GREEN FUNCTIONALIZATION OF CARBON NANOFIBERS FOR HEAVY METAL REMOVAL

BY:

MOHAMMAD ZAHID BIN ZAHARI

13566

Dissertation submitted in partial fulfillment

of the requirement for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

May 2014

Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

____

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CERTIFICATION OF ORIGINALITY

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

____

(Mohammad Zahid Bin Zahari)

ABSTRACT

Heavy metal is one of the main contaminants in industrial wastewater. This project was conducted to investigate the ability to greenly functionalized Carbon Nanofibers (CNFs) by using distilled water instead of organic acid and the ability of the greenly functionalized CNFs to adsorb heavy metal from aqueous solution. Greenly functionalizing the CNFs by using distilled water instead of the common acidic treatments method will not only reduce the effect of chemicals waste into the environment, but also can reduce the cost of production. The functionalization process is done by controlling 3 parameters, which are; contact time, temperature and stirring frequency. The functionalized CNFs will then be tested for their adsorption ability to adsorb heavy metals from aqueous solutions. This research will also involve the characterization of the CNFs by using Fourier Transform Infrared (FTIR) and the concentration of the heavy metal in the aqueous solution is will be analyzed using Atomic Adsorption Spectrometry (AAS).

ACKNOWLEDGEMENT

In the name of Allah The Most Gracious and The Most Merciful

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TABLE OF CONTENT

CERTIFICATION OF ORIGINALITY **i**

ABSTRACT **ii**

ACKNOWLEDGEMENT **iii**

LIST OF TABLE **vi**

LIST OF FIGURES **vi**

CHAPTER 1 **1**

INTRODUCTION **1**

1.1 BACKGROUND OF STUDY 1

1.2 ENVIRONMENTAL QUALITY ACT 1974, ENVIRONMENTAL QUALITY (SEWAGE AND INDUSTRIAL EFFLUENTS) REGULATIONS 1979, MALAYSIA 2

1.3 PROBLEM STATEMENT 3

1.4. OBJECTIVE AND SCOPE OF STUDY 3

1.4.1 Objective 3

1.4.2. Scope of Study 3

CHAPTER 2 **4**

LITERATURE REVIEW **4**

2.1. INTRODUTION 4

2.2. NANOMATERIALS 4

2.2.1. Carbon Nanofibers (CNF) 4

2.3. PRINCIPLE OF FUNCTIONALIZATION 5

2.3.1. Parameters for CNF functionalization 6

2.4. PRINCIPLE OF ADSORPTION 7

2.4.1. Characteristic of Physical Adsorption and Chemical Adsorption 8

2.4.2. Adsorption of Heavy Metal by Functionalize carbon surface 8

2.5 LITERATURE REVIEW ON PAST WORK DONE BY PREVIOUS RESEARCHER 9

CHAPTER 3 **14**

METHODOLOGY **14**

3.1. INTRODUCTION 14

3.2. FLOW OF THE EXPERIMENT 14

3.3. FUNCTIONALIZATION OF CNF BY WATER 15

3.3.1 Taguchi Method 15

3.3.2 Functionalization Method 16
3.4. FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY 16
3.5. METAL ION ADSORPTION STUDY 17
3.5.1 Preparation of Heavy Metal Solution 17
3.5.2 Heavy Metal Adsorption Study 17
3.6. ATOMIC ABSORPTION SPECTROMETER (AAS) 17
CHAPTER 4 **18**
RESULTS AND DISCUSSION **18**
4.1 FUNCTIONALIZATION OF CNF 18
4.2 HEAVY METAL ADSORPTION STUDY 21
4.3 COMPARISON WITH ACIDIC TREATED CNF ADSORPTION STUDY 24
CHAPTER 5 **25**
CONCLUSION AND RECOMMENDATION **25**
5.1 CONCLUSION 25
5.2 RECOMMENDATION 26
REFERENCES **27**
APPENDIX **I**
PROJECT SCHEDULE (GANTT CHART) I
ORIGINAL FTIR RESULT III
ORIGINAL AAS RESULT IX

LIST OF TABLE

Table 1: Selected parameter limits of effluents of Standard A and B 2
Table 2: Various CNF functionalization method (M. Peng-Cheng et al, 2010). 5
Table 3: Characteristic Of Physical and Chemical Adsorption (R. M. Douglas, 1984) 8
Table 4: Summary of Literature Review 10
Table 5: Parameters and Levels Used in and Carbon Nanofiber Functionalization 15
Table 6: Orthogonal Array for Carbon Nanofiber Functionalization 15
Table 7: Peak identification of FTIR spectra of CNFs 20
Table 8: Final Percentage of Chromium Adsorption 22

LIST OF FIGURES

Figure 1: CNF with: a) Platelet and b) Herringbone structure (Sufian, 2010) 4
Figure 2: Example of functionalization of nanotubes by carboxyl group (B. Kannan et al., 2005). The procedure for carbon nanofiber is identical. 5
Figure 3: Example results from FTIR Spectroscopy (Syahir, 2013) 7
Figure 4: Mechanism of adsorption (R. G. Nae et al., 2013)..7
Figure 5: Cation exchange mechanism on carbon surface (Rios et al, 2003)...8
Figure 6: Flow of experiment 14
Figure 7: Functionalization of the carbon nanomaterial flow diagram...16
Figure 8: Setup of adsorption study..17
Figure 9: FTIR Spectra of Raw and Functionalized CNF 19
Figure 11: Concentration of Chromium Vs Time of Contact with Adsorbant 21
Figure 12: Percentage of Chromium Adsorbed (%) Vs Time of Contact with Adsorbant...................22
Figure 13: Source: N. Syafiqin, 2013 24

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Water pollution is one of the major environmental problem faced in our ecosystem nowadays. Contamination of heavy metal is one of the main contributor in water pollutant issue. Heavy metals are metallic chemical element which has a high density and is toxic or poisonous at low concentration. Some examples of heavy metals are mercury (Hg), Cadmium (Cd), Arsenic (As), Lead (Pb) and Chromium (Cr). (Lenntech, 2014)

The metals do not degrade into harmless end products and tend to accumulate in living organisms causing various diseases and disorders (Imamoglu and Tekir, 2008). The effects of the heavy metals contamination in living organisms can leads to serious health hazards. The excessive copper intake and lead into the body can affect gastrointestinal track and nervous system (Imamoglu et al, 2008). Cadmium exposure may damage the kidney and also leads to bone effects and fractures (Jarup, 2003) and many more.

According to (Kurniawan and Sillanpää, 2010), chromium is on the top priority list of Group A toxic pollutants defined by the U.S. EPA (Environmental Protection Agency). Chromium originated from electroplating industries could be in the form of chromates ($CrO4^{2-}$), dichromate ($Cr2O7^{2-}$) and bichromates ($HCrO^{4-}$) (Kotas and Stasicka, 2000).

From data compiled by the Malaysian Department of Environment, the overall trend points to a slow but steady deterioration in the water quality of rivers around the country. Of 116 rivers monitored, 42 are rated as clean, 61 slightly polluted and 13 polluted. In terms of heavy metal contamination, 55 rivers have been found to exceed the maximum limit of 0.001 mg/l for cadmium, 44 rivers exceeded the iron limit of 1.00 mg/I, 36 rivers exceeded the lead limit of 0.01 mg/l and 24 rivers exceeded the mercury limit of 0.0001 mg/l.

The main sources of organic water pollution are domestic and industrial sewage, effluent from palm oil mills, rubber factories and animal husbandry. Mining operations, housing and road development, logging and clearing of forest are major causes of high concentration of suspended sediment in downstream stretches of rivers.

In several urban and industrial areas, organic pollution of water has resulted in environmental problems and adversely affected aquatic lives. In the Klang Valley alone, an estimated 50-60 tons of wastes end up in the river system daily. Various method can be used to remove heavy metals ions in wastewater treatment industries. They includes electrochemical precipitation, ion exchange, reverse osmosis and adsorption.

1.2 ENVIRONMENTAL QUALITY ACT 1974, ENVIRONMENTAL QUALITY (SEWAGE AND INDUSTRIAL EFFLUENTS) REGULATIONS 1979, MALAYSIA

There are certain concentration limits of effluent of heavy metals that have been standardized under Environmental Quality Act (EQA) 1974. Table below shows the concentration limits of the metals. Standard A and B are specialised for housing and industrial area, respectively.

Table 1: Selected parameter limits of effluents of Standard A and B (Department of Environment, DOE, Malaysia)

Heavy Metal	**Parameters (mg/L)**	
	Standard A	Standard B
Mercury	0.005	0.05
Cadmium	0.010	0.02
Arsenic	0.050	0.10
Lead	0.100	0.50
Chromium	0.200	1.00
Copper	0.200	1.00
Nickel	0.200	1.00
Zinc	1.000	1.00
Iron	1.000	5.00

1.3 PROBLEM STATEMENT

Contamination of heavy metal in wastewater is an issue that need to be resolved to prevent further harm to living organisms. The usage of carbon nanomaterial such as CNFs have gained a lot of attention for last two decades. Carbon nanomaterials have high potential to act as absorbent due to its high chemical stability and unique physical properties. They have been used as absorbent due to their highly porous and hollow structure, large specific area, large mass density and strong interaction between carbon and hydrogen molecules. However, carbon nanomaterial are very hydrophobic, tend to aggregate in aqueous solution and have low adsorption capability. In order to increase its adsorption capability, its surface needs to be functionalized. Normally, to functionalize these carbon nanomaterials, acidic solution are normally used. This is disadvantaging from the economy and environmental point of view. To overcome this, this research will study on how to functionalize CNFs by green initiative, which is using water to functionalize the carbon nanomaterials. Adsorption study will also be conducted to study on the adsorption capability of the CNFs.

1.4. OBJECTIVE AND SCOPE OF STUDY

1.4.1 Objective

The object of this research is to;

1. Investigate on the ability to produce green functionalized CNFs by using distilled water instead of common acidic treatment by manipulating 3 parameters; time of contact, temperature and stirring rate.
2. Investigate the ability of raw CNF and functionalized CNFs to adsorb heavy metals from aqueous solution.

1.4.2. Scope of Study

The scope of the study focuses on the functionalization and adsorption process of the CNFs. The CNFs will be functionalized, then be used in adsorption study of heavy metal from aqueous solution. The functionalized CNFs are analyzed by Fourier Infrared Transform (FTIR) Spectroscopy and Atomic Absorption Spectrometer (AAS). These equipment are used to indicate functional groups attached to the carbon nanomaterial and to determine the metal concentration in aqueous solution before and after the adsorption process respectively.

CHAPTER 2

LITERATURE REVIEW

2.1. INTRODUTION

This chapter shows the information of carbon nanomaterial, principle of functionalization, principle of adsorption and literature review on past work done by previous researcher was discussed.

2.2. NANOMATERIALS

Nanomaterials are objects of matter in the nanoscale (1×10^{-6}). For the past couple decades, nanomaterial shown remarkable potential to overcome environmental problems. Compared to the traditional materials, nanostructure adsorbent have exhibited much higher efficiency and faster rates in water treatment (W. Xiangtao et al.). For this research, the focus will be on one nanomaterials material, the Carbon Nanofibers (CNFs).

2.2.1. Carbon Nanofibers (CNF)

CNF is thicker and longer than MWCNF. CNF have a cross sectional of ca. 500 A^2 and are between length between 10 µm to 100µm (R. Barron et al, 2010). CNF have a unique morphology in that graphene planes are canted from the fiber axis, resulting in exposed edge planes on the interior and exterior surfaces of the fiber. These morphology resulting in two CNF structures, Platelet and Herringbone structure. The graphene layers may located perpendicular or certain angle to the fiber axis (Suffian, 2010).

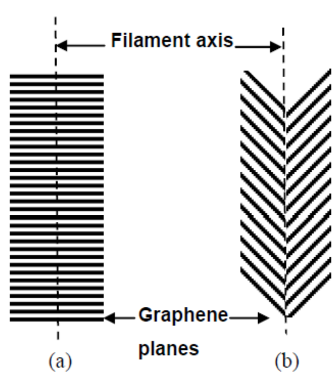

Figure 1: CNF with: a) Platelet and b) Herringbone structure (Sufian, 2010)

2.3. PRINCIPLE OF FUNCTIONALIZATION

Functionalization is adding functional groups by chemical synthesis method onto the surface of a material. The attachment of functionalization group can be done by covalent bonding and non-covalent bonding. Some example of functionalization process are listed in the **Table 2** below;

Table 2: Various CNF functionalization method (M. Peng-Cheng et al, 2010).

METHOD		**PRINCIPLE**
Chemical method	Side wall	Hybridization of C atoms from sp^2 to sp^3
	Defect	Defect formation
Physical Method	Polymer Wrapping	Van Der Walls force, π- π stacking
	Surfactant adsorption	Physical adsorption
	Endohedral method	Capillary effect

In adsorption process, functionalization of the absorbent may help to increase its adsorption efficiency to attract more adsorbates to be attached to it, thus making the adsorption process more efficient. A comparatives study of functionalize and non-functionalized carbon nanotube to remove copper (N.M Mubarak et al, 2012) shows that non functionalized MWCNTs functioned less efficient compared to the functionalized MWCNTs.

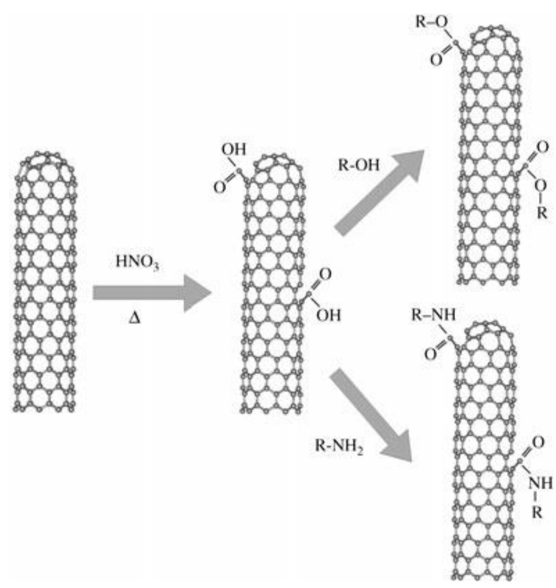

Figure 2: Example of functionalization of nanotubes by carboxyl group (B. Kannan et al., 2005). The procedure for carbon nanofiber is identical.

2.3.1. Parameters for CNF functionalization

There are several parameters influencing the functionalization process. They are oxidation temperature, type of oxidants, oxidant concentration and oxidation time.

2.3.1.1. Oxidation temperature

An increase in the amount of equilibrium adsorption of each ion increase in the amount of equilibrium adsorption of each ion with the rise in temperature may be explained by the fact that the kinetic energy of cations increase at higher temperatures, therefore, the contact between each ion is sufficient, leading to increase in adsorption efficiency. The increase in temperature may also enlarge the pores sizes of nanotube to some extent, which affect the carbon adsorption capacity. (N. M. Mubarak et al, 2012)

2.3.1.2. Type of oxidants

Oxidant are used to treat and modify the walls of CNT. Acidic solution such as sulphuric acid, nitric acid (A. Maryam et al., 2010, K. G. Vinod et al., 2011 and N.M Mubarak et al, 2012) , and hydrogen peroxide are example of normally used oxidant.

2.3.1.3. Oxidant concentration

Different concentration amount of oxidant leads to different amount of carboxylic, phenolic and lactonic group formed on the CNF surface (Zhao et. Al, 2001)

2.3.1.4. Oxidation time

Oxidation time effects towards functionalization of CNF have not really investigated. Oxygen content increase from 6.3% to 18% within 10 minutes of oxidation then decreases to 14%-15% after 10 and 24h oxidation. This shows that time have significant impact in functionalization process (Park et al. 2004).

2.3.1.5. Fourier Transform Infrared (FTIR) Spectroscopy

In order to determine the presence of additional functional groups on the CNF, they can be analyze using Fourier Transform Infrared (FTIR) Spectroscopy. This equipment can be used to determine the functional group before and after the oxidation process. Figure below shows an example of the results that one may obtain from FTIR analysis. The former peak indicates the presence of C-O stretching bands, which means that they are functionalized group attached to the CNF.

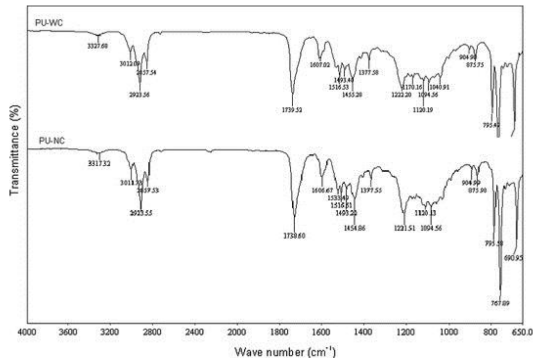

Figure 3: Example results from FTIR Spectroscopy (Syahir, 2013)

2.4. PRINCIPLE OF ADSORPTION

Adsorption is the process in which atoms, ions or molecules from a substance adhere to a surface of the adsorbent. Adsorption is a surface-based process where a film of adsorbate is created on the surface while absorption involves the entire volume of the absorbing substance.

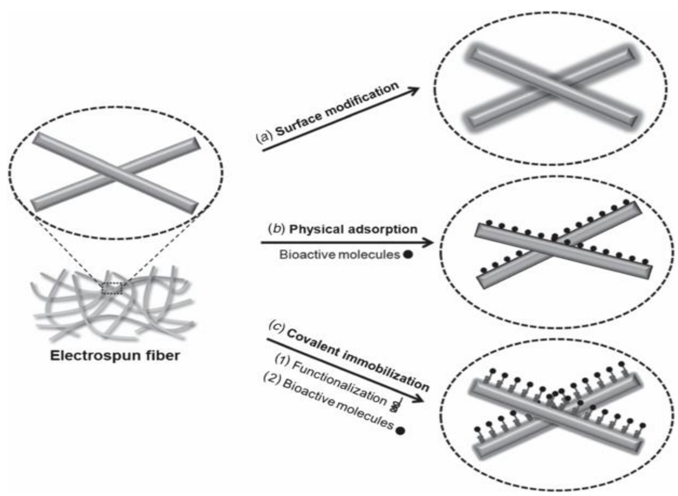

Figure 4: Mechanism of adsorption (R. G. Nae et al., 2013)

Adsorption is generally categorized into two types; physical (weak van der Waal's forces) and chemical (covalent bonding) adsorption. It may also occur due to electrostatic attraction. The molecules are held loosely on the surface of the adsorbent and can be easily removed.

2.4.1. Characteristic of Physical Adsorption and Chemical Adsorption

The Characteristic of Physical Adsorption and Chemical Adsorption are listed in **Table 3** below;

Table 3: Characteristic Of Physical and Chemical Adsorption (R. M. Douglas, 1984)

PHYSICAL ADSOPRTION	CHEMICAL ADSORPTION
Low heat of adsorption (<2 or 3 times latent heat of vaporization)	Low heat of adsorption (>2 or 3 times latent heat of vaporization)
Non specific	Specific
Rapid, non-activated, reversible	Activated, may be slow and reversible
Mono or multilayer	Monolayer
Fast	Slow
No electron transfer	Electron transfer leading to bond formation

2.4.2. Adsorption of Heavy Metal by Functionalize carbon surface

The cation-exchange reaction takes place between the metal ions and the attached hydrogen ions in the functional group formed on CNF surfaces. Figure below shows how the reaction where the metal ions retained on surface after replacing hydrogen ions. H^+

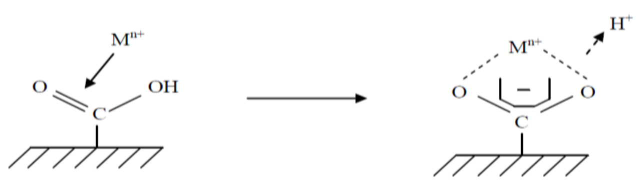

Figure 5: Cation exchange mechanism on carbon surface (Rios et al, 2003)

2.5 LITERATURE REVIEW ON PAST WORK DONE BY PREVIOUS RESEARCHER

A literature review done on past work done by previous researcher to understand the options that have already been explore for Heavy Metals Removal with Carbon Nanomaterials field. The research on green functionalization for carbon nanomaterials are very limited and have not been greatly explore. For example, Junping et al (2011) studied on the functionalization of MWCNF using Iminodiecetic Acid. Yi-Jun Xu et al. (2011), Vinod K Gupta et al. (2011) and Maryam Ahmadzadeh et al. (2011) studied on the functionalization of SWCNT using Nitric Acid, N.M Mubarak et al. (2012) studied on the functionalization of MWCNT with Nitric ad Sulphuric Acid, and Aboughaly (2012) studied on the functionalization of MWCNT using Tetrahydrofuran (THF). Therefore, this research is a good opportunity to provide new greener option for heavy metal removal by carbon nanomaterial field. **Table 4** below summarized the author, types of Carbon Nanomaterials, functionalization agent, functionalization condition and the heavy metals used in the adsorption study.

Table 4: Summary of Literature Review

No	Year	Author	Title	Material	Heavy metal	Agent/ Solution	Functional Group	Condition Used to Functionalized		Conclusion
1	2011	Junping Wang, Xiaoxing Ma Guozhen Fang, Mingfei Pan, Xiaoke Ye, Shuo Wang	Preparation of iminodiacetic acid functionalized multi-walled carbon nanotubes and its application as sorbent for separation and preconcentration of heavy metal iron	1) Oxidised Multi-Walled Carbon Nanotubes (MWCNTs-COOH)	V, Vr, Pb, Cd, Co,Cu,As	SOCl2	IDA	Phase 1 (Disperse in SOCl2 solution)	Stirring temperature70C	-MWCNT-IDA was a successful in heavy metal removal
									Stirring duration 24h	-Mild separation and pH value of 8 are recommended
				2) Iminodiecetic Acid (IDA)				Phase 2 (Mixed with IDA)	Stirring temperature: 70C	-MWCNT-IDA reuse (adsorption and desorption) was successful when passing solutions containing analytes through the column
									Stirring duration 48h	
2	2011	Yi-Jun Xu et al.	Characterization and use of functionalized carbon nanotubes for absorption of heavy metal anions	1) Carbon Nanotube	CrO4	Nitric Acid	O	Phase 1	-20mg of CNT-O	Only absorb CrO4
				2) Abundance Oxygen (Air)					-room temperature	
								Phase 2	-helium flow rate: 15mL/min	
									-temperature : 830 C	
									-Ramp rate: 10C/min	

3	2011	O. Moradi	The removal of ions by functionalized carbon nanotube: Equilibrium, Isotherms and Thermodynamic Studies	1) Single Walled Carbon Nanotube	Pb, Cd,Cu	Fresh double-distillation -ionized water	COOH	-stirring rate : 250 rpm		Single-Walled Carbon Nanotube with carboxylate functionalized croup (SWCNTs-COOH) was commercially bought. Not synthesised
				2) Single-Walled Carbon Nanotube with carboxylate functionalized croup (SWCNTs-COOH)				-Stirring Time: 120 min		
								-Temperature	1) 283 K	
									2) 293 K	
									3) 303 K	
									4) 313 K	
4	2011	Vinod K Gupta et al.	Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal	1) Multi-Walled Carbon Nanotubes	Pb	Nitric Acid	Al2N3	Phase 1 (Concentrated Nitric Acid)	Temperature: 70C	Coating. Not functionalized.
				2) Aluminium Nitrate					Stirring duration: 12h	
								(Drying)	Temperature: 110C	
									Duration: 6h	
								Phase 2 (50% Nitric Acid)	Temperature: 120C	
									Stirring duration: 12h	
								(Drying)	Duration: Overnight	
								Phase 3 (Preparation of Al2O3/MWCNTs	Stirring duration: 12h	
								(Drying)	Temperature: 110C	
								(Heating)	Temperature: 400C	
									Heating duration: 90mins	

5	2010	Maryam Ahmadzadeh et al.	Adsorption of divalent heavy metal ions from the water using carbon nanotube sheets	1)Carbon nanotube	Cu,Zn, Pb,Cd, Co ions	Nitric Acid	None	1) Dissolve in nitric acid (Duration:20h) 2) Wash with deionized until pH become constant 3) Dried at 110C for 24h	Carbon nanotube is not functionalized with a functional group
6	2011	Ali Can Zaman et al.	OH and COOH functionalized single walled carbon nanotubes-reinforced alumina ceramic nanocomposites	1) Single Walled Carbon Nanotube Alumina Ceramic Nanocomposites	None	Ethanol	COOH OH	1) Ball milled 3 hours 2) Ultrasonicated 30 min 3) Dried 100C for 30 min	
7	2012	Nuruzatlifah Bt Asari @ Mansor et al.	Chemically Modifies Multi-Walled Carbon Nanotubes (MWCNTs) with Anchored Acidic Groups	1) Multi-Walled Carbon Nanotubes	None	SO3 gas	1) At 100C: Carboxyl & Lactone 2) At 200: Carboxyl & Phenol 3) At 300: Carboxyl & lactone	1) Carried out by gas phase treatment in a Universal Temperature Programme reactor flowing SO3 gas onto CNTs while being heated to different end temperature End Temperatures: 1) 100C 2) 200C 3) 300C	The aim of modification is to introduce oxygen, & sulphur containing functional group as well as to increase its dispersibility in aqueous environment
8	2012	Mohamed Ahmed Aboughaly	Dispersion of Multiwalled Carbon Nanotubes in Polar Solvent by Adding a Functional Hydroxyl Group to its aided with sonication	1) Multi-Walled Carbon Nanotubes 2) Sodium Zincate	None	Tetrahydrofuran (THF)	OH	1) THF & MWCNTs was sonicated for 3 hours at 60 KHz 2) Sodium Zincate was sonicated with mixture of THF & MWCNTs for 12 hours	Usage of Ultra-sonification in Dispersion of CNT. Usage of double sonic source causes intermittency chaos which result into increase of dispersion.

9	2012	N.M Mubarak et al.	Comparative study of functionalized and non-functionalized carbon nanotube for removal of copper from polluted water	1) Multi-Walled Carbon Nanotubes	Cu	For Funtionali-zed MWCNTs- Nitric & Sulphuric Acid	**Functionaliz-ed MWCNTs:**	For functionalized MWCNTs:	1) MWCNTs refluxed for 4hr at 20C	Non functionalized MWCNTs functioned less efficient compared to the functionalized MWCNTs
							1) Carboxyl		2) MWCNTs washed until pH reached 7	
							2) Hydroxyl		3)Dried at 120C for 4h	
							3) Carbonyl	For non-functionalized MWCNTs:	None	
10	2011	Yong-Chein Ling et al.	Microwave-Assisted Preparation of Carbon Nanotubes with Versatile Functionalization	1) Carbon Nanotube	None	HNO3 (for microwave purification assisted with Solvent)		1) Microwave-assisted purification (With solvent)	120C-180C	
									30min	
								2) Solvent free microwave-assisted purification	100C-150C	
									5 min	

CHAPTER 3

METHODOLOGY

3.1. INTRODUCTION

This chapter discussed about the methods to prepare functionalize CNFs using three different parameters; time of contact, temperature and stirring rate. The description on the preparation of chromium (Cr) solution and the methodology of the adsorption study are also discussed. Characterizations and adsorption analysis of the CNFs using various instruments and metals adsorption at different experimental conditions are also discussed in this chapter.

3.2. FLOW OF THE EXPERIMENT

Flow of the experiment are shown in **Figure 6 below;**

Figure 6: Flow of experiment

3.3. FUNCTIONALIZATION OF CNF BY WATER

Parameters and levels used in activated carbon functionalization are listed in the **Table 5** below. These parameters were defined based on the research studies;

Table 5: Parameters and Levels Used in and Carbon Nanofiber Functionalization

Parameters	**Levels**		
	Low	*Medium*	*High*
Type of oxidant	Distilled Water		
Time of contact (h)	2	4	6
Reaction temperature (C)	25	30	35
Stirring frequency (rpm)	100	150	200

3.3.1 Taguchi Method

Design of experiment based on Taguchi method was applied for CNFs functionalization. Taguchi method enables to optimize the experimental design within selected parameters (Sufian, 2010). The optimizations of parameters were done through Taguchi method with orthogonal array of L9. Three variables with three levels were chosen in functionalization parts which are type of oxidants, oxidant concentrations and oxidation time. These parameters were defined based on past research studies and are considered as a proposal. The orthogonal array are listed in the **Table 6** below;

Table 6: Orthogonal Array for Carbon Nanofiber Functionalization

L_9	Time of contact (h)	Temperature (C)	Stirring frequency
1	2	25	100
2	2	30	150
3	2	35	200
4	4	25	150
5	4	30	200
6	4	35	100
7	6	25	200
8	6	30	100
9	6	35	150

3.3.2 Functionalization Method

The **Figure 7** below shows the flow of method in functionalizing the carbon nanofiber;

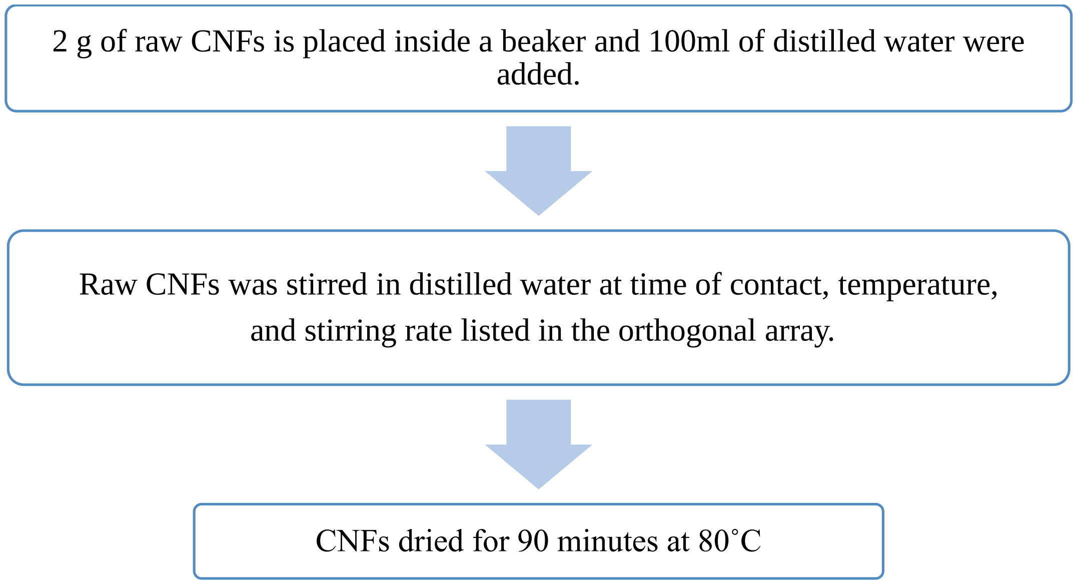

Figure 7: Functionalization of the carbon nanomaterial flow diagram

3.4. FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

The characterization of the CNFs are done by using FTIR analysis. FTIR analysis identify the chemical bonds in a molecule through production of infrared spectrum for each component in a sample. This method is used to detect functional groups on CNFs surface.

3.5. METAL ION ADSORPTION STUDY

3.5.1 Preparation of Heavy Metal Solution

Cadmium (III) Nitrate was used to prepare the Cadmium Solution. 1 g of Cadmium (III) Nitrate is dissolved using distilled water in a 1000ml volumetric flask. For the AAS calibration solution, Cadmium Standard Solution of 1000ppm was diluted into 100ppm, 50ppm and 25ppm. These solution must be freshly prepared before the AAS test to prevent degradation of the metal ion.

3.5.2 Heavy Metal Adsorption Study

This adsorption study a batch adsorption study. It will be conducted in a water bath ultrasonicator. 100 ml of Cadmium (III) Nitrate solution is agitated with an adsorbent dosage of 0.1g. Three parameters to be studied are contact time, initial metal concentration and final metal concentration. The setup of the apparatus are illustrated below;

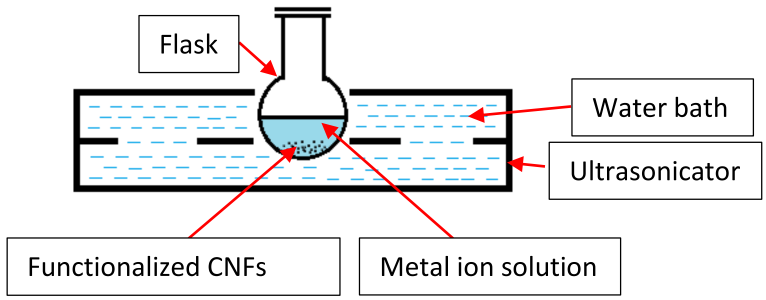

Figure 8: Setup of adsorption study

Sample from the adsorption study will be collected every 15 minutes for 1 hour to determining the adsorption percentage of the heavy metal by the CNFs.

3.6. ATOMIC ABSORPTION SPECTROMETER (AAS)

AAS is principal tool used for metallic element analysis. Atomic spectroscopy measured element by aspirated a liquid sample through a plastic tube into a flame and vaporizes. The metal atoms absorb light of a specific frequency, and the amount of light absorbed is a direct measure of the number of atoms of the metal in the solution. Initial and final metal concentration are measured using Atomic Absorption Spectrometer

CHAPTER 4

RESULTS AND DISCUSSION

4.1 FUNCTIONALIZATION OF CNF

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

The experiments were done based on the orthogonal array in order to ensure that the set parameters are capable and suitable for the process of functionalization of CNFs. The raw CNF is used as main reference. The functionalized CNFs are compared to the raw CNF to identify the presence of new and significant peaks and intensity of the functionalized group. FTIR spectra of raw and functionalized CNFs are shown in **Figure 9** below;

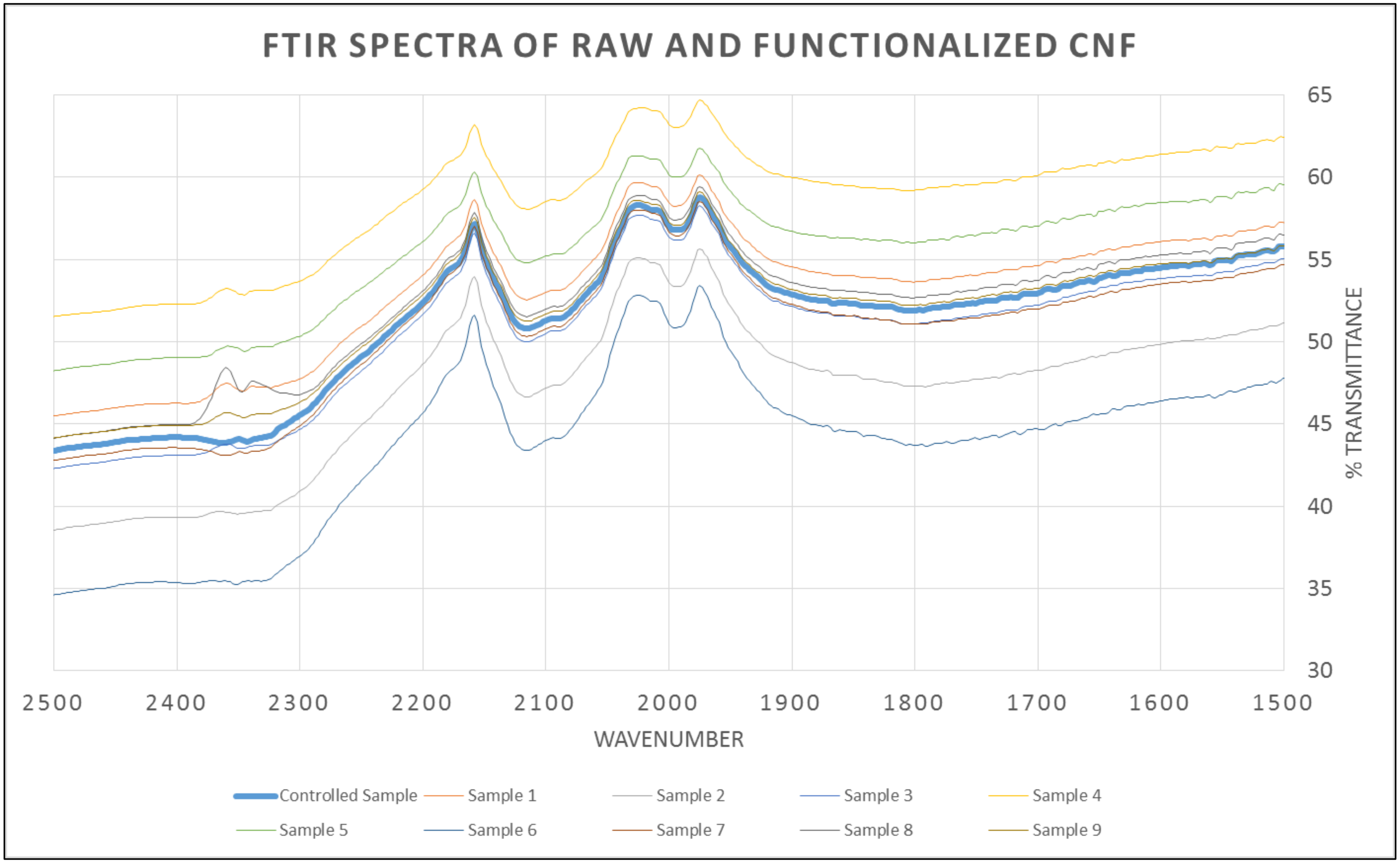

Figure 9: FTIR Spectra of Raw and Functionalized CNF

Based on Figure, it can be observed that there are no newly formed peak to all of the functionalized CNFs when compared to the raw CNF. The available peak indicates the presence of C=O stretching bands at wave number 1827.411-1875.18. The presence of O-C-O stretch band are also identified at wave number 2324.388-2350.23.

Table 7: Peak identification of FTIR spectra of CNFs

Wave No. (cm-1)	**Functional Group**
1827.411-1875.18	C=O stretch
1990.978-1995.579	C=C stretch
2090.36-2115.751	-C≡C- stretch
2324.388-2350.23	O-C-O stretch

What defers the CNFs are the transmittance of the functional group available. The transmittance shows the intensity of the functional group attached to the CNFs.

Presence of the functional groups with oxygen content on CNFs surface plays an important role for the removal of metal ions as it increases the adsorption active sites (Park and Jang, 2002). Shifting in transmittance & wavenumber in FTIR result confirms new functional group on the surface of the adsorbant. (Daffala, 2010). This is in good agreement with other literatures which the metal adsorption uptake increase after the functionalization.

Sample 4 shows the highest increment of O-C-O intensity, which is 20%. Followed by Sample 5, which is 14%. Sample 1, 8 and 9 shows small increment, which are between 2% to 7%. On the other hand, Sample 6 shows the highest decrease in O-C-O intensity, which is 20%. Sample 2, 3 and 7 shows small decrease in the intensity, which is between 2% to 9%.

For C=O stretch intensity, Sample 4 shows the highest increment, which is 16%. Followed by Sample 5, which is 10%. Sample 1, 8 and 9 shows small increment, which are between 2% to 4%. Sample 6 shows the highest decrease in O-C-O intensity, which is 16%. Sample 2, 3 and 7 shows small decrease in the intensity, which is ranged from 0% to 8%.

4.2 HEAVY METAL ADSORPTION STUDY

In order to test and investigate the efficiency of the functionalized CNFs in removing heavy metal, the functionalized CNFs undergo heavy metal adsorption study in which the result will later be tested using the AAS Spectrophotometer. All the samples including the raw sample are tested for the heavy metal adsorption study. **Figure 10 and Figure 11** below shows the result from the AAS Spectrometry for the heavy metal adsorption study.

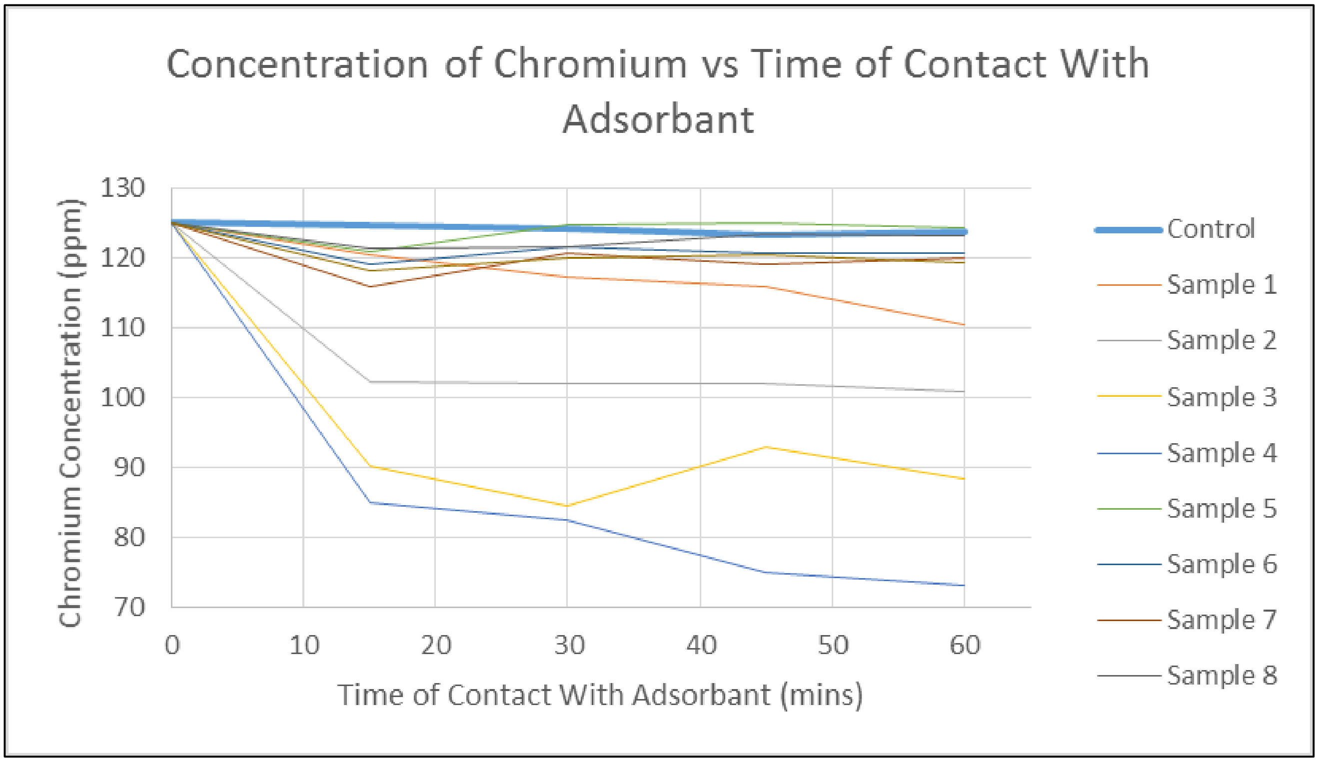

Figure 10: Concentration of Chromium Vs Time of Contact with Adsorbant

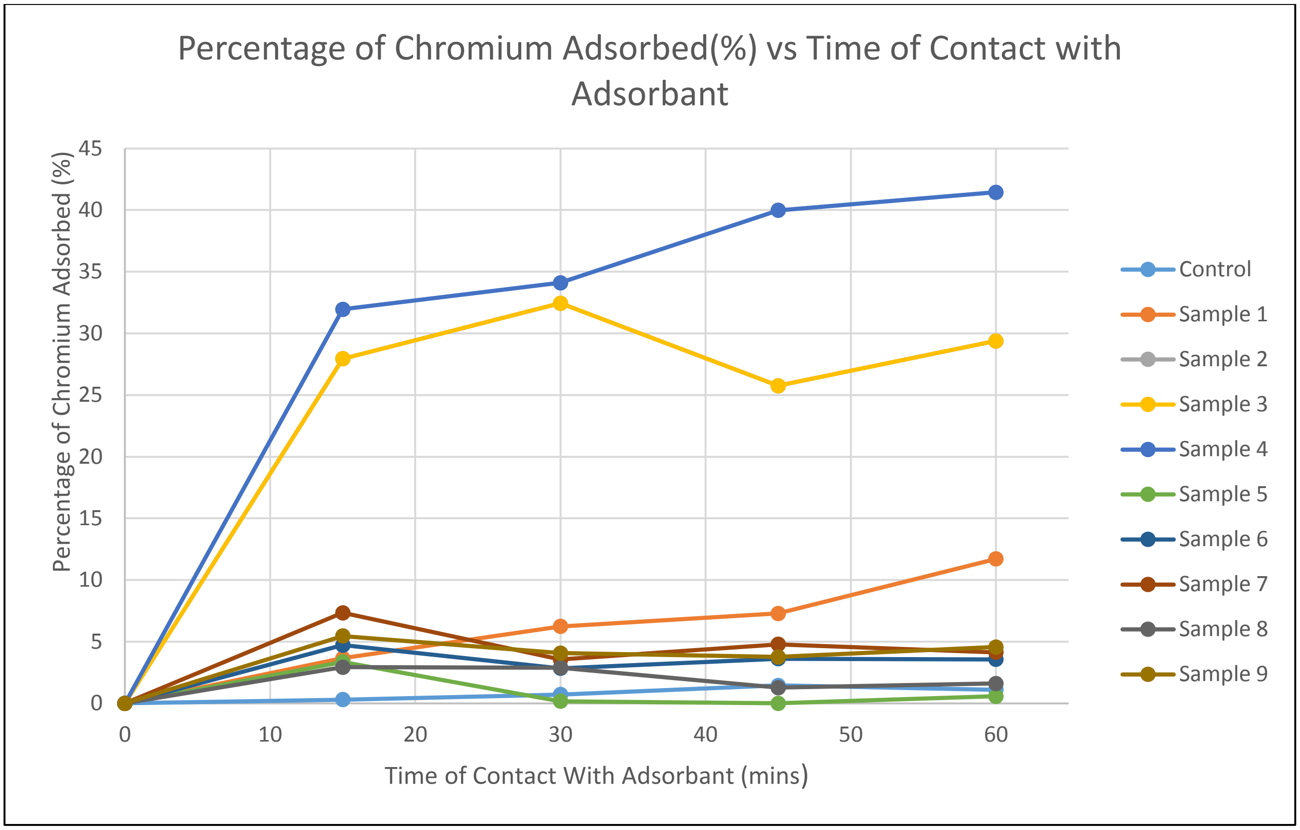

Figure 11: Percentage of Chromium Adsorbed (%) Vs Time of Contact with Adsorbant

The final percentage of adsorption are calculated and the result are listed in **Table 8** below;

Table 8: Final Percentage of Chromium Adsorption

Sample Name	**Percentage of Adsorption (%)**
Raw	1.103558577
1	11.71531387
2	19.3922431
3	29.3802479
4	41.43942423
5	0.575769692
6	4.134346261
7	4.134346261
8	1.607357057
9	4.566173531

The metal adsorption rate is crucial to be investigated as it is important to determine the adsorption equilibrium time for real application in wastewater treatment industry.

Based on **Table 8,** the Raw Sample shows only 1.10% of heavy metal adsorption. Sample 4 shows the highest chromium adsorption, which is 41.43% of heavy metal adsorption, followed by Sample 3, which is 29.38% and Sample 2, which is 19.39%.

On the contrary, other sample shows lower adsorption percentage which lies from 1.61% to 4.57%. Surprisingly, Sample 5 shows lower percentage of heavy metal adsorption compared to the Raw Sample.

FTIR analysis prove that Sample 4 has the highest intensity of O-C-O and C=O absorption bands compared to other adsorbents. Presence of the functional groups with oxygen content on CNFs surface plays an important role for the removal of metal ions as it increases the adsorption active sites (Park and Jang, 2002). This is in good agreement with other literatures which the metal adsorption uptake increase after the functionalization.

4.3 COMPARISON WITH ACIDIC TREATED CNF ADSORPTION STUDY

Adsorption study done by previous student (N. Syafiqin, 2013) which used acid to functionalize the CNFs, shows that the adsorption uptake for chromium is as high as 80%.

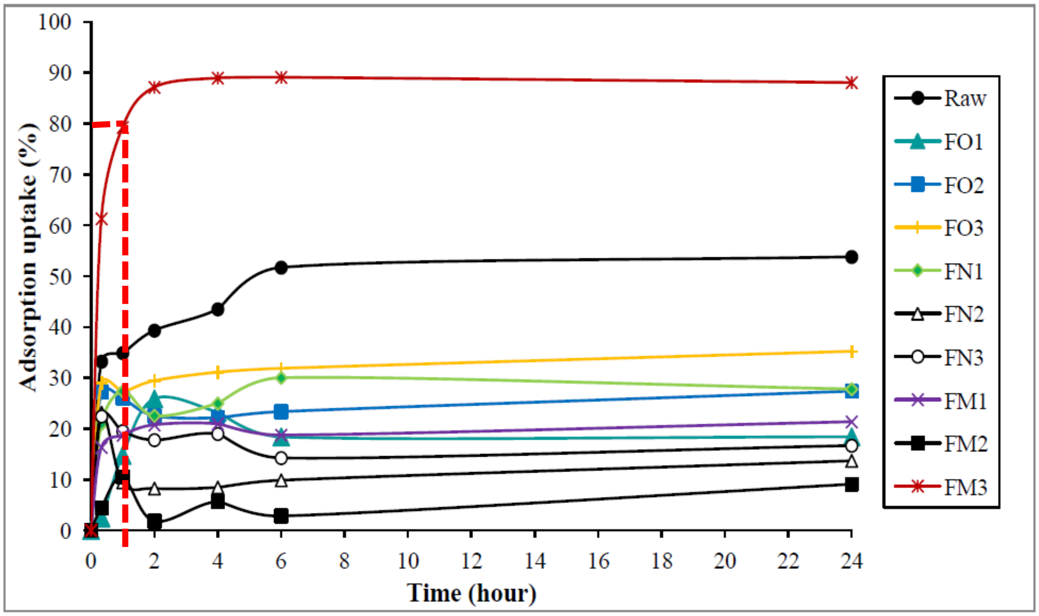

Figure 12: Source: N. Syafiqin, 2013

On the other hand, the adsorption uptake for greenly functionalized CNFs is as high as 41.43%. Which is half of the adsorption uptake of the acid functionalized CNFs. This might shows that the greenly functionalized CNFs may have lower adsorption capability, however, it is proven to be possible to greenly functionalize the CNFs by using only water.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

This researched is aim to study the ability to greenly functionalized CNFs by using water instead of organic acid and the ability of the greenly functionalized CNFs to adsorb heavy metal from aqueous solution.

For the first part of the research, the ability to greenly functionalized CNFs by using water instead of organic acid is studied. The changes in the level of transmittance from FTIR analysis proves that the functionalization procedures and parameters are correct and useful. The optimum conditions of functionalization of CNFs has also been determined through this study. The optimum parameter for functionalization is 4 hours, 25 minutes and 150 rpm.

For the second part of the research, the ability of the greenly functionalized CNFs to adsorb heavy metal from aqueous solution. The AAS result proves that heavy metal adsorption can be achieved. The best CNF from FTIR analysis shows the CNF is able to adsorb up to 40.13% of heavy metal from the aqueous solution.

As conclusion, this research has been a success as all objectives are fulfilled. Recommendation for the improvement of this research are discussed in the next section.

5.2 RECOMMENDATION

Below are some recommendation for this project;

- Use of real industry wastewater effluent for the testing of the functionalized CNFs is highly recommended for the betterment of this study as it will really show the application in real industry.
- Expand the research to study on the effect of time of contact, temperature and rotation speed on the functionalization process.
- Expand the research to study the ability to regeneration of CNFs. CNFs cost around RM2000 per 100 grams. Expanding this research can help to safe cost of buying CNFs and reduce the impacts of waste on the environment.

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APPENDIX

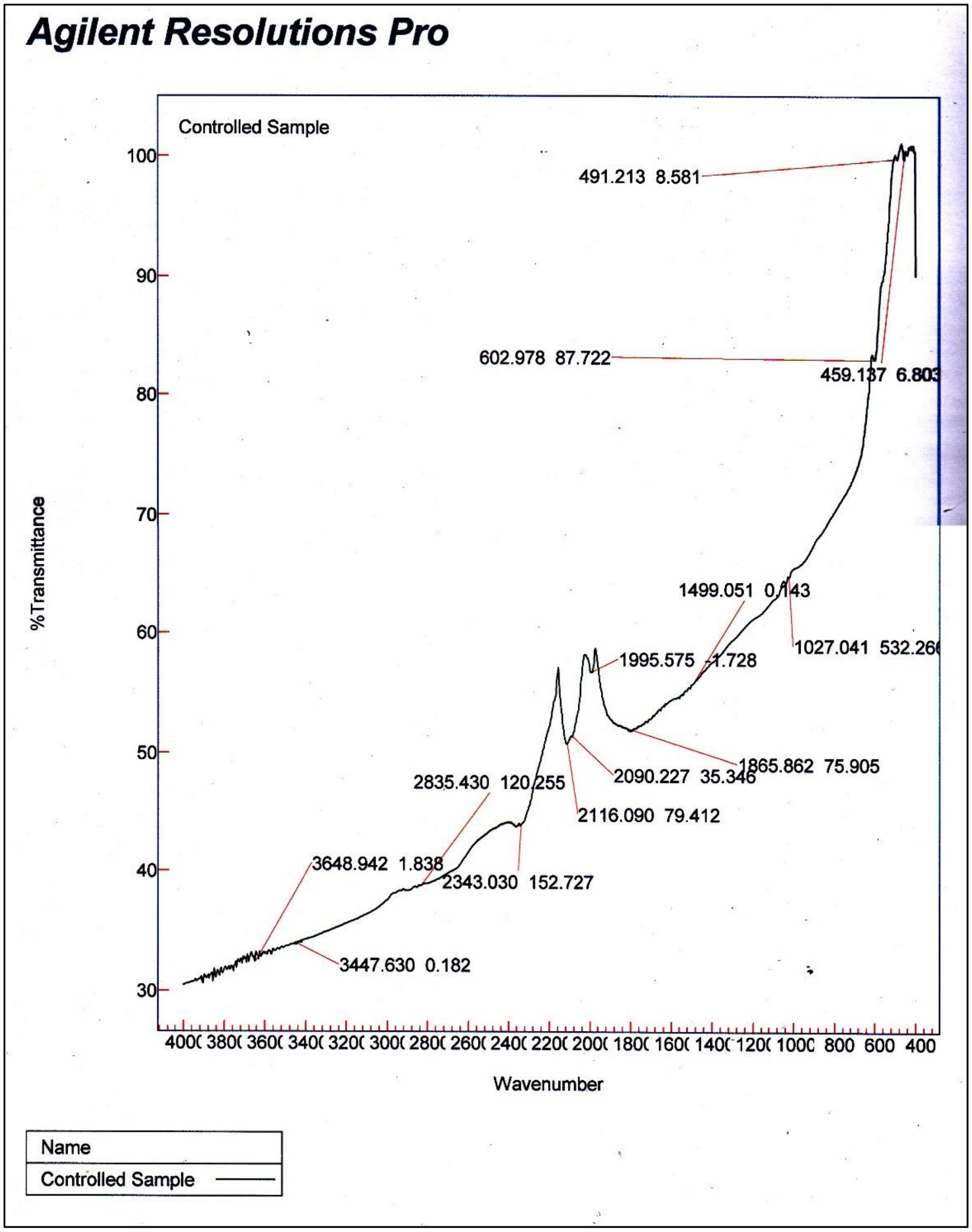
PROJECT SCHEDULE (GANTT CHART)

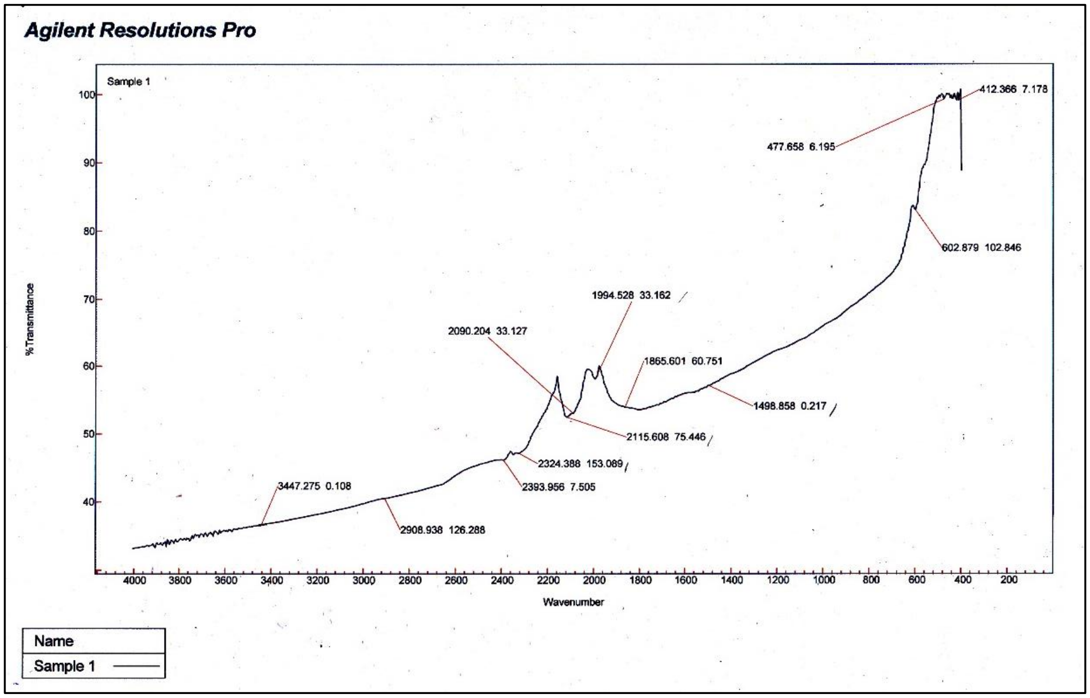
No.	Project Activities	Week														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Preparation of Chemicals Material Safety and Data Sheet															
2	Booking of Lab Space Location															
3	Arrival of Chemicals for Experiments															
4	Preparation of lab apparatus and equipment															
5	Functionalization of CNFs															
6	FTIR Analysis of CNFs															
7	Progress report (9th Jul 2014)															
8	Heavy Metal Adsorption Test On Functionalize CNFs															
9	AAS Adsorption Analysis on Heavy Metals Adsorption															
10	Poster Preparation															
11	Pre-SEDEX Presentation (1 Aug 2014)															

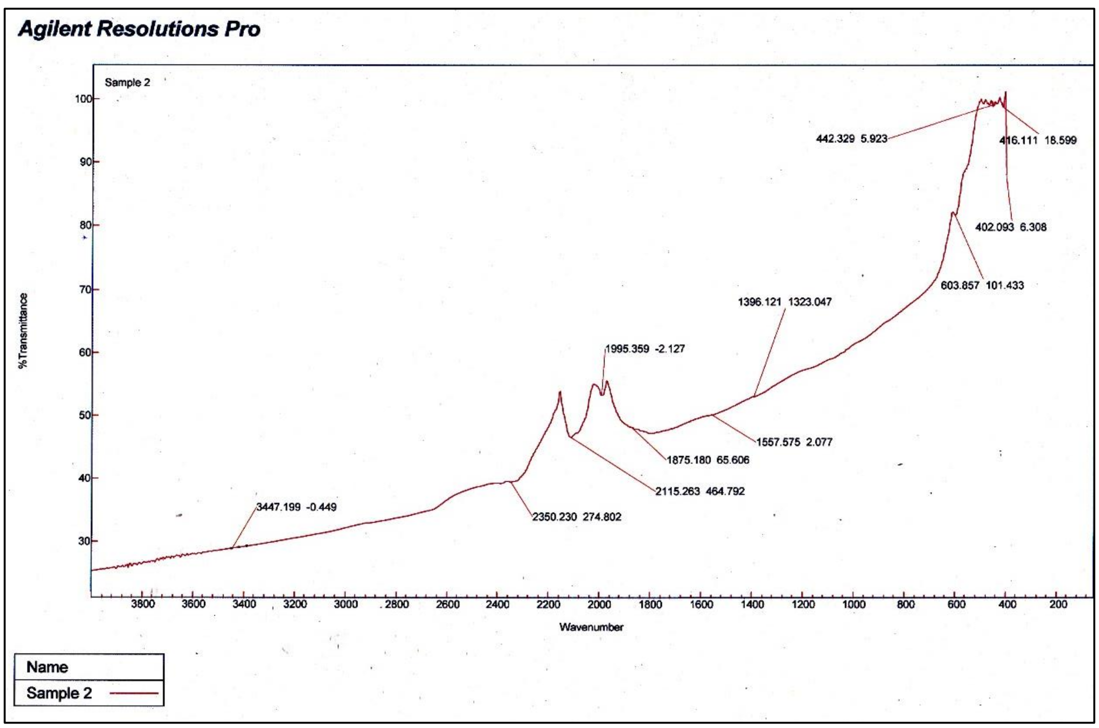
12	First Draft Report (4 Aug 2014)															
13	Submission of Dissertation (11 Aug 2014)															
14	Submission of Technical Paper (15 Aug 2014)															
15	Oral presentation (25-26 Aug 2014)															
16	Submission of Project Dissertation															

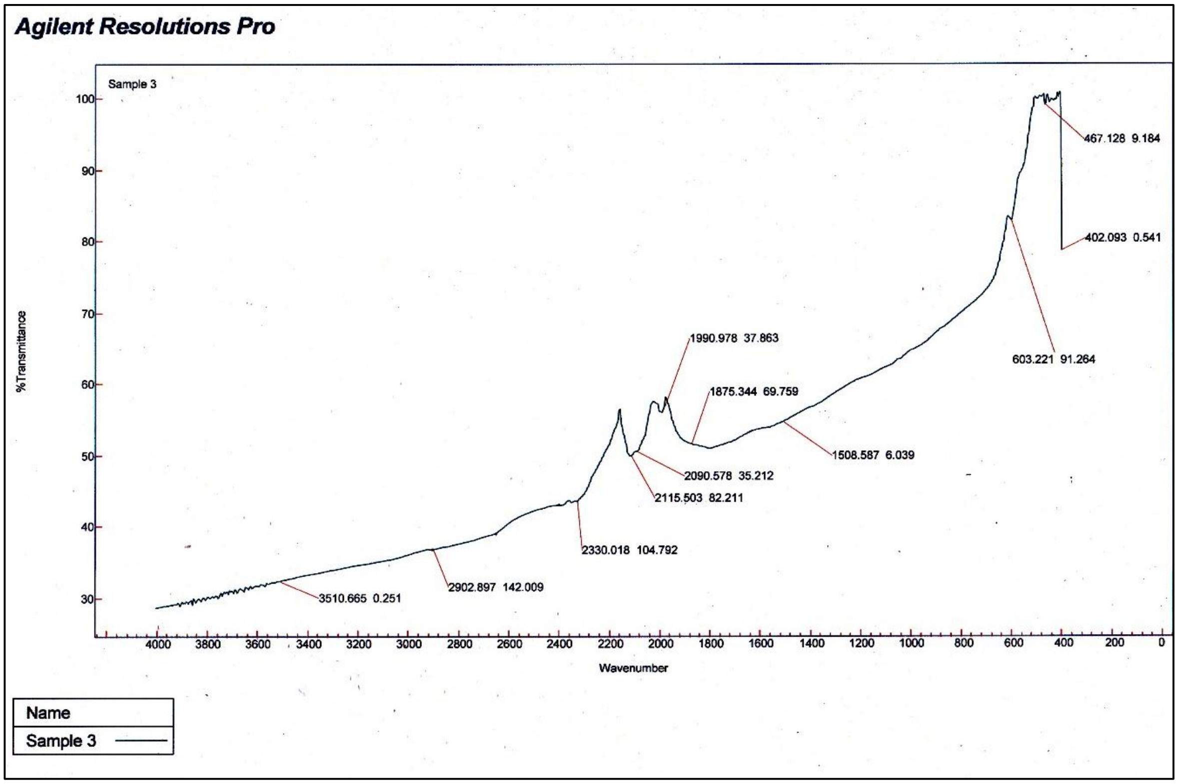
	Planned Progress
	Actual Progress

ORIGINAL FTIR RESULT

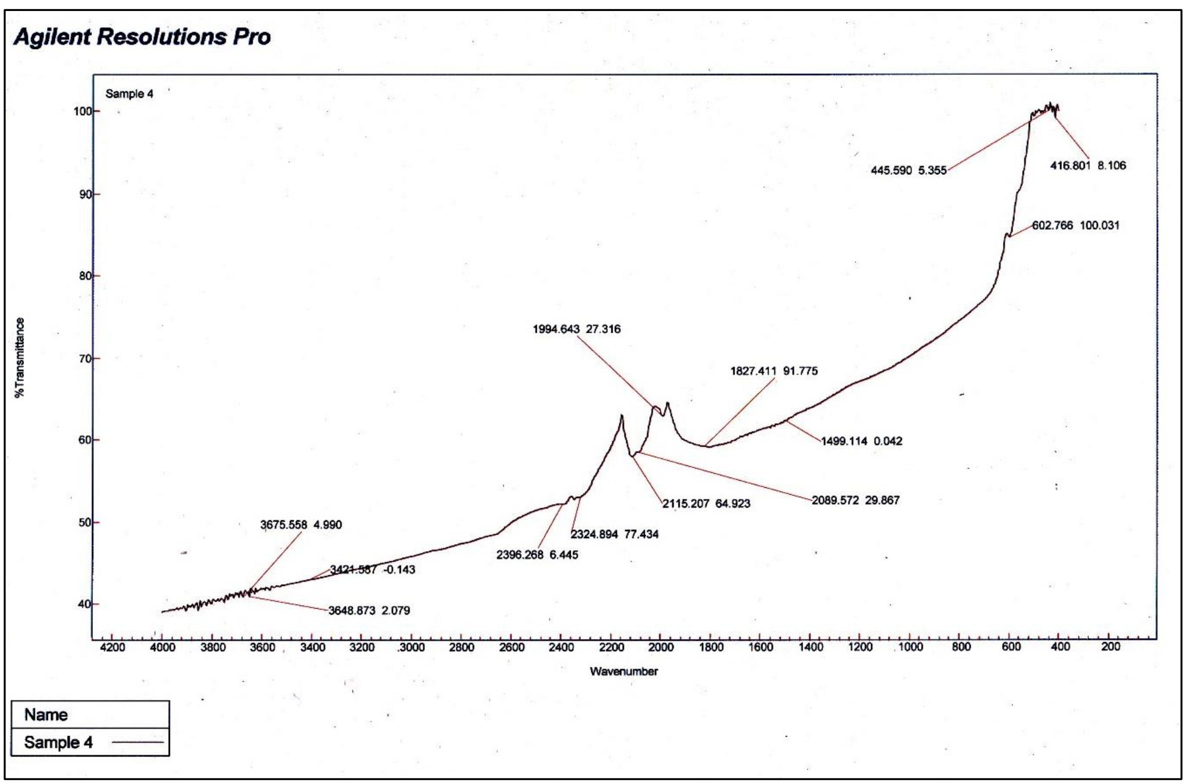



Agilent Resolutions Pro
Sample 1
% Transmittance
Wavenumber
412.366 7.178
477.658 6.195
602.879 102.846
1994.528 33.162
2090.204 33.127
1865.601 60.751
1498.858 0.217
2115.608 75.446
2324.388 153.089
2393.956 7.505
3447.275 0.108
2908.938 126.288
Name
Sample 1

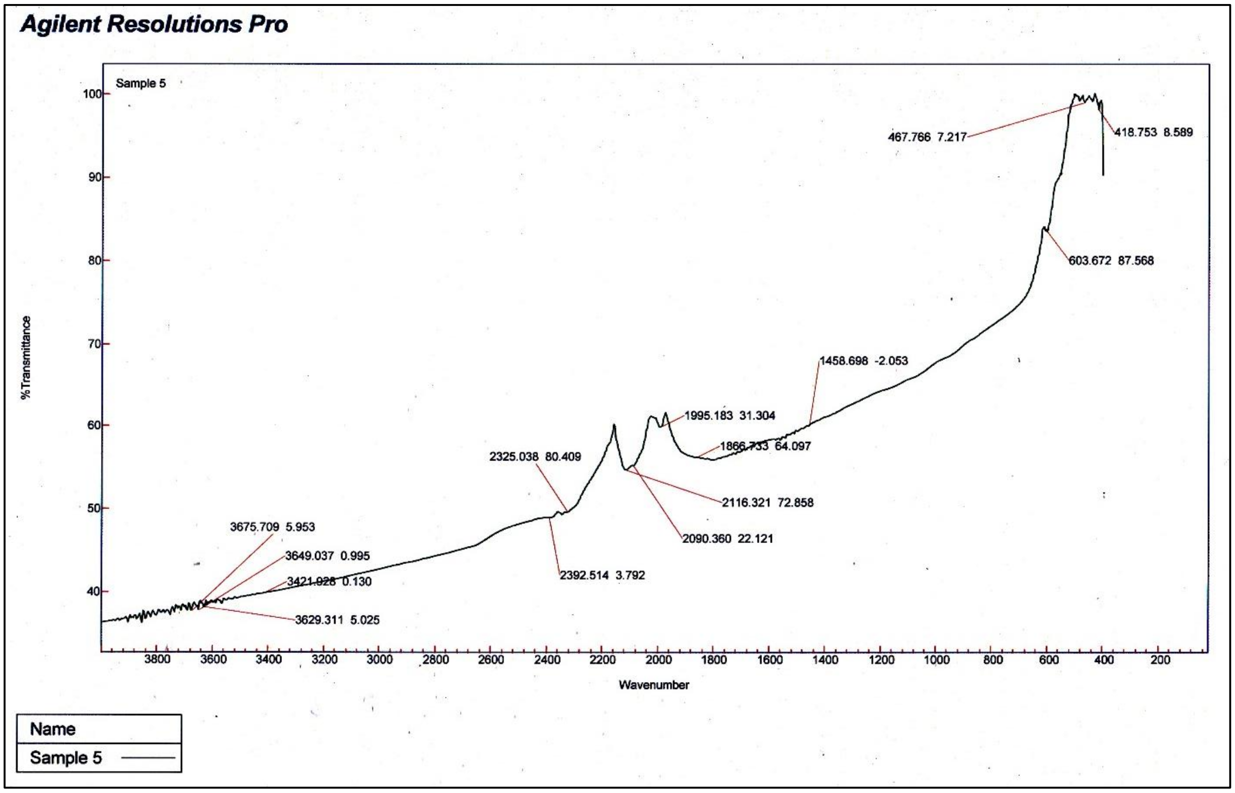

Agilent Resolutions Pro
Sample 2
% Transmittance
Wavenumber
442.329 5.923
416.111 18.599
402.093 6.308
603.857 101.433
1396.121 1323.047
1995.359 -2.127
1557.575 2.077
1875.180 65.606
2115.263 464.792
3447.199 -0.449
2350.230 274.802
Name
Sample 2

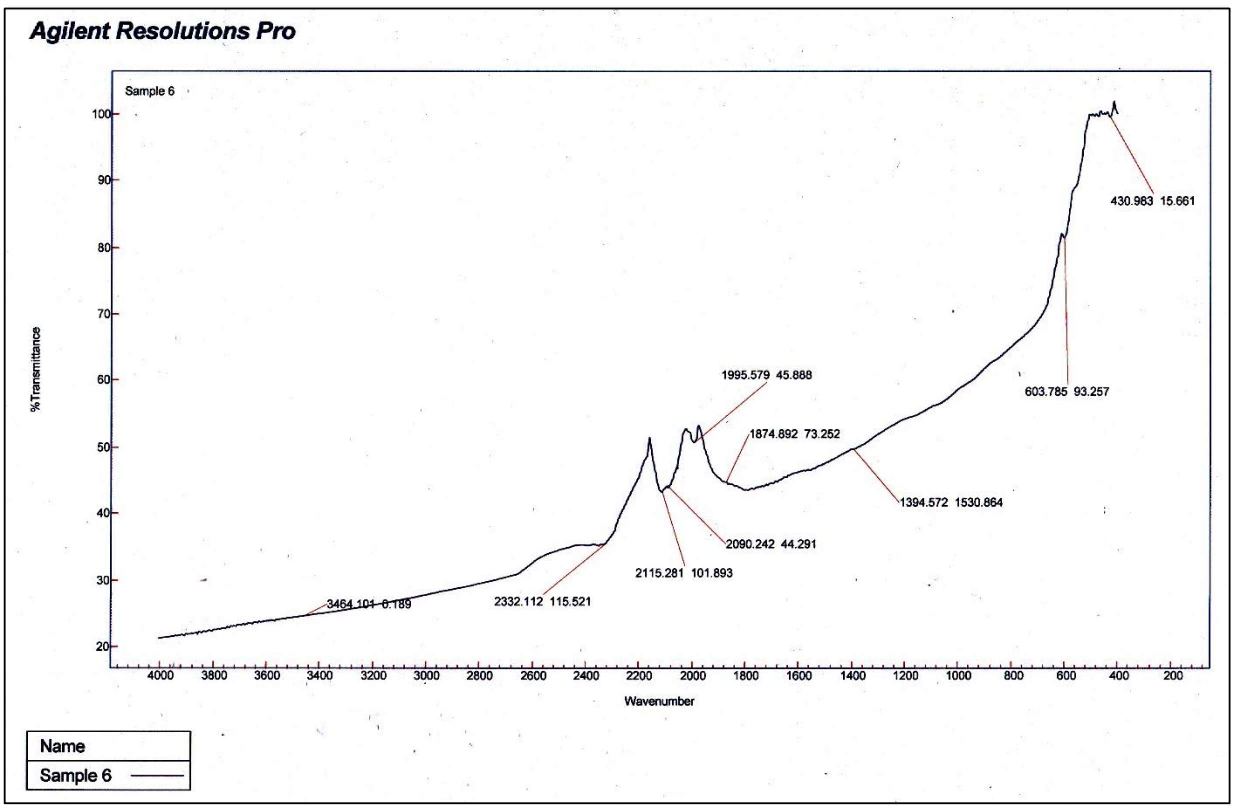


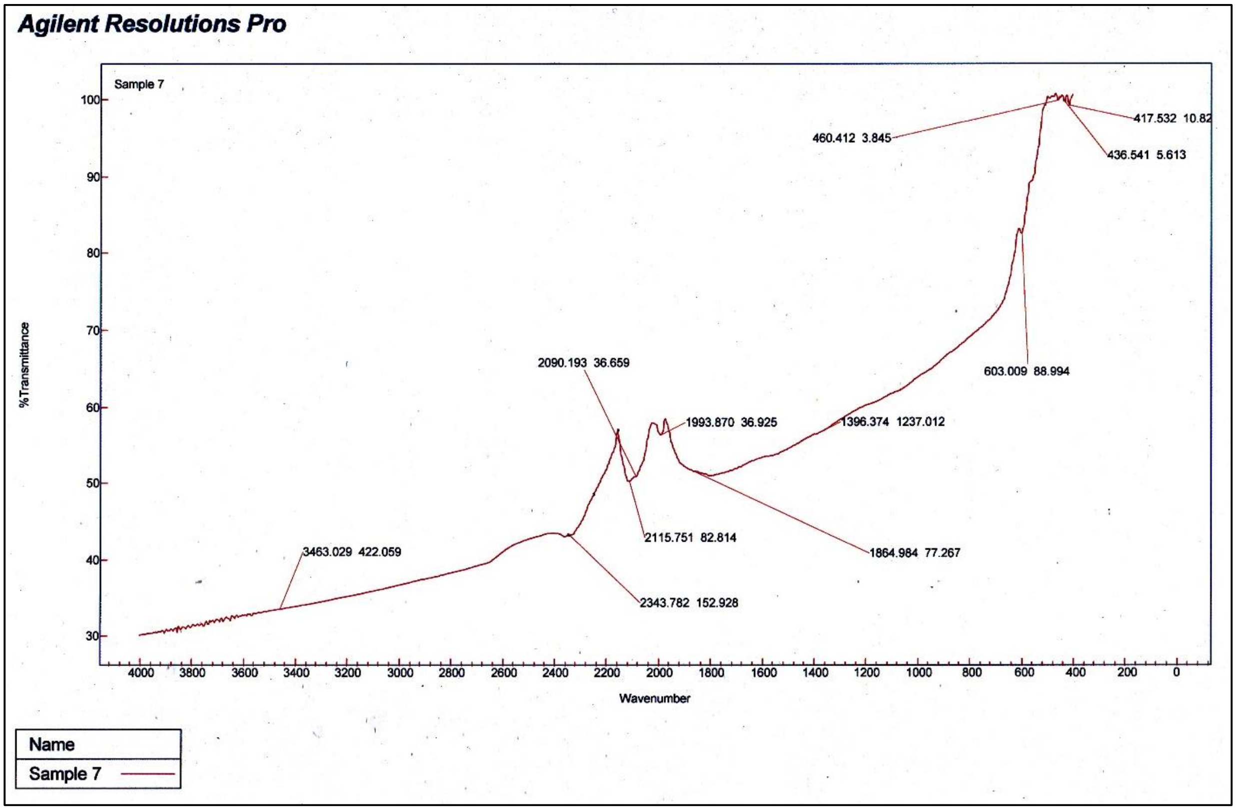
Agilent Resolutions Pro
Sample 3
%Transmittance
Wavenumber
467.128 9.184
402.093 0.541
603.221 91.264
1990.978 37.863
1875.344 69.759
1508.587 6.039
2090.578 35.212
2115.503 82.211
2330.018 104.792
2902.897 142.009
3510.665 0.251
Name
Sample 3

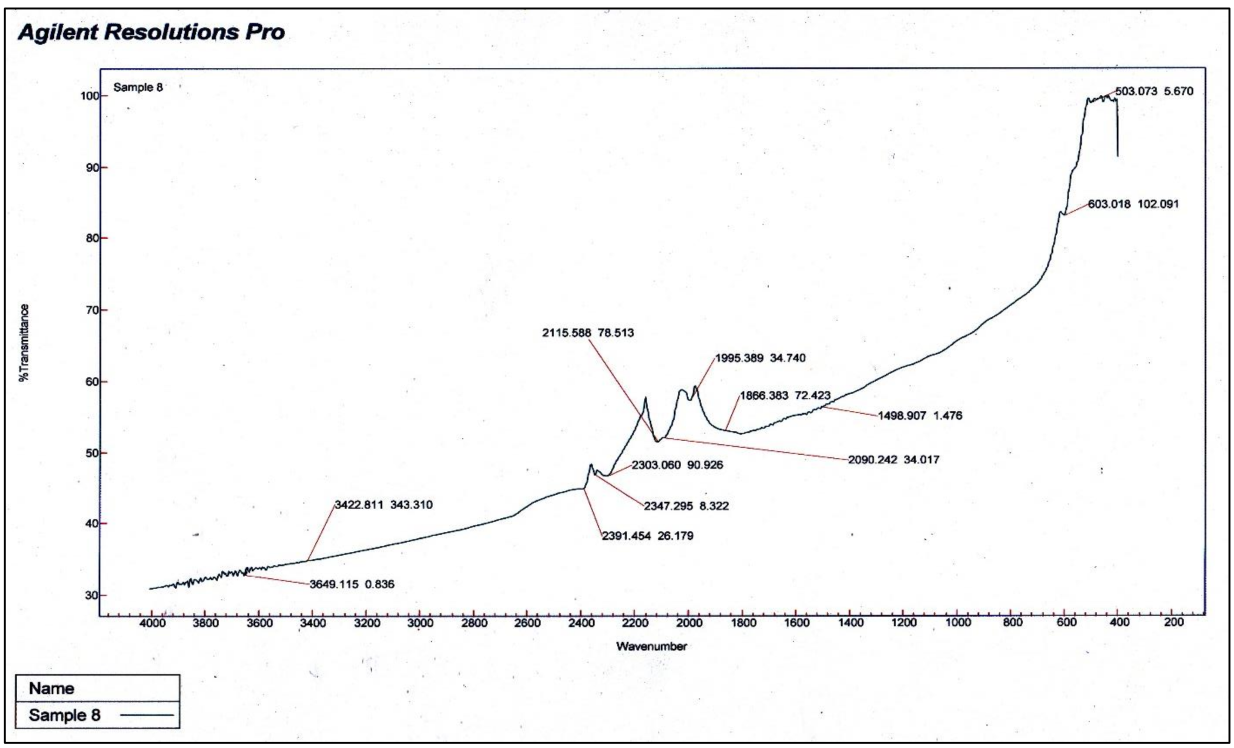


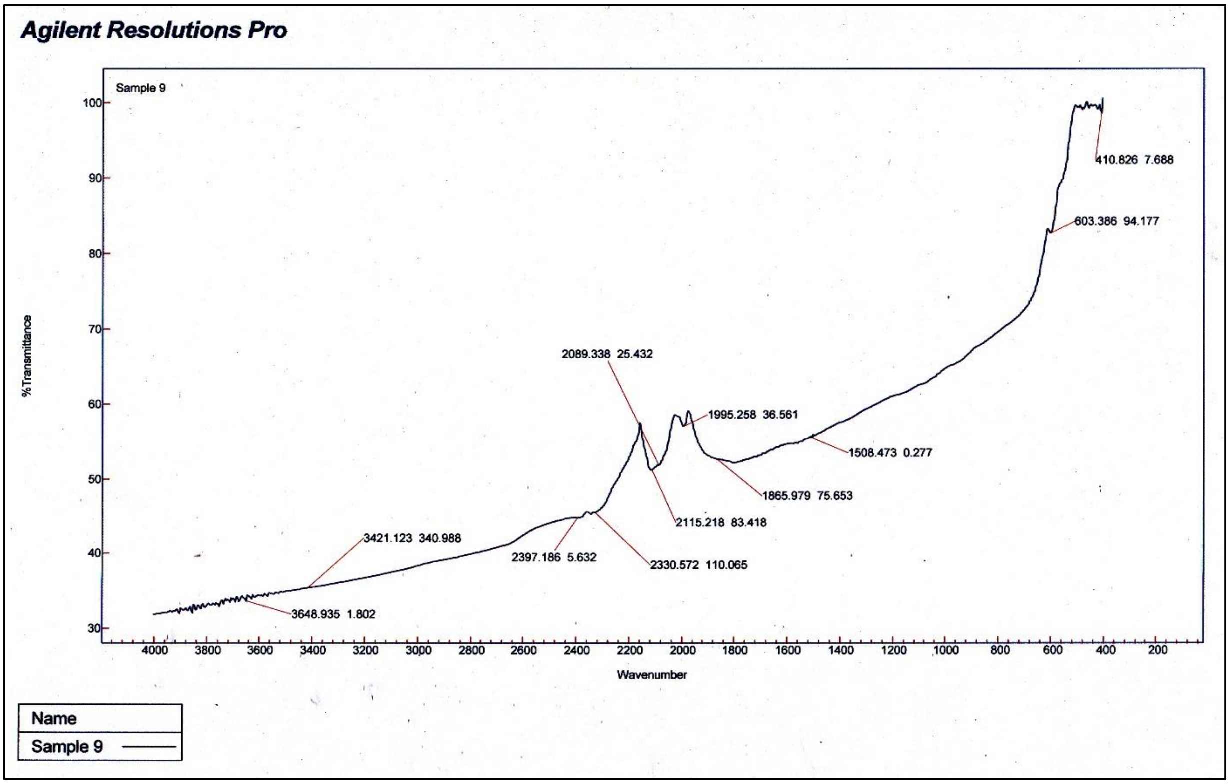
Agilent Resolutions Pro
Sample 4
%Transmittance
Wavenumber
445.590 5.355
416.801 8.106
602.766 100.031
1994.643 27.316
1827.411 91.775
1499.114 0.042
2115.207 64.923
2089.572 29.867
3675.558 4.990
2324.894 77.434
2396.268 6.445
3421.587 -0.143
3648.873 2.079
Name
Sample 4


Agilent Resolutions Pro
Sample 5
%Transmittance
Wavenumber
467.766 7.217
418.753 8.589
603.672 87.568
1458.698 -2.053
1995.183 31.304
1866.733 64.097
2325.038 80.409
2116.321 72.858
2090.360 22.121
3675.709 5.953
3649.037 0.995
3421.926 0.130
2392.514 3.792
3629.311 5.025
Name
Sample 5


Agilent Resolutions Pro
Sample 6
%Transmittance
Wavenumber
430.983 15.661
1995.579 45.888
603.785 93.257
1874.892 73.252
1394.572 1530.864
2090.242 44.291
2115.281 101.893
3464.101 0.189
2332.112 115.521
Name
Sample 6


Agilent Resolutions Pro
Sample 7
%Transmittance
Wavenumber
460.412 3.845
417.532 10.82
436.541 5.613
603.009 88.994
2090.193 36.659
1993.870 36.925
1396.374 1237.012
2115.751 82.814
1864.984 77.267
3463.029 422.059
2343.782 152.928
Name
Sample 7


Agilent Resolutions Pro
Sample 8
%Transmittance
Wavenumber
503.073 5.670
603.018 102.091
2115.588 78.513
1995.389 34.740
1866.383 72.423
1498.907 1.476
2090.242 34.017
2303.060 90.926
2347.295 8.322
3422.811 343.310
2391.454 26.179
3649.115 0.836
Name
Sample 8



Agilent Resolutions Pro
Sample 9
% Transmittance
Wavenumber
410.826 7.688
603.386 94.177
2089.338 25.432
1995.258 36.561
1508.473 0.277
1865.979 75.653
2115.218 83.418
3421.123 340.988
2397.186 5.632
2330.572 110.065
3648.935 1.802
Name
Sample 9

ORIGINAL AAS RESULT

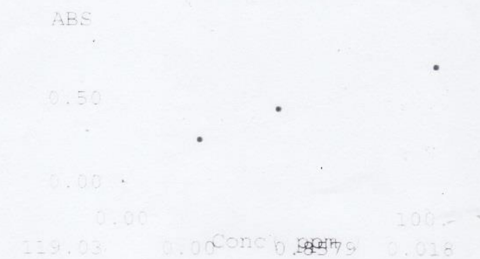
Table of Each Element 8/8/14 3:34 PM

Analysis Mode :Flame/Manual
Analysis Name :Cr
Comment :Cr080814
Description :

Meas. Date :8/8/14 3:33 PM
Element:Cr STD Unit :ppm UNK Unit :ppm

Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF
STD1		0.00	0.00	-0.0001	0.000
STD2		25.00	0.00	0.2588	0.004
STD3		50.00	0.00	0.4415	0.008
STD4		100.00	0.00	0.6947	0.014

Coefficient :K3=--
K2=--
K1=6.763543E-003
K0=5.282000E-002
Corr.Coef. :0.9846



		Sample ID	Conc.	RSD(%)	ABS	REF
control		UNK-001	119.03	0.00	0.8579	0.018
		UNK-002	124.68	0.00	0.8961	0.018
		UNK-003	124.16	0.00	0.8926	0.018
		UNK-004	123.23	0.00	0.8863	0.017
		UNK-005	123.67	0.00	0.8893	0.017
sample 1	15	UNK-006	122.31	0.00	0.8801	0.017
	30	UNK-007	120.47	0.00	0.8676	0.016
	x	UNK-008	117.24	0.00	0.8458	0.015
	x	UNK-009	115.93	0.00	0.8369	0.015
	75	UNK-010	110.40	0.00	0.7995	0.013
	45	UNK-011	103.21	0.00	0.7509	0.011
	60	UNK-012	103.70	0.00	0.7542	0.011
sample 2		UNK-013	102.31	0.00	0.7448	0.011
		UNK-014	102.07	0.00	0.7432	0.011
		UNK-015	101.93	0.00	0.7422	0.011
		UNK-016	100.80	0.00	0.7346	0.011
		UNK-017	104.69	0.00	0.7609	0.011
sample 3		UNK-018	90.11	0.00	0.6623	0.009
		UNK-019	84.48	0.00	0.6242	0.008
		UNK-020	92.85	0.00	0.6808	0.009
		UNK-021	88.31	0.00	0.6501	0.008
		UNK-022	94.12	0.00	0.6894	0.009
sample 4		UNK-023	85.09	0.00	0.6283	0.008
		UNK-024	82.41	0.00	0.6102	0.008
		UNK-025	75.06	0.00	0.5605	0.007
		UNK-026	73.23	0.00	0.5481	0.007
		UNK-027	74.06	0.00	0.5537	0.007
	x	UNK-028	39.19	0.00	0.3179	0.005
sample 5		UNK-029	120.85	0.00	0.8702	0.017
		UNK-030	124.83	0.00	0.8971	0.018
		UNK-031	125.05	0.00	0.8986	0.018
		UNK-032	124.33	0.00	0.8937	0.018
		UNK-033	121.84	0.00	0.8769	0.017
sample 6		UNK-034	119.15	0.00	0.8587	0.016
		UNK-035	121.50	0.00	0.8746	0.016
		UNK-036	120.53	0.00	0.8680	0.016
		UNK-037	120.58	0.00	0.8684	0.016
		UNK-038	120.29	0.00	0.8654	0.016

	Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF
	UNK-039		115.87	0.00	0.8365	0.015
sample 7	UNK-040		120.61	0.00	0.8686	0.016
	UNK-041		119.06	0.00	0.8581	0.015
	UNK-042		119.88	0.00	0.8636	0.015
X	UNK-043		100.62	0.00	0.7334	0.015
	UNK-044		120.08	0.00	0.8650	0.015
	UNK-045		121.38	0.00	0.8738	0.016
	UNK-046		121.43	0.00	0.8741	0.016
sample 8	UNK-047		123.45	0.00	0.8878	0.016
X	UNK-048		116.27	0.00	0.8392	0.016
	UNK-049		123.04	0.00	0.8850	0.016
	UNK-050		122.97	0.00	0.8845	0.016
	UNK-051		118.22	0.00	0.8524	0.015
	UNK-052		119.96	0.00	0.8642	0.015
sample 9	UNK-053		120.35	0.00	0.8668	0.015
	UNK-054		119.34	0.00	0.8600	0.015
	UNK-055		120.76	0.00	0.8696	0.015
	UNK-056		119.46	0.00	0.8608	0.015
	UNK-057		116.76	0.00	0.8425	0.015