

A STUDY OF NICKEL AND CADMIUM ADSORPTION USING  
GRANULATED CHARCOAL ACTIVATED CARBON (GCAC)

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CHEMICAL ENGINEERING  
UNIVERSITI TEKNOLOGI PETRONAS  
DECEMBER 2010

**A Study of Nickel and Cadmium Adsorption using  
Granulated Charcoal Activated Carbon (GCAC)**

by

Nurul Syafiqin binti Mohamad Shah

Dissertation submitted in partial fulfilment of  
the requirements for the  
Bachelor of Engineering (Hons)  
(Chemical Engineering)

DECEMBER 2010

Universiti Teknologi PETRONAS  
Bandar Seri Iskandar  
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CERTIFICATION OF APPROVAL

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(CHEMICAL ENGINEERING)

Approved by,

---

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UNIVERSITI TEKNOLOGI PETRONAS  
TRONOH, PERAK  
DECEMBER 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.

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NURUL SYAFIQIN BINTI MOHAMAD SHAH

## ABSTRACT

Waste stream coming from industries which reaches water resources and soil is spotted containing various contaminants such as heavy metals. This phenomenon is potentially hazard to human and the environment as the metals not degrade into harmless end products and tend to accumulate in living organisms, causing various diseases and disorders. Adsorption is one of the methods for removing heavy metals from contaminated effluents and the most effective among all. The present study was undertaken to investigate ability of granulated charcoal activated carbon (GCAC) as an adsorbent in adsorption process of removing nickel and cadmium ions from aqueous solutions. The analyses of heavy metal removal are performed on three operational parameters which are initial ion concentration, pH and agitation time. The experiments were carried out at room temperature (25°C) and metal solutions were agitated on a rotary shaker at constant speed of 240 rpm. BET surface area of GCAC was found to be 898 m<sup>2</sup>/g. Batch adsorption test showed that the nickel and cadmium uptake increase as agitation time increase. As initial metal ion concentration increase, nickel adsorption percentage decrease and cadmium adsorption percentage increase. Nickel adsorption percentage decreased as the nickel ion concentration increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in decreases in the adsorption efficiency. Cadmium adsorption percentage increase due to the increase in the driving force of the concentration gradient produced by the increase in the initial cadmium concentration. The equilibrium time for both metals uptake were 120 minutes and optimum initial metal concentration were 100 mg/L and 5 mg/L for cadmium and nickel, respectively. Adsorption was found to be low at acidic pH and kept increasing as pH increased. The highest cadmium and metal adsorptions were achieved at pH 10. At low pH, solution has high concentration of H<sup>+</sup> ions compared to high pH solution as it is acidic. Presence of high H<sup>+</sup> ions in metal solutions created great competition between H<sup>+</sup> ions and Cd<sup>2+</sup> ions for vacant adsorption sites of adsorbent. The competitive adsorption results in low metal uptake by GCAC. The equilibrium data fitted is more well fitted to Freundlich isotherm as the R-squared value of Freundlich were higher than Langmuir's which were 0.995 and 0.98 for nickel and cadmium, respectively. This indicates that the cadmium and nickel adsorption are multilayer adsorption on the GCAC surface.

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# CHAPTER 1

## INTRODUCTION

### 1.1 Background of study

Pollution of the environment by heavy metal ions becomes one of major problems in ecosystem nowadays. Heavy metal ions such as cobalt, cadmium, copper, nickel, chromium, lead and zinc are detected in the waste streams from mining operations, tanneries, electronics, electroplating and petrochemical industries, as well as in textile mill products (Patterson and Passino, 1987). These toxic metals do not only reach seas, lakes, ponds and reservoirs, but can also contaminate underground water in trace amounts by leaking from the soil after rain.

The other common scenario is the accumulation of toxic metals in food chain. As a result of accumulation, the concentrations of metals can be more than those in water and air. As 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). Example of serious impact of metals pollution on living health is where the excessive intake of copper and lead into the body can affect the gastrointestinal track and nervous system (Imamoglu and Tekir, 2008). Besides, effects of cadmium exposure may occur at lower exposure levels than previously anticipated, primarily in the form of kidney damage but possibly also bone effects and fractures (Jarup, 2003).

Several methods have been used in wastewater treatment which includes filtration, precipitation, ion exchange and membrane separation. Adsorption is one of the best alternatives with activated carbon being the most widely used adsorbent for this purpose (Keskinan et al., 2004). It is very economical as activated carbon has high efficiency of adsorbing heavy metal from contaminated water.

## 1.2 Problem Statement

Previously, researchers have experimented and applied several methods for removing heavy metals from contaminated effluents. The methods include precipitation, ion exchange, membrane filtration, electroplating, evaporation and adsorption. All of these methods except adsorption are inefficient as they are costly and amount of hazardous chemicals present in lakes and rivers are still continuously increasing even the methods are applied to remove the heavy metals.

Adsorption is the most effective techniques among the stated methods. Silica gels, activated alumina, oxides and hydroxides of metals, zeolites, clay minerals, synthetic polymers and carbonaceous materials, such as activated carbon and molecular carbon sieves are used as adsorbents (Imamoglu and Tekir, 2008) in the adsorption process. The most commonly and widely used adsorbents is activated carbon. Commercial activated carbons are prepared from a variety of carbonaceous raw materials (Imamoglu and Tekir, 2008).

In this study, activated carbon being analysed is made from charcoal which is in granulated form and has gone through steam activation. It will be used for nickel and cadmium removal from aqueous solution by batch method. Effect of pH, initial metal concentration and agitation time towards metal adsorption will be investigated. Its natural characteristics which are surface area, pore size distribution and chemical nature of their surface are the additional factors that highly influence the metal adsorption. Optimum sorption of heavy metal from contaminated water by granulated coal activated carbon (GCAC) will reduce the risk of hazard exposure to living organisms in terms of health.

## 1.3 Objectives and Scope of Study

### 1.3.1 Objectives

- To study the effect of agitation time on the nickel(II) and cadmium(II) uptake of granulated coal activated carbon
- To study the effect of solution pH on the nickel(II) and cadmium(II) uptake of granulated coal activated carbon
- To study the effect of initial metal ion concentration on the nickel(II) and cadmium(II) uptake of granulated charcoal activated carbon (GCAC).
- To find best adsorption isotherm that fit the adsorption behaviour.
- To determine optimum agitation time, pH and initial metal ion concentration for maximum nickel(II) and cadmium(II) uptake by granulated charcoal activated carbon.

### 1.3.2 Scope of study

- The project will be conducted throughout two semesters of Final Year and is a bench scale experimental type. It composed of two stages which are preliminary research work and laboratory work stage.
- In the first semester, preliminary research work is conducted which covers adsorption theory, characteristics of granulated coal activated carbon and heavy metal removal using various type of adsorbents done by previous researchers. This stage enable student to have concrete and deep understanding of the project.
- In the second semester, laboratory work is conducted. Series of experiments will be undertaken examining the effect of agitation time, solution pH and initial metal ion concentration on the heavy metal uptake by granulated coal activated carbon. Optimum contact time of every metal at constant pH and concentration is being determined first

which then will be the optimum constant value used for examining the other two parameters.

- Both parameters (pH and initial metal ion concentration) are varied to monitor the changes of adsorption behaviour of different metals. In this study, there are two types of heavy metals are investigated which are nickel, Ni(II) and cadmium, Cd(II). These metals had been chosen as they are the most common heavy metal contaminants of industrial wastewaters.
- Experimental result then will be analysed by finding out the amount of heavy metals have been removed from the solution. The amount of metal removed could be tested by using Atomic Absorption Spectrometer (AAS).
- Through the gained data, equilibrium value of pH and initial metal ion concentration to give maximum heavy metal uptake and best fit adsorption isotherm can be determined.

## CHAPTER 2

### LITERATURE REVIEW AND THEORY

#### 2.1 Principle of Adsorption

Adsorption is described as the enrichment of one or more components in the interfacial layer, i.e. an excess of molecules exists at the adsorbate/adsorbent interface, upon exposure of an adsorbing solid to a gas or vapour (Singh et al.,1985). According to (Mithra, 2010), adsorption is defined as a process; similar to absorption, by which a substance in a gas or liquid becomes attached to a solid. The substance can be a pollutant (heavy metals), called an adsorbate, which is attracted to the surface of a special solid (adsorbent). Adsorbent targets these particles and bonds the adsorbate to its surface. Some solids are ideal for adsorption. They have a lot of surface area for their volume because they are pockmarked with micropores.

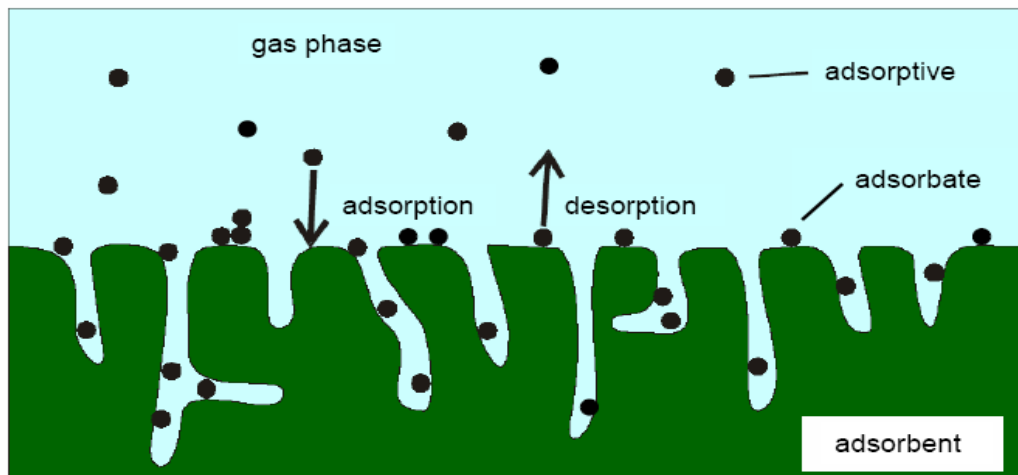


Figure 2.1. Adsorption on the solid/gas interface. ( Zoltan, 2003)



## **2.2 Types of Adsorption**

Adsorption is divided into two categories which are:

- a) physical adsorption (physisorption) or van der Waals adsorption
- b) chemical adsorption (chemisorption)

### **2.2.1 Physical adsorption**

Physisorption is applicable to all adsorbate-adsorbent systems provided the conditions of pressure and temperature are suitable whereas chemisorptions may only occur if the system is capable of making a chemical bond (Fletcher A., 2008). During physisorption, there are no chemical bonds being formed. Chemical bond is defined as attraction between the adsorbate and adsorbent exists by formation of intermolecular electrostatic or physical configuration of the adsorbent.

According to (Fletcher A., 2008), example of intermolecular electrostatic are London dispersion forces, or van der Waals forces from induced dipole-dipole interactions, and the physical configuration of the adsorbent such as the porosity of activated carbons. Adsorption mechanism is influenced by the size of admolecule in comparison with the pore width due to the energetic interactions between the chosen adsorbate and the pores.

### **2.2.2 Chemical adsorption**

Chemical adsorption is far less common than physical adsorption and due to the chemical bonds formed regeneration of the adsorbent for subsequent re-use is often difficult or impossible (Cheremisinoff, 1993). According to Everett (1985), chemisorption is an adsorption process where valence forces are involved; forces that involve in the formation of chemical compounds. During chemisorptions, chemical bonds are being formed which enhance probability of desorption of the adsorbed phase to yield products which are different to the original adsorbate in terms of its chemical properties.

### 2.3 Comparison between physisorption and chemisorptions

	<b>Physical Adsorption</b>	<b>Chemical Adsorption</b>
Heat of Adsorption / kJmol <sup>-1</sup>	20 - 40 c.f. heats of liquefaction	> 80 c.f. bulk-phase chemical reactions
Rate of Adsorption (at 273K)	Fast	Slow
Temperature Dependence of Uptake (with Increasing T)	Decreases	Increases
Desorption	Easy- by reduced pressure or increased temperature	Difficult - high temperature required to break bonds
Desorbed Species	Adsorbate unchanged	May be different to original adsorptive
Specificity	Non-specific	Very Specific
Monolayer Coverage	Mono or multilayer condition dependent	Monolayer

Table 2.1. Characteristics Associated with Physical/Chemical Adsorption, (Atkins, 1994)

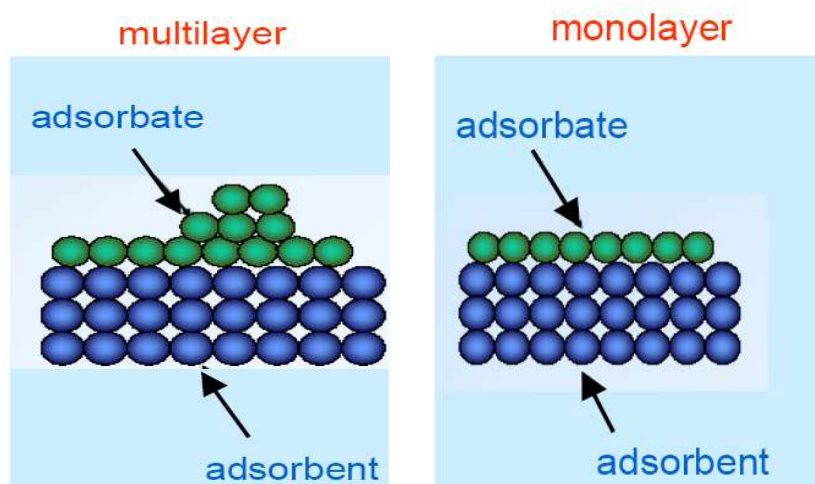


Figure 2.2. Layer coverage of adsorbate on the adsorbent during physisorption and chemisorptions process. (Zoltan, 2003)

## 2.4 Activated Carbon

Activated Carbon is a black, solid (powdered, granular or palletized) material resembling charcoal. It is a versatile adsorbent. Their adsorptive properties are due to their high surface area, a microporous structure and a high degree of surface reactivity. They are used to purify, decolorize, deodorize, dechlorinate, separate, and concentrate in order to filter or remove harmful constituents from gases and liquid solutions. Consequently, activated carbon is used in many sectors such as chemical, petroleum as well as for the drinking water and industrial wastewater treatment.



Figure 2.3. Granular Activated Carbon

### 2.4.1 Type of source materials

Activated carbon could be originated from various types of raw sources. Example of source materials are coconut shells, wood, peat, apricot stone and hazelnut husk. Pore size distribution and surface area of activated carbon which influence heavy metal adsorption capacity is highly dependant on type of materials used to produce activated carbon. Activated carbon made from different raw materials will have different surface area.

For example, activated carbon made from mangrove food (Zulkarnain et al., 1993) and apricot stone (Kobyas, 2005) has surface area of 500 m<sup>2</sup>/g and 566 m<sup>2</sup>/g, respectively.

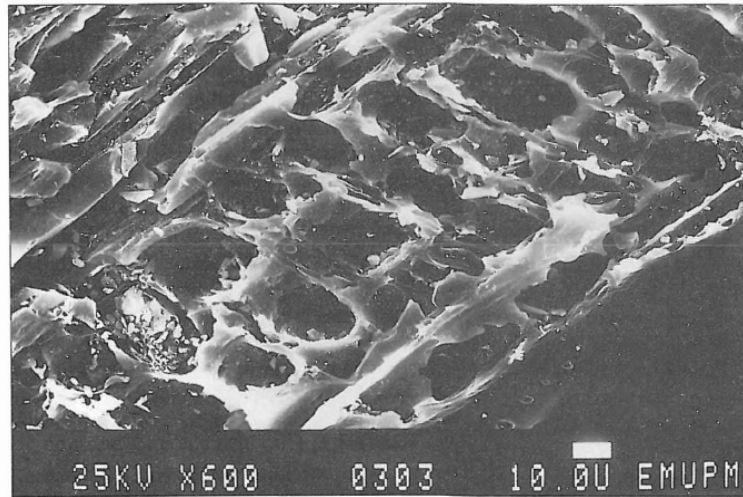


Figure 2.4 Longitudinal section of activated carbon made from mangrove wood. (Zulkarnain et. al,1993)

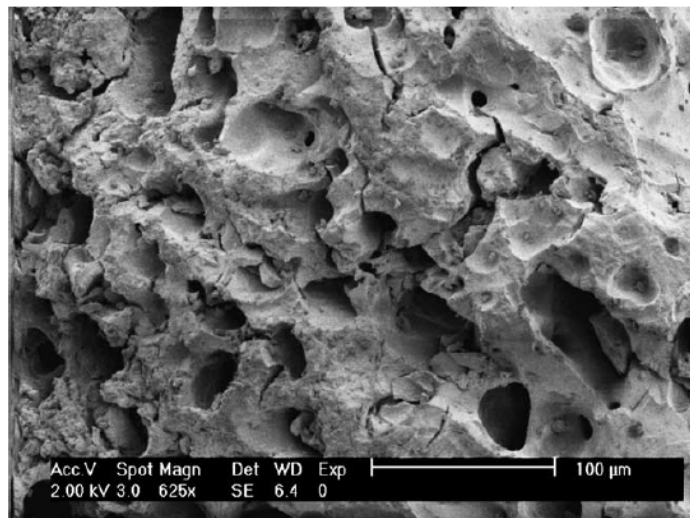


Figure 2.5 SEM Image of Activated Carbon from Apricot Stone(Kobyas et al., 2005),

### 2.4.2 Type of physical form

Physical form of activated carbon could be divided into two main types which are:

- a) Powder



Figure 2.6 : Powder activated carbon. (9a)United Carbon Website)

Powder Activated Carbon (PAC) is a form of activated carbon with a very small particle size which is less than 0.21 mm. It has large surface area which is usually applied in process of raw water intakes and gravity filters. PAC used in water treatment process cannot be regenerated, produces large amount of sludge which could cause bad water filtration.

- b) Granular ( Refer to Figure 2.3)

Granular activated carbon, also known as GAC, has a larger particle size than PAC which is in irregular shape size range from 0.21 to 5 mm. Granular activated carbon is larger than the powder shape and has a smaller surface area to volume ratio.

### 2.4.3 Porosity

#### *Definition*

The word pore is originated from Late Latin word ‘porus’ and Greek word ‘poros’. Porosity is the ratio of the volume of openings (voids) to the total volume of material. It also carries mean of any tiny hole admitting passage of a liquid (fluid or gas). Pore plays role as a passage between the external and the internal surfaces of a solid, allowing material, such as gases and vapours, to pass into, through or out of the solid (Fletcher A., 2008). Porosity is main characteristic which posses surface area of an adsorbent for adsorption process.

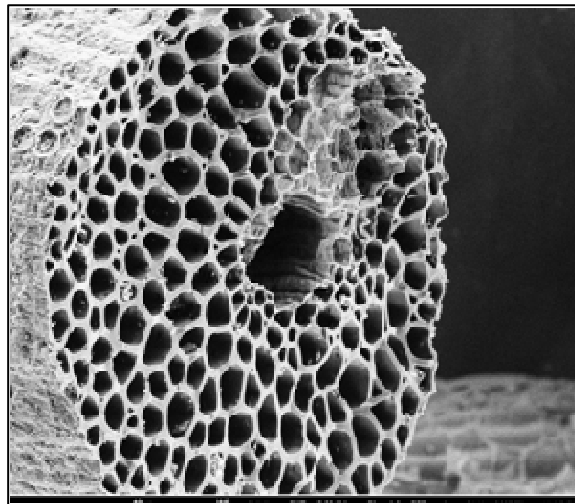


Figure 2.7: Pore structure of activated carbon.  
(School of Engineering, University of Science Malaysia)

### *Types of pores*

There are four terms to define types of pores:

- i) Open pore
- ii) Closed pore
- iii) Transport pore
- iv) Blind pore

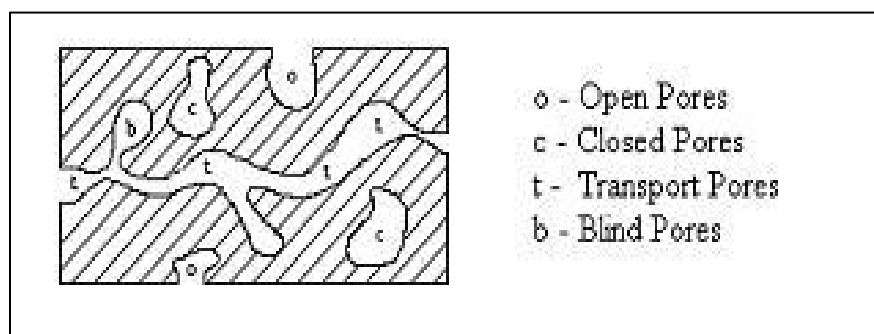


Figure 2.8 : Type of pores.( Fletcher A., 2008)

<b>Types of pores</b>	<b>Definition</b>
Open pore	Pore which is on the external surface of a solid/adsorbent and allows the passage of an adsorbate through the solid.
Closed pore	Pore which is in the internal surface of a solid and isolated from external surface.
Transport pores	Pore which connects parts of the external surface of the solid to the inner microporosity.
Blind pores	Pores which are connected to transport pores in the internal surface but do not related to any other.

Table 2.2 : Type of pore in activated carbon

### ***Type of Pores Shape***

There are 4 types of pore shape could be found in activated carbon:

- i) cylinder
- ii) ink-bottle
- iii) slit
- iv) wedge

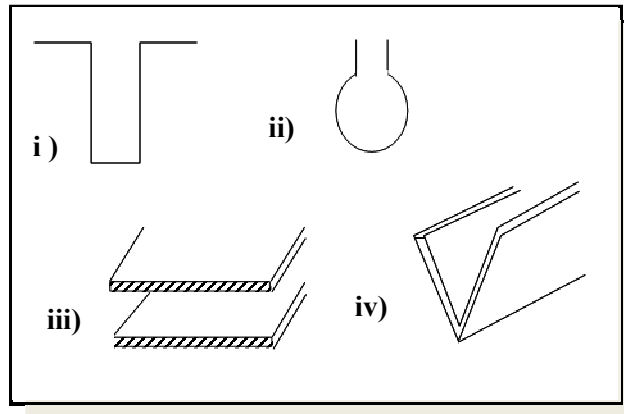


Figure 2.9 : Type of pore shape ( King, L.Y., Unknown)

### ***Types of Pores Size***

The pores are divided into three groups: micropores, mesopores (transitional pores) and the macropores.

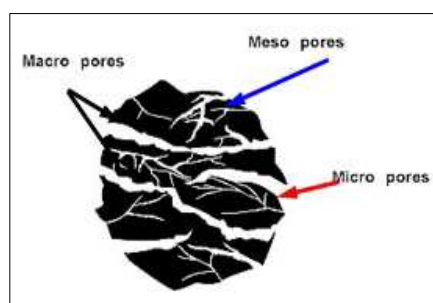


Figure 2.10 : Type of pores size of activated carbon  
(American Filtration and Separations Society Website,2009)



<b>Types of pores</b>	<b>Diameter of pore size</b>
Micropores	Less than 2 nm
Mesopores	Between 2 nm and 50 nm
Macropores	Greater than 50 nm

Table 2.3 : Classification of pore size

The specific surface area of micropores constitutes about 95% of total surface area of activated carbon. Most of adsorption in activated carbon takes place in micropores. Macropores contribution to surface area of activated carbon is very small, thus adsorption is rarely occur in mesopores area. But mesopores region is most efficiently adsorbing large molecular species such as colour molecules.

Dominance of pore size type in activated carbon is influenced by the raw materials used to produce it. Activated carbon made from coconut shells, carbon and wood will have different dominant of pore size type which are micropores, mesopores and macropores, respectively.

## 2.5 Steam Activated Carbon

Steam activation is used throughout for the activation of carbon made from various raw materials includes charcoal. The aims of steam activation is to develop pores inside the coal either micropores, mesopores or macropores. Types of pore sizes developed in the carbon dependant on the hardness of material and steam activation period. A hard material, like coconut shell, leaves almost nothing but micropores, while a soft material like peat always get many meropores as well .If steam is blowed in for long period, some of the carbon will turn to gas and leave empty spaces (pores) behind. At this level, pore developed is called micropores. Continuously blowing the steam will enhanced the change of carbon to gas and pores developed to mesopores and further steam blowed expand the pores to macropores.

## 2.6 Adsorption Isotherm

Adsorption isotherm is a complete adsorption/desorption analysis. It is a plot of equilibrium amounts adsorbed (in mmol g<sup>-1</sup>) against the relative pressure (p/p<sub>0</sub>) of the adsorbate for gas and concentration if liquid.

According to Fletcher (2008), isotherms provide a significant amount of information about the adsorbent used and the interaction with the adsorbate in the system,including:

- i) assessment of the surface chemistry and fundamentals involved in the adsorption process;
- ii) estimates of the surface area, pore volume and pore size distribution;
- iii) efficiency profiles for carbons used in industrial processes.

The extent of adsorption is a function of temperature, pressure and nature of adsorbent and adsorbate.

$$n = f(P, T, \text{adsorbate}, \text{adsorbent})$$

There are six IUPAC standard adsorption isotherms which are differ in gas/solid interaction. All adsorption isotherms should fit at least one, or at least a combination of two or more, of the six recognised types classified by Brunauer, Deming, Deming and Teller (Brunauer et. al, 1940).

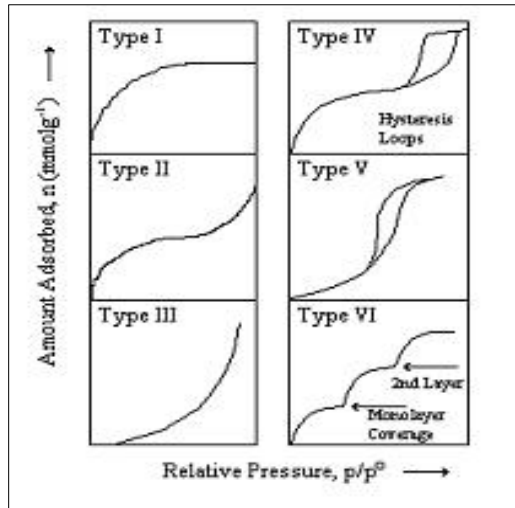


Figure 2.11 : Type of adsorption isotherms ( Fletcher, 2008)

Type I Isotherm is typical of adsorbent majorly with microporous structure. The adsorption process is usually complete at a partial pressure of  $\sim 0.5$ . Type II Isotherm is commonly produced by physical adsorption process of gases by non-porous solids and carbons comprised of mixed micro- and meso-porosity structure. Type III Isotherm usually involved by non-porous and microporous adsorbent. Due to weak interactions between adsorbate and adsorbent, there are low uptakes at low relative pressure. However, the uptakes will increase at higher relative pressure due to stronger interaction as once a molecule is adsorbed at primary adsorption site.

Type IV Isotherm shows a hysteresis loop and commonly associated with mesoporosity adsorbent. Capillary condensation gives rise to a hysteresis (Singh, 1983). Type V Isotherm is indicative of microporous or mesoporous solids. Type VI Isotherm shape is due to the complete formation of monomolecular layers before progression to a subsequent layer. It involves homogeneous, non-porous surfaces.

**2.7 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 specialized for location near to housing area and sea, respectively.

Parameter (mg/L)	Standard	
	A	B
Mercury	0.005	0.05
Cadmium	0.01	0.02
Arsenic	0.05	0.10
Lead	0.10	0.50
Chromium	0.20	1.0
Copper	0.20	1.0
Nickel	0.20	1.0
Zinc	1.0	1.0
Iron	1.0	5.0

Table 2.4 : Environmental Quality Act 1974, Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979, Malaysia: Selected parameter limits of effluent of Standards A and B (Department of Environment, DOE, Malaysia).

## **2.8 Methodology of previous researchers**

Previous researchers have conducted series of experiments in removing heavy metal using various types of adsorbents. The objective of experiment was to find important parameters affecting adsorption process and their optimum value to give maximum uptake of heavy metals. Table 2.5 shows summary of findings from experiments involving heavy metal adsorption by using adsorbent from different raw sources.

Table 2.5: Findings of previous researchers on metal adsorption using various types of adsorbents

FINDINGS									
AUTHOR	YEAR	TITLE	OBJECTIVE	METAL ION	ADSORBENT & SURFACE AREA	CONDITION	ADSORPTION UPTAKE	PARAMETERS (pH, Conc.)	CONCLUSION
M. Kobya	2004	Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone	To remove selected heavy metals from aqueous solutions and study effect of pH on adsorption	Chromium (VI), Lead, Cadmium, Cobalt, Copper, Chromium (III), Nickel,	Activated carbon from apricot stone Surface area :642 m <sup>2</sup> /g	T = 25°C Bath shaker speed = 200 rpm Contact time = 48 hour	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	<ul style="list-style-type: none"> <li>Adsorptions of the metal ions were found to be highly pH dependent. Optimum pH for removal was 1 for Cr(VI) while that for the rest of the metal ions varied from 3 to 6.</li> </ul>
Ali Hakan Ören and Abidin Kaya	2005	Factors affecting adsorption characteristics of Zn <sup>2+</sup> on two natural zeolites	To remove zinc ions from aqueous solutions.	Zinc	Zeolite (Gordes and Bigadic type) Surface area : 95 m <sup>2</sup> /g	Bath shaker speed = 100 rpm Temperature = 25°C	<ul style="list-style-type: none"> <li>Adsorption increased when the initial pH of the solution was increased from 3 to 4</li> <li>The maximum adsorption capacity of Gordes and Bigadic zeolite is 6 and 3 mg/g, respectively.</li> </ul>	pH = 3-8 Initial concentration = 2.5 – 20 mg/l	<ul style="list-style-type: none"> <li>Zn<sup>2+</sup> adsorption behavior of both zeolites is highly dependent on pH.</li> <li>Increase in the initial concentration of Zn<sup>2+</sup> in the system causes an increase in the adsorption capacity.</li> </ul>

Table 2.5: Findings of previous researchers on metal adsorption using various types of adsorbents (*cont.*)

FINDINGS									
AUTHOR	YEAR	TITLE	OBJECTIVE	METAL ION	ADSORBENT & SURFACE AREA	CONDITION	ADSORPTION UPTAKE	PARAMETER (pH, Conc.)	CONCLUSION
Amir Mossein Mahvi	2009	Teawaste as An Adsorbent for Heavy Metal Removal from Industrial Wastewaters	To remove heavy metals contains in wastewater using teawaste as an adsorbent.	Nickel, Lead, Cadmium	Teawaste	Bath shaker speed = 120 - 130 rpm Contact time = 1 hour	Adsorption capacity of lead was the highest reached almost 100 % at concentration of 5 mg/l.	Conc. = 5, 10, 15, 30 and 100 mg/L	The concentration of heavy metal has an important effect on the result of this treatment.
Mustafa Imamoglu, Oktay Tekir	2008	Removal of copper (II) and lead (II) ions from aqueous solutions by adsorption on activated carbon from a new precursor hazelnut husks.	To study the effect of activated carbon from a new precursor hazelnut husks on the lead and copper removal.	Copper (II), Lead (III)	Activated carbon from a new precursor hazelnut husks Surface area : 1092 m <sup>2</sup> /g	Bath shaker speed = 200 rpm	Adsorption of Cu (II) and Pb(II) on ACHH decreased from 99.6% and 97.2% to 39.1% and 73.2% by increasing the Cu (II) and Pb (II) concentrations from 5 mg/L to 200 mg/L respectively.	i) pH = 2.5 - 7 ii) adsorbent dosage = 0.01 - 0.5g/25 ml solution iii) contact time = 1-60 minute iv) Concentration = 5-200 mg/l	<ul style="list-style-type: none"> <li>Optimum pH values of Cu(II) and Pb (II) solution is 6.7.</li> <li>The optimum ACHH dosages were selected 0.30 g/25 ml.</li> <li>As contact time increase, adsorption increase and optimum at contact time 50 minutes.</li> <li>Percentage of adsorption decrease as concentration increase.</li> </ul>

Table 2.5: Findings of previous researchers on metal adsorption using various types of adsorbents (*cont.*)

AUTHOR	YEAR	TITLE	OBJECTIVE	FINDINGS					
				METAL ION	ADSORBENT	CONDITION	ADSORPTION UPTAKE	PARAMETER (pH, Conc.)	CONCLUSION
Upendra Kumar and Manas Bandyopadhyay	2005	Sorption of cadmium from aqueous solution using pretreated rice husk	To remove cadmium from aqueous solution	Cd <sup>2+</sup>	Epichlorohydrin treated rice husk (ERH), NaOH treated rice husk (NRH) and sodium bicarbonate treated rice husk (NCRH)	Temperature = 40°C Contact time = 6h	At pH 3 the sorption was about 36%, 45% and 46% by ERH, NRH and NCRH. At pH 5, the uptake increased to about 78%, 85% and 89%. The optimum uptake of 86.2%, 97.0% and 97.2% by ERH, NRH and NCRH, respectively was observed at pH 9.	pH = 1-3	<ul style="list-style-type: none"> <li>Increasing the pH, increasing the adsorption.</li> <li>Decreasing trend in uptake was observed above pH 9 due to formation of soluble hydroxyl complexes.</li> </ul>
Saima Q. Memon, Najma Memon, S.W. Shah, M.Y. Khuhawar, M.I. Bhanger.	2006	Sawdust—A green and economical sorbent for the removal of cadmium (II) ions	To remove cadmium using sawdust as an adsorbent.	Cd <sup>2+</sup>	Sawdust	Contact time = 24 h	The least metal ions were removed when the solution pH was maintained at 2. Adsorption decreases at pH value above 8 due to the hydrolysis of metal ions as at pH 9 Cd(II).	pH = 2-12	The optimal uptake occurred at pH 5.



Table 2.5: Findings of previous researchers on metal adsorption using various types of adsorbents (*cont.*)

AUTHOR	YEAR	TITLE	OBJECTIVE	FINDINGS					
				METAL ION	ADSORBENT	CONDITION	ADSORPTION UPTAKE	PARAMETERS (pH, Conc.)	CONCLUSION
O.S. Amuda, A.A. Giwa, I.A. Bello.	2007	Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon	To remove heavy metal from industrial wastewater.	Zn <sup>2+</sup>	Modified activated coconut shell carbon	Temperature = 25 °C Bath shaker speed = 200 rpm,	At pH above 6, the adsorption capacity was decreasing as the metal ion started to precipitate at that pH level.	pH = 1-11	<ul style="list-style-type: none"> <li>Increasing pH of the solution from 2 to 6 caused linear increase in Zn removal efficiency.</li> <li>The removal efficiency remained almost constant above pH 6.</li> </ul>
F. Noeline, D.M. Manohar, T.S. Anirudhan	2005	Kinetic and equilibrium modelling of lead(II) sorption from water and wastewater by polymerized banana stem in a batch reactor	To remove lead (II) from water and wastewater.	Pb <sup>2+</sup>	Polymerized banana stem	Temperature = 30 °C	Adsorption is 95% at pH 5 and above.	pH = 2.0–9.0	<ul style="list-style-type: none"> <li>Percentage removal of lead(II) was maximum at pH range 5.0–9.0</li> </ul>

Table 2.5: Findings of previous researchers on metal adsorption using various types of adsorbents (*cont.*)

AUTHOR	YEAR	TITLE	OBJECTIVE	FINDINGS					
				METAL ION	ADSORBENT	CONDITION	ADSORPTION UPTAKE	PARAMETERS (pH, Conc.)	CONCLUSION
Isabel Villascusa, Nuria Fiola, Maria Martinez, Nuria Miralles, Jordi Poch, Joan Serarols	2003	Removal of copper and nickel ions from aqueous solutions by grape stalks wastes	To remove copper and nickel ions from aqueous solutions.	Cu <sup>2+</sup> , Ni <sup>2+</sup>	Grape stalks waste	Contact time = 2h	Optimum value was reached at around pH 5.5–6.0	pH = 1.0–6.5	<ul style="list-style-type: none"> <li>• Metal removal with increasing pH and the optimum value was reached at around pH 5.5–6.0.</li> <li>• The same trend has also been reported in the removal of these ions by some other materials.</li> </ul>
O. mer Yavuz	2001	Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite	To remove copper, nickel, cobalt and manganese from aqueous solution using kaolinite as adsorbent.	Copper, nickel, cobalt, manganese	Kaolinite	Bath shaker speed = 3500 rpm	Cu(II) is the most adsorbed because of its smaller ionic radius (easily takes place in the pores of the kaolinite) and because of its lower affinity to sorbent (low solubility) then easily adsorbed on kaolinite.	T = 25°C and 40°C Contact time = 0 -350 min	<ul style="list-style-type: none"> <li>• Adsorption affinity order for metal ions: Cu(II) &gt; Ni(II) &gt; Co(II) &gt; Mn(II)</li> <li>• Linear form of Langmuir adsorption equation.</li> </ul>

The removal of chromium, lead, cadmium, cobalt, copper, chromium and nickel from aqueous solutions has been studied by Kobya et al.( 2005), using activated carbon from apricot stone. The pH of solution was varied in the range of 1 to 6 with known constant concentration. The sample was put in 100 ml conical flask containing 0.1 g of adsorbent and was agitated at a speed of 200 rpm in a thermostatic shaker bath at 25°C for 48 h. The initial concentration of metal ions and corresponding concentrations after fixed time periods were measured by atomic absorption spectrophotometry .The results found that adsorption capacity of all metal ions except chromium increased as the pH increased. Optimum pH for chromium is 1 while other metals are in the range 3 to 6.

In the experiment conducted by Imamoglu and Tekir (2008), lead and copper removal using activated carbon from a new precursor hazelnut husks (ACHH) has been studied. The adsorption capacity was found to be dependant on pH, adsorbent dosage, contact time and concentration of solution. As pH increased from 2.5 to 7, the adsorption capacity for both metals seemed increased and optimum at 6.7. Increment of both adsorbent dosage and contact time increase the adsorption capacity. Adsorbent dosage range was between 0.01 to 0.5g/25 ml solution and the highest adsorption capacity was achieved at 0.5g/25 ml and 50 minutes of contact time. Increment of concentration value from 1 to 200 mg/l decrease the adsorption capacity. Both metals have almost 100% adsorption capacity at 5 mg/l.

Amir et.al (2009) investigated the adsorption of nickel, lead and cadmium on teawaste as a function of concentration of the solution. The metal concentrations varied were 5, 10, 15, 30 and 100 mg/L using different amount of adsorbents which are 0.5,1, 1.5 g in single solution.

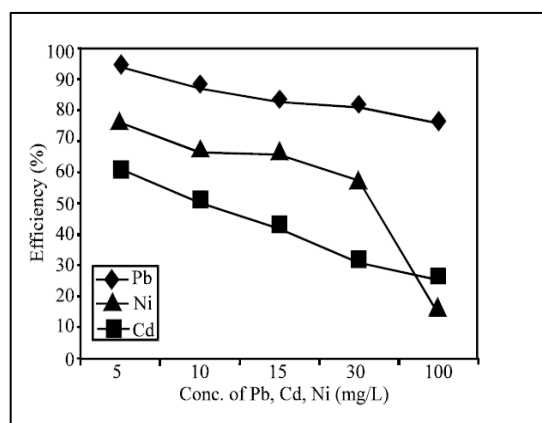


Figure 2.12 : Adsorption Percent of Lead,Cadmium and Nickel by 0.5 g teawaste (Amir et. al,2009)

Results showed that adsorption capacity of lead was the highest reached almost 100 % at concentration of 5 mg/l in the three different amount of adsorbent. All three metal ions shows decrement in adsorption capacity as concentration increases to 100 mg/l.

Ali et al. (2005) discussed the removal of zinc from aqueous solution using two types of zeolite as adsorbents. The experiment varying pH and concentration of solution which were the range from 3 to 8 and 2.5 mg/l to 20 mg/l, respectively. Adsorption capacity of both materials were found to be increased when the initial pH of the solution was increased from 3 to 4 and the maximum adsorption capacity of two different zeolite are 6 and 3 mg/g, respectively.

The effect of pH on the adsorption of cadmium, Cd (II) from aqueous solution was studied by Kumar and Bandyopadhyay (2006), using activated carbon from rice husk. The adsorbent used are divided into three types which are epichlorohydrin treated rice husk (ERH), NaOH treated rice husk (NRH) and sodium bicarbonate treated rice husk (NCRH). The solution pH was to be in the range of 3–10 as the metal solutions were precipitated above pH 11.

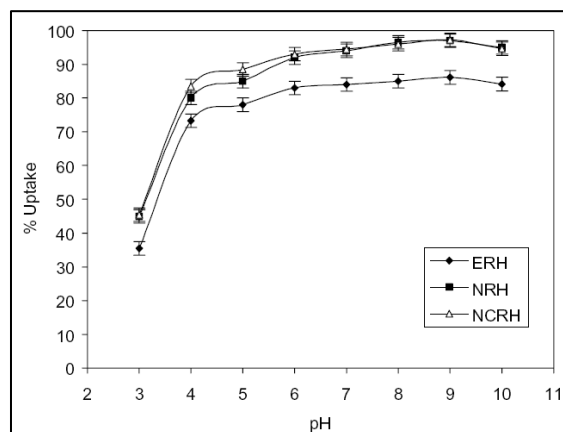


Figure 2.13 : Effect of pH on the uptake of Cd(II) (Kumar and Bandyopadhyay, 2006)

At pH 3 the sorption was about 36%, 45% and 46% by ERH, NRH and NCRH. Increasing the pH by 2 units i.e. 5, the uptake increased to about 78%, 85% and 89%. the optimum uptake of 86.2%, 97.0% and 97.2% by ERH, NRH and NCRH, respectively was observed at pH 9. Decreasing trend in uptake was observed above pH 9 due to formation of soluble hydroxyl complexes.

Memon et al.( 2007) studied the removal of Cd(II) from environmental water using activated carbon from sawdust. The optimal uptake occurred at pH 5. The least metal ions were removed when the solution pH was maintained at 2.

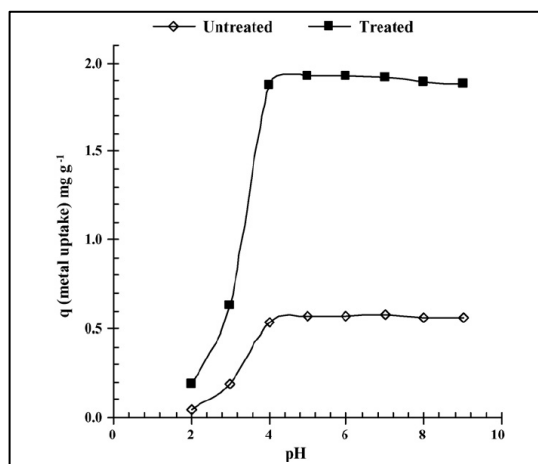


Figure 2.14 : Cd(II) ions uptake as a function of pH on treated and untreated sawdust ( Memon et. al, 2007)

At pH values less than 3, the carboxylic groups become protonated and thus are no longer available to attract metal ions from solution. Percent sorption of cadmium decreases about 4% at pH value above 8 due to the hydrolysis of metal ions as at pH 9 Cd(II).

The adsorption of zinc, Zn (II) on adsorbent made from coconut shell as function of pH, adsorbent concentration and initial ion concentration was studied by Amuda et al.(2007).The pH range was 2-6 and optimum adsorption capacity of Zn(II) was at pH 6. At pH above 6, the adsorption capacity was decreasing as the metal ion started to precipitate at that pH level. As adsorbent dose increase, adsorption capacity of Zn(II) also increase. This happened as more binding sites for ions are available at higher dose of adsorbents. However, there is limit in the increment of adsorbent dose where at certain dose of adsorbent, adsorption peak is reached and hence, no adsorption of metal ion to the adsorbent. At above 18 g/L for chitosan coated acid treated coconut shell carbon (CCASC) yielded no increase in the Zn removal efficiency as the activated carbon had already saturated with the adsorbed metal.

The highest Zn removal efficiency for CACSC was 90% at 18 g/L dose of the adsorbent. The percentage removal of Zn (II) ion by the adsorbent initially increased rapidly with increasing Zn concentration and slowed down when Zn concentration reached 25 mg/L. At lower concentrations, Zn ion in the solution would interact with the binding sites and thus facilitated 100% adsorption. At higher concentrations, more Zn ions are left un-adsorbed in solution due to the saturation of binding sites.

The adsorption of copper and nickel ions from aqueous solutions by grape stalk waste was studied by Isabel et al. (2003). The pH of initial metal solutions was varied within the range 1.0-6.5. Metal removal increased with increasing pH solution and the optimum value was reached at around pH 5.5–6.0. The same trend has also been reported in the removal of these ions by some other materials.

Noeline et al. (2005) investigated Pb(II) sorption from water and wastewater by polymerized banana stem as adsorbent. The investigated parameters are pH, initial metal concentration and contact time. The temperature is set to be constant at 30 °C. The pH range was 2.0-9.0 and percentage removal of Pb(II) was maximum at pH range 5.0-9.0. The higher the initial concentration of Pb(II), the larger the amount of Pb(II) adsorption. Adsorption was found optimum at 100 mg/l and contact time of 60 minutes. A further increase in contact time had a negligible effect on the amount of adsorption.

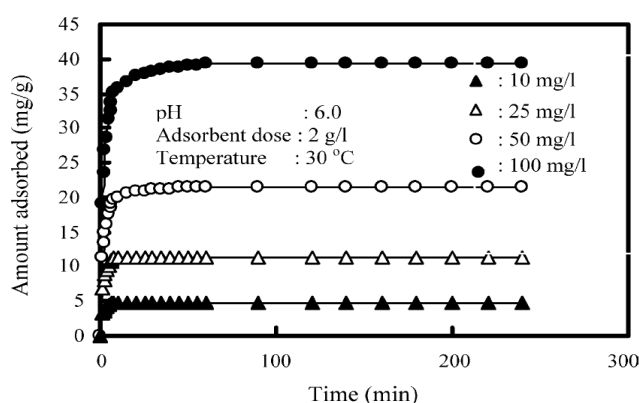


Figure 2.15 : The variation of amount of the amount of adsorption of Pb(II) with time for different concentrations at 30°C. (Neoline et. al, 2005)

Omer (2002) used kaolinite to remove manganese, cobalt, nickel and copper from aqueous solutions. Introduced concentrations were 1029, 1000, 1010 and 3159 ppm, respectively which containing accurately weighed amounts (1.00 g) of the adsorbent in 100ml glass bottles. The bottles were shaken at 25°C and /or 40°C temperatures using immersed water bath for a prescribed length of time to attain equilibrium. The adsorbent was then removed by centrifugation at 3500 rpm. The equilibrium concentrations of heavy metal concentrations were determined by flame atomic absorption spectrophotometer (AAS). It was found that Cu(II) is the most adsorbed because of its smaller ionic radius (easily takes place in the pores of the kaolinite). Besides, because of its low solubility, then it was easily adsorbed on kaolinite.

## CHAPTER 3

### METHODOLOGY

#### 3.1 Chemicals & Adsorbent Used


Chemicals	Purity	
Cadmium sulphate, CdSO <sub>4</sub>	99%	
Hydrochloric acid, HCl	95 - 98%	
Nickel sulphate, NiSO <sub>4</sub>	99%	
Sodium Hydroxide, NaOH	99%	
Adsorbent	Characteristics	Supplier
<b>Granulated Charcoal Activated Carbon (GCAC)</b>  	<p>It is a granular activated carbon produced by steam activation of select grades of coal.</p>	<p><b>Norit</b></p>

Table 3.1 : Chemicals and adsorbent used in the research

#### 3.2 Experimental Set Up

Equipment used	Purpose	Amount
Test tube ( 25 ml) + Stopper	Fill in chemical samples	8
Volumetric flask ( 200 ml)	Metal solution preparation	5
Graduated cylinder ( 50 ml)	To measure volume of metal solution	2
Pipet	Metal solution preparation	2
Funnel	Metal solution preparation	1

Table 3.2 : Equipment / Tools required for experiment



<b>Equipment used</b>	<b>Purpose</b>	<b>Amount</b>
Test tube rack	To place sample test tube	1
Beaker	Miscellaneous purpose	2
Digital weigh	Adsorbent (Activated carbon) weight measurement	1
Filter paper	To filter activated carbon from samples	50
Stopwatch	To record agitation time between samples and activated carbon	1
Glass plate / Petri Dish	Used for activated carbon weight measurement	2
Atomic Absorption Spectrometer	To test concentration of heavy metals remained	1
Bath shaker	To provide shaking motion to samples and activated carbon	1
Surface area analyzer	To test surface area of GCAC	1

Table 3.2 : Equipment / Tools required for experiment (*cont.*)

### 3.3 Experimental Methods

#### 3.3.1 Granular Charcoal Activated Carbon (GCAC) BET Surface Area and Pore size distribution Testing

BET surface area and pore size distribution of GCAC was been tested using Surface Area Analyzer. It determines surface area by measuring amount of nitrogen gas adsorbed as a function of pressure.



Figure 3.1 : Surface Area Analyzer

### 3.3.2 Batch Adsorption Studies

The experiments were carried out at room temperature (25°C). The metal solution were placed in conical flask and agitated on a rotary shaker at constant speed of 240 rpm. The metal concentration was tested using Atomic Absorption Spectrometer.

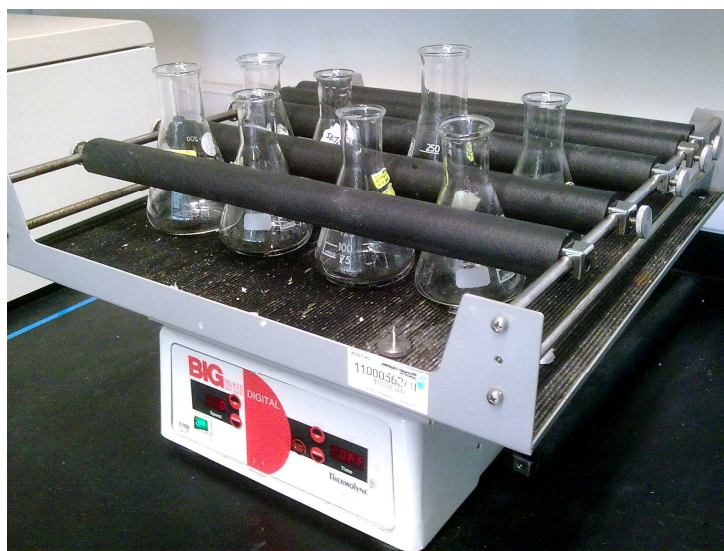


Figure 3.2 : Rotary shaker



Figure 3.3 : Atomic Absorption Spectrometer

### 3.3.3 Metal Solution Preparation

Separate metal solutions of  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  with 5 different concentrations of 5, 25, 50, 75 and 100 mg/L are prepared by diluting in respective amount of deionised water using 1000 ml volumetric flask. The pH of the metal solutions then varied to five different pH which are 2,4,6,8 and 10. The pH of solution is controlled by addition of 0.1 M NaOH and 0.1 M HCl.



Figure 3.4 : Sample of five different metal concentrations

### 3.3.4 Effect of agitation time on metal adsorption

Four samples of nickel solutions with initial metal concentration of 5 mg/L and pH 6 were poured into 25ml conical flask. 0.3 g of Granulated Charcoal Activated Carbon (GCAC) is added into flask. The flasks then were agitated on shaker for 30, 60, 90 and 120 minutes, respectively. The solutions were filtered using Whatman filter paper and concentrations of remaining metal ion in the solutions,  $C_e$  were measured by Atomic Adsorption Spectrometer (AAS).

$$\% \text{ Adsorption} = (C_o - C_e / C_o) \times 100$$

$C_o$  and  $C_e$  are the initial and final concentration of the adsorbate, respectively. The procedures were repeated with initial metal concentration of concentration of 25, 50, 75 and 100 mg/L. Same procedures were applied to experiment of cadmium.

### 3.3.5 Effect of pH on metal adsorption

Four samples of nickel solutions with pH 2 and average concentration of 50 mg/l is poured into 25ml conical flask. 0.3 g of Granulated Charcoal Activated Carbon (GCAC) is added into each flask. The flasks then were agitated on shaker for 30, 60, 90 and 120 minutes, respectively. The solutions were filtered using Whatman filter paper and concentrations of remaining metal ion in the solutions,  $C_e$  were measured by Atomic Adsorption Spectrometer (AAS).

$$\% \text{ Adsorption} = (C_o - C_e / C_o) \times 100$$

$C_o$  and  $C_e$  are the initial and final concentration of the adsorbate, respectively. The procedures were repeated with pH of 4,6,8 and 10. Same procedures were applied to experiment of cadmium.

### 3.3.4 Effect of initial metal concentration on metal uptake

Four samples of nickel solutions with initial metal concentration of 5,25, 50,75 and 100 mg/l is poured into 25ml conical flask. 0.3 g of Granulated Charcoal Activated Carbon (GCAC) is added into flask. The flasks then were agitated on shaker for 30 minutes. The solutions were filtered using Whatman filter paper and concentrations of remaining metal ion in the solutions,  $C_e$  were measured by Atomic Adsorption Spectrometer (AAS).

$$\% \text{ Adsorption} = (C_o - C_e / C_o) \times 100$$

$C_o$  and  $C_e$  are the initial and final concentration of the adsorbate, respectively. The procedures were repeated with agitation time of 60,90 and 120 minutes. Same procedures were applied to experiment of cadmium.

### 3.4 Gantt Chart for the First Semester of Final Year Project

No.	Project Activities	Week No.														
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Approval of Selected Project Topic															
2	Preliminary Research Work															
3	Submission of Progress Report															
4	Seminar															
5	Submission of Interim Report															
6	Oral presentation															
7	Project Work															

▲ Suggested milestone      ■ Process

### 3.5 Gantt Chart for the Second Semester of Final Year Project

No.	Project Activities	Week No.													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Sample Testing														
2	Submission of Progress Report 1														
3	Submission of Progress Report 2														
4	Seminar														
5	Poster Exhibition														
6	Submission of Dissertation ( soft bound )														
7	Oral Presentation														
8	Submission of Project Dissertation ( Hard Bound)														

▲ Suggested milestone      ■ Process

## CHAPTER 4

### RESULT AND DISCUSSION

#### 4.1 BET Surface area of Granulated Charcoal Activated Carbon (GCAC)

GCAC surface area is analysed by using Surface Area Analyser. Their BET surface areas are found to be 897.58 m<sup>2</sup>/g.

#### 4.2 Pore Size Distribution

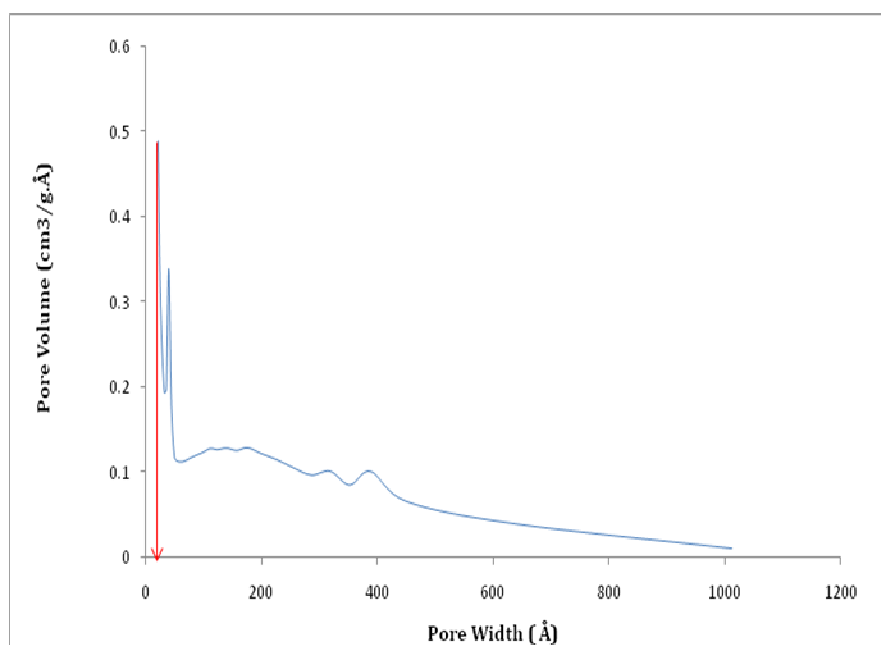


Figure 4.1: Pore size distribution of Granular Charcoal Activated Carbon

The figure above shows pore volume, cm<sup>3</sup>/g.Å versus the pore width, Å of granulated charcoal activated carbon (GCAC). Pore volume is highly dominated by pore width of 20.55 Å which covers pore volume of 0.489 cm<sup>3</sup>/g.Å. It shows that the granulated activated carbon (GCAC) is microporosity adsorbent as 20.55 Å equal to 2.055 nm and it is the characteristics of micropores.

### 4.3 Adsorption isotherm

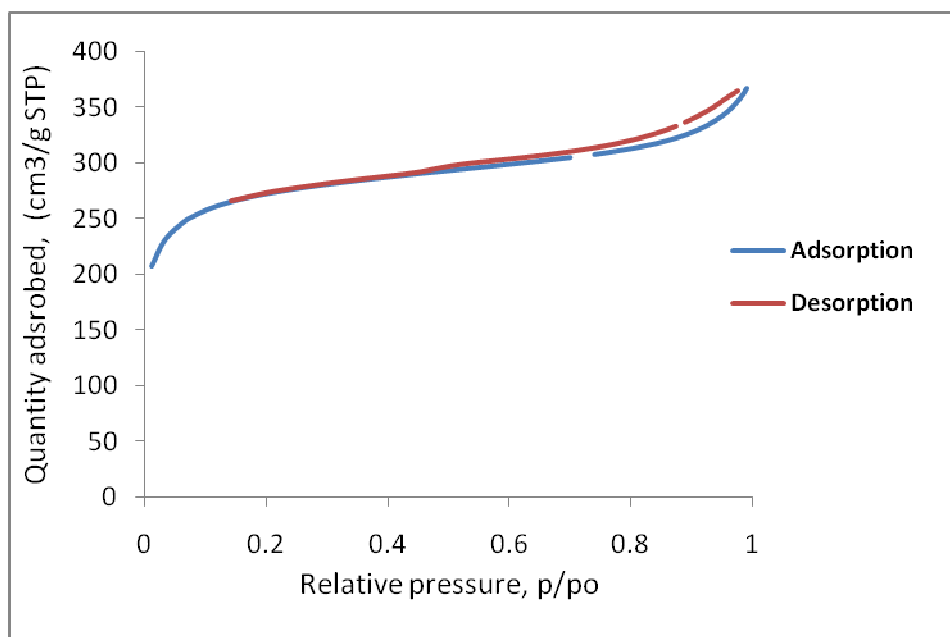


Figure 4.2 : Adsorption isotherm

The figure above shows the graph of quantity adsorbed,  $\text{cm}^3/\text{g}$  versus relative pressure,  $p/p^0$  of liquid nitrogen adsorption by granulated charcoal activated carbon (GCAC). The maximum adsorption is at relative pressure equal to 0.990774687 or  $\approx 1$  where the amount adsorbed is  $367.78 \text{ cm}^3/\text{g}$ . The desorption process starts to occur at relative pressure is 0.977 and the amount decreased to  $365.04 \text{ cm}^3/\text{g}$ . The adsorption behaviour shown is parallel to Type IV adsorption isotherm which commonly associated with mesoporosity adsorbent. In this case, the dominant pore size is  $20.55 \text{ \AA}$  which equals to  $2.055 \text{ nm}$ . The size is slightly on the boundary of size range between micropores and mesopores. As GCAC has high surface area which is  $897.58 \text{ m}^2/\text{g}$ , it has been concluded that it is a mixed microporosity-mesoporosity adsorbent.



#### 4.4 Effect of agitation time on metal adsorption

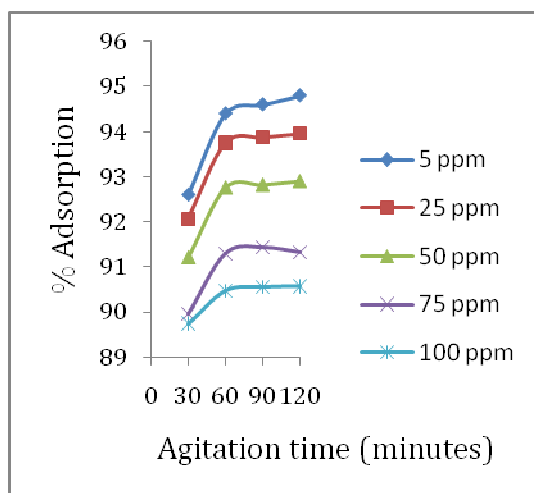


Figure 4.3 : Effect of agitation time on nickel adsorption with different initial metal concentration

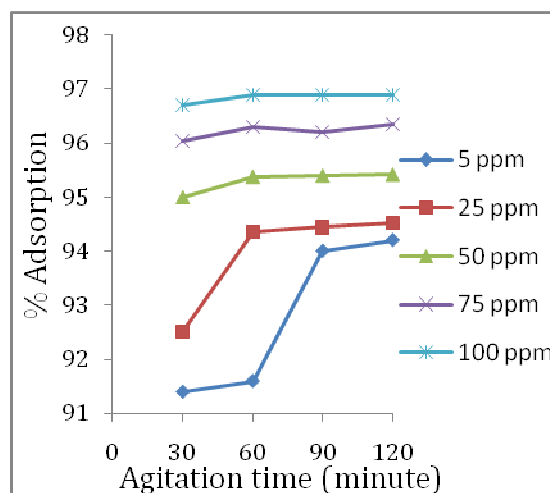


Figure 4.4: Effect of agitation time on cadmium adsorption with different initial metal concentration

The percentage of nickel and cadmium adsorption with five different of initial concentrations, adsorbent dose of 12 g/L, agitation speed of 240 rpm at room temperature 25°C are shown in the Figure 4.3 and Figure 4.4. Same trend showed by both metals as their adsorption were the highest at 120 minutes. For nickel concentration of 5,25,50,75 and 100 ppm, the adsorption percentage were 94.8%, 93.96%,92.9%,91.33% and 90.57%,respectively. For cadmium concentration of 5,25,50,75 and 100 ppm, the adsorption percentage were 94.2%, 94.52%,95.42%,96.35% and 96.9%,respectively.The adsorption seems to keep increasing with increase of time and could be higher if the time is extended for longer period. Same optimum time achieved by both metals at different initial metal concentration proved that initial metal concentration do not have impact in determining the equilibrium time and it only affects on the adsorption percentage which will be further discussed on the page 41.

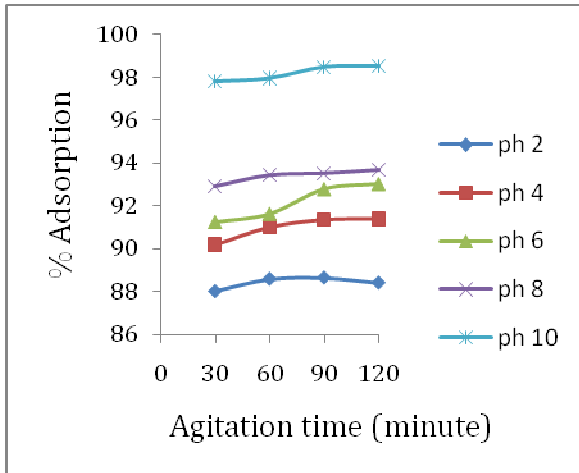


Figure 4.5: Effect of agitation time on cadmium adsorption with different pH

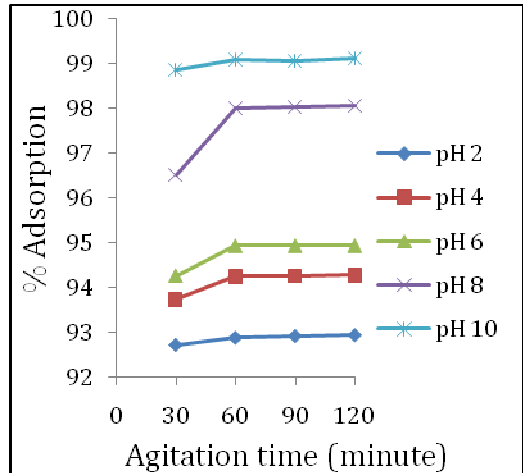


Figure 4.6: Effect of agitation time on nickel adsorption with different pH

The figure shows percentage of nickel and cadmium adsorption with initial concentration of 50 mg/L of five different pH, adsorbent dose of 12 g/L, and agitation speed of 240 rpm at room temperature 25°C. As agitation time was increased, both metal adsorptions keep increased and achieved maximum value at 120 minutes. The adsorption seems to keep increasing with increase of time and could be higher if the time is extended for longer period. Same optimum time achieved by both metals at different pH proved that pH do not have impact in determining the equilibrium time and it only affects on the adsorption percentage which will be further discussed on page 40.

## 4.2 Effect of pH on metal adsorption

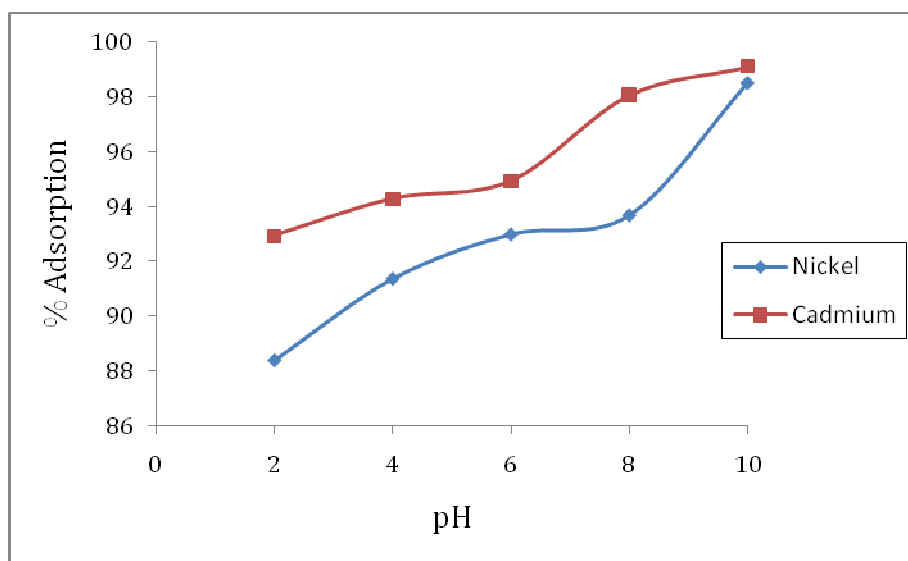


Figure 4.7: Effect of pH on nickel and cadmium adsorption

Figure 4.5 shows percentage of nickel and cadmium adsorption with initial concentration of 50 mg/L, adsorbent dose of 12 g/L, agitation speed of 240 rpm at room temperature. The agitation speed for nickel and cadmium are 120 minutes. The pH of solution is controlled by addition of 0.1M NaOH and 0.1M H<sub>2</sub>SO<sub>4</sub>. The research was conducted in the pH range 2-10 as both metals will precipitate at pH 11. During metal precipitation, there will be formation of soluble hydroxyl complexes which complicated the metal removal from solution. According to ( Schiewer et. al, 1995), too high pH values, which cause precipitation of metal complexes, should be avoided during sorption experiments where distinguishing between sorption and precipitation metal removal becomes difficult. Adsorption percentages of both metals kept increasing as pH increased. For nickel, at pH 2,4,6,8 and 10, the adsorption percentage were 88.58%,91%, 91.6%,93.45% and 97.98%.For cadmium, at pH 2,4,6, 8 and 10 the sorption were 92.94%, 94.29%,94.94%, 98.08% and 99.11%.,respectively. The adsorption percentage achieved was about 2% higher than result achieved by Kumar et. al using rice husk which was 97.2% adsorption percentage at pH 9.The result explains that the percentage of metal adsorption increase with increasing pH from 2 to 10 and concluded that adsorption was the highest at pH 10. At low pH, solution has high concentration of H<sup>+</sup> ions compared to

high pH solution as it is acidic. Presence of high  $H^+$  ions in metal solutions created great competition between  $H^+$  ions and  $Cd^{2+}$  ions for vacant adsorption sites of adsorbent. The competitive adsorption results in low metal uptake by GCAC. Optimum pH obtained for cadmium and nickel adsorption by Saima et. al (2006) using sawdust and Isabel et. al (2003) using grape stalk waste were 5 and 5.5, respectively. Compared to both of researchers' result, optimum pH of metals adsorption by GCAC was higher and alkaline. From the side of industrial application, optimum pH of metal adsorption by GCAC was much better than others as it was alkaline and will not corrosive to equipments.

#### 4.3 Effect of initial metal concentration on metal adsorption

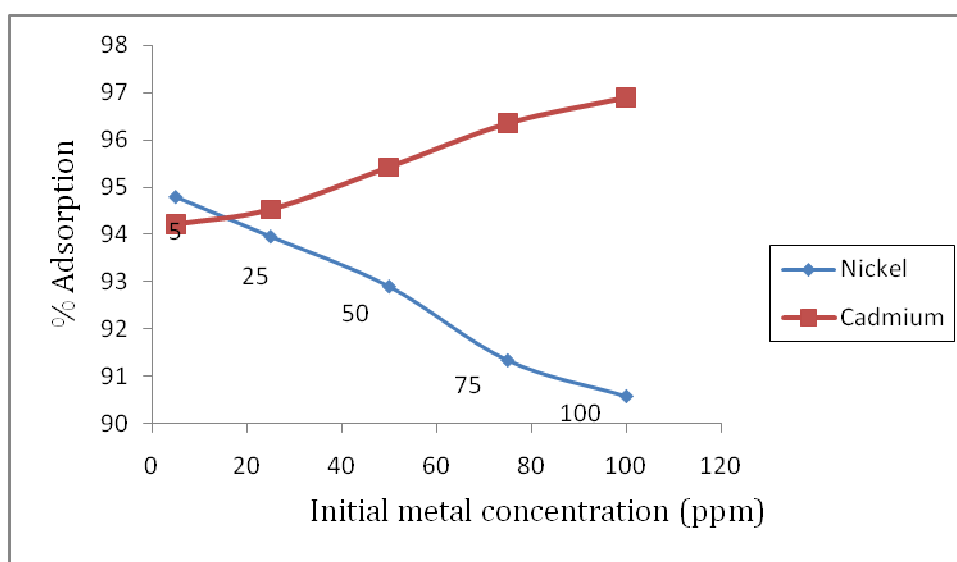


Figure 4.8: Effect of initial metal concentration on nickel and cadmium adsorption

Based on above figure, cadmium adsorption percentage increase with increase in initial cadmium concentration. At 5,25,50,75 and 100 ppm, the adsorptions were 94.2%, 94.52%, 95.42%, 96.35% and 96.9%, respectively. An increase in initial concentration of cadmium enhances the adsorption uptake of cadmium. This is due to the increase in the driving force of the concentration gradient produced by the increase in the initial cadmium concentration (Kumar, 2010). Different trend showed by nickel adsorption. The percentage of nickel adsorption decrease with increase in

initial ion concentration. At 5,25,50,75 and 100 ppm, the adsorptions were 94.8%, 93.96%, 92.9%, 91.33% and 90.57%, respectively. At low nickel ion concentration ratios, metal ion adsorption involves higher energy sites. As the nickel ion concentration increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in decreases in the adsorption efficiency (Bhattacharya et. al,2006). The same trend was achieved by Vijayakumaran *et. al* in their research on Adsorption of Nickel Ion by Low Cost Carbon-Kinetic, Thermodynamic and Equilibrium Studies. They stated that there was decrement in adsorption percentage, but the actual amount of nickel ion adsorbed per unit mass of carbon,  $Q_e$  was actually increased as in Figure 4.9 . Amount metal adsorbed per unit mass of adsorbent (mg/g),  $Q_e$  can be determined from equation below :

$$Q_e = (C_0 - C_e) V/m$$

$Q_e$  : amount metal adsorbed per unit mass of adsorbent (mg/g)

$C_0$  : initial metal concentration (mg/L)

$C_e$  : final metal concentration (mg/L)

$V$  : volume of solution (L)

$m$  : mass of adsorbent ( g)

Initial nickel concentration (mg/L)	$C_e$ (mg/L)	$Q_e$ (mg/g)	Initial nickel concentration (mg/L)	$C_e$ (mg/L)	$Q_e$ (mg/g)
5	0.26	0.395	5	0.29	0.3925
25	1.51	1.9575	25	1.37	1.96917
50	3.55	3.87083	50	2.29	3.975833
75	6.5	5.70833	75	2.74	6.021667
100	9.43	7.5475	100	3.1	8.075

Table 3.3 : Equilibrium parameters for the adsorption metal ion onto GCAC

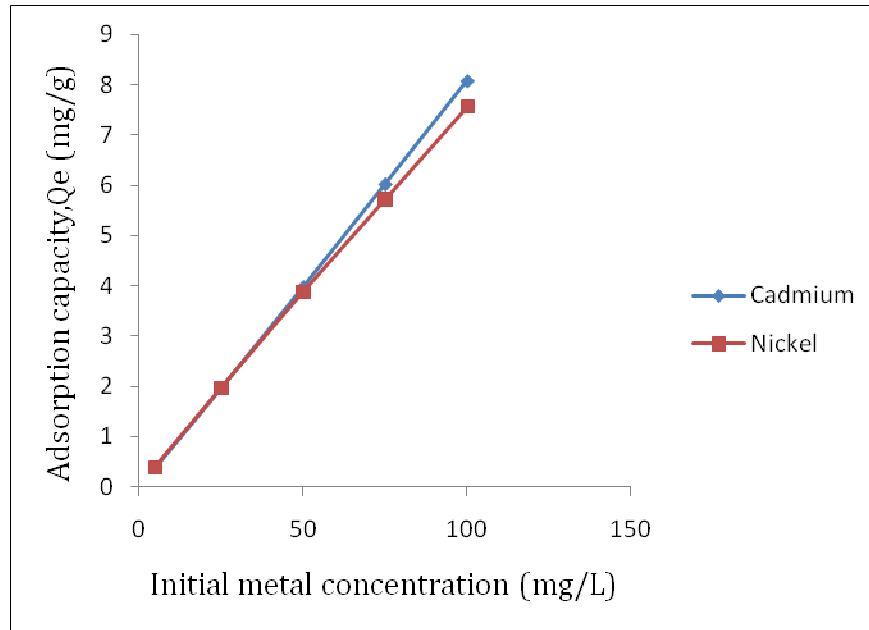


Figure 4.9 : Adsorption Capacity of Nickel and Cadmium

#### 4.6.1 Adsorption isotherm

Two types of isotherm were developed from the experimental data which are Freundlich and Langmuir isotherm. Freundlich and Langmuir isotherms assume that the adsorption is multilayer and monolayer, respectively. Freundlich isotherm equation is defined as follows :

$$Q_e = K_f C_e^{1/n}$$

where;

$K_f$  = multilayer sorption capacity

$C_e$  = final concentration of solution after adsorption (mg/L)

$1/n$  = Freundlich intensity parameter

$Q_e$  = amount metal adsorbed per unit mass of adsorbent (mg/g)

The constant can be determined by plotting  $\log Q_e$  versus  $\log C_e$  following below equation :

$$\log Q_e = \log K_f + (1/n) \log C_e$$

For the Langmuir isotherm, adsorption is described by :

$$C_e/Q_e = 1/x_m K + (1/x_m)C_e$$

Where;

$C_e$  = final concentration of solution after adsorption (mg/L)

$x_m$  = monolayer sorption capacity

$K$  = constant related to adsorption energy

$Q_e$  = amount metal adsorbed per unit mass of adsorbent (mg/g)

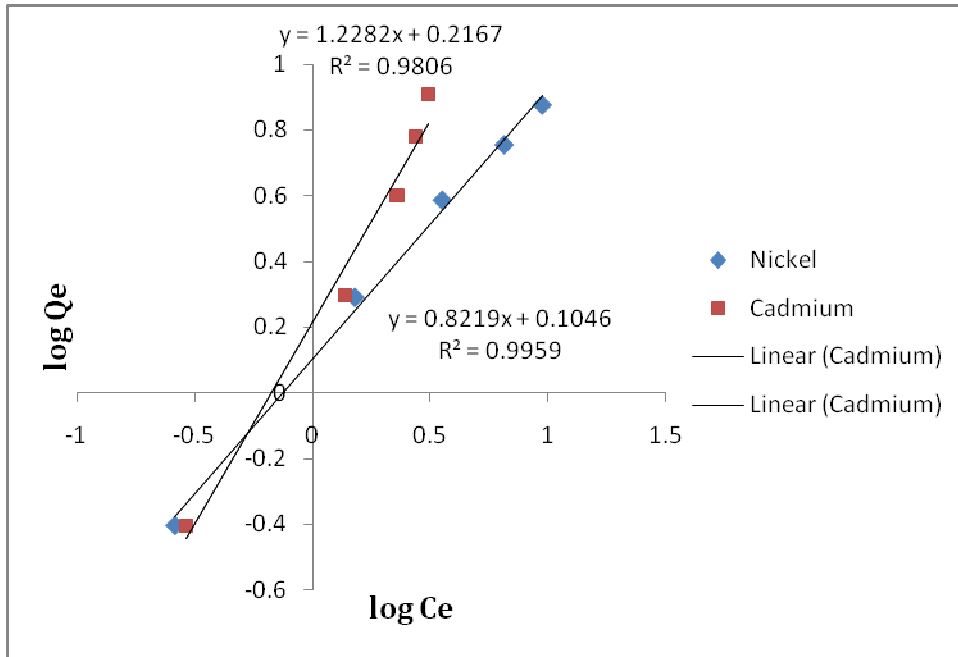


Figure 4.10 : Freundlich isotherm for nickel and cadmium adsorption

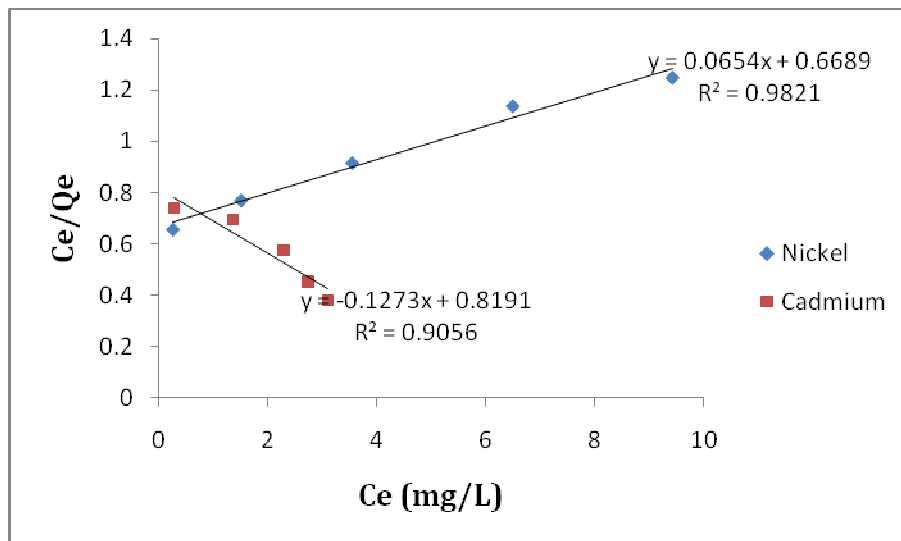


Figure 4.11: Langmuir isotherm for nickel and cadmium adsorption

The figure showed that Freundlich isotherm has R-squared value for nickel and cadmium was 0.995 and 0.980, respectively. For Langmuir isotherm, R-squared value for nickel and cadmium were 0.982 and 0.905, respectively. The higher R-squared value of Freundlich clearly proved that the GCAC adsorption data is well fitted to Freundlich isotherm compared to Langmuir. This means that the cadmium and nickel adsorption are multilayer adsorption on the GCAC surface.



## **CHAPTER 5**

### **CONCLUSION AND RECOMMENDATIONS**

#### **5.1 Conclusion**

In conclusion, Granulated Charcoal Activated Carbon (GCAC) has high potential as an adsorbent for removing nickel and cadmium ions from aqueous solutions. It was experimentally proved that GCAC able to adsorb nickel and cadmium up to range of 88 – 98.5% and 91.4 – 99.1 %, respectively. Adsorptions of both metal ions were dependent on agitation time, initial metal concentration and pH. Nickel adsorption was found optimum at 120 minutes with initial concentration of 5 ppm and pH 10 while for cadmium, its adsorption was optimum at 120 minutes with initial concentration of 100 ppm and pH 10. The equilibrium data fitted to both Freundlich and Langmuir isotherm but it is more well fitted to Freundlich as the R-squared value of Freundlich were higher than Langmuir's which were 0.995 and 0.98 for nickel and cadmium, respectively. This indicated that the cadmium and nickel adsorption are multilayer adsorption on the GCAC surface.

#### **5.2 Recommendation**

##### **5.2.1 Prolong agitation time and pH**

The agitation time could be prolonged to 3 or 4 hours and increase pH up to 14. The extension of parameters may be able to determine the point where maximum adsorption occurs.

##### **5.2.2 Use contaminated water or wastewater**

Contaminated water or wastewater could be used as heavy metal sample rather than using mixture of metal and deionized water.

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## APPENDIX I

Effect of agitation time and initial metal concentration on nickel adsorption

Initial concentration, (ppm)	Agitation time (min)	Final concentration. (ppm)	% Adsorption
5	30	0.37	92.6
	60	0.28	94.4
	90	0.27	94.6
	120	0.26	94.8
25	30	1.98	92.08
	60	1.56	93.76
	90	1.53	93.88
	120	1.51	93.96
50	30	4.39	91.22
	60	3.62	92.76
	90	3.59	92.82
	120	3.55	92.9
75	30	7.53	89.96
	60	6.52	91.31
	90	6.42	91.44
	120	6.5	91.33
100	30	10.25	89.75
	60	9.53	90.47
	90	9.45	90.55
	120	9.43	90.57

## APPENDIX II

Effect of pH on nickel adsorption

pH	Initial concentration (ppm)	Agitation time (min)	Final concentration (ppm)	% Adsorption
2	50	30	6	88.00
	50	60	5.71	88.58
	50	90	5.68	88.64
	50	120	5.8	88.40
4	50	30	4.91	90.18
	50	60	4.5	91.00
	50	90	4.33	91.34
	50	120	4.31	91.38
6	50	30	4.39	91.22
	50	60	4.2	91.60
	50	90	3.62	92.76
	50	120	3.5	93.00
8	50	30	3.5439	92.91
	50	60	3.2758	93.45
	50	90	3.2298	93.54
	50	120	3.1501	93.70
10	50	30	1.08	97.84
	50	60	1.0083	97.98
	50	90	0.7542	98.49
	50	120	0.7345	98.53

### APPENDIX III

Effect of agitation time and initial metal concentration on cadmium adsorption

Initial concentration (ppm)	Agitation time (min)	Final concentration (ppm)	% Adsorption
5	30	0.43	91.40
	60	0.42	91.60
	90	0.3	94.00
	120	0.29	94.20
25	30	1.87	92.52
	60	1.41	94.36
	90	1.39	94.44
	120	1.37	94.52
50	30	2.5	95.00
	60	2.31	95.38
	90	2.3	95.40
	120	2.29	95.42
75	30	2.97	96.04
	60	2.78	96.29
	90	2.85	96.20
	120	2.74	96.35
100	30	3.3	96.70
	60	3.1	96.90
	90	3.1	96.90
	120	3.1	96.90

## APPENDIX IV

### Effect of pH on cadmium adsorption

pH	Initial concentration (ppm)	Contact time (min)	Final concentration (ppm)	% Adsorption
2	50	30	3.64	92.72
	50	60	3.56	92.88
	50	90	3.54	92.92
	50	120	3.53	92.94
4	50	30	3.13	93.74
	50	60	2.87	94.26
	50	90	2.8634	94.2732
	50	120	2.8559	94.2882
6	50	30	2.86	94.28
	50	60	2.5304	94.9392
	50	90	2.5281	94.9438
	50	120	2.5279	94.9442
8	50	30	1.734	96.532
	50	60	0.9904	98.0192
	50	90	0.9765	98.047
	50	120	0.9621	98.0758
10	50	30	0.5672	98.8656
	50	60	0.4584	99.0832
	50	90	0.467	99.066
	50	120	0.443	99.114



