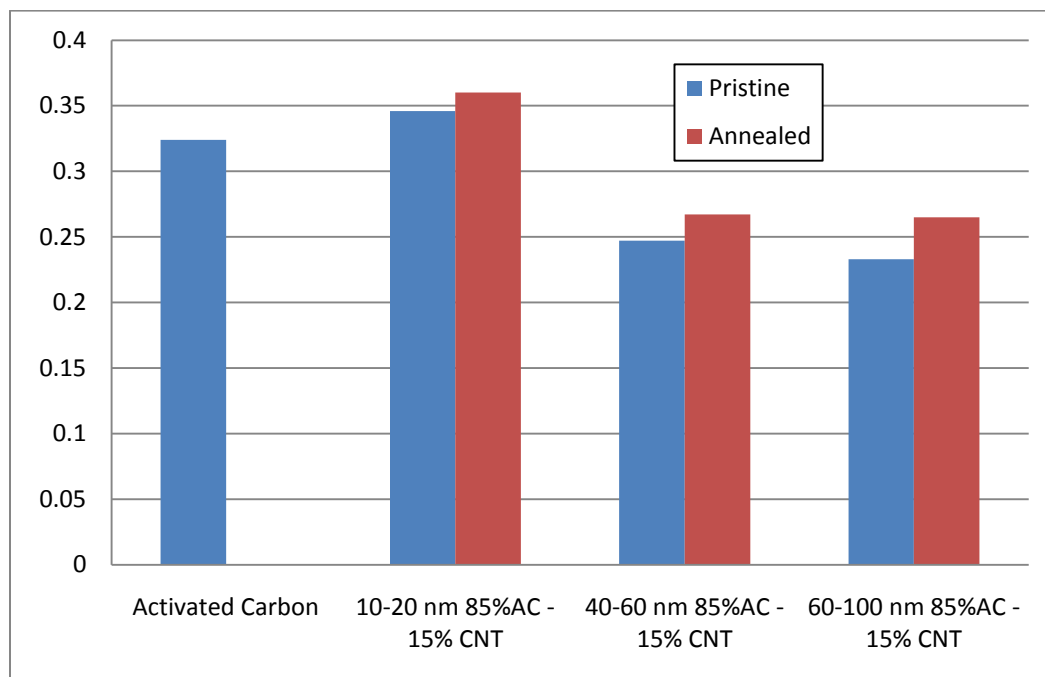


Figure 36: Density variation of the 85% activated carbon - 15% CNT mixture

The density values of the activated carbon- carbon nanotube mixture are shown in Fig. 36. It was found that the density values of 40-60 nm and 60-100 nm CNT were lower than the density of activated carbon. Thus these two sets of nanotubes take more volume for the same mass of sample than activated carbon. To estimate the effect of CNT density on the availability of void spaces in the activated carbon matrix, the following equation should be used.

$$V_{total} = V_{CNT} + V_{ActivatedCarbon} + V_{Void}$$

$$\frac{m_{total}}{\rho_{total}} = \frac{m_{CNT}}{\rho_{CNT}} + \frac{m_{ActivatedCarbon}}{\rho_{ActivatedCarbon}} + V_{Void}$$

$$V_{Void} = \frac{m_{total}}{\rho_{total}} - \left(\frac{m_{CNT}}{\rho_{CNT}} + \frac{m_{ActivatedCarbon}}{\rho_{ActivatedCarbon}} \right)$$

where, V_{void} is the amount of void spaces available for adsorption of methanol,

$V_{Activated\ carbon}$ is the volume occupied by the activated carbon

V_{CNT} is the volume of the carbon nanotubes

ρ and m represent the density and mass for each parameter(activated carbon, CNT and total)

If the density of CNT is not a function of CNT diameter, and the mass of CNT and activated carbon are the same for all cases (i.e. 85% AC + 15%CNT), then the amount of void volume is inversely proportional to matrix density. From Fig. 36, it is evident that the mixtures containing 40-60 and 60-100 nm CNT result in greater void volume. This supports the notion that a decrease in matrix density results in greater availability of adsorption sites including micropores. Furthermore, the amount of methanol adsorbed for these two sets were found to be higher than the methanol adsorbed by activated carbon, confirming this hypothesis.

Kinetics and mass transport

The kinetics of the adsorption process is important because it has been observed that it affects the level of adsorption [21]. It is hypothesized that mixing carbon nanotubes with activated carbon increases the kinetics of the methanol adsorption of

methanol on activated carbon. This could be attributed to the enhanced diffusion process that takes place when methanol flows inside the carbon nanotubes. Since adsorption is a surface phenomenon, it can be assumed that the methanol gets adsorbed on the top surface the adsorbent first and thereby prevents the penetration of methanol into the lower layers of the adsorbent. Addition of nanotubes could help solve this problem, because the hydrophobic nature of the nanotubes will help in transport of methanol molecules through the adsorbent material.

Joseph et. al. [23] suggested that the hydrophobic nature of CNT nanotubes is responsible for increasing the speed of water molecules flowing through them in part driven by the inter-atomic potential between the adsorbent and adsorbate. The effect of the hydrophobic nature of CNT seems to have a greater effect when CNT of certain sizes are used. This concept still is under investigation by several research teams [23]. This concept is also applied to our adsorption data and it can be said that the kinetics of the process is improved when nanotubes of a certain size range are added to activated carbon.

The adsorption rate of ethanol on activated carbon fibers was investigated by B.B. Saha et. al [21]. The Linear Driving Force equation and the Arrhenius equation were used to calculate the kinetics of the reactions. In this thesis, we use a more direct approach by using a pressure ratio P/P_0 (where P_0 is saturation pressure) over the duration of the test for estimating the kinetics of the adsorption process for each adsorbent sample. According to the Dubinin-Radushkevitch equation (Equation 1), the level of adsorption is dependent upon P/P_0 .

$$\ln W = \ln W_o - D \left[T \cdot \ln \left(\frac{P}{P_o} \right) \right]^2$$

In the study, it was found that the kinetics of the adsorption process can best be characterized by using a logarithmic equation during the initial stages of adsorption (when $P/P_o < 0.8$). The final stages of adsorption were found to be linear and all the kinetics constants had almost the same value regardless of adsorbent type. For the initial stage of adsorption, the following equation was used.

$$P(t) = k_1 \cdot \ln(t) + C_1 \quad (4)$$

where $P(t)$ refers to the Pressure corresponding to time t . k_1 refers to the kinetic constant for the first stage of the adsorption process when $P/P_o < 0.8$, and C_1 is an empirical constant.

The initial phase refers to the adsorption process when the cell pressure is below $0.8 P_o$, where P is the absolute pressure at time t , and P_o refers to the saturation pressure of the process at Temperature T . The value of $P(t)$ was normalized using equation (5) and was plotted against time t .

$$\theta_p = \frac{P(t) - P(i)}{P(f) - P(i)} \quad (5)$$

The kinetic constant k_1 was calculated for each adsorbent and is plotted in Table 13. The final phase of the adsorption process was considered when pressure $P > 0.8P_o$ and was characterized by a linear curve, calculated through equation (6)

$$P(t) = k_2 \cdot t + C_2 \quad (6)$$

where k_2 is the kinetic constant for the second and final stage of the adsorption process and C_2 is the intercept of the linear equation. k_2 values for each adsorbent are also listed in table 13.

It was found that k_2 was nearly constant for most of the adsorbent samples. The value of k_1 can be used to indirectly determine the speed of adsorption of the process. It was found that k_1 was less for the pristine and acid treated nanotubes while higher for the mixtures (represented by a M in the table).

It is noted that the value of k_1 for the mixture containing acid treated 60-100 nm CNT was lower than for the mixture containing annealed 60-100 nm CNT. This could be because of the presence of functional groups in the acid treated nanotubes which apparently made the carbon nanotubes less hydrophobic, prevented the fast transport of methanol through the nanotube [23].

We can conclude that the kinetics of the reaction is aptly characterized by the equations that were obtained using the corresponding k_1 , k_2 values for each adsorbent. From Table 13, it is evident that adsorption is driven by kinetics and not solely by the number of adsorption sites. Interestingly enough, the mixtures reach $P/P_0 = 0.8$ much faster than activated carbon alone. Moreover, CNT samples alone took more time to reach $P/P_0 = 0.8$ and exhibited less adsorption. Therefore, it can be inferred that adsorption depends strongly both in the availability of porous cavities and faster diffusion transport. Furthermore, mixing annealed CNT in activated carbon results in greater adsorption and faster diffusion than the other combinations (i.e. acid-treated or pristine).

Table 13: Calculation of kinetic constants

Adsorbent	Logarithmic $P/P_0 < 0.80$			Linear $P/P_0 > 0.80$			CH ₃ OH Adsorbed g/kg
	$P(t) = k_1 * \ln(t) + C_1$			$P(t) = k_2 * t + C_2$			
	k_1	C_1	R^2	k_2	C_2	R^2	
Activated carbon	0.196	-0.015	0.95	0.001	0.813	0.96	161.43
10-20nm Pristine	0.171	0.28	0.99	0.001	0.798	0.982	84.41
40-60nm Pristine	0.165	0.23	0.99	0.001	0.778	0.994	52.75
60-100 nm Pristine	0.149	0.298	0.99	0.001	0.777	0.98	68.58
10-20 nm Annealed	0.103	0.472	0.94	0.001	0.833	0.99	73.85
40-60 nm Annealed	0.141	0.323	0.99	0.001	0.777	0.99	63.3
60-100 nm Annealed	0.141	0.3	0.99	0.001	0.78	0.99	58.03
10-20 nm Acid Treated	0.133	0.335	0.99	0.001	0.799	0.99	58.03
10-20 nm Acid+Sonic	0.09	0.502	0.99	0.001	0.798	0.99	52.75
60-100 nm Acid Treated	0.18	0.231	0.99	0.001	0.816	0.99	52.75
60-100 nm Acid+Sonic	0.145	0.327	0.99	0.001	0.818	0.99	52.75
M:75% 60-100 nm	0.245	-0.146	0.99	0.001	0.766	0.98	116.06
M: 50% 60-100 nm	0.273	-0.324	0.96	0.001	0.801	0.99	147.71
M: 25% 60-100 nm	0.266	-0.368	0.90	0.001	0.765	0.98	200.46
M:15% 60-100 nm	0.239	-0.207	0.96	0.001	0.776	0.99	211.01
M:15% 60-100 nm Annealed	0.316	-0.562	0.92	0.001	0.817	0.94	226.84
M:15% 60-100 nm Acid Treated + Sonicated	0.282	-0.433	0.94	0.001	0.761	0.96	237.39
M:50% 40-60 nm	0.266	-0.294	0.971	0.001	0.79	0.99	158.26
M: 25% 40-60 nm	0.31	-0.498	0.941	0	0.919	0.717	189.91
M: 15% 40-60 nm	0.278	-0.419	0.941	0.001	0.743	0.99	221.56
M:15% 40-60 nm Annealed at 25 °C	0.298	-0.472	0.944	0.001	0.791	0.98	253.22
M:15% 40-60 nm Annealed T = 30 °C	0.226	-0.074	0.988	0.001	0.782	0.99	137.16
M:15% 40-60 nm Annealed T = 35 °C	0.212	0.011	0.987	0.001	0.802	0.99	126.61
M:15% 10-20 nm	0.253	-0.373	0.933	0.002	0.547	0.99	200.46
M:15% 10-20 nm Annealed	0.308	-0.546	0.932	0.002	0.707	0.99	242.67

CHAPTER VI

CONCLUSION AND FUTURE WORK

An adsorption test system was designed to find the amount of methanol adsorbed for different adsorbents that were used. Different adsorbents were experimented with to find the best possible adsorbent material to be used which can adsorb the maximum quantity of methanol.

It was found that activated carbon was a good adsorbent. However carbon nanotubes of three different diameter ranges were tested as adsorbents and the level of adsorption was found to be lower than the level of adsorption found in activated carbon.

The pristine nanotubes were annealed in high temperature under vacuum to open the ends of the carbon nanotubes. Also, the pristine nanotubes were treated with concentrated nitric acid under reflux to provide functional groups on the ends of the nanotubes. These treatments were characterized using transmission electron microscopy, scanning electron microscopy, X-Ray diffraction and Raman spectroscopy. The treated nanotubes were tested in the adsorption cell for methanol adsorption and no significant improvement in the level of adsorption was found.

A mixture of activated carbon and carbon nanotubes was proposed to be used as adsorbent material. Mixtures of various concentrations of activated carbon and carbon nanotubes were prepared. The adsorption of methanol was found to increase in these samples.

Mixtures that used a 85% concentration of activated carbon and 15% of carbon nanotubes was found to be the optimal mixture that enabled maximum adsorption into

the carbon nanotubes. It was found that using a higher or lower concentration of activated carbon in the mixture resulted in a lower adsorption of methanol.

Based on experimental data, it was concluded that the level of adsorption of the optimal mixture increases if the nanotubes used in the mixture are annealed under vacuum conditions. Also it was found that acid treated nanotubes did not perform as well as annealed nanotubes in the mixture.

The increase in the level of adsorption of the mixture is attributed to an increase in the interstitial space on the activated carbon surface which is available for adsorption. Also, the kinetics of the adsorption process was increased due to a faster diffusion through carbon nanotubes in the mixture.

Future work

Many improvements can be expected if the parameters used in the experiment are changed. The annealing temperature of carbon nanotubes could play an important role. If the nanotubes are heated to higher temperatures, a higher level of adsorption could be expected.

Once the best possible adsorbent is obtained, the adsorption cycle must be combined with a desorption cycle as part of a solar refrigerator setup. The solar refrigerator must be tested for its coefficient of performance (COP) using the optimal adsorbent. A higher COP is expected because of the higher capacity of the adsorbent to adsorb methanol.

Another area which can be investigated is the type of adsorbate fluid used. Methanol is found to be an effective adsorbate. Different fluids can be tested for the

same adsorption setup to find the best possible adsorbate that can be used in the solar refrigerator.

REFERENCES

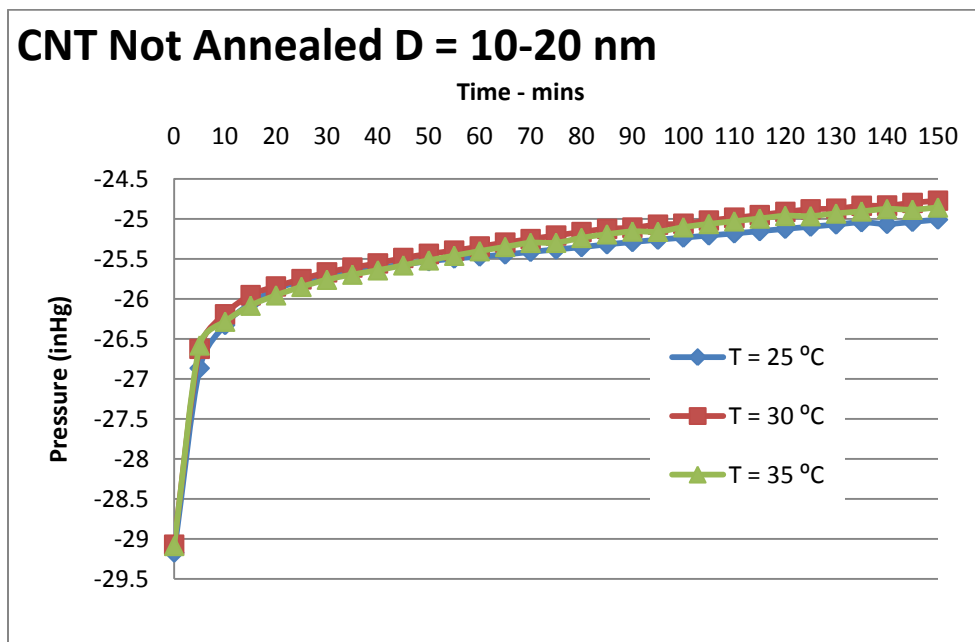
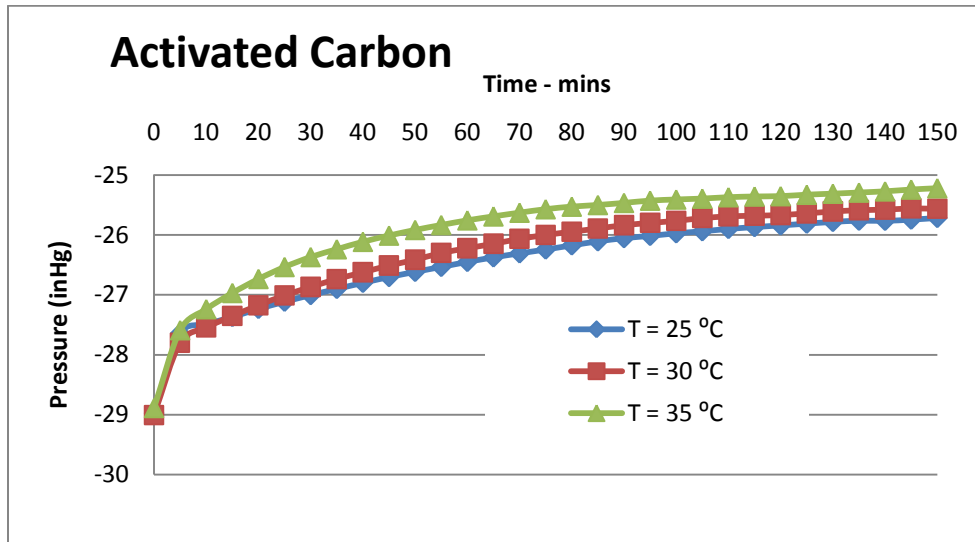
- [1] Li ZF, Sumathy K. A solar powered ice-maker with solid adsorption pair of activated carbon and methanol. *International Journal of Energy Research*, 1999; 23:517-27.
- [2] Anyanwu EE, Ezekwe CI. Design, construction and test run of a solid adsorption solar refrigerator using activated carbon/methanol as adsorbent/adsorbate pair. *Energy Conversion and Management*, 2003; 44: 2879- 92.
- [3] Hildbrand C, Dind P, Pons M, Buchter F. A new solar powered adsorption refrigerator with high performance. *Solar Energy*, 2004; 77: 311-8.
- [4] Boubakri A. A new conception of an adsorptive solar-powered ice maker. *Renewable Energy*, 2003; 28: 831-42.
- [5] Iijima, S. Helical microtubules of graphitic carbon. *Nature*, 1991; 354: 56-8.
- [6] Komarneni M, Sand A, Lu M, Burghaus U. Adsorption kinetics of small organic molecules on thicker and thinner layers of carbon nanotubes. *Chemical Physics Letters*, 2009; 470: 300-3.
- [7] Ajayan PM, Ebbesen TW, Ichihashi T, Iijima S, Tanigaki K, Hlura H. Opening carbon nanotubes with oxygen and implications for filling. *Nature*, 1993; 362: 522-5.
- [8] Eswaramoorthy M, Sen R, Rao CNR. A study of micropores in single-walled carbon nanotubes by the adsorption of gases and vapors. *Chemical Physics Letters*, 1999; 304: 207-10.
- [9] Talapatra S, Zambano AZ, Weber SE, and Migone AD. Gases do not adsorb on

- the interstitial channels of closed-ended carbon nanotubes. *Physical Review Letters*, 2000; 85(1): 138-41.
- [10] Andrews R, Jacques D, Qian D, Dickey EC. Purification and structural annealing of multiwalled carbon nanotubes at graphitization temperatures. *Carbon*, 2001; 39: 1681-7.
- [11] Ci L, Zhu H, Wei B, Xu C, Wu D. Annealing amorphous carbon nanotubes for their application in hydrogen storage. *Applied Surface Science*, 2003;205:39-43.
- [12] Huang W, Wang Y, Luo G, Wei F. 99.9% purity multi-walled carbon nanotubes by vacuum high temperature annealing. *Carbon*, 2003; 41: 2585-90.
- [13] Kim YA, Hayashi T, Osawa K, Dresselhaus MS, Endo M. Annealing effect on disordered multi-wall carbon nanotubes. *Chemical Physics Letters*, 2003; 380: 319-24.
- [14] Babaa MR, McRae E, Gomes C, Delpoux S, Medjahdi G, Blacher, Beguin F. Characterization and gas adsorption on multi-walled carbon nanotubes before and after controlled chemical opening. *Electronic Properties of Synthetic Nanostructures*, 2004; 723: 133-6.
- [15] Kuznetsova A, Mawhinney DB, Naumenko V, Yates JT, Liu J, Smalley RE. Enhancement of adsorption inside of single-walled nanotubes. *Chemical Physics Letters*, 2000; 321: 292-6.
- [16] Kyotani T, Nakazaki S, Xu W, Tomita A. Chemical modification of the inner walls of carbon nanotubes. *Carbon*, 2001; 39: 782-5.
- [17] Moon JM, An KH, Lee YH. High-yield purification process of single-walled

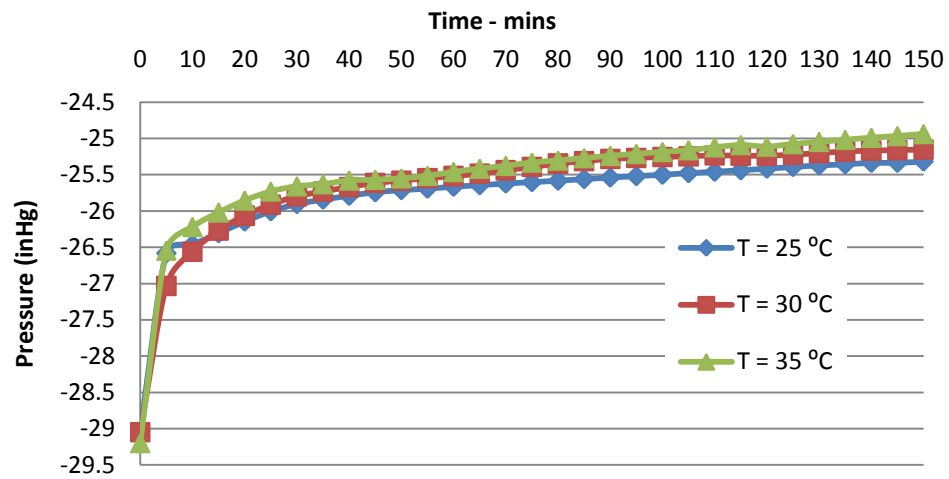
- carbon nanotubes. *Journal of Physical Chemistry*, 2001; 105: 5677-81.
- [18] Rosca ID, Watari F, Uo M, Akasaka T. Oxidation of multiwalled carbon nanotubes by nitric acid. *Carbon*, 2005; 43: 3124-31.
- [19] Zhan D, Shi L, Fang J, Li X, Dai K. Preparation and modification of carbon nanotubes. 2005; 59: 4044-7.
- [20] Reyhani A, Mortazavi SZ, Nozad Golikand A, Moshfegha AZ, Mirershadi S. The effect of various acids treatment on the purification and electrochemical hydrogen storage of multi-walled carbon nanotubes. *Journal of Power Sources*, 2008; 183: 539-43.
- [21] Saha BB, El-Sharkawy II, Chakraborty A, Koyama S, Yoon S and Ng KC. Adsorption rate of ethanol on activated carbon fiber. *Journal of Chemical Engineering Data*, 2006; 51: 5187-92.
- [22] Gregg SJ, Sing KSW. In: Gregg SJ, editor, *Adsorption, surface area and porosity*. London; New York: Academic Press; 1982, 195 - 245.
- [23] Joseph S, Aluru NR. Why are carbon nanotubes fast through water? *Nanoletters*, 2008; 8: 452-8.

APPENDIX

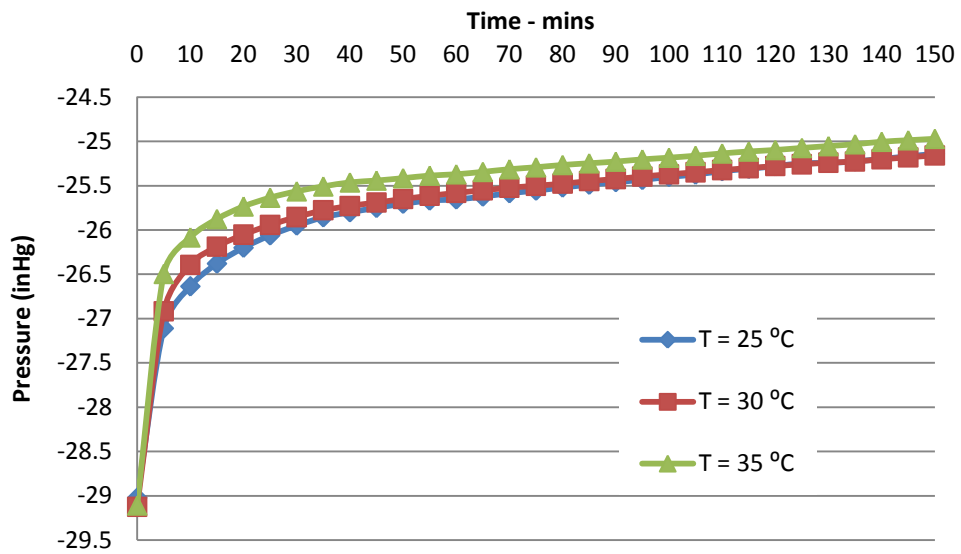
PRESSURE VS. TIME PLOTS FOR VARIOUS ADSORBENTS



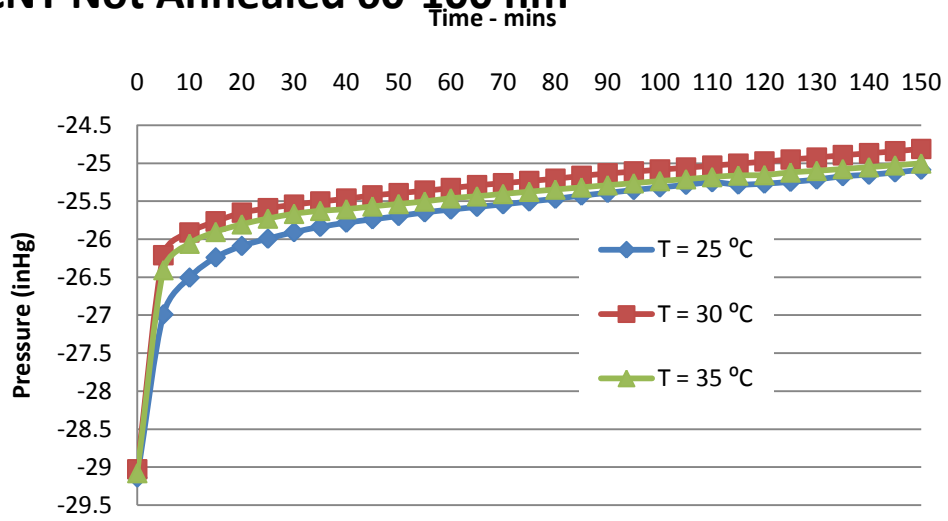
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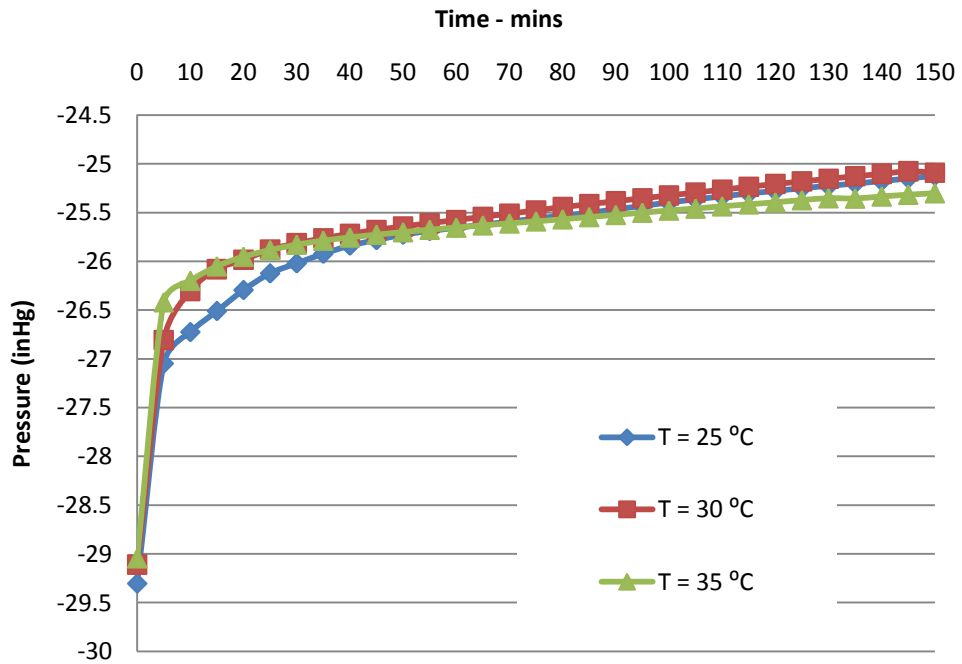
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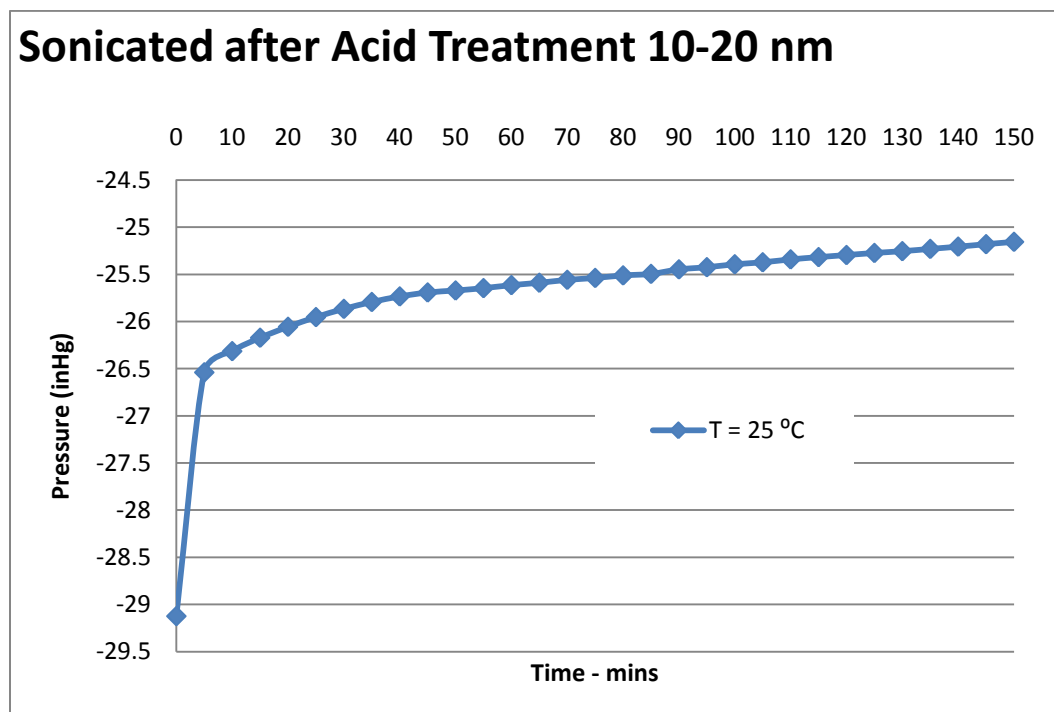
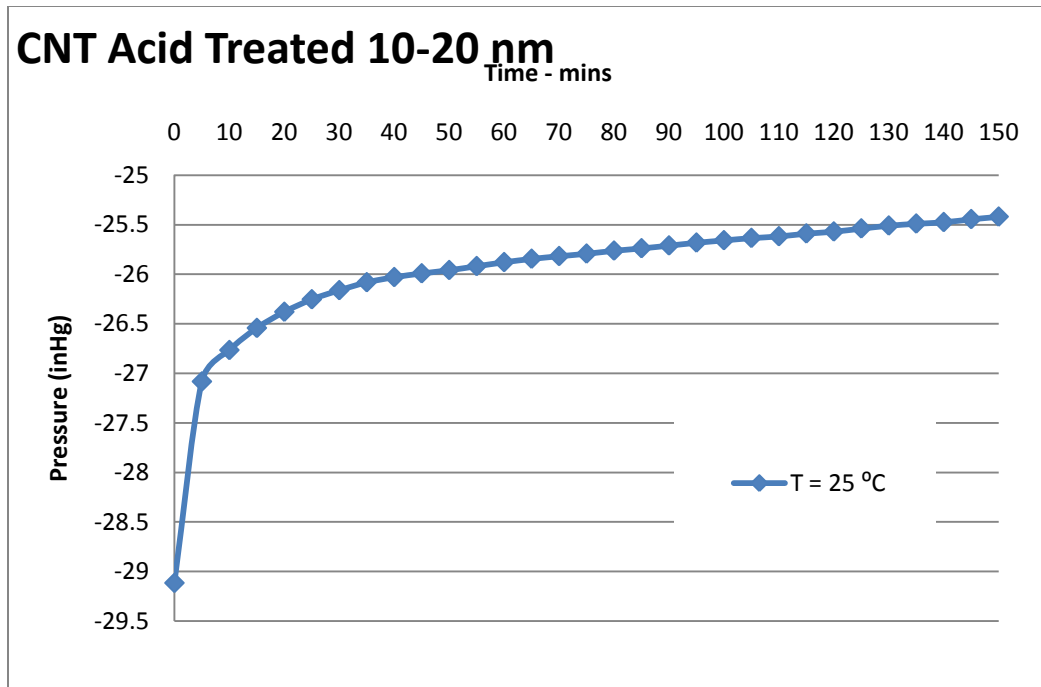


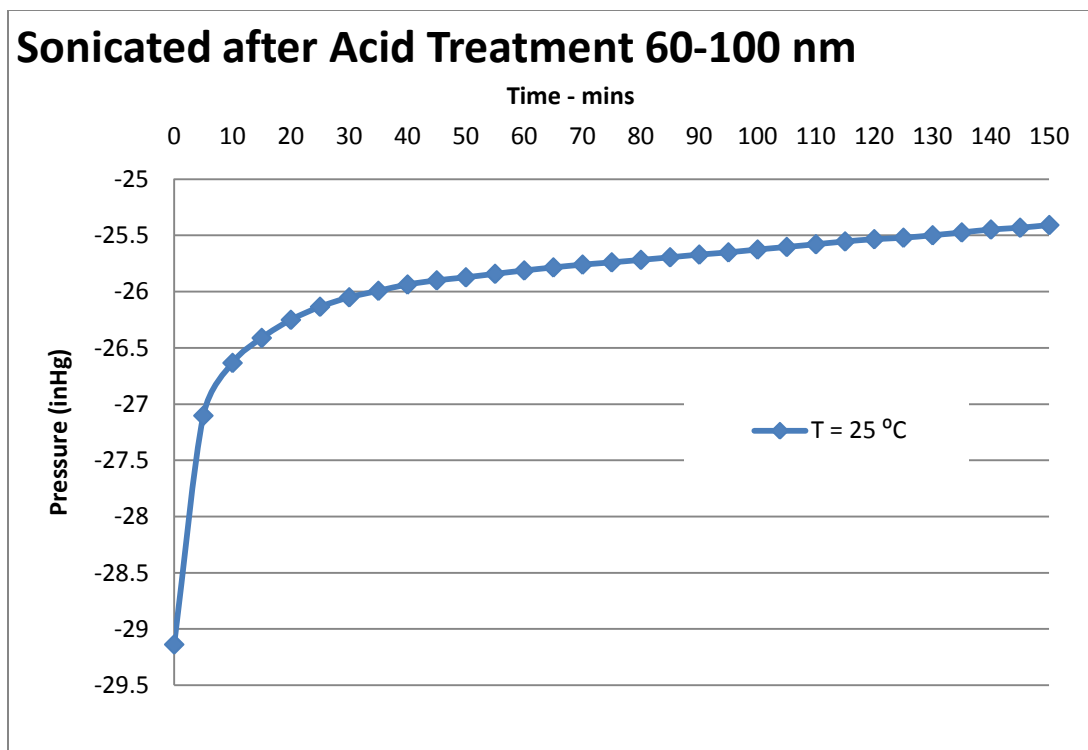
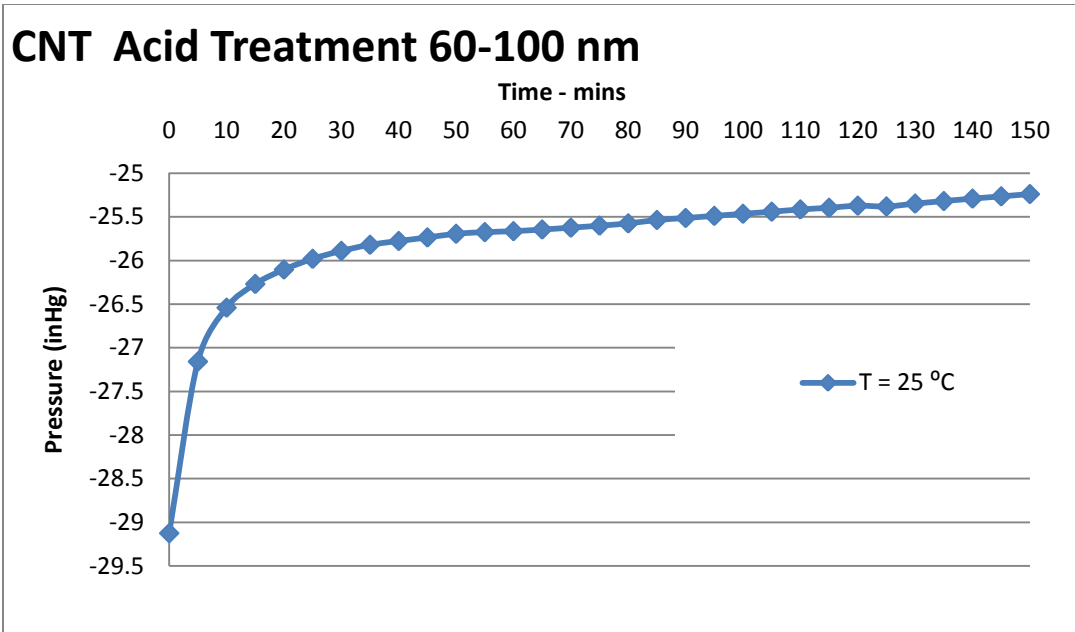
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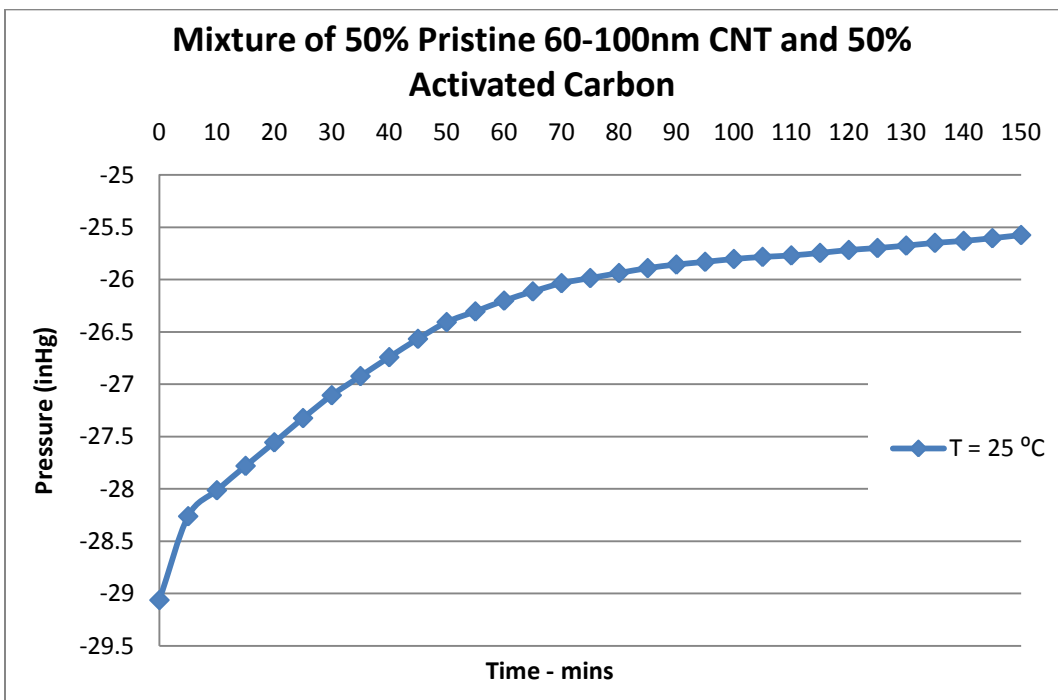
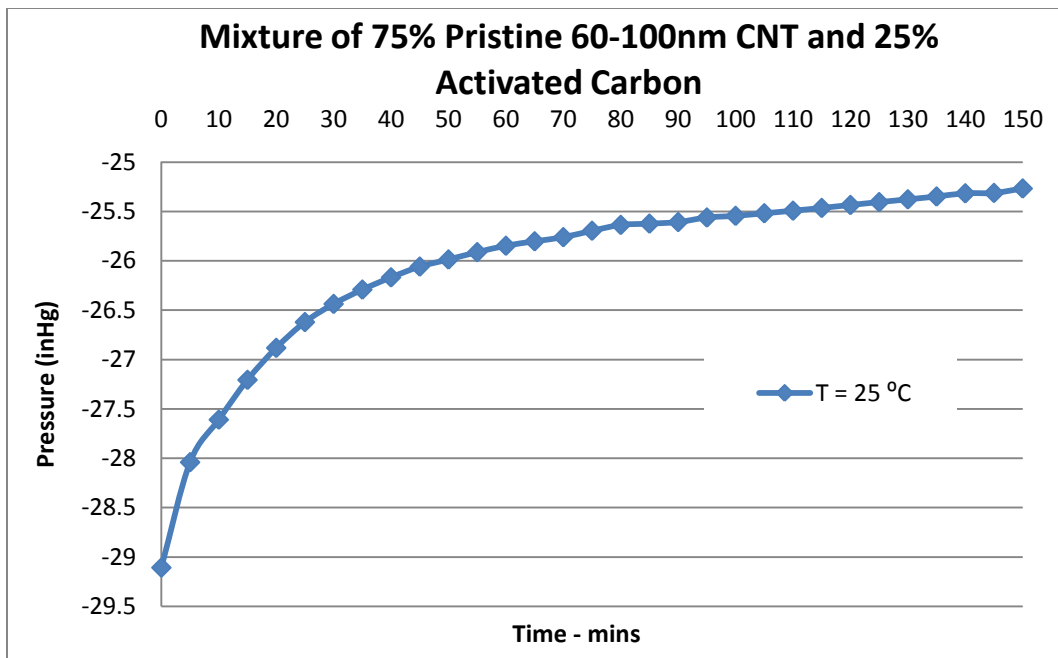


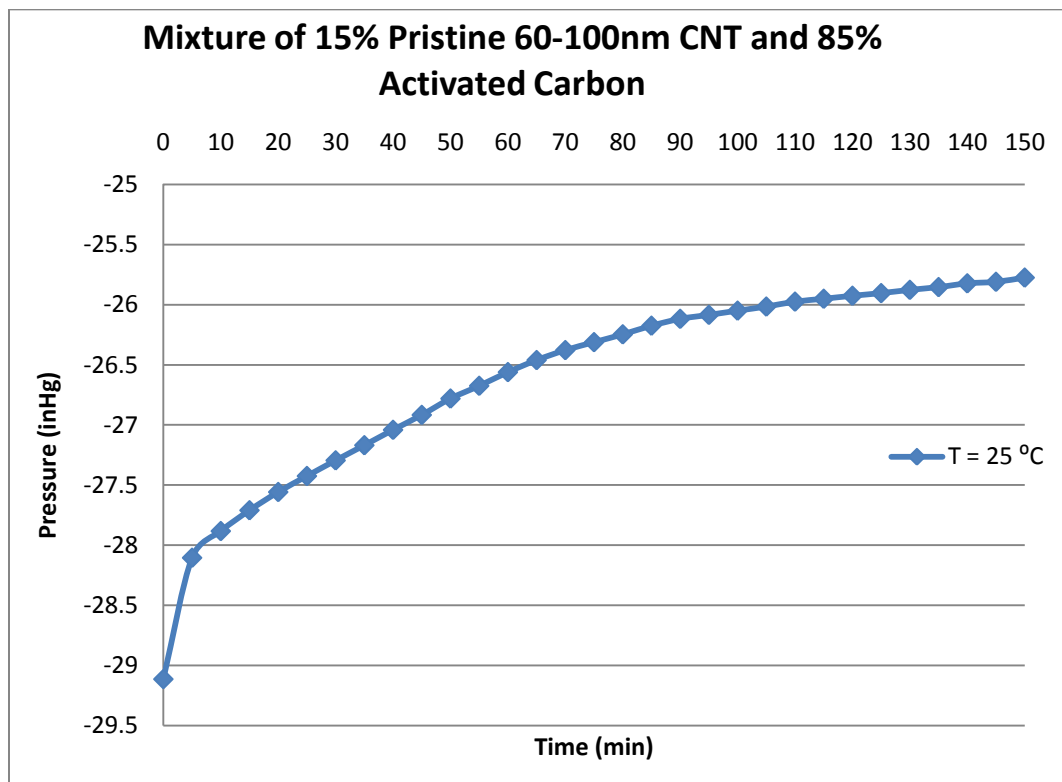
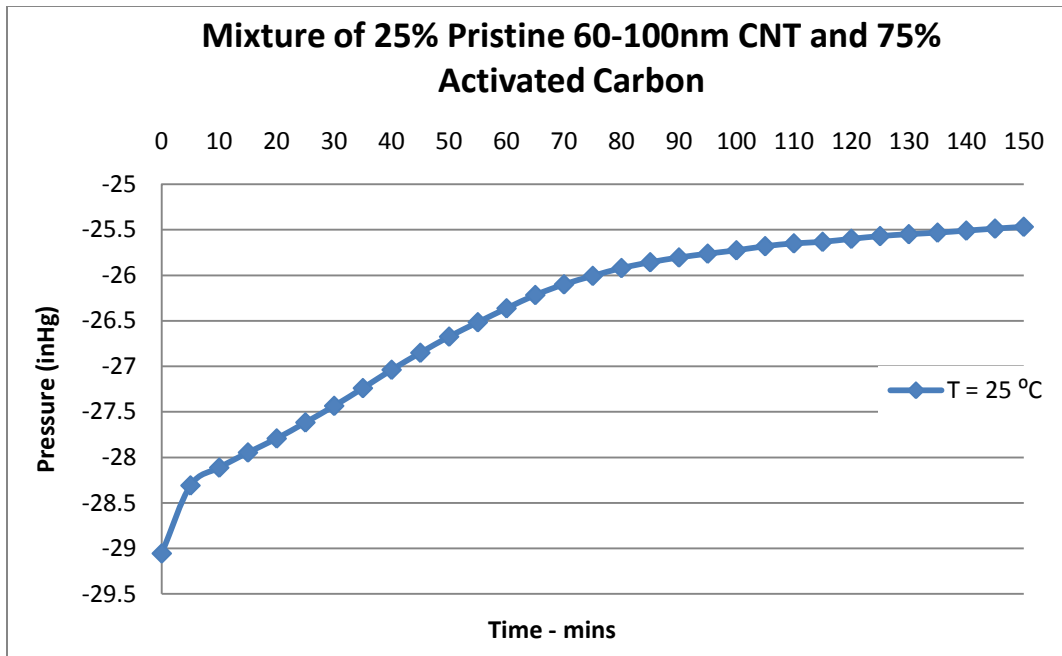
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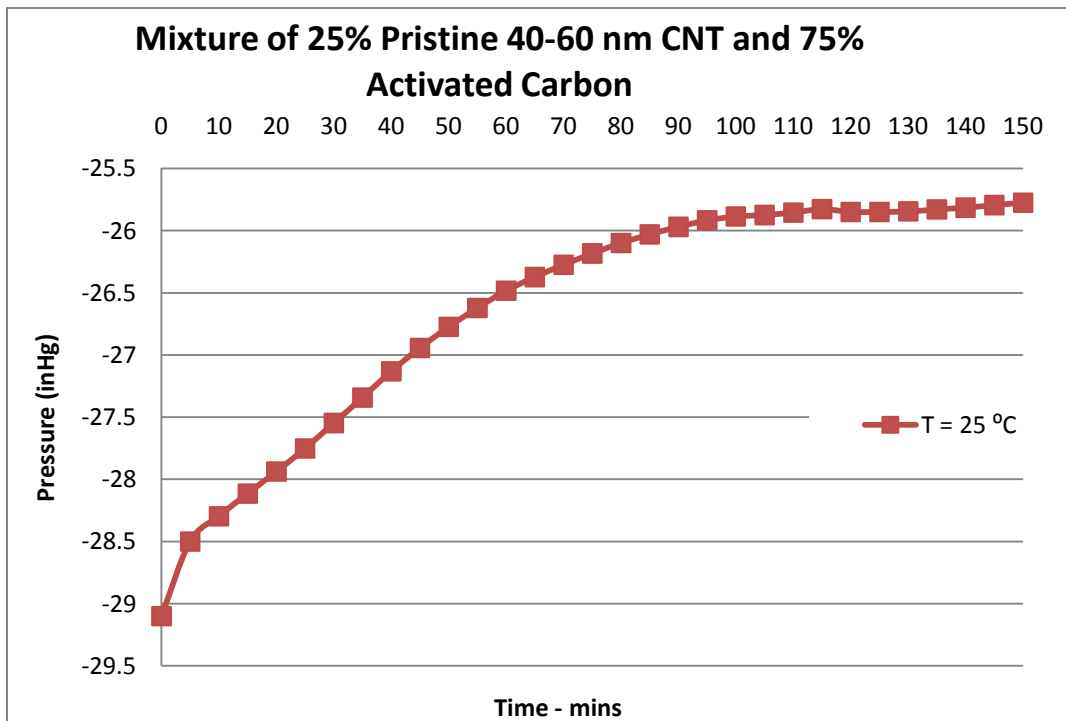
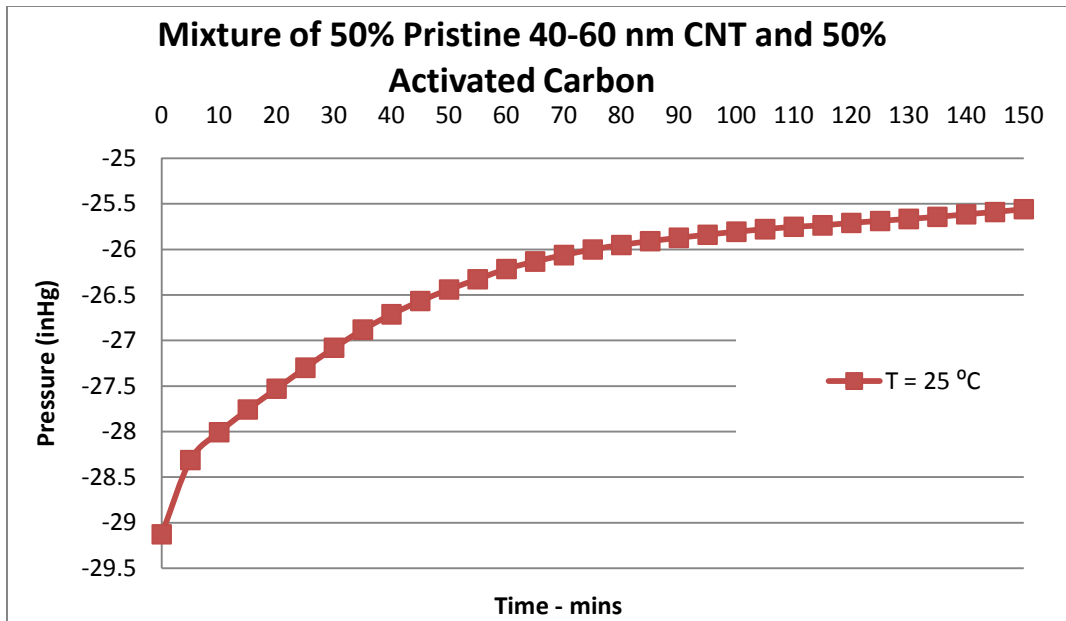


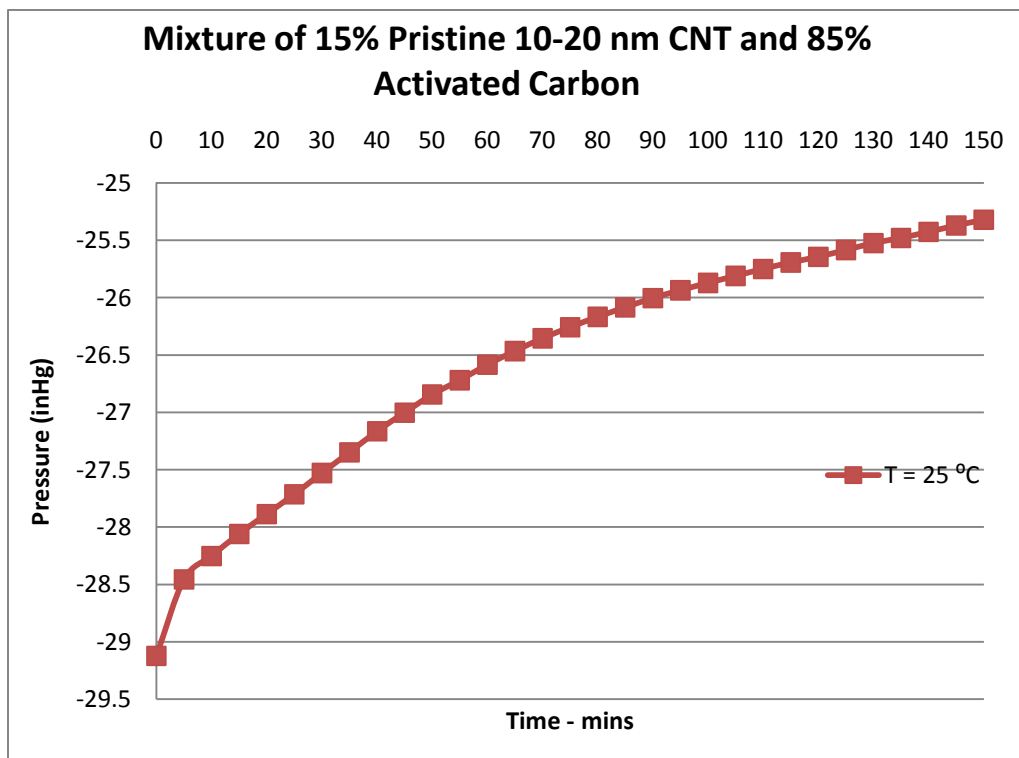
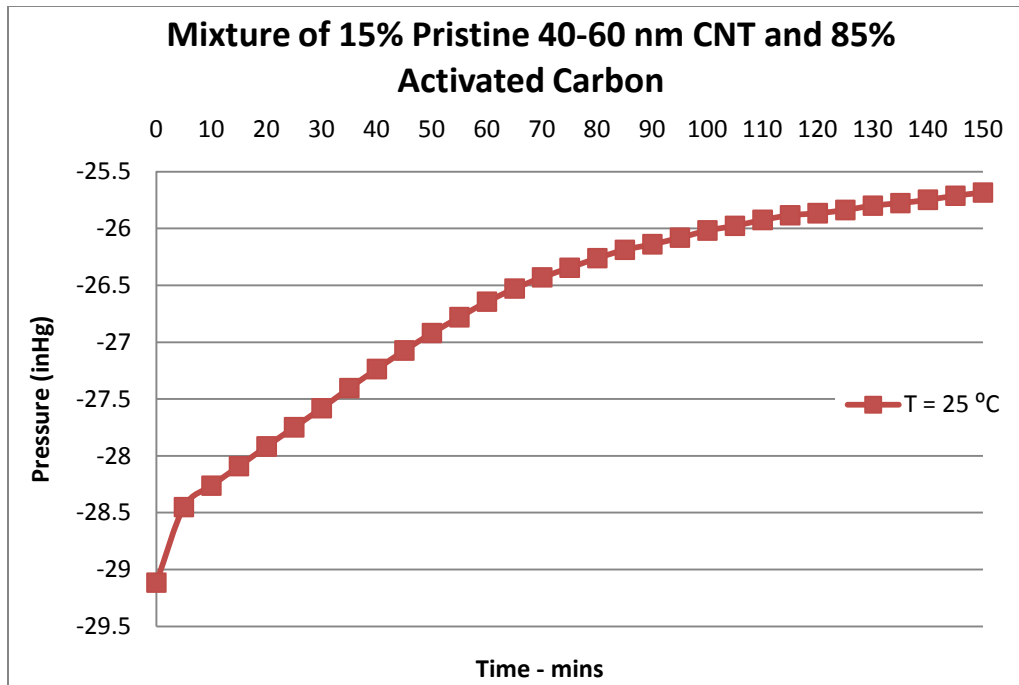


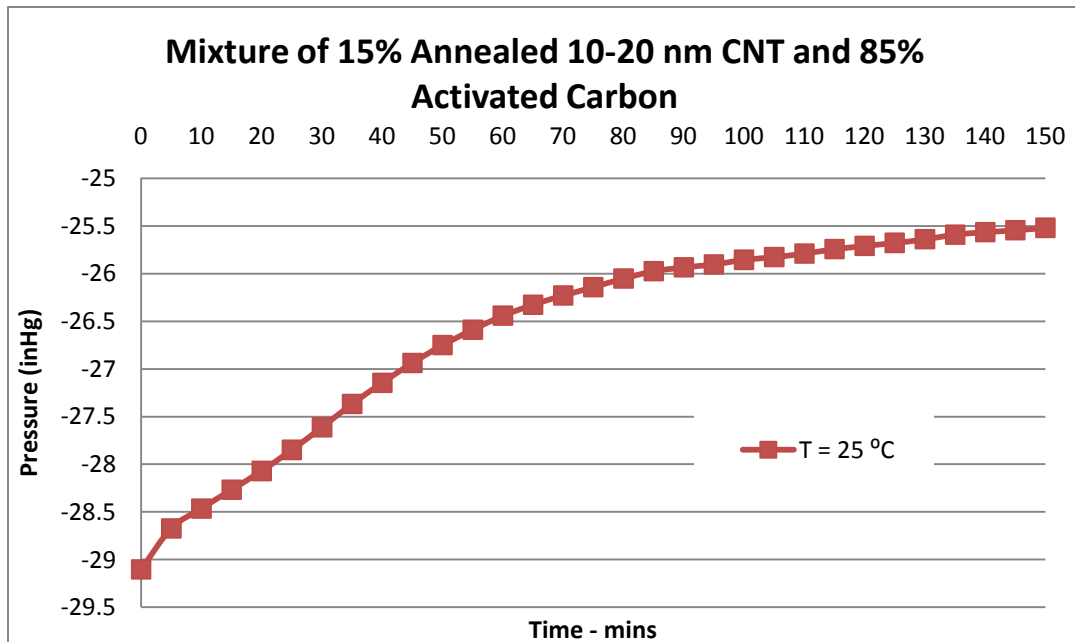
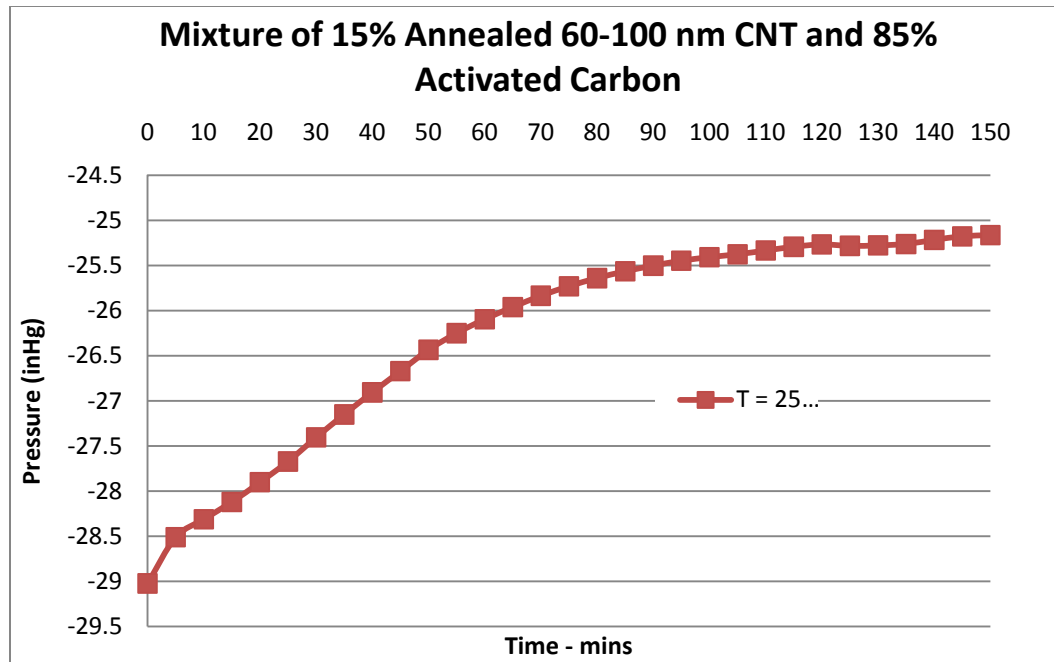


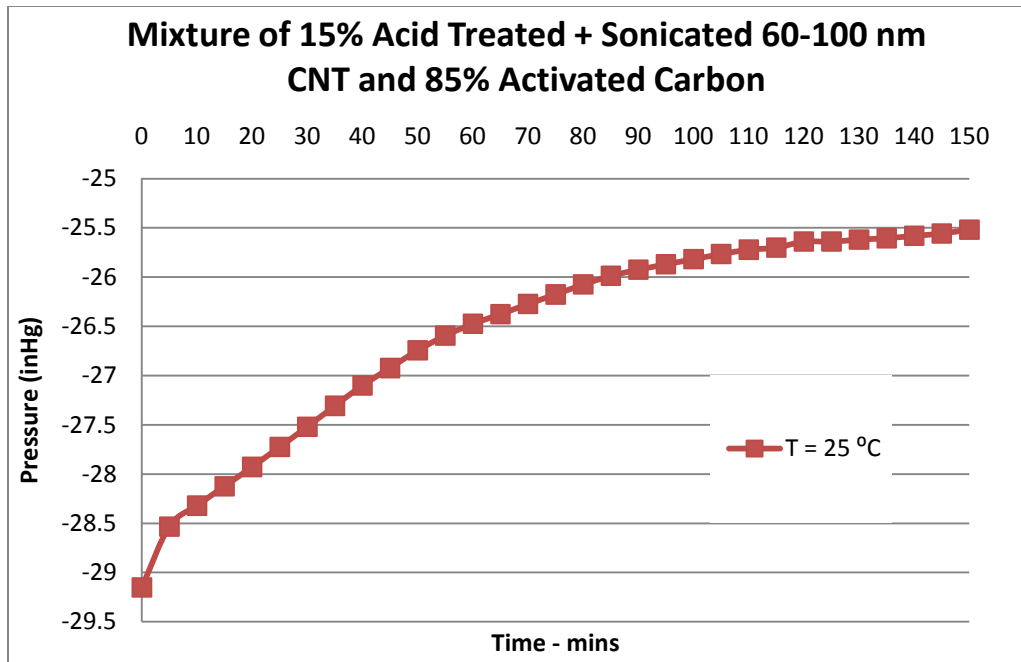












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