A Study of Cadmium, Nickel and Copper Adsorption Using Multi-walled Nanotubes

by

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CERTIFICATION OF APPROVAL

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July 2010

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.

NOOR AZURAH ZAINA ABIDIN

ACKNOWLEDGEMENT

Abstract

Water contaminated with heavy metals has harmful effects not only to human being but the environment as well. Their non-biodegradable characteristic may possess possible accretion in living organism and may accumulate to toxic concentration and causes ecological damage under certain environmental condition. This dissertation promotes the adsorption process of heavy metal ions by adopting Multi-walled Carbon Nanotubes (MWNTs) as an adsorbent. MWNTs have been identified as promising materials for use in a wide range of applications. In combination with the large surface area, they have also strapped up with d-spacing more compatible with most heavy metal ions and endowed with exceptionally high material properties such as electrical and thermal conductivity, strength, stiffness, and toughness. The optimum contact time, effect of pH and the effect of concentration were investigated. Experiments were done in a batch process mode using water bath shaker at shaking speed of 200 rpm. The highest removal efficiency achieved at 99.8% for copper followed by 99.7% and 94.6% for cadmium and nickel respectively. The affinity order was determined to be Cu (II) > Cd (II) > Ni (II).

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CHAPTER 1
INTRODUCTION

Water that is contaminated with cadmium (Cd), Nickel (Ni) and copper (Cu) have harmful effect on human beings as well as the environment. Their non biodegradable characteristic may possess possible accumulation in living organisms. Under certain environmental conditions metals may accumulate to toxic concentration and they cause ecological damage. In aquatic systems, metals are present as dissolved ions and complexes, suspended and colloids ions and solid in sediments (Özmen, Külahcı et al., 2004). These pollutants are present in many industrial wastewaters such as those produced by metal plating facilities, mining operations, battery manufacturing processes, the production of paints and pigments, and the glass production industry (Argun, Dursun et al., 2007)

Excessive human intake of copper (Cu) leads to severe mucosal irritation and corrosion, the widespread capillary damage, hepatic and renal damage, and central nervous system irritation followed by depression. Severe gastrointestinal irritation and possible necrotic changes in the liver and kidney can also occur. The high concentration intake of cadmium causes *itai itai* disease (Mukesh, Puneet et al., 2008). The effects of Ni exposure vary from skin irritation to damage to the lungs, nervous system, and mucous membranes. Some heavy metals are also known carcinogens (Argun, Dursun et al., 2007) Therefore, the removal of excess heavy metal ions from wastewater is essential to protect human and environmental health.

Several methods have been reported for removing heavy metals from wastewater. These include chemical precipitation, reverse osmosis, adsorption, ion exchange or electrolytic recovery (Stafiej & Pyrzynska, 2007). However, some of these methods suffer from drawback. For instance, both chemical and electrochemical precipitation, pose a

significant problem in terms of disposal of the precipitated wastes. Same goes to ion exchange which does not appear to be economical (Argun, Dursun et al., 2007)

On the other hand, aquatic plants, microorganisms and wood-based materials such as sawdust and bark increase the COD of water even though these types of adsorbent used in removing heavy metal by adsorption are economical.

This dissertation introduced a fairly new adsorbent in removing heavy metal ions by adsorption process. The aim of this project is for the removal of cadmium Cd (II), nickel Ni (II) and copper Cu (II) using a type of carbon nanotubes which is the multi-walled carbon nanotubes (MWNTs).

Carbon nanotubes (CNTs) have been reported to hold massive impending in eradicating many sorts of impurities. These include chlorobenzenes, herbicides and as well as lead (Pb) and dioxin (Stafiej & Pyrzynska, 2007). MWNTs that consist of cylindrical graphitic polymeric structures are endowed with exceptionally high material properties such as electrical and thermal conductivity, strength, stiffness, and toughness (cefic, 2009). These properties provide a huge potential for a good adsorbent in removing heavy metal pollutants.

Wide variety of studies on adsorption process in removing metal ions were reported in the literature but with regards to carbon nanotubes (CNTs) are limited to only a few parameters and the type of metals reported in previous studies were very general. To that extent, this dissertation will focus only on three types of metal ions that are cadmium (Cd), nickel (Ni) and copper (Cu) and widen the parameters of study. The optimum contact time, the effects of metal ions concentrations and the effect of pHs of solution as well as the effect of temperature on the absorption efficiency using MWNTs were investigated.

The next chapter of this dissertation discussed in details on legislations which concern on wastewater contaminants. Four regulation under environmental quality act (EQA) 1974 applied by Malaysian department of environment (DOE) with regards to water safety regulations .Also been discussed in the literature review is the background information of carbon nanotubes. Detail information including characteristics and a bit on the d-spacing of multi-walled carbon nanotubes (MWNTs) were discussed. Moreover, a bit on heavy metal definition, characteristic and the effect to human were conferred. More thorough elaboration on adsorption processes and principles were thrashed out. Detailed discussion on equilibrium isotherms such as Freundlich, Langmuir and BET theory were conversed as well. Methodologies on previous study with regards to adsorption processes in removing heavy metals pollutants were also reported in the literature. Comparison on methodologies, lesson learnt and outcome of previous studies were well thought-out in this chapter as well. It is wise to revise and learned from previous research to get a better understanding in order to develop good methodology and reduce possibility to repeat the same mistake.

Chapter 3 conversed about the methodologies being applied for this project. This chapter entails specifically on the step by step procedure used for each experiment including the material and experimental preparations. In brief, experiments were operated in a batch process mode using water bath shaker. Experiments were performed in sequence to ensure optimum adsorption capacity obtained starting from studying the effect of contact time, followed by determining the effect of concentration and the effect of pH as well as the effect of temperature.

The exciting chapter in this study is chapter 4 which is the results and discussion chapter. This chapter provides the outcome of the experimental works. Data distributions were sorted accordingly into tables and graph for easier observation. Nickel with 20 mg/l of concentration provides high adsorption capacity. A period of 4 hours

demonstrated the best duration for the experimental study. On the other hand cadmium illustrated the best performance of adsorption with 98% of removal efficiency. More detail elaboration on the results obtained as well as the comparison on the adsorption peak was conferred in details in this chapter.

Following results and discussion chapter is the conclusion chapter where outcomes of this study were concluded. In brief, this chapter highlights the important result and so as the important key of discussion. Any flaws or the need to further study on this dissertation were discussed on recommendation section.

CHAPTER 2
LITERATURE REVIEW

2.1 Legislation

Malaysia has adopted Environmental Quality Act (EQA) as a pragmatic approach in dealing with climate change and environmental issues. EQA is an enabling piece of legislation for preventing, abating and controlling pollution, and enhancing the environment, or for other related purposes. Pollution, as declared in EQA, includes the direct or indirect alteration of any quality of the environment or any part of it by means of a positive act or act of omission (UNESCAP, 2010)

2.1.1   Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979

These Regulations may be cited as the Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979 and shall be deemed to have come into force on the 1st January 1979; except for those sources in existence before this date, these regulations shall come into force on January 1, 1981(DOE, 2006). There are 7 parts under this regulation. These regulations shall apply to discharges of effluent into any inland waters, other than the effluents discharged from prescribed premises or other premises specified in the first schedule or both.

2.1.2   Environmental Quality (Sewage and Industrial Effluents) (Amendment) Regulations 2000

These regulations are an addition of the Environmental Quality (Sewage and Industrial Effluents) Regulations 1979. There are 7 parts with 24 regulations falls under Environmental Quality (Sewage and Industrial Effluents) (Amendment) Regulations 2000. These regulations encompasses of parameter limits of effluent of standards A and

B, list of catchment areas where standard A applies and parameter limits of effluent other than of standard A or B to name a few (DOE, 2006)

2.1.3 Environmental Quality (Prescribed Premises) (Scheduled Wastes Treatment and Disposal Facilities) Regulations, 1989

These Regulations may be cited as the Environmental Quality (Prescribed Premises) (Scheduled Wastes Treatment and Disposal Facilities) Regulations 1989 and shall come into force on the 1st May 1989. Scheduled wastes means any waste falling within the categories of waste listed in the First Schedule to the Environmental Quality (Scheduled Wastes) Regulations 2005. There 9 regulations highlighted by this order (DOE, 2006).

2.1.4 Environmental Quality (Scheduled Wastes) Regulations, 2005

These regulations may be cited as the Environmental Quality (Scheduled Wastes) Regulations 2005. This regulation is the amendment of Environmental Quality (Scheduled Wastes) Regulations, 1989 and come into operation on 15 August 2005. There are 17 regulations have been highlighted which encompasses of citation and commencement until revocation (DOE, 2006).

2.2 Heavy Metals

The term "heavy metals" defined as commonly held for those metals, which have specific weights more than $5gcm^{-3}$ (Mukesh, Puneet et al., 2008). These heavy metal ions include cobalt, copper, nickel, chromium and zinc (Kobya, Demirbas et al., 2005). Heavy metals are not biodegradable and their presence in streams and lakes leads to bioaccumulation in living organisms, causing health problems in animals, plants, and human beings (Argun, Dursun et al., 2007).

Cadmium is used extensively in the manufacture of batteries, paints, and plastics. In addition, it is used to plate iron products, such as nuts and bolts for corrosion prevention.

It is from plating operations that most of the cadmium reaches the water environment. At extreme levels, it causes an illness called "Itai-Itai" decease, characterized by brittle bones and intense pain (Mukesh, Puneet et al., 2008). At low level of exposure over prolonged periods, it causes high blood pressure, sterility among males, kidney damage and flu-like disorders (Sawyer & McCarty, Perry L.: Parkin, Gene F., 1994).

(UCSC, 2008)

Figure 2.1 "Itai Itai disease symptom

Although **copper** is used commercially for many purposes, its major source in drinking water is corrosion of copper pipes used for water conveyance. Excessive human intake of Cu leads to severe mucosal irritation and corrosion, the widespread capillary damage, hepatic and renal damage, and central nervous system irritation followed by depression. Severe gastrointestinal irritation and possible necrotic changes in the liver and kidney can also occur. In surface waters, copper is toxic to aquatic plants at concentrations sometimes below 1.0 mg/l and has frequently been used as a sulfate salt to control growth of algae in water supply reservoirs. Concentration near 1.0 mg/l can be toxic to

some fish (Argun, Dursun et al., 2007; Mukesh, Puneet et al., 2008; Sawyer & McCarty, Perry L.: Parkin, Gene F., 1994).

Nickel is used in electroplating and the rinse waters from these operations constitute the major avenue by which salts of these metals gain access to aquatic environment. The effects of Ni exposure vary from skin irritation to damage to the lungs, nervous system, and mucous membranes (Argun, Dursun et al., 2007). Nevertheless, it appears to be of low toxicity in humans (Sawyer & McCarty, Perry L.: Parkin, Gene F., 1994).

Several processes have been used and developed over the years to remove metal ions, such as chemical precipitation, reverse osmosis, electrolytic recovery, ion exchange or adsorption (Stafiej & Pyrzynska, 2007).

2.3 Carbon Nanomaterial

Carbon nanomaterial defined as materials with a nanoscale component or structure that exerts the significant influence on properties or function (Richard, 2008). Carbon nanomaterial is all materials that are composed of grains, which in turn comprise many atoms. These grains can be visible or invisible to the naked eye, depending on their size. Conventional materials have grains varying in size anywhere from hundreds of microns to centimeters (Michael, Kamali et al., 2002). A common type of nanomaterial is carbon nanotubes and carbon nanofibers.

2.4 Carbon nanotubes

Carbon nanotubes on the other hand are molecular-scale tubes of graphitic carbon with outstanding properties. They are among the stiffest and strongest fibers known, and have remarkable electronic properties and many other unique characteristics (Peter, 2009). Carbon nanotubes have generated huge activity in most areas of science and engineering due to their unprecedented physical and chemical properties. No previous material has

displayed the combination of superlative mechanical, thermal and electronic properties attributed to them (Coleman, Khan et al., 2006). There are two main types of nanotubes available today which are single walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs).

2.4.1 Single-walled nanotubes (SWNTs)

Single-walled nanotubes are generally narrower than the multi-walled tubes, with diameters typically in the range 1-2 nm, and tend to be curved rather than (Peter, 2009). Single Walled Nanotubes (SWNT) can be considered as long wrapped graphene sheets. Nanotubes generally have a length to diameter ratio of about 1000 so they can be considered as nearly one-dimensional structures.

More detailed, a SWNT consists of two separate regions with different physical and chemical properties. The first is the sidewall of the tube and the second is the end cap of the tube. The end cap structure is similar to or derived from a smaller fullerene, such as $C_{60}C$-atoms placed in hexagons and pentagons form the end cap structures. It can be easily derived from Euler's theorem that twelve pentagons are needed in order to obtain a closed cage structure which consists of only pentagons and hexagons.

2.4.2 Multi-walled nanotubes (MWNTs)

Multi-walled nanotubes (MWNT) consist of an array of such cylinders formed concentrically and separated by 0.34 nm, similar to the basal plane separation in graphite. MWNTs can have diameters from 2 to 100 nm and lengths of tens of microns (Coleman, Khan et al., 2006).

Multi-walled carbon nanotubes (MWCNTs) are of special interest for the industry and Structurally MWCNTs consist of multiple layers of graphite superimposed and rolled in on themselves to form a tubular shape. Three properties of MWCNTs are specifically

interesting for the industry which is the electrical conductivity (as conductive as copper), their mechanical strength (Up to 15 to 20 times stronger than steel and 5 times lighter) and their thermal conductivity (same as that of diamond and more than five times that of copper). A combination of these impressive properties enables a whole new variety of useful and beneficial applications (cefic, 2009).
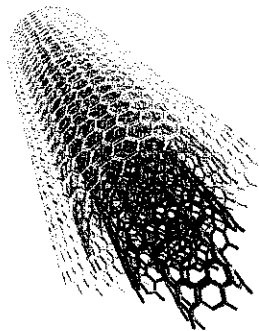
(Daenen, de Fouw et al., 2003)   (Catalyticmaterials.com, 2009)
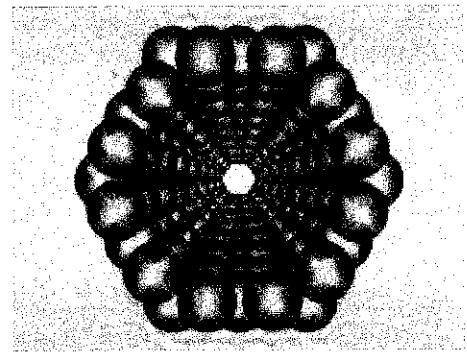
Figure 2.2: MWNTs structures
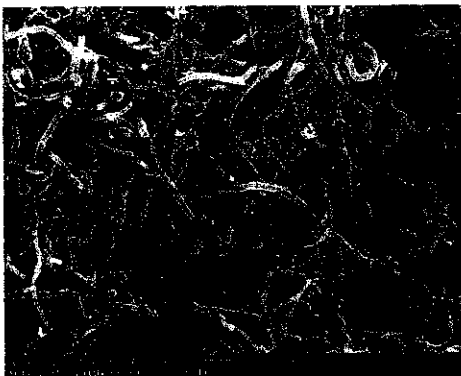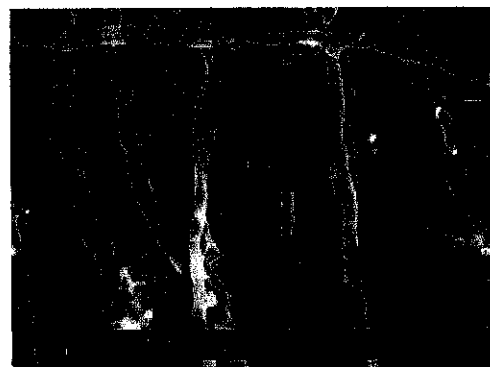
(Zhao, Lei et al., 2006)   (areeweb.polito.it, 2007)

Figure 2.3: SEM and TEM image of MWNTs

Previous study shows that the average thermal conductivity of multi-walled carbon nanotube films, with the film thickness from 10 to 50 mm, is around 15 W/m K at room temperature and independent of the tube length. Taking a small volume filling fraction of CNT's into account, the effective nanotube thermal conductivity could be 23102 W/m K, which is smaller than the thermal conductivity of diamond and in-plane graphite by a factor of 9 and 7.5, respectively (Jiang Yang, Qing Zhang et al., 2002).

2.4.3 Atomic radius and the d-spacing

In comparison to other available adsorbent, nanotube has a d-spacing which is more compatible with the atomic radius of metal ions. This d-spacing provide higher possibility for ions uptake. The commercial d-spacing size for graphitic carbon nanotubes is 0.355 nm. Figure 2.4 illustrates the high resolution image of the d-spacing in nanotubes. The physical characteristics of multi-walled nanotubes and atomic radius of cadmium, nickel and copper (Dean, 1999) are as illustrated in table 3.1 and table 2.1 respectively.

Element	Atomic radius, (pm)	Effective ionic radii, (pm)				
		Ion charge	Coordination number			
			4	6	8	12
Cadmium	148.9	2+	78	95	110	131
Copper	128	1+	60	77	-	-
		2+	57	73	-	-
		3+	-	-	54 LS	-
Nickel	124	2+	55	69	-	-
		3+	-	56 LS	-	-
				60 LS		

Table 2.1: Atomic radius and effective ionic radii of cadmium, copper and nickel
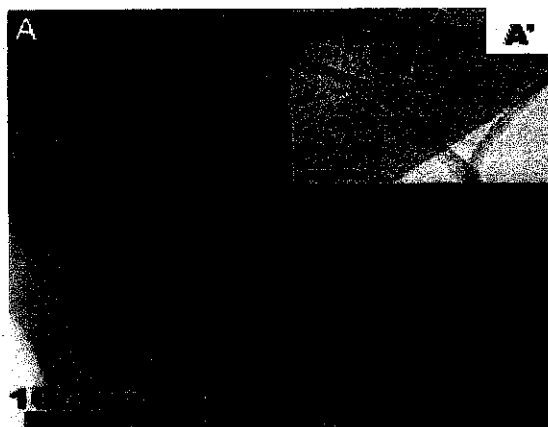
(Wang, Zhao et al., 2004)

Figure 2.4: Wall d-spacing of MWNTs

2.5 Adsorption

2.5.1 Adsorption principle

The process of adsorption implies the presence of an "adsorbent" solid that binds molecules by physical attractive forces, ion exchange, and chemical binding (Demirbas, 2008). In adsorption process, one or more components of a gas or liquid stream are adsorbed on the surface of a solid adsorbent and a separation is accomplished. In commercial processes, the adsorbent is usually in the form of small particles in a fixed bed. The fluid is passed through the bed and the solid particles adsorb components from the fluid. When the bed is almost saturated, the flow in the bed is stopped and the bed is regenerated thermally or by other methods so that desorption occurs. The adsorbed material (adsorbate) is thereby recovered and the solid adsorbent is ready for another cycle of adsorption (Christie, 2003).

2.5.2 Adsorption of heavy metals

Removal of heavy metal ions existed in water is always an issue because they cause a serious biological danger. An exclusion of the heavy metal ion is commonly carried out by an adsorption based on an ionic interaction between positively charged metal ions and negatively charged matrices (Ki, Gang et al., 2007). A dispersible adsorbent with large surface area and suitable chemistry would be very advantageous for the removal of heavy metals from aqueous solutions (Yantasee, Warner et al., 2007). Studies on the adsorption of heavy metals by activated carbon and various low-cost materials have been reported in the literature. These include activated carbon prepared from peat, coconut shells and coal to name a few (Kobya, Demirbas et al., 2005).

(Won, Hye et al., 2010)

Figure 2.5: Heavy metal ion adsorption onto CNTs

2.5.3 Adsorption Isotherm

Equilibrium adsorption isotherms (capacity studies) are of fundamental importance in the design of adsorption systems since they indicate how metal ions are partitioned between the adsorbent and liquid phases at equilibrium as a function of metal concentration. When an adsorbent comes into contact with a metal ion solution, the concentration of metal ions on the surface of the adsorbent will increase until a dynamic equilibrium is reached; at this point, there is a clearly defined distribution of metal ions between the solid and liquid phases (Argun, Dursun et al., 2007).

The process of Adsorption is usually studied through graphs known as adsorption isotherm. It is the graph between the amounts of adsorbate (x) adsorbed on the surface of adsorbent (m) and pressure at constant temperature. Different adsorption isotherms have been Freundlich, Langmuir and BET theory (Xamplified, 2010).

In the process of adsorption, adsorbate gets adsorbed on adsorbent.

$$\text{Adsorbate} + \text{Adsorbent} \underset{\text{desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} \text{Adsorption}$$

$$A + B \rightleftharpoons AB$$
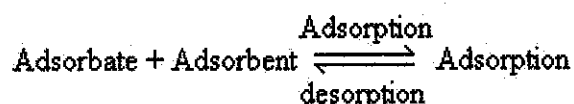
According to Le-Chatelier principle, the direction of equilibrium would shift in that direction where the stress can be relieved. In case of application of excess of pressure to the equilibrium system, the equilibrium will shift in the direction where the number of molecules decreases. Since number of molecules decreases in forward direction, with the increases in pressure, forward direction of equilibrium will be favored (Xamplified, 2010)

2.5.3.1 Langmuir Adsorption Isotherm

This isotherm was based on different assumptions one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules.

$$A(g) + B(S) \underset{\text{desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} AB$$
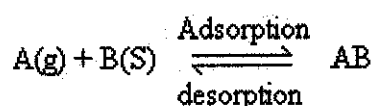
Where A(g) is unadsorbed gaseous molecule, B(s) is unoccupied metal surface and AB is Adsorbed gaseous molecule.

2.5.3.2 Freundlich Adsorption Isotherm

$$\frac{x}{m} = kp^{\frac{1}{n}}$$

Where x is the mass of the fluid adsorbed on mass m of the adsorbent at pressure p and k, n are constants whose values depend upon adsorbent and fluid at particular temperature. Though Freundlich Isotherm correctly established the relationship of adsorption with pressure at lower values, it failed to predict value of adsorption at higher pressure (Xamplified, 2010).

2.5.3.3 BET adsorption Isotherm

The multilayer formation was explained by BET Theory. The BET equation is given as

$$V_{total} = \frac{V_{mono}C\left(\frac{P}{P_0}\right)}{\left(1-\frac{P}{P_0}\right)\left(1+C\left(\frac{P}{P_0}\right)-\frac{P}{P_0}\right)}$$

Another form of BET equation is

$$\frac{P}{V_{total}(P-P_0)} = \frac{1}{V_{mono}C} + \frac{c-1}{V_{mono}C}\left(\frac{P}{P_0}\right)$$

Where Vmono be the adsorbed volume of fluid at high pressure conditions so as to cover the surface with a unilayer of the fluid molecules, K_1/K_L the ratio is designated C. K1 is the equilibrium constant when single molecule adsorbed per vacant site and KL is the equilibrium constant to the saturated vapor liquid equilibrium (Xamplified, 2010).

2.6   Literature on previous studies

Studies on the adsorption of heavy metal ions from aqueous solutions basically initiate the investigations on the effect of concentrations and pH on the adsorption capacity. Some studies leads to determining the optimum shaking speed, adsorbent mass and

contact time as well in order to acquire maximum uptake of heavy metal ions. Mostly, adsorption isotherm was determined using Langmuir isotherm model. Also reported in the literature, the adsorption experiments were performed in a batch mode.

Many kind of adsorbent found in previous studies have higher than 50% porosity and could achieved removal efficiency of more than 90%. However, some of the adsorbent suffers from drawback in term of cost and availability in the market. Some of the adsorbent are creative and obviously effective but apparently difficult to obtain. Only a few can be classified as a good adsorbent. For instance, (Kobya, Demirbas et al., 2005) discussed on the usage of apricot stone as an adsorbent. (Božić, Stanković et al., 2009) uses sawdust of linden (*tilia*), poplar (*samsun clone*) and beech (*fagus sylvatica*) while (Argun, Dursun et al., 2007) uses modified oak sawdust.

List of studied adsorbents for the removal of metal ions from liquid phase with regards to the surface area, removal efficiency and studied parameters as reported in the literature were summaries in table 2.2 below.

(Kobya, Demirbas et al., 2005) discuss on the usage of apricot stone as an adsorbent. The porosity of this adsorbent is 74% with a surface area 566 m^2/g. Only the effect of pH was studied and the results indicate that maximum removal of up to 99% for Cr (VI), Pb (II), Cd (II) and Co (II) at pH 1, pH3, pH 5 and pH 6 respectively. Moreover, at pH 4 removals of Ni (II) and Cu (II) give 97.59% and 96.24% correspondingly. As solution pH was increased, the onset of metal hydrolysis and precipitation was dominant at higher pHs ($\geq$ 5).

On the other hand, (Božić, Stanković et al., 2009)performed adsorption experiment for Cu, Zn, Mn as well as Cd, Fe and Ni onto sawdust of linden (*tilia*), poplar (*samsun clone*) and beech (*fagus sylvatica*) which act as adsorbents. The surface areas are 1.22 m^2g^{-1},

0.89 m^2g^{-1} and 1.08 m^2g^{-1} respectively. On lowering the initial pH, the adsorption capacity was achieved at a pH between 3.5 and 5 for all kinds of sawdust studied. The initial concentration of the adsorbate and the concentration of sawdust strongly affect the process. A degree of adsorption higher than 80% achieved for Cu^{2+} ions but it is very low for Fe^{2+} ions, not exceeding 10%.

(Stafiej & Pyrzynska, 2007) employed carbon nanotubes (CNTs) as an adsorbent to study the adsorption characteristics of some divalent metal ions such as Cu, Co, Cd, Zn, Mn and Pb. However, the study was limited to only a few parameters and the type of metals reported in previous studies were very general. The effect of solution conditions such as pH and metal ions concentration was investigated. The initial pH values were adjusted from 3.0 to 9.0 using various phosphate buffers. The initial metal concentration was increased from 1 to 20 mg/L. Copper ions are more favorably adsorbed on CNTs and the adsorption capacity of Cu (II) attained 3.49 mg/g at a equilibrium concentration of 20 mg/L, while the adsorption capacity for Co (II) and Pb (II) were 2.60 and 2.96 respectively. The highest adsorption capacity achieved at pH 9 with affinity order of the metal ions towards Carbon Nanotubes (CNTs) is Cu (II) > Pb (II) > Co (II) > Zn (II) > Mn (II).

Table 2.2: Previous studies on heavy metal removal

Sources	Objectives	Metal ion	Adsorbent	Condition	Adsorption uptake	Parameters
(Kobya, Demirbas et al., 2005)	• Investigate the effect of pH	Cd (II), Ni(II), Cu (II), Co(II), Pb (II) and Cr (VI)	Apricot stone porosity: 74% surface area: 566 m²/g.	Agitating speed: 200 rpm T = 25 °C duration: 48 h	Maximum removal: 99.99% for Cr (VI) at pH 1, 99.86% for Pb (II) at pH 3, 99.67% for Cd (II) at pH 5, 99.11% for Co (II) at pH 6, 98.56% for Cr (III) at pH 4, 97.59% for Ni (II) at pH 4 96.24% for Cu (II) at pH 4,	pH 1 - 6
(Božić, Stankovic et al., 2009)	• Determine the effect of pH • Determine the effect of concentration	Cu, Zn, Mn, Cd, Fe and Ni	Sawdust: linden (Tilia): 1.22 m²g⁻¹ poplar (Samsun Clone): 0.89 m²g⁻¹ beech (Fagus Sylvatica): 1.08 m²g⁻¹	Agitating speed: 300 rpm, T=25⁰C Duration: 1-90 minute	Maximum adsorption: At pH 3.5 -5 for all the studied kinds of sawdust. 80% for Cu²⁺ ions Very low for Fe²⁺ ions, not exceeding 10%.	Concentration: 7–8 mg g⁻¹ pH: 3-6
(Stafiej & Pyrzynska, 2007)	• Determine the effect of pH • Determine the effect of concentration	Cu, Co, Cd, Zn, Mn and Pb.	CNTs outer diameter: 5–10 nm surface area: 40–600 m²/g	Agitating speed: 350 rpm, T=25⁰C Duration: 4h	Adsorption capacity: Affinity order of the metal ions towards CNTs is Cu (II) > Pb (II) > Co (II) > Zn (II) > Mn (II).	Concentration: 1-20 mg/L pH: 3-9
(Argun, Dursun et al., 2007)	• Determine the optimum shaking speed • Determine the optimum adsorbent mass and pH • Determine the optimum contact time	Cu, Ni and Cr	modified oak sawdust	T= 25 °C	Maximum removal: At 250 rpm: 87% Cu(II), 82% Ni(II), 80% Cr(VI) Contact time: 62% for Cu(II) at 4h 88% for Ni(II) at 8h 93% for Cu(II) at pH 4, 82% for Ni(II) at pH 8, 84% for Cr(VI) at pH 3.	shaking speed: 100-450 rpm concentration: 0.1-100mg/L contact time: 0.5 -12 hours pH: 2-9

Modified oak sawdust is another adsorbent studied by (Argun, Dursun et al., 2007) that capable in adsorbing heavy metal ions from aqueous solution. The study tested the removal of three heavy metals which are Cu, Ni, and Cr on the optimum shaking speed, adsorbent mass, contact time, and pH. The effect of shaking speed was studied by varying speed for 100-450 rpm for 2 hours. The maximum removal efficiencies were obtained at 250 rpm: 87, 82, and 80% for Cu (II), Ni (II), and Cr (VI), respectively.

The effect of adsorbent mass was determined as well by varying the mass of adsorbent from 5 – 8 g/L. Adsorption increased gradually with increasing adsorbent mass, to a maximum at 40 g L^{-1} for Cu (II), 30 g L^{-1} for Ni (II), and 60 g L^{-1} for Cr (VI). After this maximum equilibrium value, the removal efficiency did not increase with increasing adsorbent mass. In terms of contact time, the adsorption rate initially increased rapidly, and that the optimal removal efficiencies were reached within about 2 h for 56, 78, and 72% for Cu (II), Ni II), and Cr (VI), respectively. However, the equilibrium (maximum) value was attained at around 4 h for Cu (II) and 8 h for Ni (II) and Cr (VI), with adsorption rates of 62, 88, and 81%, respectively. The effect of pH and concentration were studied as well. The pH of the aqueous solution was clearly an important parameter that controlled the adsorption process. Maximum removal efficiency reached 93% for Cu (II) at pH 4, 82% for Ni (II) at pH 8, and 84% for Cr (VI) at pH 3. For the effect of concentration, the removal efficiencies decreased from 98% to 80% for Cu (II), 98% to 66% for Ni(II), and 97% to 66% for Cr(VI) as the metal concentration increased.

In comparison with the methodologies and results obtained from these studies, it is wise to revise the parameters and condition of experiments in order to further study the adsorption uptake of heavy metals for this project. Taking the best conditions of experiment and gather information on the adsorption uptake based on previous study is important to ensure the maximum adsorption capacity obtained for this project.

Chapter 3
Methodology

3.1 Material Preparation

1 g/l of copper (Cu), Nickel (Ni) and cadmium (Cd) stock solutions were prepared from their respective sulfate salts. The concentrations of metal ions used in this experiment were prepared from these sulfates stock solutions.

Multi-walled carbon nanotubes (MWNTs) used in this study was purchased from Nanostructure & Amorphous Materials Inc. The MWNTs with 95% of purity and outer diameter that ranges from 10-20 nm were produced from catalytic vapor decomposition.

3.1.1 Physical characteristic of MWNTs

Element	Surface Area (m²/g)	Outer Diameter (nm)	Length (μm)	ρ_{bulk} (g/cm³)	ρ_{true} (g/cm³)	Purity %
MWNTs	180 – 213	10-20	0.5 - 200	0.04 – 0.05	2.1	95

Table 3.1: Physical characteristic of MWNTs

3.2 Experimental

The ability of MWNT in removing Cu, Ni and Cd ions were determined by determining the effects of concentration and pH of the metal solutions. The experiments were done in a batch process mode using *Julabo* water bath shaker. Setting speed of 200 rpm was elected for agitation throughout the experiment. Experiments were performed in sequence to ensure optimum adsorption capacity obtained. The concentration gained from the second experiment was used for the next experiment to investigate the effect of pH. Determinations of the effect of

temperatures were performed next using the best pH and concentration obtained previously.

3.2.1 Determination of contact time

The varying times were chosen to be at 2h, 4h and 6h. Bath shaker temperature was fixed at 25°C with a fixed parameter for concentration and pH and agitation speed of 200 rpm. Metal ion concentrations as well as the pH were fixed alternately to determine the contact time. Meaning that the determination of contact times were operates for each concentration and pH. This is to observe whether concentrations and pHs effects the position of equilibrium time. The initial and final concentration of metal ions was performed using Zeeman atomic absorption spectrophotometer (Z-5000).

3.2.2 Determination of concentration effects

50 mg of MWNT were soaked in 20 ml of a single metal ion solution. The concentrations of appropriate metal ion solution were varied by a factor of five starting from 5-25 mg/l. pHs of the metal solution were fixed at pH 9. The experiments were run for 2h, 4h and 6h with constant speed of 200 rpm. Temperature of water bath of 25°C was fixed. The initial and final concentration of Cu, Ni and Cd ions were determined using Zeeman atomic absorption spectrophotometer (Z-5000).The value of metal concentration that gives the highest adsorption efficiency was used as the fixed concentration to determine the effect of pH.

3.2.3 Determination of pH effects

Similar to the previous method, 50 mg of MWNT were soaked in 20 ml of a single metal ion solution. Except this time the pHs of appropriate metal ion solution were varied by a factor of two starting from pH 4 – pH 12. The initial pH values were adjusted using 0.1M and 0.01M H_2SO_4 and similar molarities was used for NaOH. The concentrations of the metal solutions were fixed according to the highest value

of metal concentration obtained from previous experiment. Again, the experiments were run for 2h, 4h and 6h. The final concentrations of metal ions were determined using Zeeman atomic absorption spectrophotometer (Z-5000).

3.2.4 Determination of temperature effects

The parameters were extended to observe the effect of temperature to the adsorption efficiencies. Concentration in which has given the highest adsorption climax and so as the pH were operated again in a batch process mode with constant shaking speed of 200 rpm. The contact time varies for 2h, 4h and 6h. Temperature varies for 25°C, 35°C and 45°C. The initial and final concentrations of metal ions were again determined by Zeeman atomic absorption spectrophotometer (Z-5000). Table 3.1 below show the summary of procedures been developed for this project.
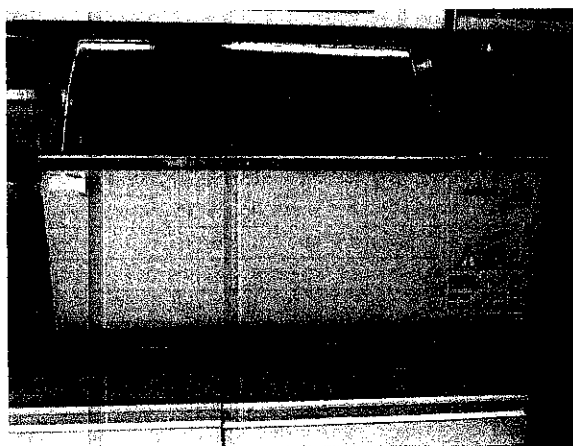

Figure 3.1: *Julabo* water bath shaker
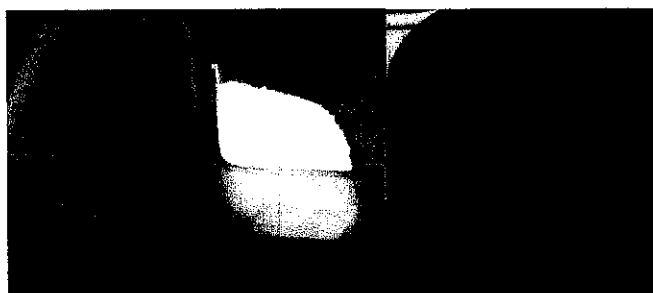
Figure 3.2: Ni (II) sulfate, Cd (II) sulfate and Cu (II) sulfate

Adsorbent: Multi-walled Carbon Nanotubes (MWNTs)					
Agitation speed: 200 rpm					
Method of experiment: Batch experiment using water bath shaker					
Parameters study	Metal ions	Agitation speed (rpm)	Operating time (hour)	pH	C_0 (mg/L)
Determine the contact time	Cd	200	2, 4, 6	4 - 12	5 - 25
	Ni	200	2, 4, 6		
	Cu	200	2, 4, 6		
Determine the effect of concentration	Cd	200	2, 4, 6	9	5 – 25
	Ni	200	2, 4, 6		
	Cu	200	2, 4, 6		
Determine the effect of pH	Cd	200	2, 4, 6	4 - 12	Optimum concentration obtained from previous experiment
	Ni	200	2, 4, 6		
	Cu	200	2, 4, 6		
Determine the effect of temperature	Cd	200	2, 4, 6	Optimum pH obtained from previous experiment	Optimum concentration obtained from previous experiment
	Ni	200	2, 4, 6		
	Cu	200	2, 4, 6		

Table 3.2: Summary of procedures

Chapter 4
Results and Discussion

4.1 Optimum contact time

Three specific periods were chosen to determine the time where highest point of adsorption obtained which are 2 hours, 4 hours and 6 hours. The highest peak normally obtained at equilibrium. According to Le Chatelier's principle, at equilibrium, concentration of reactant and product does not change with time unless disturbance being supplied to the process. Disturbances include changes in concentration, addition of catalyst and changes in temperature and pressure. Therefore, experiments to determine the contact time were run for all concentrations. Apparently, results for cadmium concentration over time as shown in figure 4.1 having highest adsorption capacity at the period of 4 hours for all concentration and start to be constant after that.
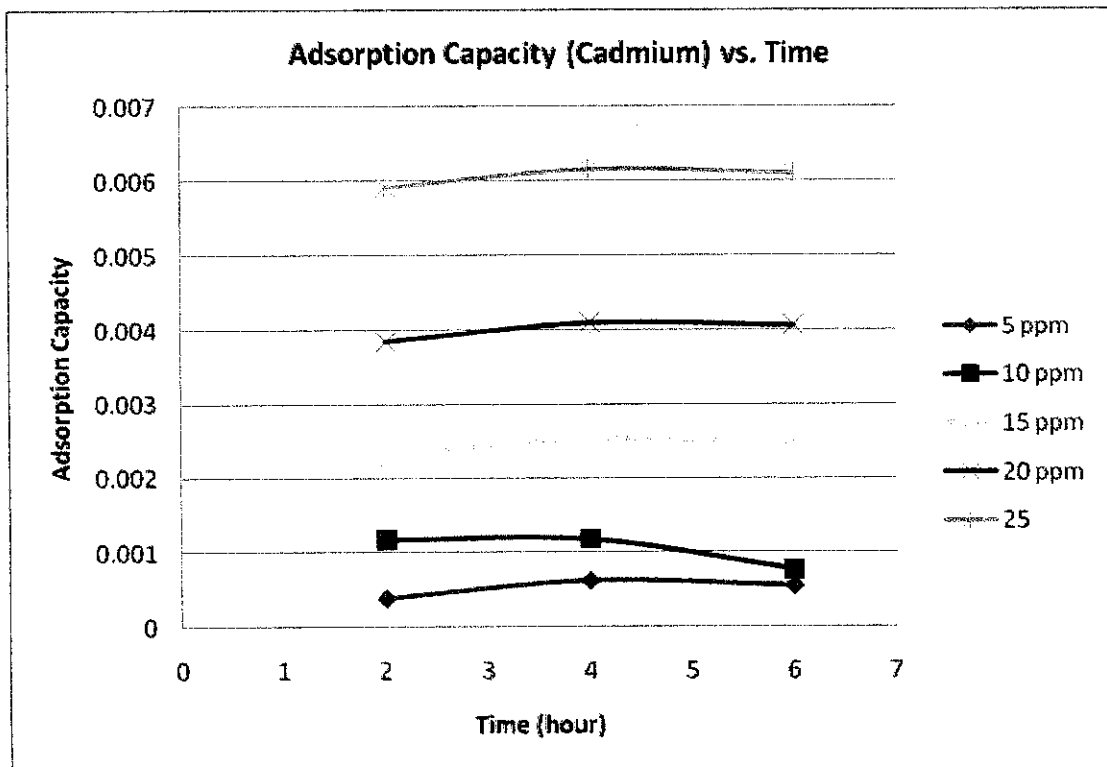

Figure 4.1: Optimum contact time for cadmium

A glance at the graph shows that the trend for all concentration is similar. Only at the concentration of 10 ppm has rapidly decreased right after 4 hours of operating. It may decrease again and keeps on fluctuating as the time extended. It could also referred to occurring of the desorption process. However for this experiment it won't be necessary to extend the time for that particular concentration since obtaining the time to reach the highest peak is the major concern.

Looking at the trend again, the starting duration of 2 hours is perfect since it can be predicted that less than 2 hours could have lower adsorption capacity. 2 hours is too short to allow cadmium to get contact with the MWNTs absorbent. Moreover, it seems like more than 4 hours is too long for the absorbent to holds cadmium ions since it already reach its equilibrium. From results obtained, duration of 4 hours is be set for the next experiment to determine the effect of pH.

Similar method was used for nickel. The experiment with concentration ranges from 5 – 25 ppm was repeated for 2 hours, 4 hours and 6 hours to find the best adsorption peak. It appears that nickel in Figure 4.2 seems not to be following the trend of cadmium. The only similarities between those two metal ions is that most of the concentration having the highest adsorption at a period of 4 hours. Only concentration of 20 ppm has a high peak of adsorption at a period of 4 hours and 42 minutes. The next experiments are operated according to the optimum time obtained.

At some point the trend may describe that the process starts to operate in reverse after their highest adsorption peak. To be exact, desorption process starts to occur after a period of 4 hours in which molecules adsorbed on a surface are transferred back into a bulk phase. Same goes to nickel at a concentration of 20 ppm where the highest adsorption climax is 42 minutes higher compared to other concentrations.

On the other hand, Figure 4.3 describes an interesting trend for copper. High percentage of adsorption could be observed at a period of 4 hour and 6 hour in a range within 99.4 % - 99.8%. The highest adsorption capacity achieved at a period of 4 hours with 99.8% adsorption and a concentration of 20 ppm.
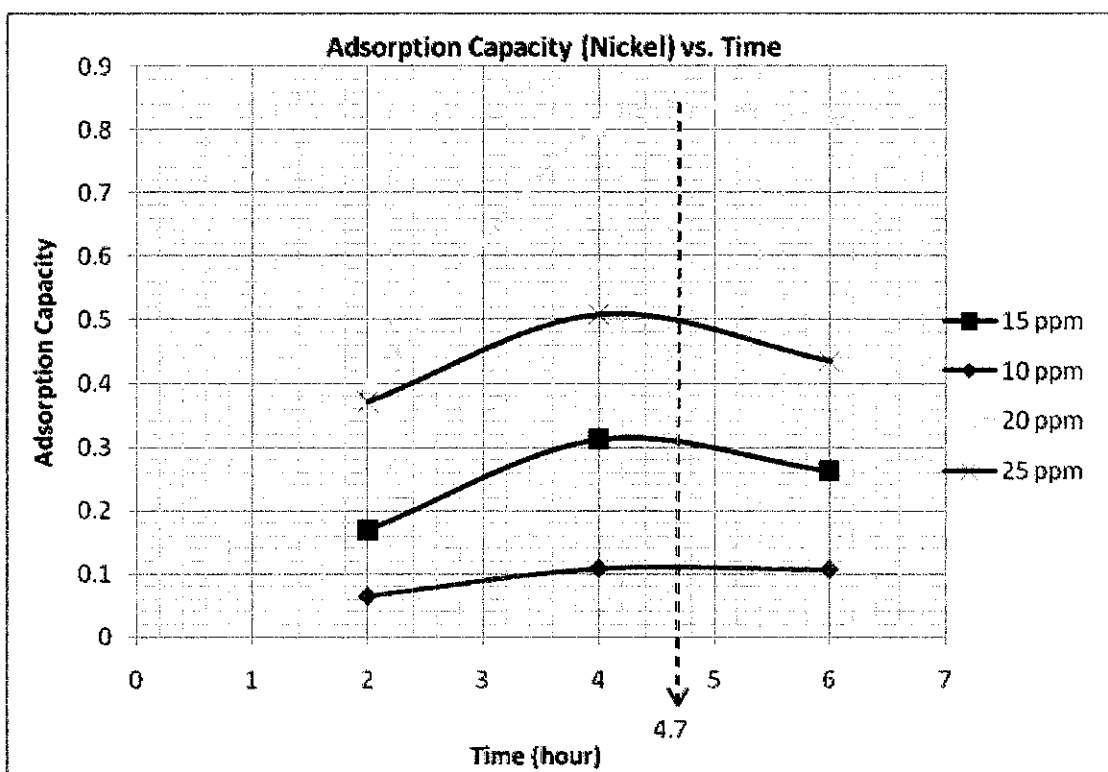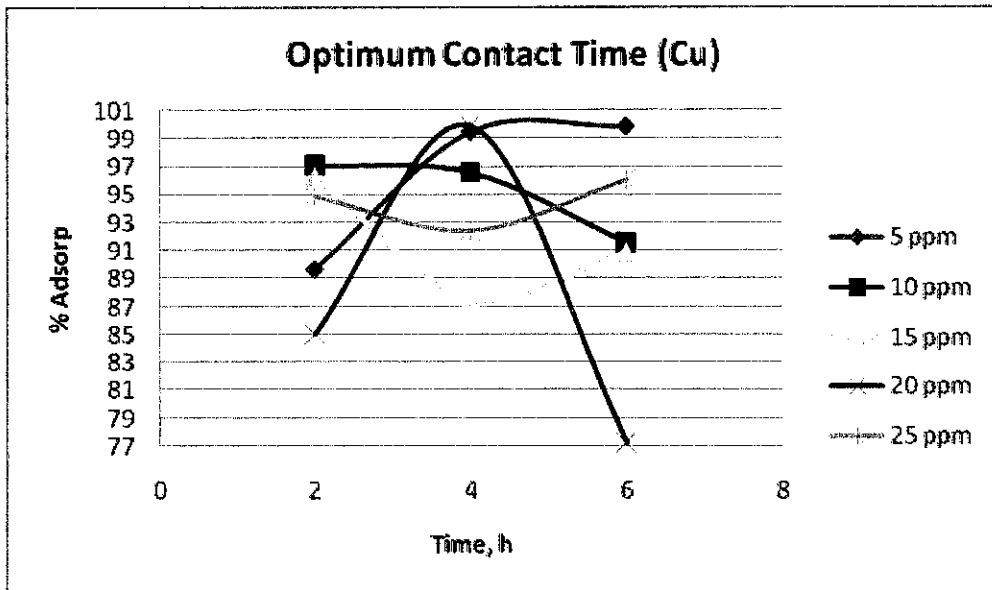

Figure 4.2: Optimum contact time for Nickel

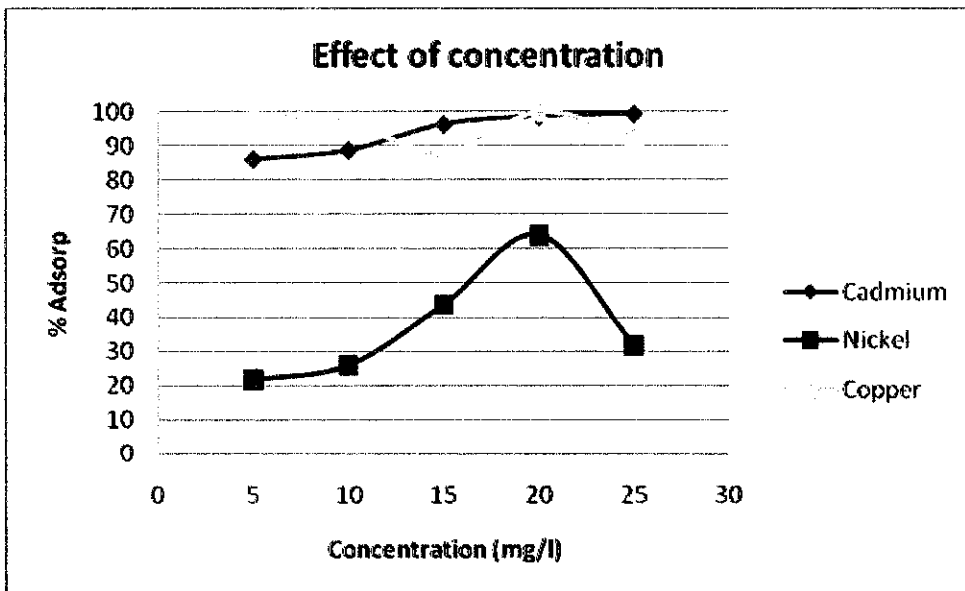Figure 4.3: Optimum contact time for Copper

Figure 4.4: Effect of concentration on the adsorption capacity

CdSO4 Feed	Adsorption capacity, q	NiSO4 Feed	Adsorption capacity, q
5	0.000608	5	0.000032
10	0.001172	10	0.0001084
15	0.002512	15	0.0003124
20	0.004100	20	0.0008044
25	0.006160	25	0.0005080

Table 4.1: Adsorption capacity per feed of metal solution

4.2 Effect of concentration

Concentration of a molecule will affect the speed of the reaction so a high concentration of cadmium should speed up the rate of reaction. The graph in figure 4.3 ought to prove this statement. The movement of the graph shows that cadmium with higher concentration provides higher adsorption capacity compared to the lower concentration. The value of adsorption capacity at 25 mg/L could reach up to 99.3%. Obviously, the lowest adsorption capacity obtained at a concentration of 5 mg/L for cadmium with an adsorption capacity, q of 0.000608 mg/g.

Different trend obtained for nickel ion. The result shows that the adsorption capacities have slightly increase from 5mg/l until concentration of 15mg/l. These values could be observed from table 4.1. The movement of the graph suddenly increases at a concentration of 20 mg/l of nickel solution providing high peak of adsorption. It illustrated that a feed of 20 mg/l for nickel solution was preferred for 50mg of MWNTs. While extended concentration of 25 mg/l shows that the adsorption capacity decreased. This is where desorption starts to occur saying that the MWNTs could no longer hold more nickel ions. It is likely that a given mass of adsorbent material has a finite number of adsorption sites, and that as metal

concentrations increase, these sites become saturated. Therefore, nickel solution at a concentration of 20 mg/l is used for the next experiment to determine the effect of pH to the adsorption process.

Copper on the other hand provide up to 99.8% of removal efficiency at a concentration of 20 ppm. According to table 4.2, the percentage of adsorption is within the range of 87 – 99.8 %. It looks like MWNTs are attracted to copper as well. By observing the trend, high copper uptake achieved at the beginning of the experiment but starts to falls after the first dose. It looks like the adsorbent could hold 5 ppm of copper easily but as the dosage increases the adsorption capacity drops. However, a rapid increase is observed after that. Here, the optimum copper uptake achieved at a concentration of 20 ppm.

Concentration ppm	Adsorption %
5	99.4964
10	99.4918
15	99.49359
20	99.84883
25	99.46514

Table 4.2: % Adsorption per feed of copper solution

4.3 Effect of pH

pH is another important factor in determining the effectiveness of an adsorbent since pHs may have changed the concentration of solution due to reaction they creates. 99.3% of cadmium can be removed from liquid solution. This result is accomplished at a pH of 12. According to graph at figure 4.5, the trend started at a pH of 4 provides low adsorption capacity. However, the adsorption has a slight increase after

that and drops bit by bit until pH 10 before increases rapidly at a pH of 12. Therefore, it can be said that cadmium at pH 12 has better removal.

Meanwhile, the highest percentage for nickel was attained at a pH of 12 as well with more than 80% of removal efficiency. The trend for nickel seems to be following the similar trend as cadmium. The adsorption process for nickel starts at a low pH which is pH 4 and has a slight increase at a pH of 6. At a pH of 8, the adsorption drops a bit before increases again after that. This fluctuation shows the process of adsorption. The highest adsorption attained at a pH of 12.

Obviously, as shown on the graph different trend was observed for copper. The adsorption process tends to increase in increasing pH. However, after pH 10, the adsorption process starts to drop. This phenomenon appears to be the beginning of desorption process. The adsorption process reaches the highest peak at a pH of 10 with 99.2% of adsorption.

The pattern of the graph seems to show that other reaction maybe occurred apart of adsorption. Further investigation needed to clarify this matter.

Figure 4.5: Effect of pH

4.3 Effect of temperature

Temperature is a crucial parameter in adsorption reaction. According to the adsorption theory, adsorption decreases with increase in temperature and molecules adsorbed earlier on a surface tend to desorbs from the surface at elevated temperatures. As illustrated in figure 4.6, copper get a hold of better removal at room temperature which is 25°C. But a different trend is noticed for both cadmium and nickel where higher temperature allows the uptake of molecules into the pores more easily, causing adsorption to increase as temperature increases. Highest adsorption for both cadmium and nickel attained at a temperature of 55°C.

Similar to previous section, the pattern of the graph seems to show that other reaction maybe occurred apart of adsorption. Further investigation needed to clarify this matter.
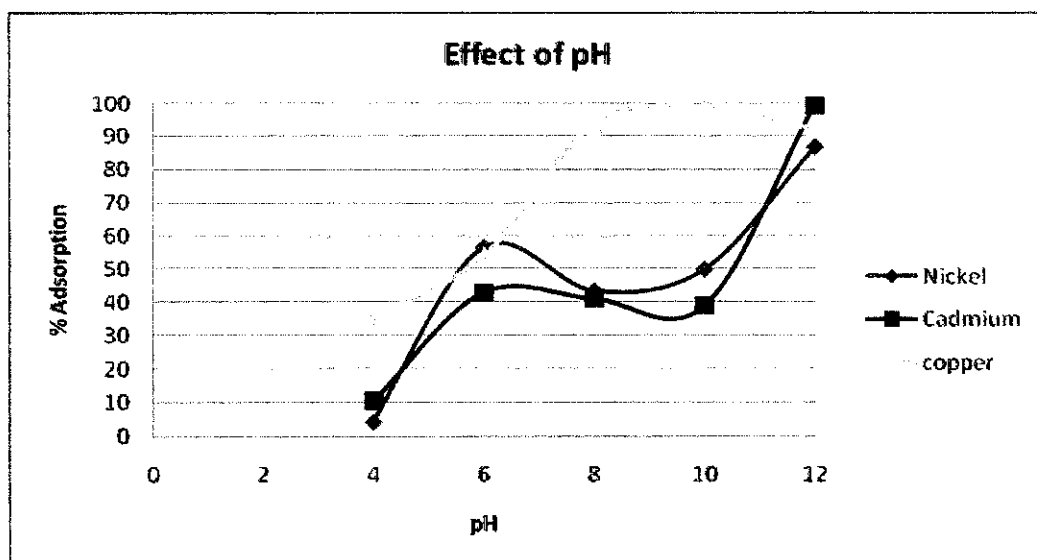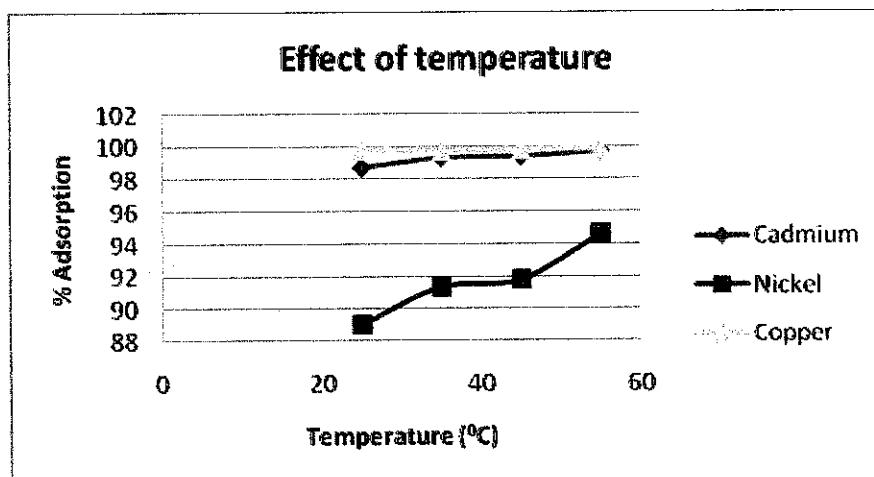

Figure 4.6: Effect of temperature

4.4 Adsorption Isotherm

Among a few available isotherm models, Freundlich adsorption isotherm is used in analyzing the experimental data with regards to metal ions uptake onto MWNTs.

Freundlich adsorption isotherm is applicable to highly heterogeneous surfaces. The original equation can be rearranged to get a linear form of equation.

$$q = K_f \ C^n$$

Where:

K_f and n are coefficients

q = weight adsorbed per unit wt of adsorbent

C = concentration in fluid

Taking logs and rearranging:

$$\text{Log } q = \text{Log } K_f + n \text{ Log } C$$

K_f and n are Freundlich constants related to adsorption capacity and intensity, respectively. The value of n is observed to determine whether the system is homogeneous or heterogeneous. If n value closes to 1, the system is homogeneous while if n value approaching zero, the system is heterogeneous.

Freundlich Plot (Cd)

y = -1.0986x - 3.2657
$R^2 = 0.8738$
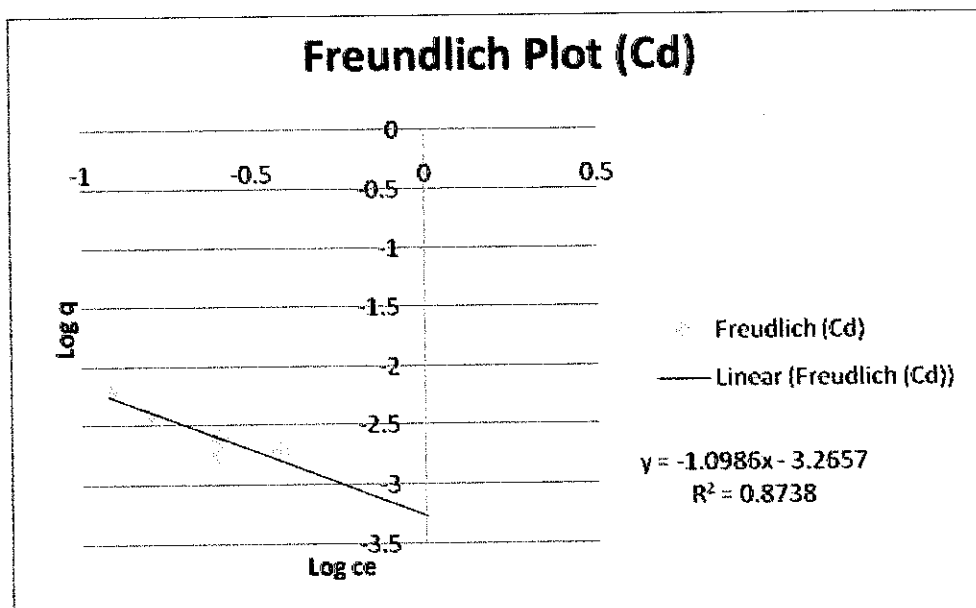
Figure 4.7: Freundlich plot for cadmium

Figure 4.8: Freundlich plot for Nickel

Figure 4.9: Freundlich plot for cadmium

Figure 4.7, figure 4.8 and figure 4.9 illustrate the freundlich plot for cadmium, nickel and copper respectively. Both cadmium and copper have a heterogeneous system while nickel ha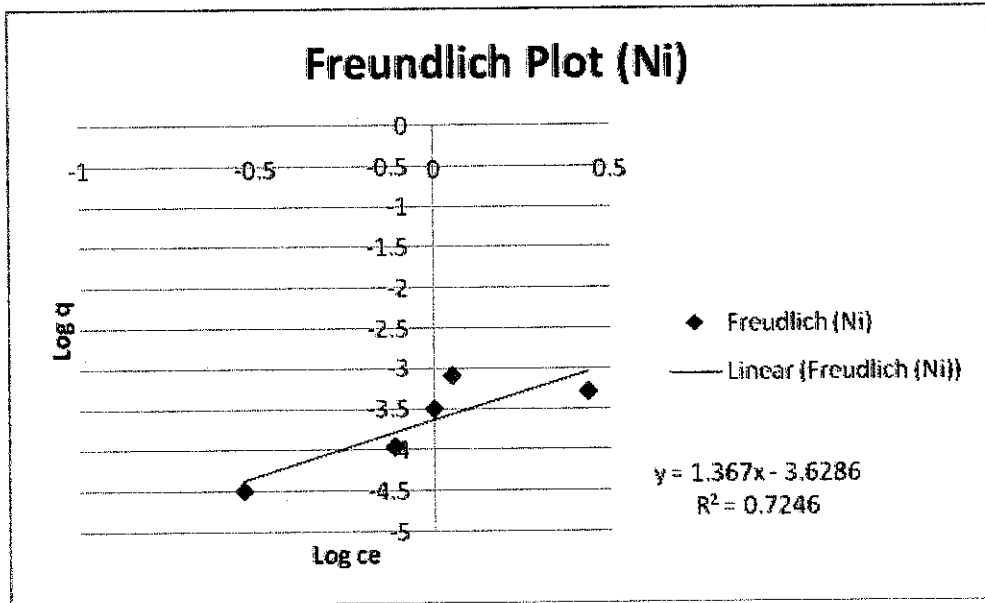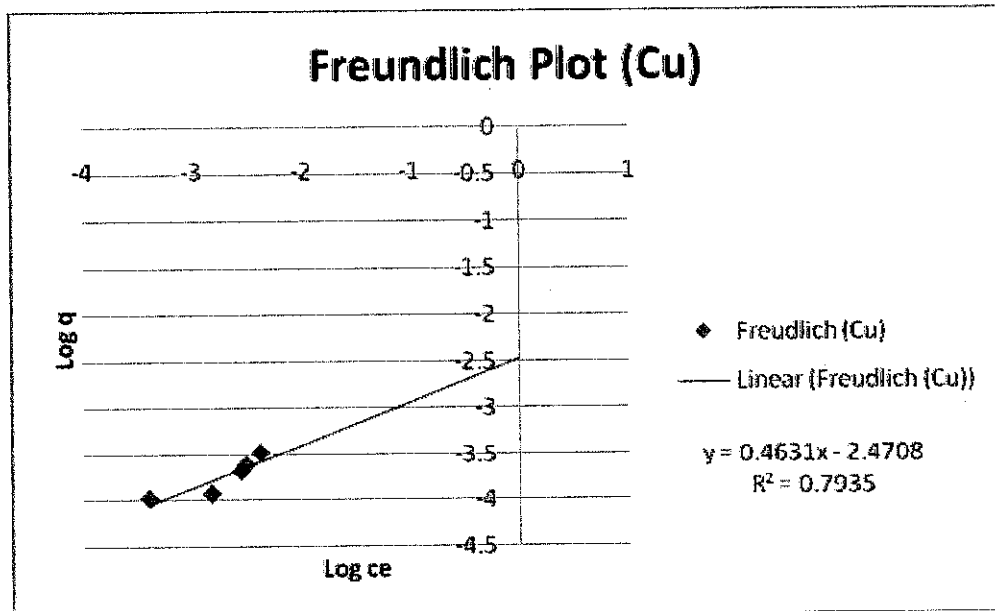s homogeneous system. (Lew, 2009) describe a homogeneous solution by the ratio of solute to solvent remains the same throughout the solution

even if homogenized with multiple sources, and stable because, the solute will not settle out, no matter how long the solution sits. Heterogeneous mixture on the other hand is the substance that is not circulated consistently. (Dean, 1999)

The correlation constant for all three metal ions have a value approaching 1. The K_f constant which relate to the adsorption capacity showing that copper has the highest adsorption capacity since the K_f constant is higher than other metal ions. On the other hand, cadmium has the second highest K_f value and followed by nickel. Therefore, the affinity order could be arrange as Cu (II)>Cd (II)>Ni (II).

4.5 Comparison with other adsorbent

The comparison could be made by comparing the results obtained with previous studies as illustrated in table 2.2. In comparison with apricot stone in terms of the pH effects, MWNTs provide higher adsorption percentage for cadmium with 99.3 % but lower percentage of adsorption for nickel. Apricot stone could give 97.59% compared to MWNTs with only 86.5%. Sawdust provides the highest removal of copper at a lower pH with 80% adsorption. Sawdust also tends to create precipitates waste at the end. (Stafiej & Pyrzynska, 2007) which also employed CNTs as adsorbent for other metal ions gives Freundlich correlation coefficient very closed to Perhaps further investigation need to be made for this dissertation to clarify the results obtained.

4.6 BET Surface Area Analysis
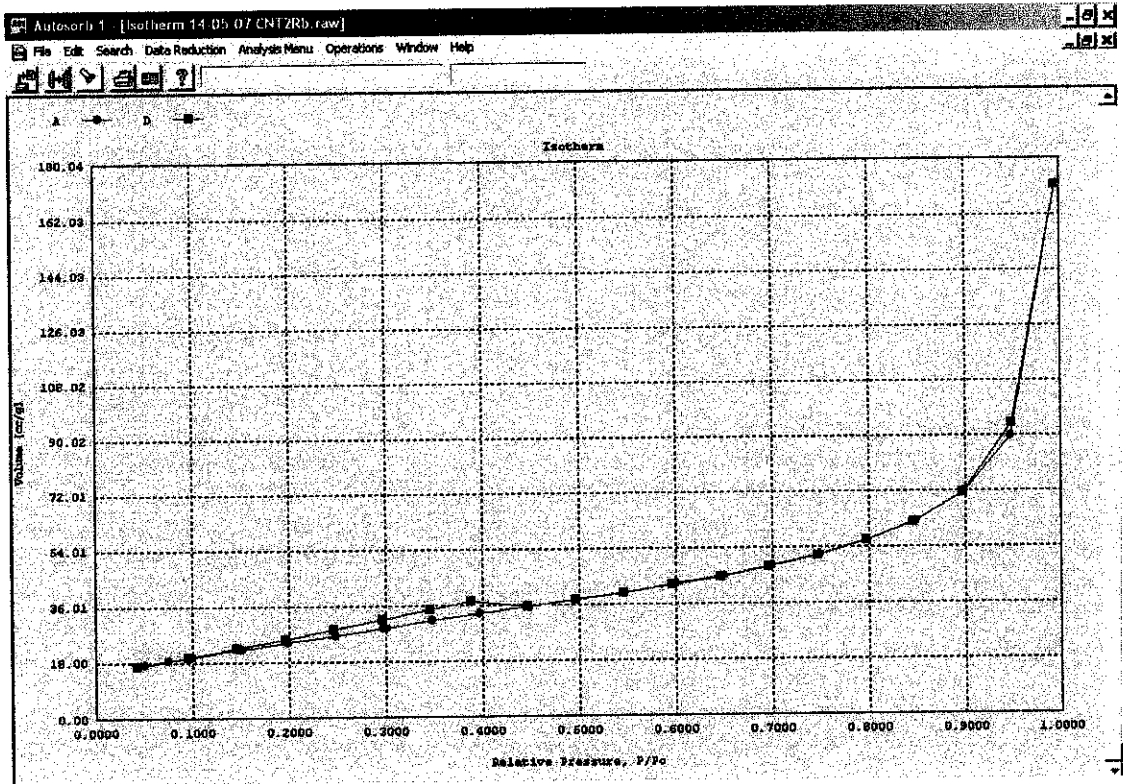
BET theory is a well-known rule for the physical adsorption of gas molecules on a solid surface, that is basis for an important analysis technique for the measurement of the specific surface area of a material.

According to above figure, maximum adsorption occurs at a relative pressure of 1 with amount adsorbed of 171.03 cm^3/g. The adsorption proceeds as in type II isotherm which commonly associated with microporosity, mesoporosity and macroporosity.

Chapter 5

Conclusion

This dissertation presented the study of MWNT adsorbent in removing Cd (II), Ni (II) and Cu (II) by adsorption process. Removal of these pollutants is a must since it is harmful to human being, animals and so as the environment. MWNT was able to remove more than 99% of these metal ions from aqueous solution.

Throughout the study, experiments were done in a batch process mode using water bath shaker. Among the parameters studied such as determination of contact time, investigation on the effects of pHs and metal ion concentration as well as the determination of the effects of temperature with regards to the adsorption capacity.

The experiment to determine the effects of contact time was operated for all concentrations and pHs to ensure highest adsorption efficiencies achieved. The highest peak normally obtained at equilibrium and at equilibrium, concentration of reactant and product changes with time since disturbances such as concentration, pH and temperature been supplied to the process.

Multi-walled carbon nanotubes (MWNTs) are able to remove up to 99% of cadmium and copper ions from aqueous solution and 95% for nickel. Both copper and cadmium shares similar contact time in which optimum adsorption occurs at a period of 4 hours and nickel at a period of 4.7 hours. It seems like more than 4 hours is too long for the absorbent to holds those ions since it's already reach its equilibrium. MWNTs work better in removing 25 mg/l of cadmium and 20 mg/l of copper both with 99% removal efficiencies.

pH could influence the adsorption capacity as well. Cadmium can achieve up to 99.8% of removal efficiency at pH 12. Meanwhile, nickel at pH 12 also manages to attain more than 95% of efficiency. Temperature is a crucial parameter in adsorption

reaction. Copper get a hold of better removal at room temperature which is 25°C. Different trend is noticed for both cadmium and nickel where higher temperature allows the uptake of molecules into the pores more easily, causing adsorption to increase as temperature increases. Highest adsorption of both cadmium and nickel attained at a temperature of 55°C with more than 99% removal efficiency. Further investigation needed to clarify whether other reaction present apart of adsorption.

Both cadmium and copper have a heterogeneous system while nickel has homogeneous system. The correlation constant for all three metal ions have a value approaching 1. Copper has the highest adsorption capacity since the K_f constant is higher than other metal ions. The affinity order could be arrange as Cu (II) > Cd (II) > Ni (II).

5.1 Recommendation

For the experiment to observed the effect of concentration, further investigation can be done to see whether by increasing the concentration of cadmium could offer higher value of adsorption capacity. Ranges of cadmium concentration could be extended even more.

Further study needed to determine whether there are other reaction present apart from adsorption for the experiment to determine both pHs and also temperature.

An auxiliary study on the adsorption of nickel (II) using MWNTs needed to clarify the adsorption efficiency. Other than that, the parameters of study could be extended even more, For instance, to determine and observed the effect of pressure on the heavy metals uptake. Since MWNTs was proven effective in removing heavy metal ions such as copper, cadmium and nickel, perhaps further study could be done for other metal ions.

Chapter 6
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xtArticle/Pdf/1290350604.pdf

A. Project time frame
B. Formula & calculation
C. Experimental data

A. Project time frame

TIMELINE / SUBJECT	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13	Week 14	Week 15
Safety Briefing		■													
Submission of chemicals requisition form					■										
workstation booking period						■									
Apparatus booking period							■								
Experimental preparation :															
> Equipment familiarization (bath shaker, AAS)								■	■	■	■				
> Chemical Preparation										■					
Progress report submission								■							
Seminar 1								■							
Experimental Work										■	■	■	■	■	
Sample submission for pore size and surface area analysis										■					
Interim Report submission														■	
Oral Presentation															■

Table A.1: Final year project time frame (1st semester)

2	Meeting with supervisor																					
	Classes on Report Writing Resources																					
4	Submission of Progress Report 1																					
	Project progress (experiments, work, sample and ...)																					
6	Submission of Progress Report 2																					
	Poster Exhibition																					
8	EDX																					
	Submission of Final Report																					
10	Final Oral Presentation																					

Table A.2: Final year project time frame (2nd semester)

B. Formula & calculation:

1. Adsorption capacity

$$q = \frac{V \times (C_0 - C_f)}{W}$$

Where:

V = Volume of metal solution

C_0 = Initial metal concentration

C_f = Final metal concentration

2. % adsorption (Efficiency)

$$\% \, Adsorption = \frac{C_0 - C_f}{C_0} \times 100\%$$

3. $Log \, q = Log \, K_f + n \, Log \, C$

	log qe	log ce
Copper	-3.479	-2.3768
	-3.6148	-2.5086
	-3.9286	-2.8239
	-3.976	-3.3979
	-3.6814	-2.5528
Cadmium	-2.7373	-0.6021
	-2.7231	-0.4202
	-2.6	-0.6021
	-2.3872	-0.7959
	-2.2104	-0.9208

Nickel	-4.4949	-0.5376
	-3.965	-0.1101
	-3.5053	0.00173
	-3.0945	0.05346
	-3.2941	0.43823

C. Experimental data

1. Concentration over time

CdSO4 Feed	Initial	2 Hour	4 Hour	6 Hour
5 ppm	1.77	0.83	0.25	0.42
10 ppm	3.31	0.4	0.38	1.42
15 ppm	6.53	0.77	0.25	0.39
20 ppm	10.41	0.83	0.16	0.26
25 ppm	15.52	0.74	0.12	0.25

NiSO4 Feed	Initial	2 Hour	4 Hour	6 Hour
5 ppm	0.37	0.04	0.29	0.1
10 ppm	1.047	0.884	0.776	0.781
15 ppm	1.785	1.362	1.004	1.129
20 ppm	3.142	2.162	1.131	1.088
25 ppm	4.013	3.088	2.743	2.928

CuSO4 Feed	Initial	2 Hour	4 Hour	6 Hour
5 ppm	0.824	0.0852	0.0047	0.0016
10 ppm	0.5998	0.0174	0.0205	0.0505
15 ppm	0.2952	0.011	0.03678	0.0268
20 ppm	0.2636	0.0395	0.0004	0.06
25 ppm	0.5225	0.0268	0.0395	0.0205

2. pH over time

   i. Cadmium

pH	initial	2h	4h	6h
4	3.42	3	3.07	3.1
6	2.1	1.64	1.2	1.47
8	2.37	1.16	1.4	0.21
10	2.5	0.92	1.53	1.24
12	1.47	0.1	0.01	0.04

ii.   Nickel

pH	initial	4h	6h
4	5.16	4.95	4.98
6	1.95	0.85	1.38
8	2.08	1.18	1.62
10	1.87	0.94	1.43
12	2.83	0.38	0.63

pH	initial	2h
4	57.84	35.95
6	42.16	30.44
8	40.81	12.4
10	38.69	26.1
12	22.82	6

iii.   Copper

pH	initial	2h	4h	6h
4	0.714	0.0852	0.4631	0.0016
6	0.4988	0.0174	0.2297	0.0505
8	0.2733	0.011	0.01833	0.0268
10	0.2349	0.0395	0.00192	0.06
12	0.4785	0.0268	0.0381	0.0205

3. Temperature

i. Cadmium

Cadmium				
Initial	25°C	35°C	45°C	55°C
3.872	1.9475	3.0571	2.3832	1.5024

ii. Copper

Copper				
Initial	25°C	35°C	45°C	55°C
0.2422	0.0004	0.0079	0.00616	0.0061