Functionalized CNF for H$_2$ adsorption study.

By

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of the requirements of the final year project guidelines.**

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CERTIFICATION OF APPROVAL

Functionalization of Carbon Nanofiber's
for Hydrogen Adsorption Study

By

THINESH NAIDU A/L BALAMORGAN

A project dissertation submitted to the

Chemical Engineering Programme

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BACHELOR OF ENGINEERING (Hons)

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Approved by

_____

(Dr. Suriati binti Sufian)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH , PERAK

SEPTEMBER 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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(THINESH NAIDU A/L BALAMORGAN)

ABSTRACT

The hydrogen is a clean source of fuel which when combusted under the presence of oxygen , it produces water vapour as the only exhaust gas. Besides that , the chemical energy density of hydrogen is about 142Mj/kg which is at least three times larger than that of other chemical fuels. Hence , in search of green alternative to replace gasoline , hydrogen has been proposed as ideal source of energy. However , the hydrogen volume is about 3000 times higher than that of gasoline at room temperature and atmosphere because it's a molecular gas. Thus , the storage of hydrogen is the main drawbacks for further improvement of hydrogen technology. Therefore , on board hydrogen energy storage need compact , light , safe and affordable containment and the US Department of Energy states to achieve a 6.5% storage capacity. Hydrogen storage in functionalized carbon nanomaterial's is a very attractive field since high gravimetric storage capacities maybe possible owing the low specific weight and high specific surface area to volume ratio and by functionalization ,it can be modified to increases certain functional groups which has the ability to attract and store hydrogen.

The project is focusing on the study of hydrogen adsorption using carbon nanofibers which are functionalized using distilled water (H_2O) and nitric acid (HNO_3) and to compare the adsorption capacity as well as to characterize it using specific equipment to obtain sufficient data pertaining to it. In addition to it , surface characterization will also be investigated using SEM and EDS to obtain a general overview of the effect of the functionalization to the surface of the carbon nanofibers.

ACKNOWLEDGEMENT

In completion of this final year project, I would like to thank Universiti Teknologi PETRONAS for providing me with the opportunity to conduct this study. I would also like to express my gratitude to my supervisor, Dr Suriati binti Sufian for her unconditional guide and support throughout the project. I am also grateful to Dr Abdus Salam for the knowledge he shared with me on conducting experiment related to this project area. Not forgetting, special thanks to lab technicians and past final year project student Amanina for their co-operation that helped me to conduct my experiment smoothly. Finally, I would like to thank my parents Mr.Balamorgan and Ms.Santharani for their continuous support and encouragement which driven me to complete this project successfully.

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NOMENCLATURE

I. HNO_3 : Nitric Acid

II.   CNF : Carbon Nanofiber

III. H_2O : Water

IV.   SEM : Scanning Electron Microscopy

V.   FTIR : Fourier Transform Infrared Spectroscopy

VI.   CNT : Carbon Nanotube

VII. HNO_3 CNF : Nitric acid functionalized carbon nanofiber

VIII. H_2O CNF : Water functionalized carbon nanofiber

CHAPTER 1
INTRODUCTION

1.1   Project Background

The consumption of fossil fuels has ever been increasing , this increase in the consumption leads to the increase in threats from global warming. Therefore, our planet needs to come up with new way to harness the inexhaustible source of energy . Hence, according to many researchers , hydrogen holds tremendous promise as a new renewable and clean energy option. Besides that , hydrogen is a convenient , safe and versatile fuel that can easily be converted to a desired form of energy without any harmful emission. However , an efficient and safe storage of hydrogen is crucial to ensure its feasibility. Common hydrogen storage technique such as , use of pressurized tank is not safe and feasible. Thus , functionalized carbon nanofibers (CNFs) provides an alternative way to store this hydrogen with much safer way and with the right modification , it pose great future .

1.2   Problem Statement

Adsorption of hydrogen is process by which the storage of hydrogen takes place. In conjunction with that , the specific surface area is very important as it affects the storage efficiency. Hence, nanostructured or porous carbon materials have received continuous interests as a potential hydrogen storage medium for their physisorption property. These property is all made possible due to their low atomic mass , relatively high chemical stability and tunable pore structure. United States'Department of Energy (DOE) has set a target of 6.5 % , much research has been done to enhance the ability of CNFs to store hydrogen. These hydrogen storage capacities are far from the target of 6 wt.% established by United States'Department of Energy (DOE). Thus , an alternative method is crucial to be developed. In another article , it states that the rapid surge in new synthetic nanomaterials demands complementary advancement in surface characterization techniques and modification methods in order to understand and utilize these materials.

1.3   Objectives

I.   To investigate on the ability to produce greenly functionalized CNFs by using distilled water.
II.   To perform surface characterization of the functionalized carbon nanofibers.

III.   To study the hydrogen uptake capacity on the greenly functionalized CNF using fixed bed reactor hydrogen adsorption and compare it with HNO_3 functionalized CNF.

1.4   Scope of Study

Throughout the research , the scope of study that will be focused on is as the following :

I.   Functionalization of CNF using distilled water as to produce a greenly functionalized CNF.
II.   The functionalized CNF and raw CNF were sent for Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) characterization.
III.   The functionalized CNF are sent for the final test to determine the hydrogen uptake capacity and make the comparison with the raw CNF.

CHAPTER 2
LITERATURE REVIEW

This chapter consists of literature review of various research and publication done on the subject of functionalization of carbon nanofibers and hydrogen adsorption. The literature review is divided into 3 sections and has been summarized as following :

1. Introduction and the basic understanding to carbon nanofibers and it's properties.
2. A basic theory and mathematics of hydrogen adsorption.
3. Past research on carbon nanofibers and its significance.

2.1 Understanding carbon nanofibers and its properties.

Carbon nanofibres (CNF) are high aspect ratio graphitic material that has been studied and done further research for it's numerous applications. This is due to the fact that that they posses a unique physical properties. The following are some of the physical properties possessed by CNF.

- High Strength

- Low Density
- Metallic Conductivity
- Tunable Morphology
- Chemical & Environment Stabilities
- Compatibility with Organochemical Modification

A study on the surface of such nanomaterials are extremely important as it's not only surface structurally and chemically different but its properties tends to dominate at the nanoscale level due to the drastically increased surface to volume ratio. . Hydrogen being abundant and providing clean energy has attracted many interest and attraction around the world in recent years. Hence, a crucial aspect is to identify a method which can store hydrogen safely and efficiently. The specific surface area is very important as it affects the storage efficiency. Hence, nanostructured or porous carbon materials have received continuous interests as a potential hydrogen storage medium for their physisorption property. These property is all made possible due to their low atomic mass , relatively high chemical stability and tunable pore structure.

2.2 A basic theory and mathematics of hydrogen adsorption

Adsorption Isotherm of Hydrogen Adsorption

Consider the adsorption of a non-reacting gas onto the surface of a catalyst. Adsorption data are frequently reported in the form of adsorption *isotherms*. Isotherms portray the amount of a gas adsorbed on a solid at different pressures but at one temperature. An example of adsorption isotherm is depicted in the figure below. It is based on the classic study of Ward who adsorbed hydrogen on powdered copper at 25°C .
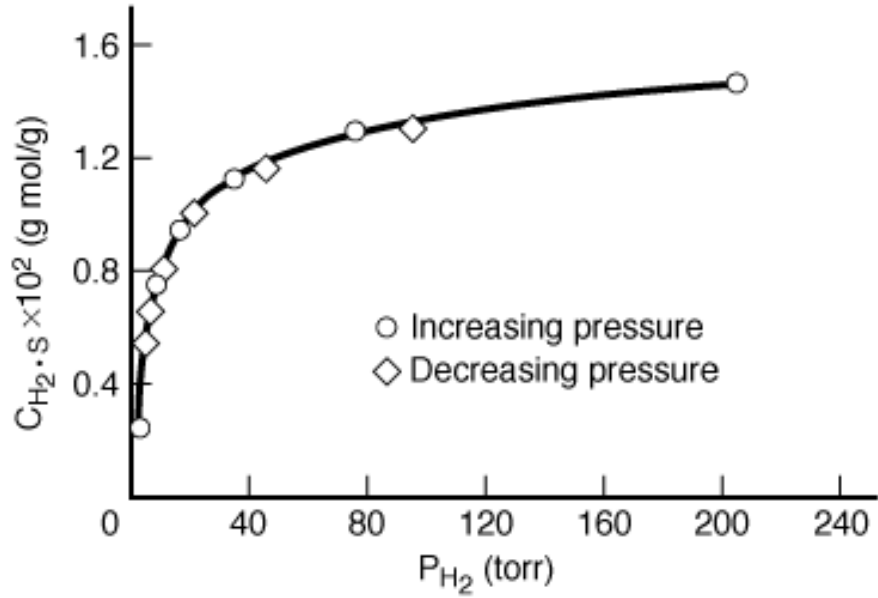
Figure 1 : Adsorption Isotherm for Hydrogen Gas

TABLE R10.1-1
Adsorption of H_2 on Cu Powder at 25°C

Increasing Pressure, P_{H_2} (torr)[a]	$C_{H_2 \cdot s} \times 10^2$ (g mol/ g Cu)	Decreasing Pressure, P_{H_2} (torr)[a]	$C_{H_2 \cdot s} \times 10^2$ (g mol/ g Cu)
3.25	0.559	45.1	1.160
8.90	0.761	21.5	0.995
17.65	0.941	10.65	0.800
36.2	1.212	5.40	0.659
74.5	1.281	2.95	0.564
204.8	1.471	1.70	0.464

[a] 1 torr = 1 mmHg = 0.133 kPa = 0.00132 atm.

Table 1 : Adsorption of Hydrogen on Copper Powder

First , a model system is proposed and then the isotherm obtained from the model is compared with the experimental data shown on the curve. If the curve predicted by the model agrees with the experimental data , the model may well describe what is happening physically in the real system.However, if the predicted curve does not agree with the experimental data , then the model fails to match the physical situation in at least one important characteristics and perhaps more. There

are two models that can be postulated , one is known as non-dissociated adsorption and the other is dissociative adsorption. The former mentioned adsorption is which hydrogen is adsorbed as molecules (H_2) , while the latter is whereby the hydrogen is adsorbed as atoms of hydrogen (H) instead of molecules. Whether a molecule adsorbs dissociatively or non-dissociatively depends on the metal surface.

Molecular adsorption

The adsorption of hydrogen molecules will be considered first. Since the hydrogen does not react further after being adsorbed, we need only to consider the adsorption process:

$$H_2 + S \rightleftharpoons H_2 \cdot S$$
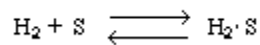
In obtaining a rate law for the rate of adsorption, the reaction in Equation (R10.1-1) can be treated as an *elementary reaction*. The rate of attachment of the hydrogen molecules to the surface is proportional to the number of collisions that these molecules make with the surface per second. In other words, a specific fraction of the molecules that strike the surface become adsorbed. The collision rate is, in turn, directly proportional to the hydrogen partial pressure, P_{H_2}. Because hydrogen molecules can adsorb only on vacant sites and not on sites already occupied by other hydrogen molecules, the rate of attachment is also directly proportional to the concentration of vacant sites, C_v. Combining these two facts means that the rate of attachment of hydrogen molecules to the surface is directly proportional to the product of the partial pressure of H and the concentration of vacant sites:

Adsorption

$$H_2 +$$

$$H_2$$

Desorption

$$H_2$$

$$+ H_2$$

13
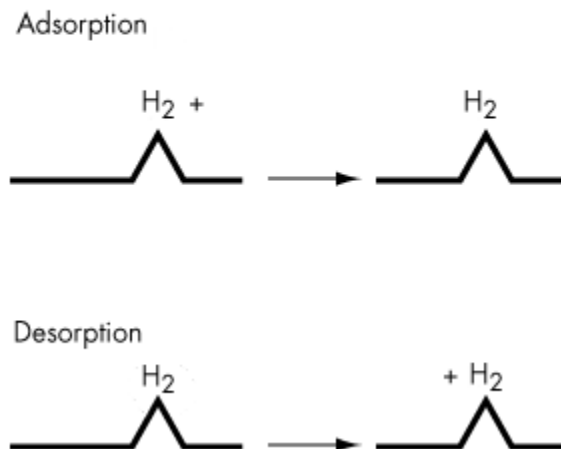
rate of attachment $k_{-A} P_{H_2} C_v$

The rate of detachment of molecules from the surface can be a first-order process; that is, the detachment of hydrogen molecules from the surface is usually directly proportional to the concentration of sites occupied by the molecules, $C_{H_2 \cdot s}$

rate of detachment $= k_{-A} C_{H_2 \cdot s}$

The net rate of adsorption is equal to the rate of molecular attachment to the surface minus the rate of detachment from the surface. If k_A and k_{-A} are the constants of proportionality for the attachment and detachment processes, then

$r_{AD} = k_A \, P_{H_2} C_v - k_{-A} \, C_{H_2 \cdot s}$; the ratio of $K_A = k_A / k_{-A}$ is the adsorption equilibrium constant

The parameters k_A, k_{-A}, and K_A are all functions of temperature, exhibiting an exponential temperature dependence. The forward and reverse specific reaction rates, k_A and k_{-A} increase with increasing temperature, while the adsorption equilibrium constant, K_A, decreases with increasing temperature. At a single temperature, in this case 25°C, they are, of course, constant in the absence of any catalyst deactivation.

Because hydrogen is the only material adsorbed on the catalyst, the site balance gives

$C_t = c_v + c_{H_2 \cdot s}$

The points plotted in Figure R10.1-1 were taken at equilibrium conditions. The experimental details present in the original work support this fact, and the absence of hysteresis confirms it. At equilibrium, the net rate of adsorption equals zero. Setting the right-hand side of Equation (R10.1-3) equal to zero and solving for the concentration of H$_2$ adsorbed on the surface, we get

$C_{H_2 \cdot s} = K_A C_v P_{H_2}$

Using the previous equation and rearranging gives us ;

$C_{H_2 \cdot s} = \dfrac{K_A P_{H_2} C_t}{1 + K_A P_{H_2}}$

This equation thus gives $C_{H_2 \cdot S}$ as a function of the partial pressure of hydrogen, and so is an equation for the adsorption isotherm. This particular type of isotherm equation is called a *Langmuir isotherm*.

However , for a dissociative molecular adsorption , the adsorption isotherm is a little complex, and thus the isotherm is as follows

$$C_{H_2S} = \frac{(K_A P_{co})^{1/2} C_t}{1 + 2(K_A P_{c0})^{1/2}}$$

2.3   Past Research On Hydrogen Adsorption Using Carbon Nanomaterials.

Various studies has been carried out by many researchers with respect to carbon adsorption. In 1997 , a study by Dillon et. al. showed that the single-walled nanotubes (SWNTs) could store hydrogen at ambient temperature. This has led with further study on hydrogen storage capacity of various carbon nanostructures such as (SWNTs) , multi-walled nanostructures (MWNTs), graphite nanofibers (GNFs) and activated carbons (ACs). To meet the ever increasing demand for hydrogen storage , much effort has been made to explore new materials with rich porosity . Hence , a new carbon material has been studied which is graphene. Graphene is composed of a monolayer of carbon atoms packed into dense honeycomb crystals structure. This structure is so unique to the extend that it posses inherent high surface area (~2630 m2g−1) , sufficient porosity , superior conductivity , broad potential window and rich surface chemistry . As a result, graphene has been attracting alot of attention for hydrogen storage recently. Srinivas et al. reported that hydrogen storage capacity of graphene sheets (GS)synthesized by the reduction of a colloidal suspension of exfoliated graphite oxide (GO) was about 1.2 wt.% and 0.1 wt.% at pressures of up to 10 bar under the temperatures of 77 K and 298 K, respectively. Ghosh et al. investigated that high hydrogen uptake on GS obtained by thermal exfoliation was 2.0–3.1 wt.% at 100 bar,298 K. Cheng et al. showed that 0.4 wt.% and ~0.2 wt.% hydrogen

uptake were obtained at 77 K under 1 bar and room temperature under 60 bar, respectively. These hydrogen storage capacities are far from the target of 6.5 wt.% mass ratio established by United States'Department of Energy (DOE). Thus , an alternative method is crucial to be developed in the preparation of single or few layered graphene samples.

In another article , it states that he rapid surge in new synthetic nanomaterials demands complementary advancement in surface characterization techniques and modification methods in order to understand and utilize these materials. The surface properties often deviates substantially from the bulk material properties due to a difference in physical and chemical structure. The surface of a nano structure holds a unique significance due to their enhanced roles in determining functional characteristics which becomes more significant as the surface to volume ratio increases. Among the different types of nanomaterials , a carbon nanostructures holds a special importance due to their mechanical strength and chemical stability. In its simplest form, such a hexagonal network terminated by hydrogen atoms is represented by a graphene sheet, [Figure 1(a)], a carbon nanotube (CNT), more specifically a single-walled carbon nanotube (SWCNT), can then be considered as a graphene sheet rolled into a cylinder, where multiple concentric sheets create a multiwalled carbon nanotube [MWCNT, Fig. 1(b)]. The introduction of five and seven member rings into the graphene allows the formation of curved structures such as "buckyballs" and nanocones. Carbon nanofibers (CNFs) are a class of these materials that have curved graphene layers or nanocones stacked to form a quasi-one-dimensional filament, whose internal structure can be characterized by the angle α between the graphene layers and the fiber axis [Fig. 1(c)]. One common distinction noted in the literature is between the two main fiber types: "herringbone" [Fig. 1(d)], with dense conical graphene layers and large α , and "bamboo" [Fig. 1(e)], with cylindrical cuplike graphene layers and small α , which is more similar to a MWCNT. However, in the case of a true CNT α is zero.
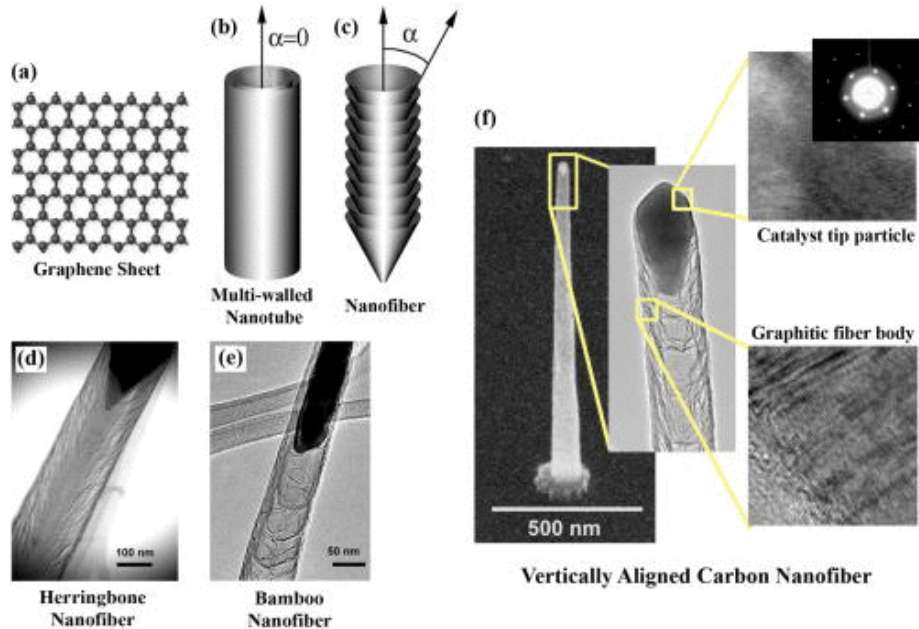
Figure 2 : Schematic of carbon nanostructures: (a) single sheet of graphite, (b) CNT consisting of concentric graphene sheets, and (c) CNF composed of stacked graphene cones at an angle alpha with respect to the axis of the fiber. The two primary CNF structures: (d) herringbone-type CNF and (e) bamboo-type CNF. (f) Representative VACNF composed of a Ni catalyst nanoparticle at the tip and a graphitic fiber body. [(a)–(e)]

A study done by Soo Jin Park and Seul Yi Lee with the title hydrogen storage behaviors of platinum supported multi walled carbon nanotubes (MWNTs) were studied. The microstructure of Pt/MWNTs was characterized using x-ray diffraction and transmission microscopy. The pore structures were experiment and studied by N_2/77 K adsorption isotherms. Hence , the storage capacity was analyzed at 100 bar and 298 K. In the study , it shows that the amount of hydrogen storage increased in proportion to the Pt amount as the Pt is homogenously distributed. Moreover, another study was conducted by Ralph T.Yang , whereby interesting results were reported for using Lithium and Potassium doped carbon nanotubes . In the study , Li- and K- doped carbon nanotubes adsorbed 20 wt % and 14 wt % of hydrogen at 1atm and mild temperature of about $200^{o}C$ to $400^{o}C$ for Lithium and near room temperature for Potassium doped nanotubes.

CHAPTER 3
METHODOLOGY

3.1   Introduction

This chapter discuss about the methods by which the experiment has been performed and the procedure the carbon nanofibers has been functionalized . Hence , to prepare the functionalized carbon nanofibers, two important parameters were controlled , the time of contact , the temperature and the solvent. The two parameters are important in the ultrasonification part as it prepares the functionalized carbon nanofibers . Characterization and adsorption analysis of the functionalized CNFs using various equipmentswere analyzed to   obtain   the   necessary   data   and   information.

3.2   Flow Of The Experiment
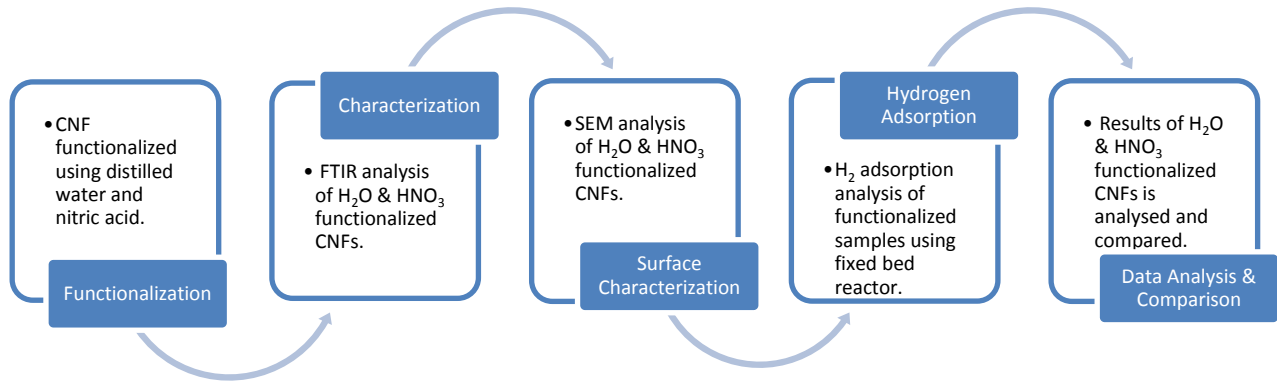
Flow of the experiment is shown below

- CNF functionalized using distilled water and nitric acid.

Functionalization

Characterization

- FTIR analysis of H_2O & HNO_3 functionalized CNFs.

- SEM analysis of H_2O & HNO_3 functionalized CNFs.

Surface Characterization

Hydrogen Adsorption

- H_2 adsorption analysis of functionalized samples using fixed bed reactor.

- Results of H_2O & HNO_3 functionalized CNFs is analysed and compared.

Data Analysis & Comparison

Figure 3 : Flow of methodology

3.3   Functionalization

- Parameters and levels used in functionalizing the carbon nanofibers are listed in the table 6 These parameter were based on the previous research studies ;

Parameters	Levels
Type of solvent	I. Distilled water (H_2O) II. Nitric Acid (HNO_3)
Time of Contact (h)	4
Reaction temperature (^oC)	25
Equipment	Ultrasonicator

Table 2 : Functionalization Parameters

Functionalization Method

The figure below show the flow of method in functionalizing the carbon nanofiber ;

For the H_2O functionalized CNF : 2 g of raw CNFs is placed inside a beaker and add 100 ml of distilled water.

For the HNO_3 functionalized CNF : 2 g of raw CNFs is placed inside a beaker and add 100 ml of HNO_3.

Stir the raw cnf with it's respective solvent (water and nitric acid) using a sonicator under the following parameters :
Temperature : 25 ^oC
Duration : 4 hours

Once the sample is stirred using the ultrasonicator , the excess solvent is removed using the solvent removal pump. The sample is then dried for 24 hours at 80 ^oC .
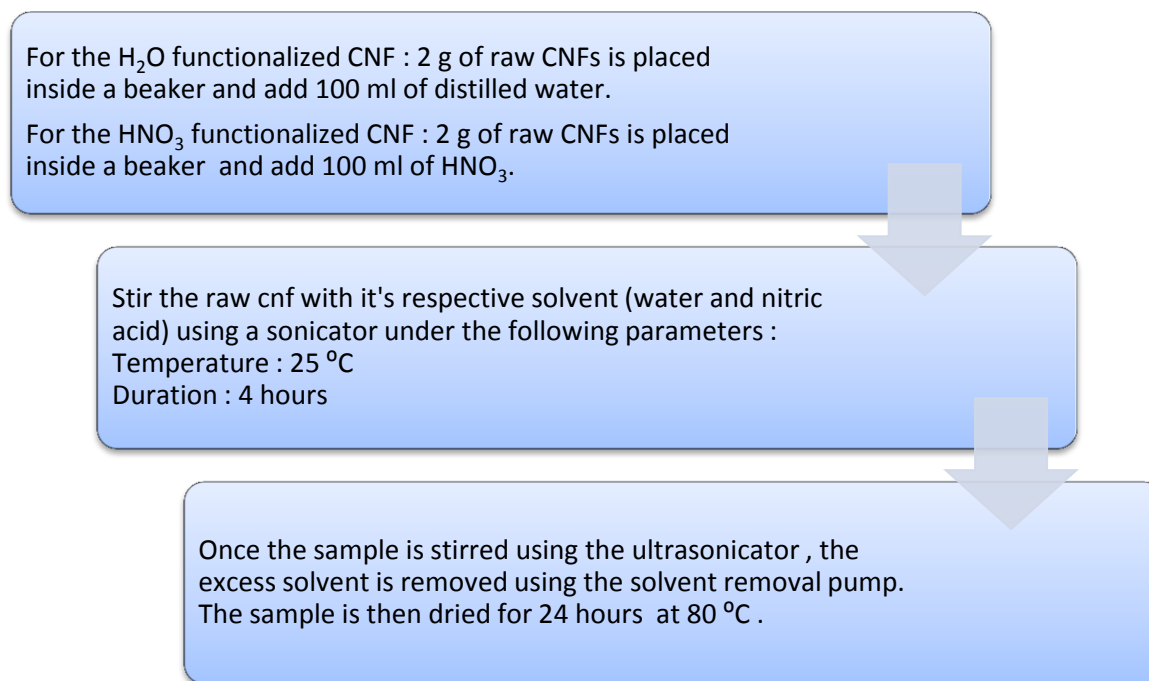
Figure 4 : Functionalization of carbon nanomaterial flow diagram

3.4   Characterization

There are two different characterization done and is listed below :

I.   Functional group characterization
II. Surface Characterization

I.   Functional group characterization was done using the Fourier Transform Infrared (FTIR) spectroscopy . The FTIR analysis identifies the chemical bonds in a molecule through the production of infrared spectrum for each component in a sample. This method is used to detect the functional groups on the functionalized CNF's surface and the transmittance amount for each functional groups present.

II. Surface characterization was done using Scanning Electron Microscopy (SEM) . The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS), crystalline structure.

3.5   Hydrogen Adsorption Study

- By referring to the previous research work as guidance (Salam , Sufian , Lwin & Muregesan , 2013) , the procedure for hydrogen adsorption using TPPCNF's experiment are as follows,

1. A sample of raw CNF , H_2O functionalized CNF and HNO_3 functionalized CNF is to be sent for hydrogen adsorption.

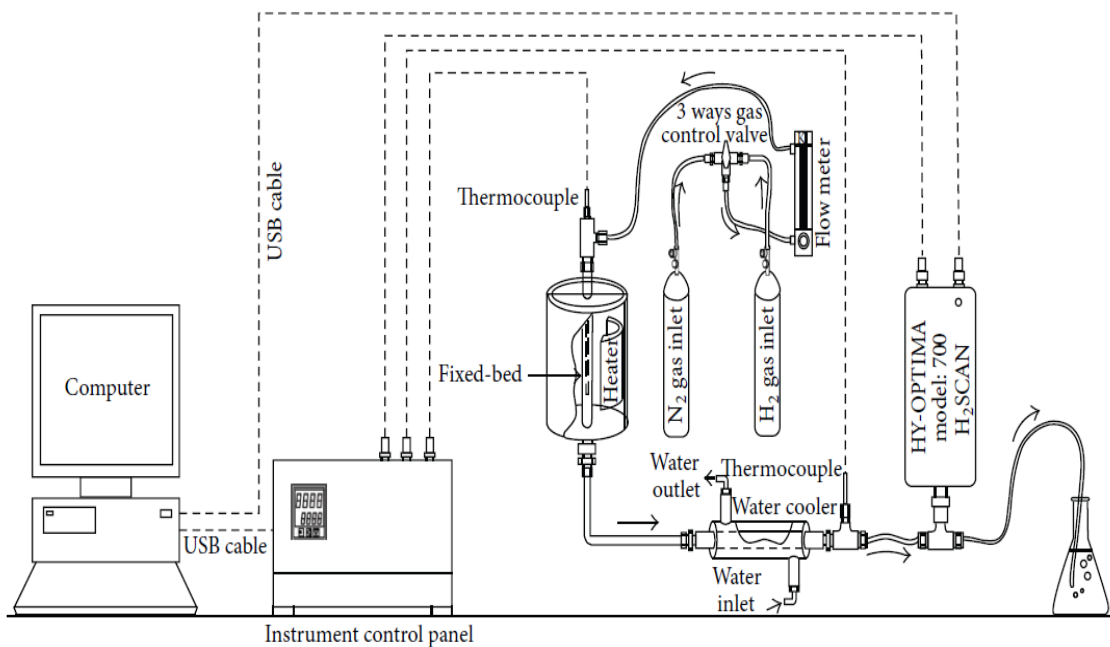2. For hydrogen capacity measurement, the full experimental setup is as shown in Figure 5.

Figure 5 : Diagram of Full Fixed Bed Setup
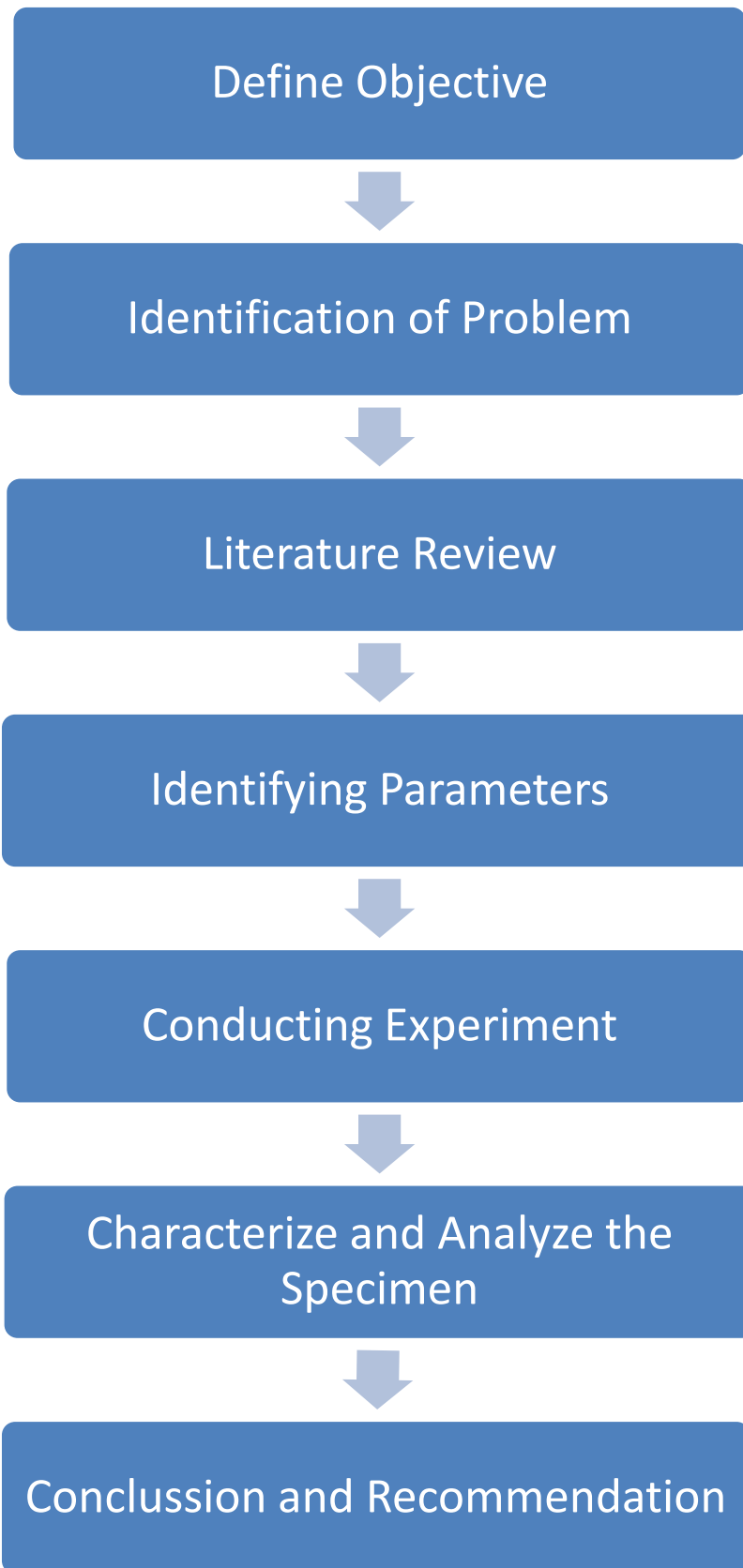*(Salam et. Al , 2013)*

The system is first to be calibrated without including the samples into the bed. Next, purified nitrogen will be used to evacuate any remaining gas in the bed. The bed is then to be kept until it reaches room temperature. The three samples will then be placed on the bed. After that, the

required amount of hydrogen gas and nitrogen gas will be exposed to fixed bed to conduct H_2 adsorption on the raw CNFs and the functionalized CNFs. The data acquisition of the gas concentration will be measured via RS232 converter using a hyperterminal of the Windows XP program.

3. The data collected will be tabulated and analyzed.

4. A comparison study of results with relevant literature reviews will be done for discussion and conclusion .

3.6 Project Activities

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┌─────────────────────────────────┐
│         Define Objective         │
└─────────────────────────────────┘
                 ↓
┌─────────────────────────────────┐
│     Identification of Problem     │
└─────────────────────────────────┘
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┌─────────────────────────────────┐
│         Literature Review         │
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│       Identifying Parameters      │
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│       Conducting Experiment       │
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│   Characterize and Analyze the    │
│            Specimen               │
└─────────────────────────────────┘
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┌─────────────────────────────────┐
│   Conclussion and Recommendation  │
└─────────────────────────────────┘
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Gant Chart and Key Milestones

Timelines for FYP 2

No.	Detail/ Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Project Work Continues	███	███	███	███	███	███	███								
2	Submission of Progress Report							●								
3	Project Work Continues								███	███	███	███	███			
4	Pre-SEDEX										●					
5	Submission of Draft Final Report											●				
6	Submission of Dissertation (soft bound)												●			
7	Submission of Technical Paper												●			
8	Viva													●		
9	Submission of Project Dissertation (Hard Bound)															●

● Suggested milestone

███ Process

25

CHAPTER 4

RESULT AND DISCUSSION

3.1 CHARACTERIZATION OF FUNCTIONALIZED CARBON NANOFIBERS

3.1.1 Fourier Transform Infrared Spectroscopy (FTIR)

Functional groups on the carbon surface can be identified by FTIR analysis. FTIR analysis were done in order to ensure that the functionalization of CNF's are successful. The presence and addition of new peaks with respect to the original results indicates the attachment of new functional groups on the surface of the functionalized CNF's. Interpretation of the FTIR results are based on the table of IR absorption frequencies. (Silverstein, Bassler & Morrill , 1981).

The raw CNF is used as a controlled standard so we can have a main reference od the unfunctionalized CNF's. The functionalized CNF's are compared to the raw CNF to identify the presence of new and significant peaks and its respective transmittance. The data of the FTIR spectra of raw and functionalized CNF's are represented in tabular form for easier comparison, the figure of the original FTIR spectra can be obtained from the appendices ;

Table 3 : FTIR transmittance data.

BOND	TRANSMITTANCE (%)		
	Raw CNF	H_2O-CNF	HNO_3-CNF
C-H (rock)	14.5	34.3	46.5
$C-O$ (stretch)	14.7	33.3	47.0
$O-H$ (bend)	12.3	31.4	45.3
$C-C$ (stretch)	10.1	31.8	46.0
C=O (stretch)	6.0	27.3	40.0
$C \equiv C$ (stretch)	3.4	30.1	37.3

Based on the table 3 above, it can be seen that there are no newly formed peaks on the functionalized CNF compared to its raw CNF. The available peaks on all three samples are the C-H bend at the wave number of 610-700 cm^{-1}. The presence of C-O stretch between the wavenumber of 1000-1320 cm^{-1} . Besides that , we have O-H stretch at the wavenumber 1400-1500 cm^{-1}. Then , we have the C=O stretch at around wavenumber 1630-1680 cm^{-1}. We also have C≡C at wavenumber 2090.4-2115.8 cm^{-1}.Finally , the hydroxyl functional group O-H is also present at wavenumber between 2500-3300 cm^{-1}. Hence , by looking at the

table , it is evident that the transmittance level of the functional groups present in each sample increases. Thus , for the water functionalized CNF , it is observed that , the transmittance level at least doubled compared to the raw CNF. The average transmittance level for the water functionalized CNF is approximately 31.35% with 10.16% of the raw CNF. Its about three times compared to raw CNF. However, the nitric acid functionalized CNF has the highest level of transmittance. It has an average 43.7 % transmittance level , higher than the water functionalized CNF. The importance of the transmittance level of each functional group can be seen for the hydrogen uptake capacity as it increases the adsorption active sites.

Transmittance (%)

HNO_3 Functionalized CNF

H_2O functionalized CNF
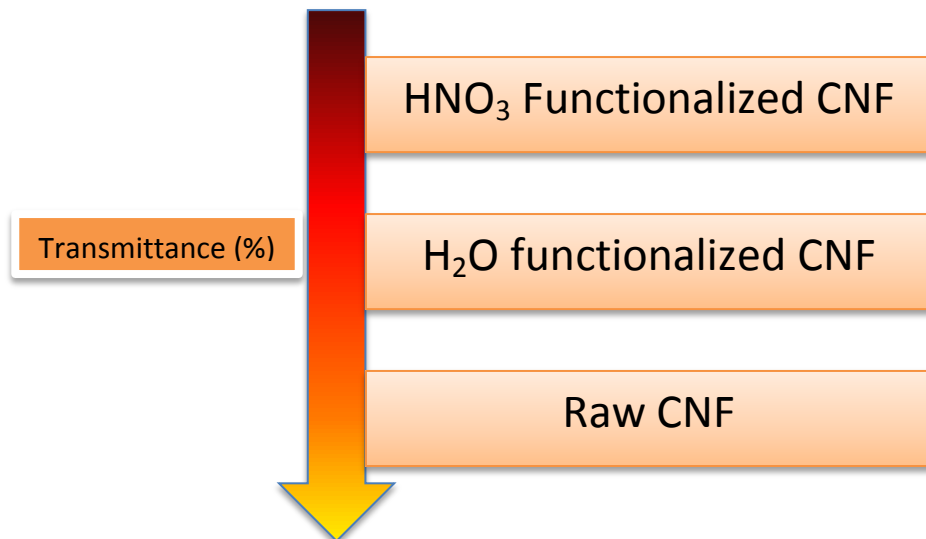
Raw CNF

3.1.2   Surface characterization using Scanning Electron Microscopy (SEM)

Figure 6 : SEM image of Raw CNF
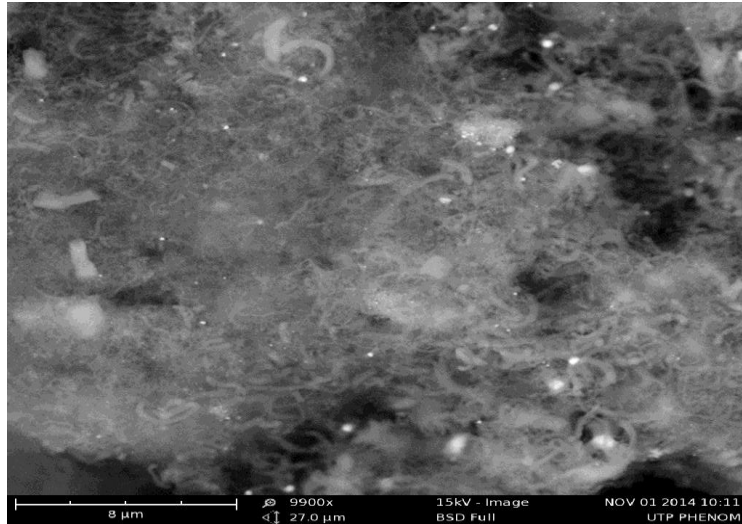
Figure 7 : SEM image of H$_2$O functionalized CNF
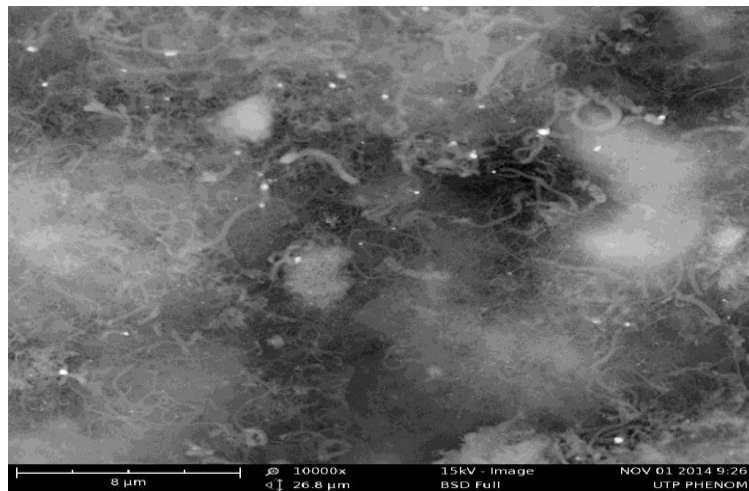
Figure 8: SEM image of HNO$_3$ Functionalized CNF
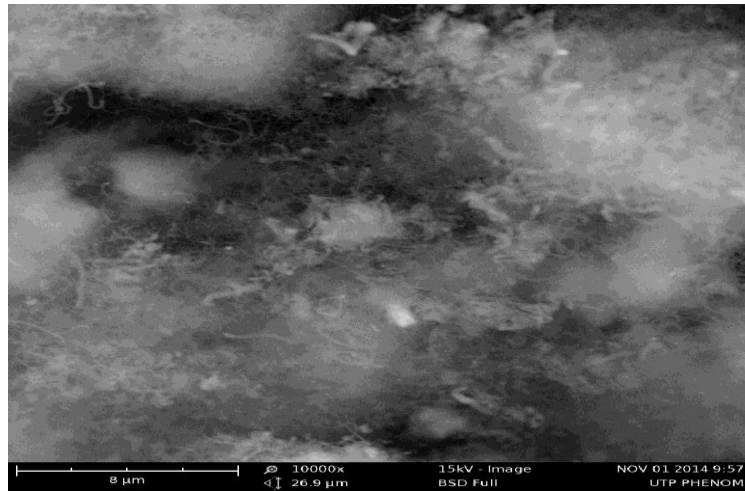
3.1.3   Hydrogen Adsorption Study

The hydrogen adsorption studies are currently done using the raw CNF and the two functionalized CNF's with the flow of 5% Hydrogen gas (balance: Nitrogen gas). After the hydrogen adsorption study is conducted, all the data are formed to breakthrough curve graphs. The pink region area on upper side of the breakthrough curve graph as shown in Figure 9 is the adsorbed amount of hydrogen.

Figure 9 : Breakthrough Curve
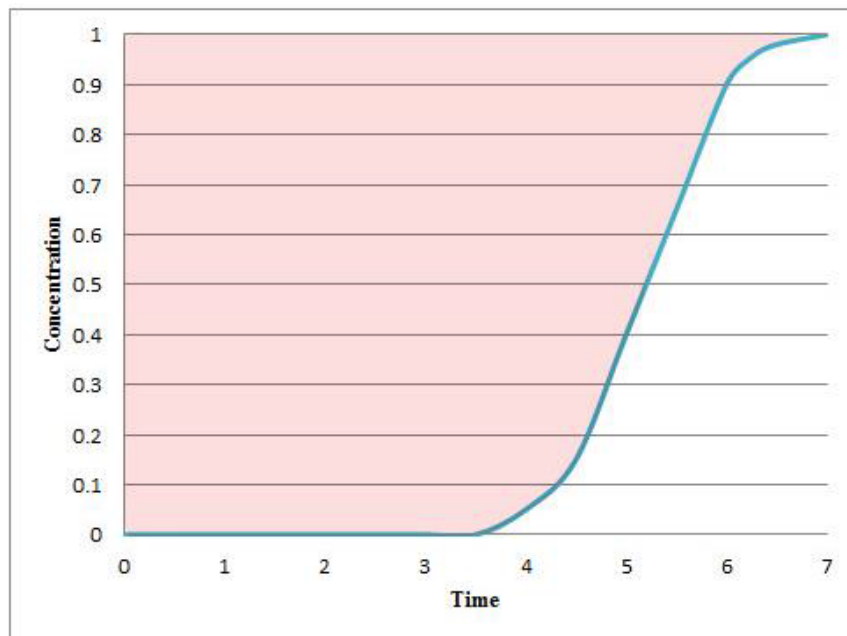
With the breakthrough curve, the capacity of the reactor for hydrogen adsorption can be calculated by using the following equation (Rodrigues, de Moraes Jr, da Nóbrega, & Barboza, 2007):

$$M_{ads} = \frac{Q_{t(MW)}}{\frac{RT}{P_A}} \left[\Delta t - \int_0^t \left(\frac{y}{y_o} \right) dt \right]$$ (1)

$$W = \frac{M_{ads}}{M_{bed}}$$ (2)

Whereby ,

t = total adsorption time
y = initial concentration
y_o = final concentration
M_{ads} = adsorbed mass
Q_t = gas flow
P_A = partial pressure of the inlet Hydrogen gas
M_{bed} = mass of bed = 0.5 g

The figure 10 below shows the first test run of hydrogen adsorption done on the first three samples

Hydrogen Breakthrough Curve for Functionalized CNF's (1)
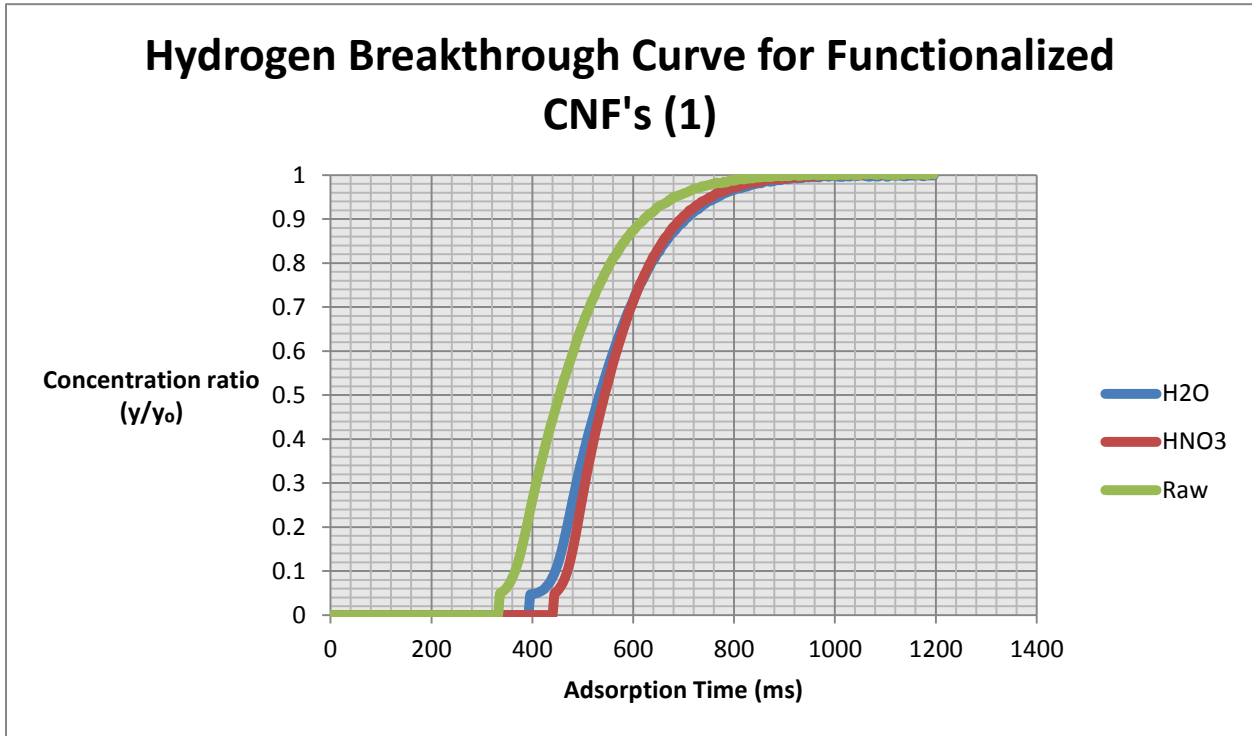
The figure 11 below shows the second test run done on the three samples.

Hydrogen Breakthrough Curve for Functionalized CNF's (2)
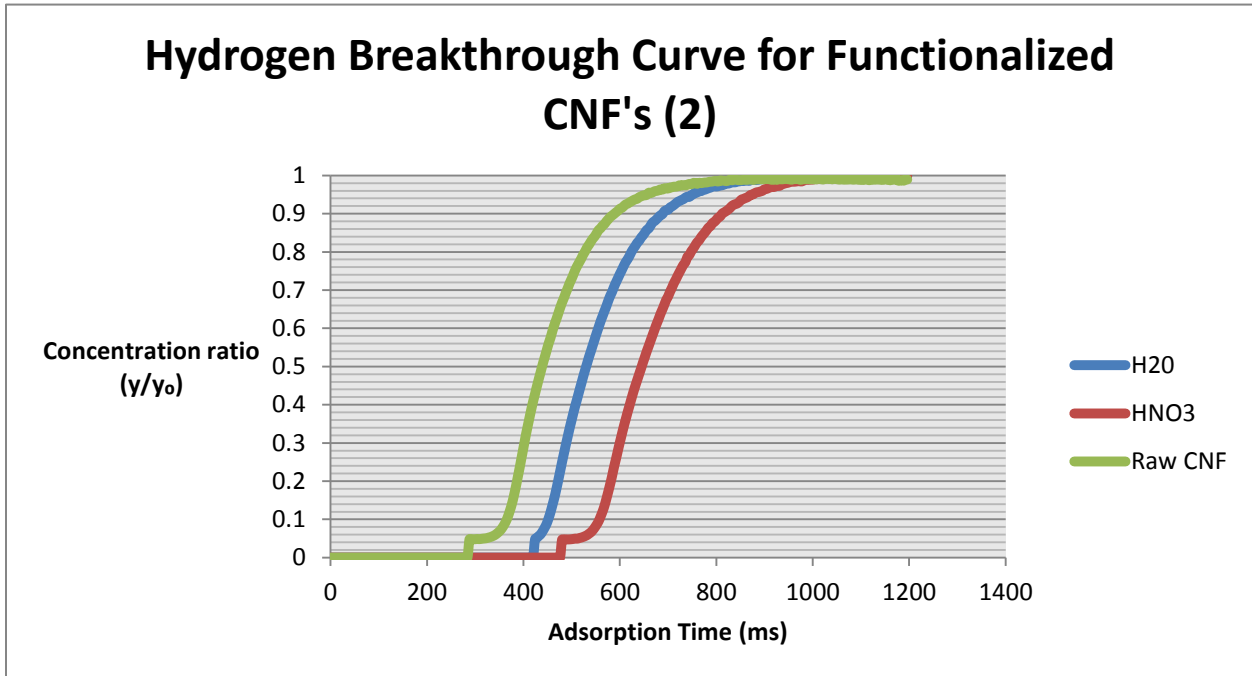
Using the equation proposed by Rodriques et. al. , the amount of hydrogen adsorbed is calculated. Hence , the table below shows it adsorbed amount and the weight percentage of adsorption.

Table 4 : Adsorption result for the 1st test run

Sample (Test Run 1)	Adsorbed Mass	Hydrogen Adsorption (wt%)
Raw CNF	0.4760	0.952
H_2O - CNF	0.5565	1.11
HNO_3 - CNF	0.5654	1.13

Table 5 : Adsorption result for the 2nd test run

Sample (Test Run 2)	Adsorbed Mass	Hydrogen Adsorption (wt%)
Raw CNF	0.4630	0.926
H_2O - CNF	0.5530	1.11
HNO_3 - CNF	0.6660	1.33

Table 6 : Average Hydrogen adsorption data

Sample (Average)	Adsorbed Mass (Average)	Hydrogen Adsorption (wt%)
Raw CNF	0.4695	0.939
H_2O - CNF	0.5548	1.11
HNO_3 - CNF	0.6157	1.23

As it can be observed at the table above, table 4 and 5 shows the hydrogen uptake capacity with the weight percentage of hydrogen adsorbed being tabulated in the last column. It is evident that the weight percentage increases with the raw CNF giving the lowest amount of hydrogen uptake of about 0.939 weight percentage and following with water functionalized CNF with an average of 1.11 weight percentage and then following with HNO_3 functionalized CNF which gives us an average of 1.23 weight percentage of hydrogen adsorbed. Hence, this increasing trend of weight percent signifies the amount of hydrogen being adsorbed in increasing. Thus , it can be justified that the adsorption amount does obey with the fourier transform infrared spectroscopy whereby as stated in the table 3 . It is evident that the increase in the transmittance level of the functional groups affects the hydrogen uptake capacity whereby the highest transmittance level

which is observed in HNO_3 functionalized CNF gives the highest amount of hydrogen adsorption followed by the H_2O functionalized CNF and then the raw CNF. Thus , this experiment shows that greenly functionalized CNF may have a lower adsorption capability but the most important fact is that it is proven to be possible to greenly functionalize the CNF by using only distilled water. Moreover , the greenly functionalized has its own advantages whereby water is much cheaper compared to most of the acids , it is safer to be used especially for experimentation purpose for a preliminary surface functionalization and last but the most evident fact that it does not pose any sort of environmental issues compared to acid functionalized CNF.

CHAPTER 5
CONCLUSSION AND RECOMMENDATION

This researched is aim to study the ability to greenly functionalize CNF by using water instead the more common organic acid and to study the ability of the greenly functionalized CNF to undergo hydrogen adsorption and measure it's uptake capacity.

For the first part of the research , the ability to greenly functionalized CNF's by using water is studied and the it compared with the nitric acid functionalized CNF as well as the raw CNF. The difference in the percentage level of transmittance of the functional groups obtained from FTIR analysis is analyzed and it proves that the functionalization procedures and parameters are correct and useful . It is evident that HNO_3 functionalized CNF possess the highest level of transmittance , followed by H_2O functionalized CNF and the lowest is evidently the raw CNF which is basically un-functionalized. Surface characterization was also done using SEM to understand and check if there is any morphological changes on the functionalized CNFs.

Hence, the sample of functionalized CNF is then used to study it's hydrogen uptake capacity using the fixed bed reactor . This is to analyze the ability of the greenly functionalized CNF to adsorb hydrogen gas. The breakthrough curve for all the samples were analyzed and proves that hydrogen adsorption on water functionalized CNF is possible whereby it adsorbs about 1.11 weight percent though slightly lower than acid functionalized CNF which has about 1.23 weight percent. As a conclusion , this research has been a success as all the objectives are fulfilled and it can be justified that greenly functionalized CNF can adsorb hydrogen though it's slightly lower than the acid based functionalization but it has its positive aspects whereby , water is much cheaper compared to acid and safer and of course it is more environmentally friendly.

The recommendation for this particular research would be as following :

   I.   To greenly functionalize carbon nanotube's (CNTs) instead of the CNF.
  II.   To vary the adsorption conditions such as lower temperature and higher pressure and analyzed the effect on hydrogen uptake capacity.

CHAPTER 6
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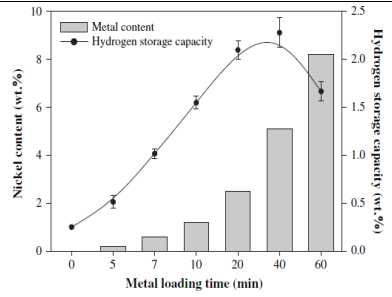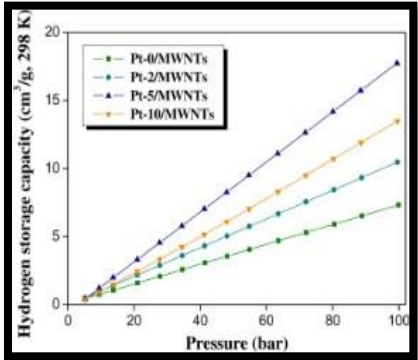
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Literature Review Table

No	Year	Author	Title	Materials for H$_2$ adsorption	Condition	H$_2$ Capacity	Method Used	Conclusion/ Remarks
1	1999	Ralph T. Yang	Hydrogen storage by alkali-doped carbon nanotubes – revisited	Li & K doped carbon nanotubes.	For Li-doped T : 200°C - 400°C P : 1atm pure H$_2$ For K-doped T : 25°C P : 1atm pure H$_2$	For Lithium doped CNT's Storage Capacity : 20 wt.% For Pottasium doped CNT's Storage Capacity : 14 wt.%	H$_2$ adsorption - desorption experiments were carried out with a Thermogravi-metric analyzer.	For Li-doped total weight differential was only 2.5%, rather than 20% For K-doped total weight differential, from 1.8% to 21%.
3	2003	Dan Lupu et. al.	Hydrogen uptake by carbon nano'bers catalyzed by palladium	Carbon Nanofiber of herringbone structure.	P : 10 MPa in pure hydrogen	P : 10MPa (constant) Increasing of the H uptake with the increasing Pd/C ratio	Evaporation of mixture of PdCl$_2$ & Lanthanum nitrate. Calcination in air @ 420°C Chemical vapor deposition technique(CVD)	At constant pressure , the H uptake increases with the increasing Pd/C ratio in the sample up to a saturation value of 1.5% of H$_2$.

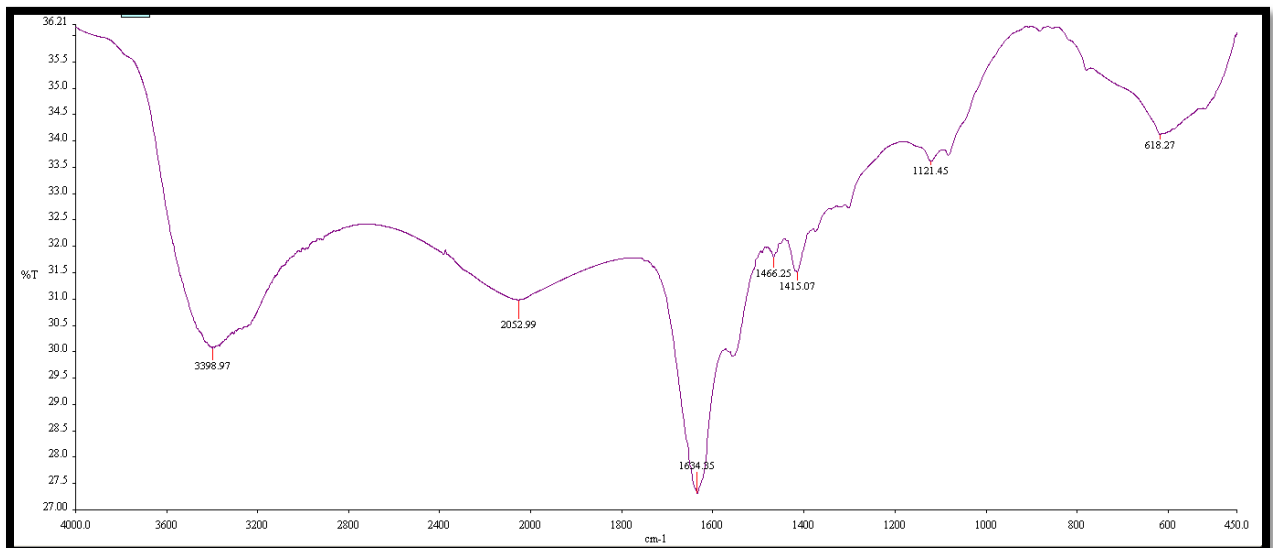| No	Year	Author	Study	Material	Conditions	Result	Method	Conclusion
4	2005	Marcello Marella & Michele Tomaselli	Synthesis of carbon nanofibers and measurements of hydrogen storage	Pd-doped graphite nanofibers	T : 450 ^oC P : 160 bar	After loading at 77 bar and T : Room Temperature Hydrogen storage of 1.38 ± 0.30 wt.%	Catalytic C_2H_4 decomposition for synthesis of CNF Impregnation by a known hydrogen "spillover" catalyst. ex : Pd	Carbon nanofibers do not seem a suitable candidate for hydrogen storage. For , Pd-doped nanofibers, hydrogen storage of 1.38 ±0.30 wt.% was measured at room temperature.
5	2007	Chao-Wei Huang, Hung-Chih Wu & Yuan-Yao Li	Hydrogen storage in platelet graphite nanofibers	Platelet graphite nanofibers (PGNFs)	T : 298 K P:4.83MPa	At Temperature 298 K & Pressure 4.83 MPa Storage Capacity : 3.3 wt %	Synthesized by thermal decomposition from a mixture containing PEG and $NiCl_2$ measured using volumetric method	PGNFs possess a 3.3 wt.% hydrogen storage capacity. High degree of graphitization and large numbers of open edges in PGNFs from the synthesis method.
6	2007	Byung-Joo Kim , Young-Seak Lee , Soo-Jin Park	A study on the hydrogen storage capacity of Ni-plated porous carbon nanofibers	Porous carbon-nanofiber-supported nickel nanoparticles	T: 298K P : 100 bar		Porous carbons were activated at 1050 ^oC, and the nickel nanoparticles were loaded by an electroless metal-plating method.	Amount of hydrogen stored was enhanced by increasing nickel content, showing 2.2 wt.% in the PCNF-Ni-40 sample The higher dispersion rate of transition metals can also enhance hydrogen uptake
7	2008	K.L Klien et al.	Surface characterization and functionalization of carbon nanofibers	-	-	-	-	An understanding on the type of carbon nanomaterials and its functionalization.
8	2009	Soo-Jin Park & Seul-Yi Lee	Hydrogen storage behaviors of platinum-supported multi-walled carbon nanotubes	Platinum supported multi walled carbon nanotubes (PtWNT)	T: 298 K P: 100bar		Chemical vapor deposition Impregnation using H_2Cl_6Pt	Hydrogen storage capacity of Pt/MWNTs increased as the Pt content increased to 3.72 wt% (Pt-5/MWNTs) and then decreased. Degree of dispersion and micropore is vital for H_2 storage.

#	Year	Author	Title	Material	Conditions	Results	Method	Conclusions
9	2010	Srinivas et al	Synthesis of graphene-like nanosheets and their hydrogen adsorption capacity	Graphene Nanosheets	T: 77 K – 298K P: up to 10bar At R.T & P=100bar	1.2wt% - 0.1wt% At R.T & P=100bar 0.72wt%	Reduction of GO using hydrazine hydrate at 80 °C followed by vacuum filtration and drying.	BET SA : 640m2/g 0.68 wt.% at 77 K and 1 bar is consistent with other carbon samples.
10	2010	Eva Dı́az, Marta Leó́n & Salvador Ordonez	Hydrogen adsorption on Pd-modified carbon nanofibres: Influence of CNF surface chemistry and impregnation procedure	Pd-modified carbon nanofibres	T: 303 K to 473 K at a heating rate of 5 K/min P : 12 MPa	(see Table 2 below)	Thermogravi-metric analyzer	Efficiency of CNF's in hydrogen storage can be optimized -adding oxygenated functional groups. -adding an active metal
11	2011	Saha & Deng	Hydrogen adsorption on Pd- and Ru- doped C60 fullrene at an ambient	1. Pd- C60 2. Ru- C60 3. Pristine C60	T= 25˚C P= 30 MPa	1. Pd- C60 Pd 2.81 2. Ru- C60 2.81 3. Pristine C60 1.35	Gravimetric method Rubotherm magnetic suspension balance	
12	2012	Aboutalebi et. al.	Enhanced hydrogen storage in graphene oxide-MWCNTs composite at room temperature	1. MWCNTs 2. GO 3. rGO-MWCNTs 4. GO-MWCNTs	T= 25˚C P= 5 MPa	1. MWCNTs 0.9 2. GO 1.4 3. rGO-MWCNTs 2.1 4. GO-MWCNTs 2.6		
13	2013	Salam et al.	Hydrogen Storage of a Fixed Bed of Nanocrystalline Mixed Oxides	Nanocrystalline hydrotalcite derived mixed oxides containing magnesium, cobalt, and aluminum (MCAM) $(M(1-x)Al x O(1+x/2)$	T= 25˚C P= 200 kPa	(see Capacity table below)	Fabricated Fixed bed reactor	
14	2006	James M.Blackman et. al.	Activation of carbon nanofiber for hydrogen storage	Carbon nanofibers	P=10MPa T=30 °C	(see activation table below)		This study has shown that an increase in BET surface area does not always result in an increase in the hydrogen sorption capacity of the CNF,

Table 2 – Hydrogen uptake at 0.1 MPa and 298 K of carbon nanofibres under study.

Material	cm³ g⁻¹ sample	cm³ g⁻¹ metal	cm³ m⁻² sample	%, w/w
CNF	6.7	–	0.21	0.055
CNF-oxi	2.4	–	0.06	0.020
1% Pd-CNF-aq	5.5	549	0.17	0.045
1% Pd-CNF-oxi-aq	12.6	1284	0.35	0.103
1% Pd-CNF-org	6.8	639	0.21	0.056
1% Pd-CNF-oxi-org	3.2	300	0.09	0.026

(Row 13)

MCAM	Capacity(mg/g)	
	Ads	Des
031	19.10	8.31
121	28.72	14.31
211	21.69	10.09

(Row 14)

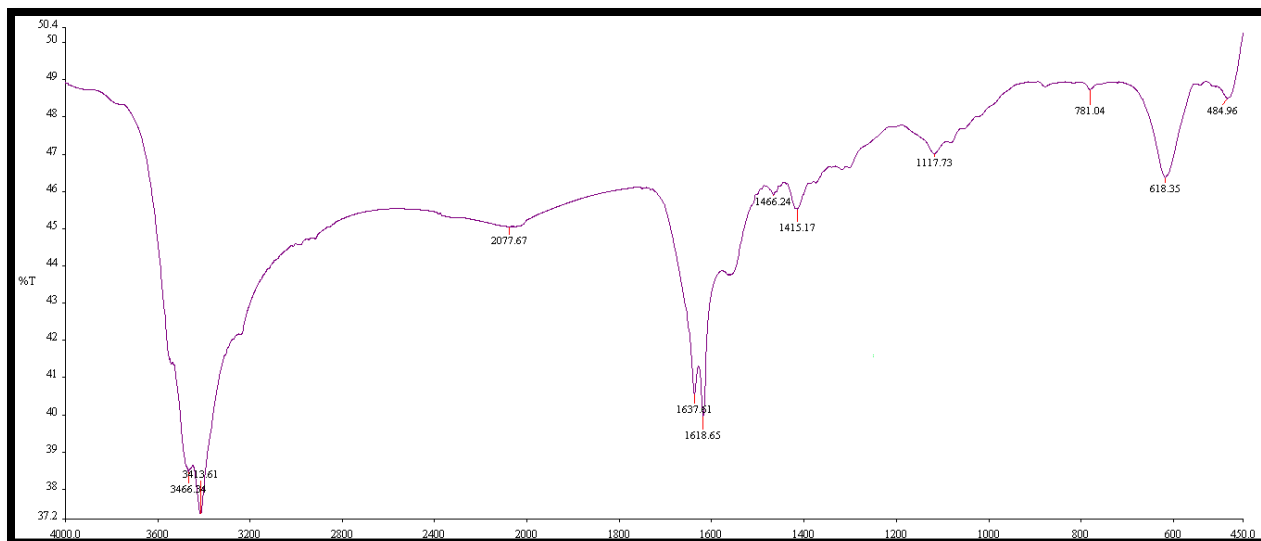| Activation condition	H2 sorption	BET
AP	0.35	475
500	-	482
700	0.28	438
900	0.42	1000
1000	0.34	562

APPENDICES

FTIR ANALYSIS RESULT
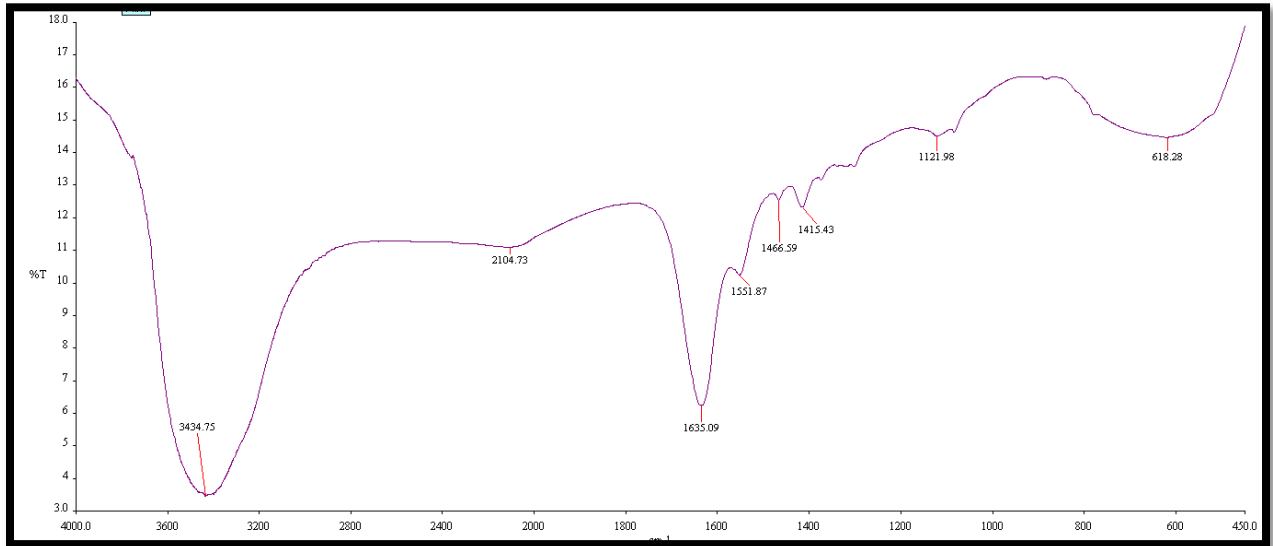
Raw CNF

H_2O functionalized CNF

HNO₃ functionalized CNF