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ADSORBENTS BASED ON CARBON NANOTUBES FOR WASTE WATER TREATMENTS.

by

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Dissertation submitted in partial fulfillment of
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CERTIFICATION OF APPROVAL

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A Project Dissertation Submitted To The
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Approved by,

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(Dr Moulay Rachid Baba)

University Technology Petronas
Tronoh, Perak
September 2011

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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Muhd Irsyaduddin Zakwan B Nor Saeran

ABSTRACT

Carbons materials are widely used adsorbent. Carbon Nanotubes (CNTs) are the new member of carbon family. They have been use in various fields such as composite reinforcements, sensors and others due to their extraordinary mechanical, electrical, thermal and structural properties. CNTs which have very large specific areas aside from high chemical and thermal stabilities make very attractive adsorbents. Many researches have been made to find the optimal condition for CNTs to operate. One of them is the affinity of the CNTs for certain type of wastewater.

In the introduction, I will describe about the waste water and heavy metals in the background study. I will also explain about why heavy metals are hazardous and the importance of removing it from the wastewater. I will also explain about the problem statement and the objective of the experiments. Lastly, I'll define my scope of study.

In the literature review, I'll first define the adsorption and introduce the CNTs. After that I'll state all the past research of several researchers about the optimal condition for CNTs adsorption including pH, temperature and others. Then I'll move to the research methodology which consist of the experiment variables, research methodology, equipment that needed for the experiment and the raw materials for this experiments.

Since the experiment is still in progress, I just put the observation that I can see during the experimentation. I'll also explain the reason behind the observation. Finally, I conclude my report.

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Chapter 1

Introduction

1.1 Background of study:

Wastewater is produced in almost all chemical plant. Most of them contain toxic and hazardous substances such as heavy metals, organic contaminants and others. If this waste water is being discharged into public without being treated, many life forms will be killed because these substances can cause many chronic and acute diseases. Therefore, it is very important for the waste water to be treated first before it is discharged. There are many methods to treat the waste water which include ion exchange, activated carbon, adsorption and others. Each of them has their own advantage and disadvantage.

Heavy metals are usual compound in any wastewater from industries. Before this wastewater is discharged to environment, it is important for the plant to treat the wastewater to remove the Heavy Metals. If the wastewater containing Heavy Metals are discharged to the river untreated, it can cause many problems to people. The heavy metals will be eaten by aquatic life forms and stored into their body. The Heavy Metals will then transfer and accumulated to the body of the one who eat those life forms since Heavy Metals are non-biodegradable. If many of Heavy Metals accumulated in body, it will cause negative impact on the body and inflict many diseases.

1.2 Problem Statement:

Carbon Nanotubes or CNT are the new member of the carbon family. CNT has two types which are single walled CNTs (SWCNT) and Multi Walled CNTs (MWCNT) and can be distinguished by observing their numbers of layers. CNT can be used directly as adsorbent or can be used after attaching functional groups to their external surface.

1) Will attaching the functional groups will increase the adsorption rate of heavy metals and selectivity of CNT.

2) Is attaching the functional group is more favorable than just using the CNT directly

1.3 Objectives:

There are several objectives for this experiment:

1) Performing experiment using pristine and functionalized CNTs to remove heavy metal from sample waste water.

2) To compare the adsorption properties of the two samples above.

3) To find the most compatible functional group for the type of wastewater used.

4) Prove that attaching functional group to CNT will yield more adsorption rate.

1.4 Scope of Study:

This study will focus on Multi-walled CNT as adsorbent. One of the experiments will focus on using pristine (as received) and functionalized CNTs. In the result, it is expected to be able to compare the adsorption rate and selectivity of both the experiment. Furthermore, this experiment will also be conducted to find the most compatible functional group for the sample waste water composition.

Chapter 2

Literature Review

2.1 Adsorption

In adsorption process, one or more components of a gas or liquid are adsorbed on the surface of the solid adsorbent and a separation is accomplished. In commercial processes, the adsorbent is usually in the form of small particle in a fixed bed. Many adsorbents have been developed for a wide range of separation. Typically, the adsorbents are in the form of small pellets, beads and granules ranging diameter from 0.1mm and 12mm. there are a number of commercial adsorbents such as activated carbon, silica gel, activated alumina, molecular sieve zeolites and synthetic polymer or resin.

In wastewater treatment, activated carbon normally used in as an adsorbent in advanced stage to remove soluble organics which may still present after secondary treatment and filtration. The refractory organic material will be adsorbed by the activated carbon. Once the adsorbent get saturated, it must be regenerated in because activated carbon is an expensive product.

2.2 Introduction to Carbon Nanotubes

Carbon Nanotubes or CNT has two kinds which are Single Walled CNT and Multi Walled CNT. Single Walled CNT is a tube made of a single graphite layer rolled up into a hollow cylinder (Stéphanie, Christian and Janina, 2004). The Single Walled CNT is distinguished from each other by their by their chirality. The chirality will determine their properties and diameter since its chirality are unique for each type of CNT. Figure 1 shows the example of Single Walled CNT (Jose Mauricio Marulanda, 2009).

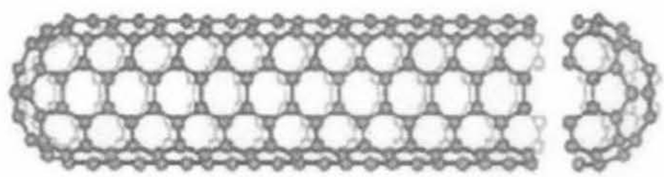

Figure 1: The microscopic view of Single Walled Carbon Nanotubes

Unlike SWCNTs, Multi Walled CNTs has multiple layers of carbon instead of one. This allows more adsorbate to be attached to its surface.

2.3 Effect of pH on the Adsorption Rate

Adsorption of MWCNTs is affected by many factors. One of them is pH. According to research by Anna Stafieja and Krystyna Pyrzynska, whenever the pH of the solutions is higher than the pH in the surface of CNTs (pH_{pzc}), the adsorption rate will increase. From the electrostatic point of view, when the pH of the solution is higher than pH_{pzc}, the surface of the CNT becomes negatively charged. The heavy metals which are positively charged are easily attracted to the negative charge on the surface of the CNT. This is proven by the zeta potential value of the each CNT used by experiment by Goran, Aleksandar, Miodrag, Mirjana, Radoslav, Aleksandra and Petar (2009).

Table 1: Physical properties of raw-MWCNT, o-MWCNT and e-MWCNT.

Sorbents	Surface area ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Av. pore diameter (nm)	pH_{PZC}	Zeta potential (mV)
raw-MWCNT	187.58	0.755	16.09	4.98	–13.7 (pH 5.30)
o-MWCNT	78.49	0.328	16.72	2.43	–50.0 (pH 3.98)
e-MWCNT	101.24	0.538	21.25	5.91	–26.9 (pH 6.60)

The o-MWCNT is the MWCNT that has been mixed with concentrated H_2SO_4 and HNO_3. The e-MWCNT is the further purified o-MWCNT with Methanol, De-Ionized water and coupling agent.

Anna Stafieja and Krystyna Pyrzynska in their research have plotted the graph of adsorption rate versus the pH. The graph is given in Figure 1.

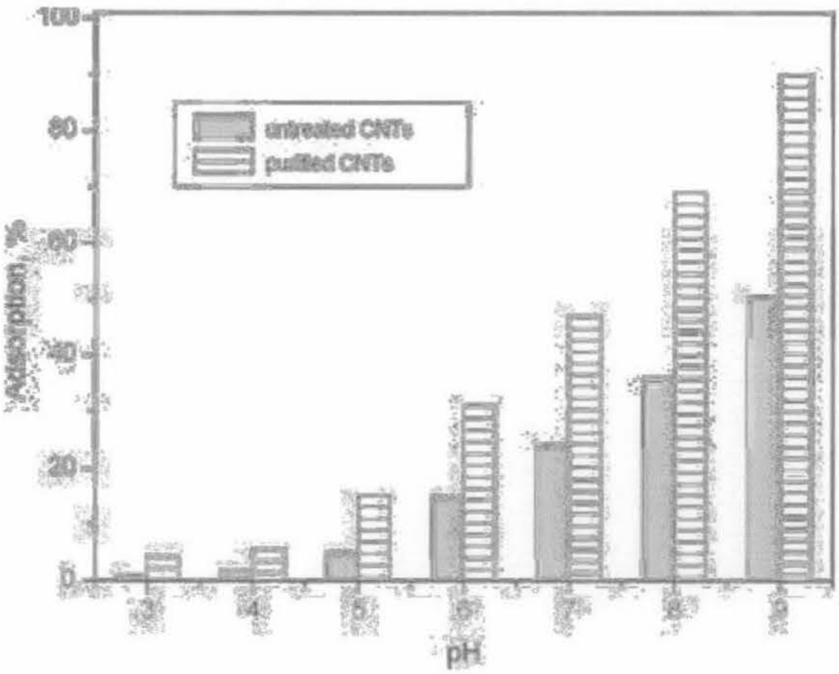

Figure 2: Effect of pH on the adsorption of Co(II) with untreated and purified HNO_3 carbon nanotubes

However, Di Xu, Xiaoli Tan, Changlun Chen and Xiangke Wang in their research has conclude that the adsorption rate of the Pb^+ started to going down at pH more than 10. It is also concluded that the best pH fall from 7 to 9. Below is the result of their research.

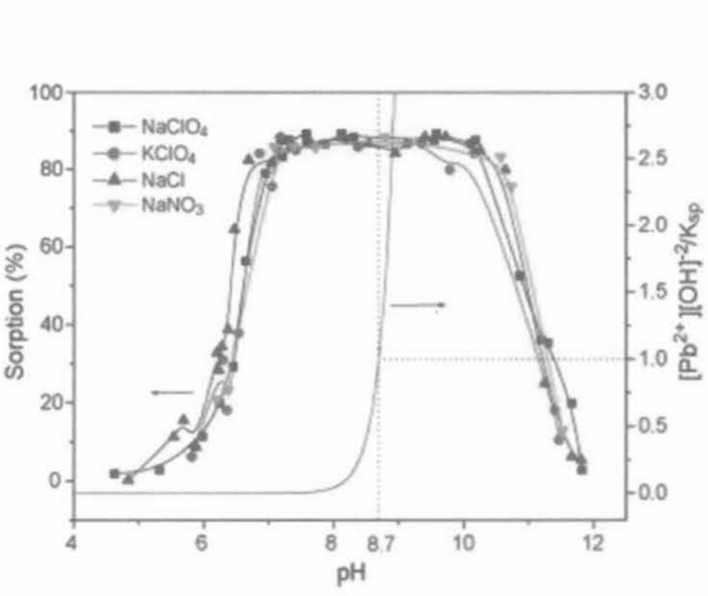

Figure 3: Variation in sorption of Pb(II) to oxidized MWCNTs as a function of equilibrium pH and foreign ions.

Apart from the journals mentioned above, there are many researches on the pH effect which is research by Gadupudi, Chungsying, and Fengsheng (2007), Chungsying and Huantsung (2008), Mustafa, Kadriye, Canan and Mustafa (2007), K., E.M. and N.J. (2008), Chao-Yin and Han-Yu (2008), Munther and Jean-Luc (2006) and Zhanming, Teresa, Zongbin, Mei and Jieshan (2009).

2.4 Effect of Temperature on the Adsorption Rate

During the process of attaching functional groups to the surface of MWCNTs, if it is refluxed multiple times or at a long time at extreme chemical condition (high temperature or high pressure), some of the groups on its surface might decompose thus decreasing the adsorption rate. Research also proves that pristine MWCNT can withstand temperature up to 800°C before starting to decompose while the functionalized CNT is having their wt% decreased at much less temperature. This proves that functionalized CNT are thermally unstable (Goran and all, 2009). Below is the result of the research by Hongjuan, Ailin, Feng, Hao and Jian (2007).

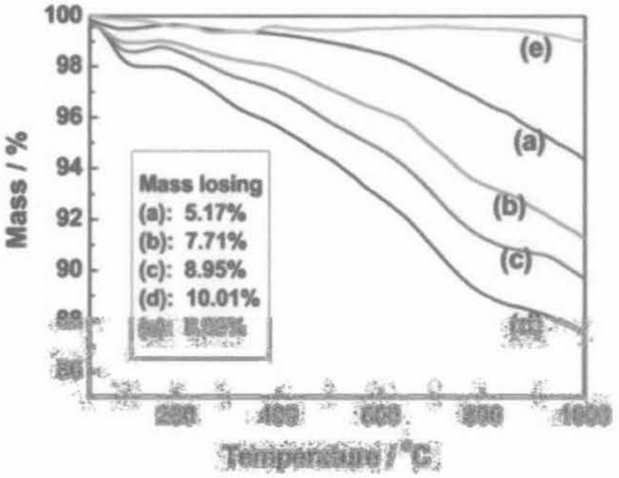

Figure 4: TG of MWCNTs with (a) Acidified for 1 hr., (b) Acidified for 2 hrs., (c) Acidified for 6 hrs., (d) Acidified for 10 hrs. and (e) Annealed 6 hrs. acidified MWCNT in 800°C.

However, the adsorption rate can increase if the temperature of the solution increases in high temperature. According to research by Gadupudi, Chungsying, and Fengsheng (2007), the sorption capability of Pb^{2+} and Zn^{2+} ions remarkably increased with a rise in temperature. The increasing temperature will result in the rise in diffusion rate of metals ions thus increasing the contact between the wall of CNTs and the metal ions. The sorption rates of metal ions are determined by the activation energy of sorption, E_a. The faster the rate of sorption process, the lower the E_a. It is also stated in their journals that SWCNTs has much lower E_a than MWCNTs. This can be explained by the fact that SWCNT consist only one layer of atomic layers. Multiple layers like MWCNTs require more E_a for the diffusion of metals ions. Plus, the E_a is affected by the diffusion of the solution. The E_a will be less with the higher diffusivity. Since the diffusion rate is increased at high temperature, the less energy is required for the sorption process.

2.5 Others Factors Affecting the Adsorption Rate

There's other factor that may increase or decrease the adsorption rate of the CNTs such as dosage (Xuemei, Changlun, Masaaki and Xiangke, 2010). Using higher dosage will increase the adsorption rate since we are providing more surface area for the adsorption to happen. The amount of functional groups attached to the CNTs will also affect the adsorption rate. Higher amount will yield more adsorption rate. To increase the amount of functional groups, we must make sure that we mix the acid with the CNTs for longer time.

Munther and Jean-Luc (2006) in their research also mention about the effect to adsorption time to the amount of heavy metals adsorbed. Below is the result of their experiments.

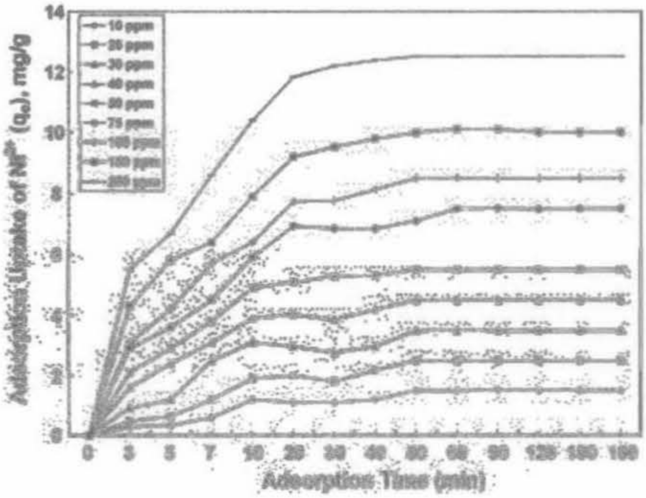

Figure 5: Effect of adsorption time and initial nickel ions concentrations on the adsorption uptake of nickel ions for the as-produced CNTs.

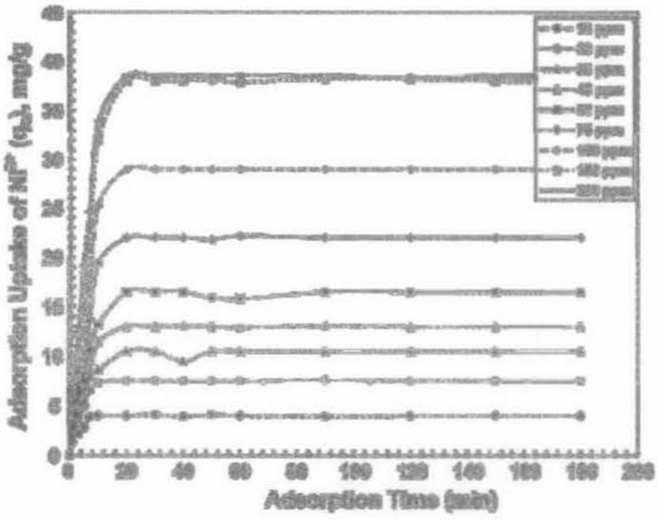

Figure 6: Effect of adsorption time and initial nickel ions concentrations on the adsorption uptake of nickel ions for the functionalized CNTs.

As you can see from figure above, we can conclude that the amount of nickel doesn't really matter since everything will be adsorbed at 60 minute. Plus, the raw CNTs and the functionalized CNTs yield the same result. However, it is clear that the functionalized CNTs have more adsorption rate than pristine CNTs.

Chapter 3

Methodology

3.1 Research Methodology

In completing this research, there are many steps that I have to takes. The first step is to understand the title of the research that I have accepted. To do this, I seek my Supervisor guidance to further understand the topic. My supervisor has explained about the topic and I got the general idea of the topic. After that I myself have made further studies about this topic to understand in depth about this topic.

Then, I was assigned to make a proposal about this topic. In doing the proposal, I have used many references such as books and journals. Books have helped me in understanding the fundamental principles of my topic while journals have help me in understanding in details about CNTs. Journals also provide me with up to date information about the CNTs based on past researches. I also acquire many useful informations such as optimal condition for CNTs reaction and effect of several condition to adsorption rates of CNTs. Then, I was assigned to present this proposal to my supervisor and internal examiner, Mrs. Suriati Binti Sufian. Lastly I need to finish this interim report to be sent to both my supervisor and internal examiner.

The next step is doing the experiment. For the experiment, first I need to fill is the Material Safety Data Sheets (MSDS) forms before I am allowed to enter the lab. This need to be done so that I realizes the danger of each chemical and takes extra caution in doing the experiment. After doing the experiment, the result will be compiled and properly analyst to conclude the experiment.

3.2 Experiment Variable

3.2.1 Controlled Variable:

1. Temperature of the solution:
   - 140°C for Functionalization Experiment
   - 25°C for Heavy Metal Removal
2. pH of the solution:
   - pH for functionalization depends on the acids used
   - pH of the wastewater will be kept as it is
3. MWCNT

3.2.2 Independent Variable:

1. Functional Groups on MWCNT

3.2.3 Dependent Variable:

1. The amount of Heavy Metals adsorbed

3.3 Project Activity

This experiment will be split into two parts. The first are functionalization and the second one is waste water removal.

3.3.1 Functionalization

1) 70 mL of Acid is added to 0.03 g of MWCNT.
2) The solution is then heated at 100°C and continuously stirred for 1 hour.
3) The solution is left overnight after it is diluted.
4) The solution will be filtered using ceramic filter and dried at 80°C.
5) The functionalization experiment is then continued by varying the acid solution to 140mL and MWCNT amount to 0.06g and the time to 3 hours.

3.3.2 Waste water HM removal experiment

1) 0.03 g of the CNT without any Functional Groups will be added into 30 ml wastewater with the pH values of the solution are kept. The solution will then be sent for Sonication (dispersion) for 1 hour. After one hour has passed, the solution will finally be sent for 5 hours of stirring.
2) After 5 hours, the suspension will be sent to be separated using Centrifuge
3) The wastewater is then sent to Atomic Adsorption Spectrometer.
4) The amount of lead adsorbed was calculated by subtracting the equilibrium lead content with initial lead content.
5) The experiment are repeated by using CNT with various Functional Groups

3.4 Raw material needed:

1) Waste water from PETRONAS Malacca.
2) Multi Walled Carbon Nanotubes.
3) Hydrochloric Acid (HCl), Sulfuric Acid (H_2SO_4) and Nitric Acid (HNO_3)

3.5 Equipment listing:

1) Sonicator
2) Atomic Adsorption Spectroscopy (AAS)
3) Stirrer
4) Fourier Transform Infra-Red (FT-IR)
5) Centrifuge

3.6 Gantt Chart

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	Submission of of Draft Report																
5	Submission of Dissertion (Soft Bound)																
6	Submission of Technical Paper																
7	Oral Presentation																
8	Submission of Dissertion (Hard Bound)																

Key Milestone
Process

Chapter 4

4.1 Findings

During the experiment, there are many observations that can be seen from the sample. Notice that this is just an observation. This observation will be discussed in discussion part.

For Functionalization experiment:

1. The color of the acid doesn't change much except for HCl at 3 hour. The color change from light yellow to gold color.
2. The weight of the CNTs becomes heavier after functionalization. Although the change was small.

The adsorption experiment

1. The color of the wastewater is become lighter. The color change from deep yellow to light yellow.
2. After the adsorption experiment, the volume of the wastewater drop. Usually, the volume drop by 5 mL even with the CNTs still inside the wastewater.

4.2 Data Gathering

For gathering data, there are two ways for getting the data. One is using Fourier Transform Infra-Red. Fourier Transform Infra-Red spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. From this equipment, the type of chemical bonding and bonds that exist in the CNTs can be analyzed.

The second ways to obtain data is by using Atomic Adsorption Spectroscopy. Atomic absorption spectroscopy (AAS) is a spectroanalytical procedure for the qualitative and quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state. In analytical chemistry the technique is used for determining the concentration of a particular element (the analyte) in a sample to be analyzed. AAS can be used to determine over 70 different elements in solution or directly in solid samples. This equipment gives the concentration of each element in the treated wastewater.

4.3 Data Analysis

Fourier Transform Infra-red (FTIR)

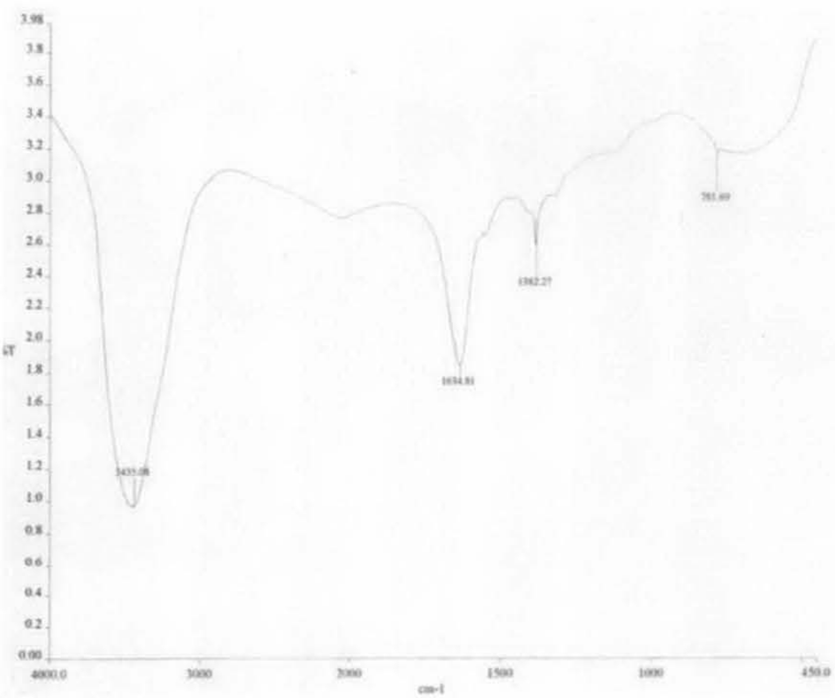

Figure 7: FTIR for NHO3

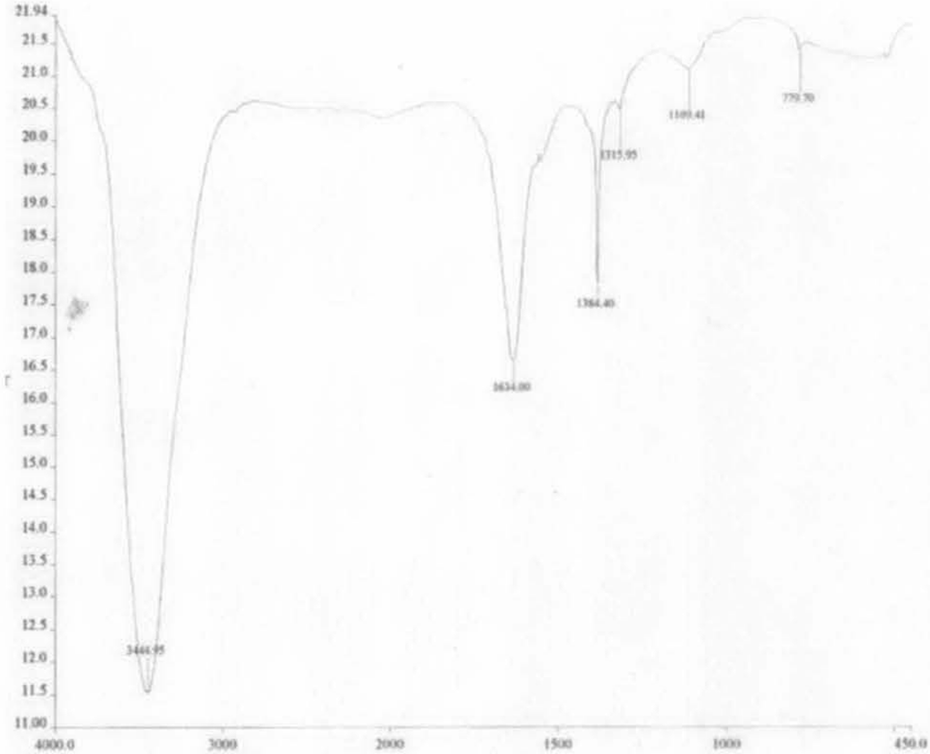

Figure 8: FTIR for NHO3 3 Hour

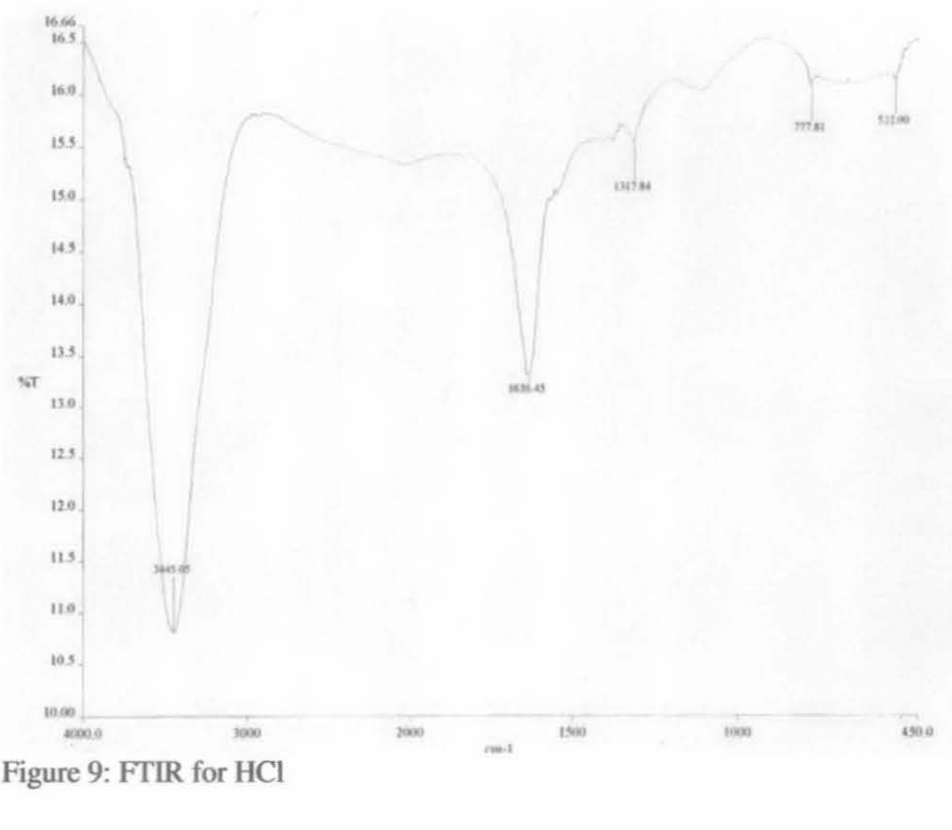

Figure 9: FTIR for HCl

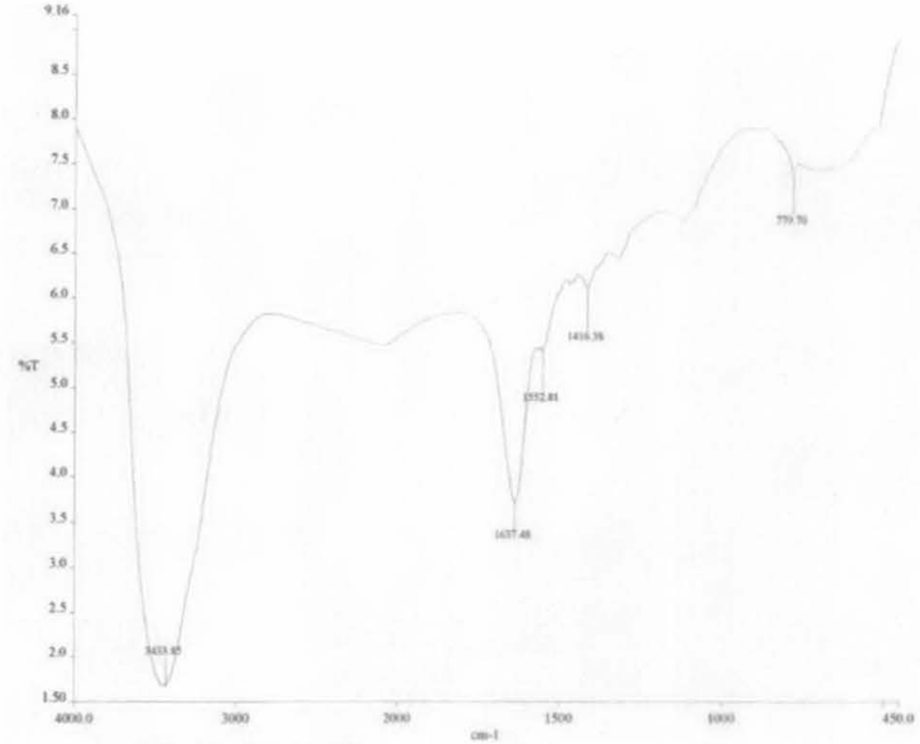

Figure 10: FTIR for HCl 3 Hour

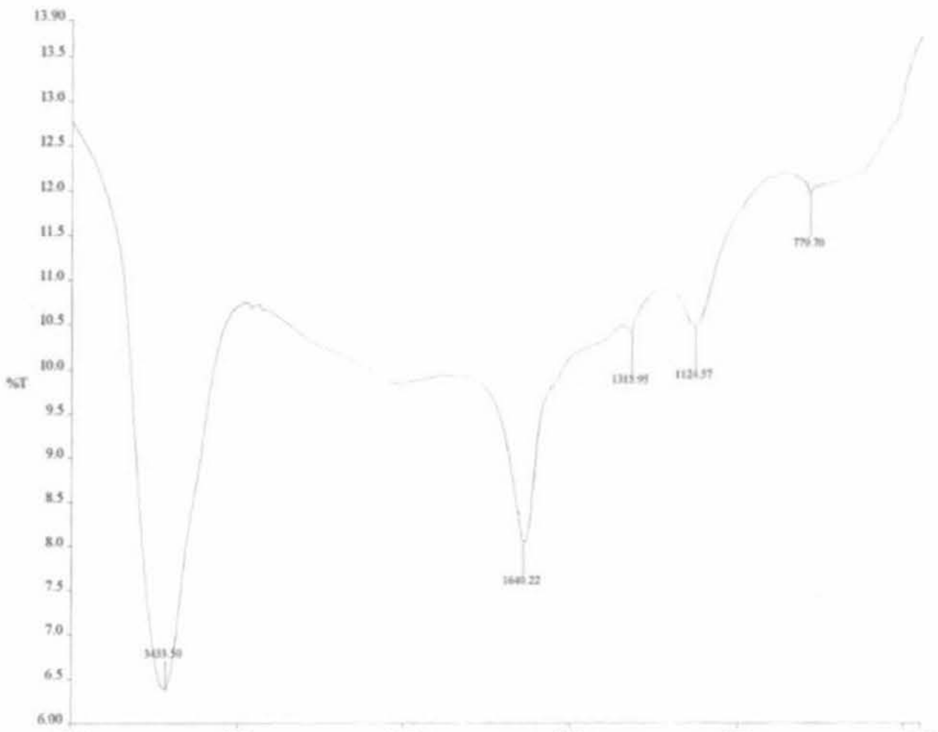

Figure 11: FTIR for H2SO4

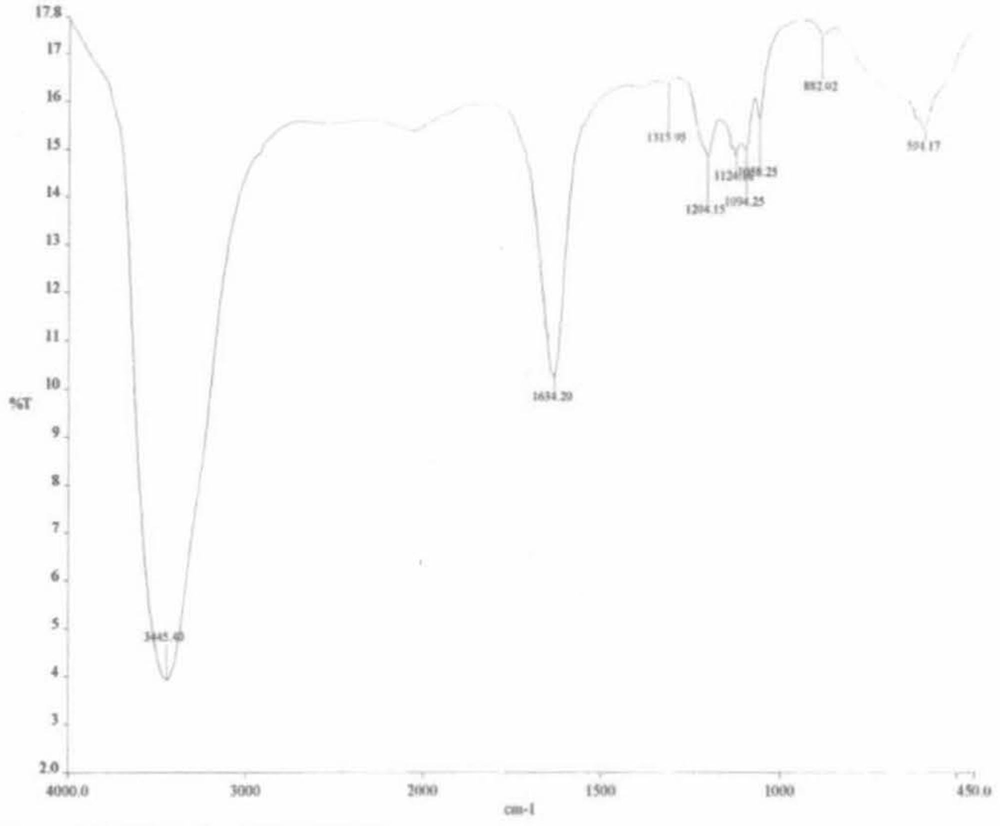

Figure 12: FTIR for H2SO4 3 Hour

4.4 Discussion

Based on the observation, the color of the acid change because the functional group that is in the acid was changes with the functional group in the surface of CNTs. The reason why only the 3 hour HCl change color because only at 3 hours that the element is enough to change the color of the acid. The weight of the CNTs also change because the functional groups attached to the CNTs contribute to the weight of functionalized CNTs. However the weight change is small and trivial.

After the adsorption experiment, we can observe that the color of the wastewater become lighter than the original wastewater. This is proof that the heavy metal is adsorbed by the CNTs. Another observation that can be seen is the volume of the wastewater is obviously reduced. This can be concluded that the wastewater has lost Heavy metal thus decreasing in volume.

Chapter 5

Conclusion

CNTs are the new family of the Carbon family. They have been used in various field such as electronic and chemicals. It is also has potential as the best adsorbents for heavy metals. K. Pillay, E.M. Cukrowska and N.J. Coville (2008) have already proven that unfunctionalised and functionalized CNTs has superior adsorption rate as compared to activated carbon. It is worth to consider using CNTs as adsorbent for a process that needs fast adsorption rate.

References

Gaoa Z. M., Bandosz T. J., Zhao Z. B., Han M. and Qiu J. H. (2009), Investigation of factors affecting adsorption of transition metals on oxidized carbon nanotubes, Journal of Hazardous Materials, Volume 167, Issues 1-3, 15 August 2009, Pages 357-365

Kandah M. I., and Meunier J. L. (2006). Removal of nickel ions from water by multi-walled carbon nanotubes. Journal of Hazardous Materials, Volume 146, Issues 1-2, 19 July 2007, Pages 283-288

Kuo C. Y. and Lin H. Y. (2008). Adsorption of aqueous cadmium (II) onto modified multi-walled carbon nanotubes following microwave/chemical treatment. Desalination, Volume 249, Issue 2, 15 December 2009, Pages 792-796

Lu C. S. and Chiu H. T. (2008), Chemical modification of multiwalled carbon nanotubes for sorption of Zn^{2+} from aqueous solution, Chemical Engineering Journal Volume 139, Issue 3, 15 June 2008, Pages 462-468

Marulanda J. M. (2009), Current Transport Modeling Of Carbon Nanotubes, VDM Verlag Dr. Müller.

Pillay K., Cukrowska E.M. and Coville N.J. (2008). Multi-walled carbon nanotubes as adsorbents for the removal of parts per billion levels of hexavalent chromium from aqueous solution. Journal of Hazardous Materials, Volume 166, Issues 2-3, 30 July 2009, Pages 1067-1075

Rao G. P., Lu C. S., and Su F. S.(2007), Sorption of divalent metal ions from aqueous solution by carbon nanotubes: A review, Separation and Purification Technology, Volume 58, Issue 1, 1 December 2007, Pages 224-231

Reich S., Thomsen C. and Maultzsch J. (2004), Carbon Nanotubes: Basic Concepts and Physical Properties, WILEY-VCH Verlag GmbH & Co. KGaA, Weinbeim.

Ren X. M., Chena C. L., Nagatsu M. and Wang X. K. (2010), Carbon Nanotubes As Adsorbents In Environmental Pollution Management: A Review, Chemical Engineering Journal, Volume 170, Issues 2-3.

Stafieja A. and Pyrzynska K. (2007), Adsorption Of Heavy Metal Ions With Carbon Nanotubes, Separation and Purification Technology, Volume 58, Issue 1.

Tuzen M., Saygi K. O., Usta C. and Soylak M. (2007). Pseudomonas aeruginosa immobilized multiwalled carbon nanotubes as biosorbent for heavy metal ions. Bioresource Technology, Volume 99, Issue 6, April 2008, Pages 1563-1570

Vuković G. D., Marinković A. D., Čolić M., Ristić M. D., Aleksić R., Perić-Grujić A. A. and Uskoković P. S. (2010), Removal Of Cadmium From Aqueous Solutions By Oxidized And Ethylenediamine-Functionalized Multi-Walled Carbon Nanotubes, Chemical Engineering Journal, Volume 157, Issue 1, 15 February 2010, Pages 238-248

Wang H. J., Zhou A., Peng F., Yu H. and Yang J. (2007). Mechanism study on adsorption of acidified multiwalled carbon nanotubes to Pb(II). Journal of Colloid and Interface Science, Volume 316, Issue 2, 15 December 2007, Pages 277-283

Xu D., Tan X. L., Chen C. L. and Wang X. K. (2007), Removal of Pb(II) from aqueous solution by oxidized multiwalled carbon nanotubes, Journal of Hazardous Materials, Volume 154, Issues 1-3, 15 June 2008, Pages 407-416