

**REMOVAL OF HEAVY METALS FROM INDUSTRIAL WASTEWATER USING
ACTIVATED CARBON**

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BORANG PENGESAHAN STATUS TESIS♦

**JUDUL : REMOVAL OF HEAVY METALS FROM INDUSTRIAL
WASTEWATER USING ACTIVATED CARBON**

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**REMOVAL OF HEAVY METALS FROM INDUSTRIAL WASTEWATER
USING ACTIVATED CARBON**

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**A thesis submitted in fulfilment of the requirements for the award of the degree
of Bachelor of Chemical Engineering**

**Faculty of Chemical & Natural Resources Engineering
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MAY 2010

I declare that this thesis entitled “removal of heavy metals from industrial wastewater using activated carbon” is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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*Special Dedication to my family members that always love me,
My friends, my fellow colleagues
And all faculty members*

For all your Care, Support and Believe in me

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ABSTRACT

The presence of heavy metals in wastewater is known to cause severe damage to aquatic life, beside the fact that these metals kill microorganism during biological treatment of wastewater with a consequent time delay of the treatment process. Chromium is one of the major heavy metals present in wastewater which has toxic effect and is a strong oxidizing agent capable of being absorbed through the skin. Palm oil mills in Malaysia produce about 4.3 million tones of shell and the significant problems in the palm fruit processing is managing the wastes generated during the process. The palm shell can be converted into useful products such as activated carbon. So, this method will reduce industrial wastewater problem and will bring benefits to society. Hence, this research aims to use activated carbon produced from palm shell to remove Chromium from industrial wastewater. Pyrolysis was applied for the preparation of activated carbon from palm shell using furnace at 600°C. The treatment of activated carbon was carried out by oxidizing it with sulphuric acid and coating with chitosan. Two adsorbents namely Palm Shell Activated Carbon (PSAC) and Palm Shell Activated Carbon coated with Chitosan (PSACC) were used to remove chromium from aqueous solution. The effects of pH of the solution, adsorbent dosage, agitation speed, and contact time on adsorption of chromium were studied. The experimental results proved that the chromium removal efficiency of PSACC was better compared PSAC. Freundlich and Langmuir isotherms were used to analyze the adsorption of chromium from aqueous solution. The results concluded that Freundlich isotherm captured the adsorption of Chromium better compared to Langmuir isotherm as the former have higher correlation regression coefficient.

ABSTRAK

Logam berat yang hadir di dalam air kumbahan diketahui menyebabkan beberapa kerosakan kepada hidupan akuatik, di samping fakta yg menyatakan bahawa logam-logam ini membunuh mikroorganisma semasa rawatan biologi terhadap air kumbahan dengan akibat penundaan masa proses rawatan itu. Chromium adalah salah satu major logam berat yang hadir di dalam air kumbahan yang mempunyai kesan toksik dan mampu menyerap melalui kulit kerana merupakan ejen pengoksidaan yang tinggi. Minyak kelapa sawit di Malaysia menghasilkan 4.3 juta tan metrik kulit sawit dan masalah utama di dalam proses buah sawit adalah mengendalikan sisa-sisa yang terhasil semasa proses itu. Kulit sawit boleh ditukar kepada hasil yang berguna seperti karbon aktif. Jadi, kaedah ini akan mengurangkan masalah industri air kumbahan dan akan membawa kebaikan kepada masyarakat. Dengan itu, kajian ini bertujuan untuk menggunakan karbon aktif yang terhasil daripada kulit sawit, untuk menyingkirkan Chromium daripada industri air kumbahan. Pyrolysis akan digunakan untuk penyediaan karbon aktif daripada kulit sawit menggunakan dapur leburan pada suhu 600°C. Rawatan karbon aktif dilaksanakan melalui pengoksidaannya dengan asid sulfurik dan selaput menggunakan chitosan. Dua bahan penyerap iaitu Karbon Aktif Kulit Sawit (PSAC) dan Karbon Aktif Kulit Sawit dibalut dengan Chitosan (PSACC) digunakan untuk menyingkirkan Chromium daripada larutan. Kesan-kesan pH larutan, dos bahan penyerap, kelajuan dan masa terhadap penyerapan Chromium akan dikaji. Keputusan eksperimen membuktikan bahawa efisien penyingkiran Chromium daripada PSACC adalah lebih baik berbanding PSAC. Isoterma Freundlich dan Langmuir digunakan untuk menganalisis penyerapan Chromium daripada larutan. Keputusan menyimpulkan bahawa isoterma Freundlich adalah lebih baik daripada isoterma Langmuir kerana mempunyai hubungkait pekali regresi yang tinggi.

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LIST OF SYMBOLS

PSAC	-	Palm Shell Activated Carbon
PSACC	-	Palm Shell Activated Carbon coated with Chitosan
°C	-	Degree Celsius
q_e	-	Amount of metal ions adsorbed
K_L	-	Langmuir equilibrium constant
K_F	-	Freundlich equilibrium constant
C_e	-	Solution phase metal ion concentration
AAS	-	Atomic Absorption Spectrometer
cm	-	Centimetre
mm	-	Millimeter
hr	-	Hour
min	-	Minute
g	-	Gram
mg	-	Milligram
L	-	Liter
ml	-	Milliliter
rpm	-	Revolution per minute
%	-	Percentage
E	-	Removal efficiency
C_0	-	Initial concentration
C_1	-	Equilibrium concentration

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Recently, heavy metal pollution around all factories has been pointed out with the expansion of the industries in developing countries (Morgan and Lee, 1997 and Brower *et al.*, 1997). Wastewater from the all factories is divided into two types, which are from manufacturing process and from rinsing process (Gotoda *et al.*, 1992; M.K.Denki *et al.*, 1986). In advanced countries, removal of heavy metals in wastewater is normally achieved by advanced technologies such as precipitation–filtration, ion exchange and membrane separation (Tohyama *et al.*, 1973). However, in developing countries, these treatments cannot be applied because of technical levels and insufficient funds. Therefore, it is desired that the simple and economical removal method which can utilize in developing countries are established. Although the treatment cost for precipitation–filtration method is comparatively cheap, the treatment procedure is complicated. On the other hand, adsorption method such as ion exchange and membrane separation is simple one for the removal of heavy metals. However, there is a limit in the generality in developing countries because chelating and ion-exchange resins are expensive. Therefore, it is worthwhile to develop the economical adsorbents to remove heavy metals which can be generally utilized in developing countries.

A heavy metal is a member of an ill-defined subset of elements that exhibit metallic properties, which would mainly include the transition metals, some

metalloids, lanthanides, and actinides. Many different definitions have been proposed, some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity (John H. Duffus, 2002). The term 'heavy metal' refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), lead (Pb), zinc (Zn), and copper (Cu). Heavy metals are natural components of the earth's crust. They cannot be destroyed. As trace elements, some heavy metals like copper, selenium and zinc are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning (Aremu, 2002).

A number of technologies have been developed over the years to remove heavy metals from industrial wastewater. The conventional chemical methods include precipitation, ion-exchange, electrochemical processes, ultra filtration, reverse osmosis and membrane technology (Abdel-Shafy *et al.*, 1996; Amuda *et al.*, 2006). A major disadvantage with precipitation is production of sludge. Ion exchange is considered a better alternative technique for remove heavy metals or such a purpose. However, it is not economically appealing because of high operational cost. Adsorption using commercial activated carbon can remove heavy metals from wastewater, such as Cd, Ni, Cr, Zn and Cu.

Activated carbon is one of the most important types of industrial carbon with very high porosity and surface area. It is prepared by carbonization and activation of a large number of raw materials of biological origin such as coconut shells, wood, peat, coal and fruit stones (Rodriguez and Linares, 1988; Rodriguez, 1997). In general, the raw materials to make activated carbon must accomplish a sort of requirements like high carbon content, low mineral content, easily activation, low degradation during storage, and, of course, low cost (Rodriguez, 1997). Agro-industrial by-products such as coconut shells, almond shells, hazelnut shells, cherry stones, eucalyptus, apricot stones, nuts, grape seeds, olive and peach stones, sugar cane bagasse and oil palm trunks are materials usually inexpensive and abundantly available for which the effective utilization has been desired (Guo and Lua, 2001; Hussein *et al.*, 1996; Hayashi *et al.*, 2002). Palm shells from palm oil processing mills are an agricultural solid waste in some tropical countries (Guo and Lua, 2001).

Palm shell is a good raw material for preparation and production of activated carbon (Nomanbhay *et al.*, 2005).

1.2 Problem Statement

Rapid industrialization has led to increased disposal of heavy metals into the environment. The tremendous increase in the use of the heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substances in the aquatic environment. The metals are special because of their persistency in the environment. At least 20 metals are classified as toxic, and half of these are emitted into the environment in quantities that pose risks to aquatic life (Kortenkamp *et al.*, 1996). Chromium is one of the major heavy metals present in wastewater which has toxic effect and is a strong oxidizing agent capable of being absorbed through the skin. The sources of chromium mostly from chemical industry, paint, metallurgy, leather, fertilizers, petroleum refining and coal burning (Mishra, 2008). Chromium has both beneficial and detrimental properties. Two stable oxidation states of chromium persist in the environment, Cr (III) and Cr (VI), which have contrasting toxicities, mobilities and bioavailabilities. Whereas Cr (III) is essential in human nutrition (especially in glucose metabolism), most of the hexavalent compounds are toxic, several can even cause lung cancer. While Cr (III) is relatively innocuous and immobile, Cr (VI) moves readily through soils and aquatic environments and is a strong oxidizing agent capable of being absorbed through the skin (Park and Jung, 2001). Palm oil mill is one of the most important agro-industry in the Malaysia. Palm oil mills in Malaysia produces about 4.3 million tones of shell and the significant problems in the palm fruit processing is managing the wastes generated during the process (Diego *et al.*, 2004). One possibility of managing the waste is to convert it into useful product such as activated carbon. This approach will reduce the problem of managing waste during palm fruit processing and also helpful in removing heavy metals from industrial wastewater.

1.3 Research Objective

The objectives of this study are as follows:

- a) To prepare activated carbon from palm shell using pyrolysis process
- b) To improve the adsorption capacity of palm shell activated carbon by coating with chitosan
- c) To determine the optimum conditions for removal of Chromium from industrial wastewater
- d) To find out suitable adsorption isotherm to capture the adsorption of Chromium using palm shell activated carbon

1.4 Scope of Research

The scopes of this study are as follows:

- a) Activated carbon, which is prepared from low cost palm shell has been utilized as the adsorbent for the removal of heavy metals from industrial wastewater.
- b) Chitosan is an excellent adsorbent and adsorption capacity of palm shell activated carbon can be improve by coating activated carbon with chitosan.
- c) To study the effect of pH, adsorbent dosage, agitation speed and contact time on removal of chromium from an aqueous solution.
- d) To study the adsorption phenomena using Freundlich and Langmuir adsorption isotherm.

1.5 Research Contribution (Significance of Study)

This research can help in minimizing the environmental impact and aid by removal of heavy metals from industrial wastewater. Whereas the present of heavy metals is strongly influence the human safety and health and of course environment factor. So the adsorbent such as activated carbon can be used to remove heavy metals

from industrial wastewater to make the better safety and health life with good environment.

The significant of study for this project are as follows:

a) Aquatic environment

When wastewater containing heavy metals was discharged from industry, will create water pollution to aquatic environment. The aquatic ecosystem will also damage. So, this project will protect aquatic environment by the removal of heavy metals from wastewater.

b) Convert palm shell into useful products

Palm oil mills in Malaysia produces about 4.3 million tones of shell and the significant problems in the palm fruit processing is managing the wastes generated during the process. This palm shell can be converted into useful products such as activated carbon. So, this approach will reduce the problem of managing waste during palm fruit processing and also helpful in removing heavy metals from industrial wastewater.

c) Health concern

Industrial wastewater containing many heavy metals and most of the metals are emitted into the environment in quantities that pose risks to human health. Some of heavy metals can give advantages to human body, but, at higher concentrations they can lead to poisoning. So, removal of heavy metals from industrial wastewater is necessary to make sure good health for human and society.

d) Industrial purposes

Some industries, such as power-generation plants can use treated wastewater. A lot of water is needed to cool power-generation equipment, and using wastewater for this purposes means that the facility won't have to use higher-quality water that is best used somewhere else.

1.6 Thesis Layout

This thesis has 5 chapters. Chapter 1 introduces a background of the study and also about the problem of heavy metals whereas become an environment issues and the effects to human health and also the way to solve that problem. It is also includes research objective, scope and significance of study. Chapter 2 is about literature review which includes topic extensively researched of heavy metals, adsorption process with use palm shell activated carbon, activated carbon treatment and using of chitosan and also adsorption isotherm. Literature research contains information relevant and directly related to research in this study. In Chapter 3, the methodology develops the steps needed to study about preparation of activated carbon and the steps of removal of heavy metals will be discussed. Chapter 4 will be discussing about the results obtained from the experiment. It includes preparation of palm shell activated carbon, preparation of chitosan, the factor influencing adsorption process, and study of adsorption isotherm. Lastly Chapter 5 will provide some concluding remarks of this research and also provide recommendations on how to improve the heavy metals removal from wastewater.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metals

Water pollution by heavy metal and dyes remains a serious environmental problem nowadays. According to Mishra (2008), water pollution occurs when too much of an undesirable or harmful substance flows into a body of water, exceeding the natural ability of that water body to remove the undesirable material or convert it to a harmless form.

Industrial wastewater, which contains raw materials, processed chemicals, final products, processed intermediates, processed by-product and impurities of the industry (Mishra, 2008), can be classified as one of the sources of water pollution. Table 2.1 enlists the source of eight most common heavy metals that contribute to their appearance in water ways.

Table 2.1: Source of Eight Most Common Heavy Metals (Mishra, 2008)

No.	Source	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
1.	Mining and ore processing	X	X			X	X		X
2.	Metallurgy	X	X	X	X	X	X	X	X
3.	Chemical Industry	X	X	X	X	X	X		X
4.	Alloys					X			
5.	Paint		X	X		X			X
6.	Glass	X				X	X		
7.	Pulp and paper mills			X	X	X	X	X	
8.	Leather	X		X			X		X
9.	Textiles	X	X		X	X	X	X	X
10.	Fertilizers	X	X	X	X	X	X	X	X
11.	Petroleum refining	X	X	X	X	X	X		X
12.	Coal burning	X	X	X	X	X	X	X	

2.2 Heavy Metals Removal

Various Chemical treatment methods have been developed for the removal and recovery of heavy metals from wastewaters. There are four major classes of chemical separation technologies: chemical precipitation, electrolytic recovery, adsorption/ ion exchange, and solvent extraction/ liquid membrane separation (Tohyama *et al.*, 1973). These major classes involves various methods include chemical treatment with lime, caustic oxidation and reduction, ion exchange, adsorption, reverse osmosis, solvent extraction, membrane filtration, electrochemical treatment and evaporative recovery. Chemical treatment methods for removal of heavy metals ions from waste are schematically illustrated in Figure 2.1. But most of these methods are often not economically viable especially when the effluents contain a large concentration of heavy metals (Bailey *et al.*, 1998). Most metal rich wastewater is treated by precipitation process. In this process, soluble metal ions are removed as insoluble metal hydroxide precipitates. But this process also has several disadvantages. The presence of aqueous organic ligands in wastewater can hinder metal hydroxide precipitation, which may result in residual metal concentrations that

may no longer meet the increasingly stringent effluent discharge standards. The results are also not satisfactory with complex metals. Further, the major disadvantage with these treatment techniques is the production of sludge. As a result, an aquatic problem is changed into solid waste problem (Lewinsky, 2006). Comparison of the major features, advantages and disadvantages of chemical processes technologies for removal of heavy metal ion from wastewater are provided in Table 2.2.

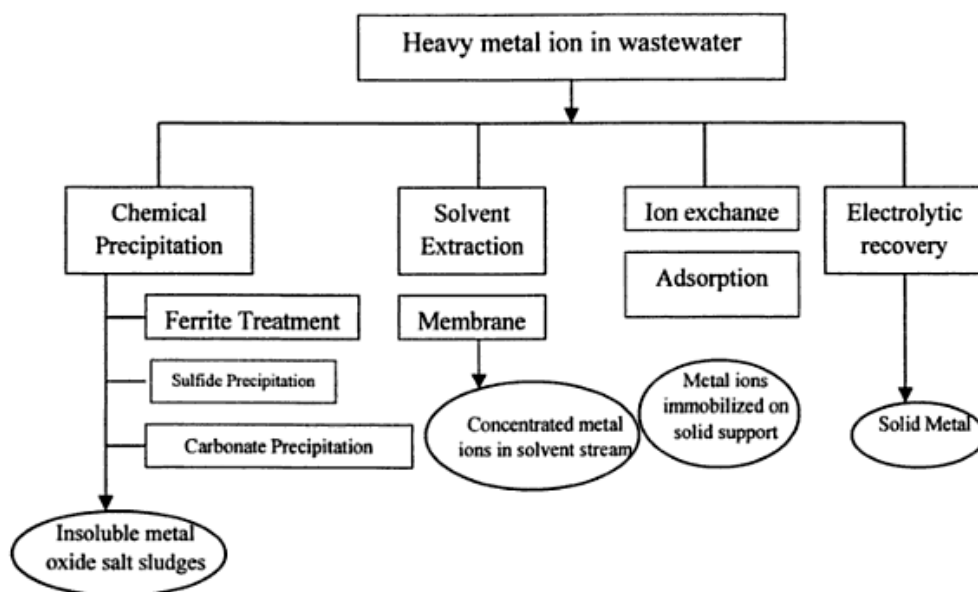


Figure 2.1: Available Chemical Treatment Methods for Hazardous Heavy Metals Ion Removal from Wastewater (Lewinsky, 2006)

Table 2.2: Comparison of Chemical Process Technologies for Heavy Metals Ion Removal

Process	Chemical/Energy Input	Major Advantages	Major Disadvantages	References
Chemical precipitation	Precipitant/flocculant, acid, base, mixing and fluid handling	Low metal concentration in the effluent are achieved	High chemical requirement, sludge disposal problem	Stum <i>et al.</i> , 1970
Electrolytic recovery	Electrical energy	Lesser chemical consumption, recovery of pure metal is the added economic value	Energy intensive, high capital cost, reduced efficiency at dilute concentrations	Lewinsky, 2006
Adsorption/ Ion exchange	Fluid handling unit/ regenerating solution	Highly effective for removing metal ions to a very low concentration	Chemical regeneration requirement, fouling and corrosion of plant. Disposal of exhausted adsorbent.	Ghosh, 2006
Solvent extraction	Stripping solvent, makeup extraction solvent; fluid handling	Selective heavy metal removal, continuous concentrated metal solution recovery	Capital costs, toxic solvent discharges	Lewinsky, 2006
Membrane	Extractant for liquid supported membrane; fluid handling	Selective heavy metal removal	Fouling and lesser durability of membranes	Lewinsky, 2006

2.2.1 Chemical Precipitation

Chemical precipitation is the most common technique for the removal of heavy metals from water and wastewaters. The most frequently used chemicals for precipitation of metals are lime, caustic and sodium carbonates. The precipitation method has been used for the removal of iron, copper, zinc, tin cadmium and nickel from the effluents of metal finishing industries (Stum *et al.*, 1970) and for removal of iron and aluminium in sewage water (Anon, 1978). In the process of lime precipitation of heavy metals, caustic is added usually to reach the pH of minimum solubility. This process has limitation where multiple metals present have a pH range of minimum solubility. The disadvantage of sulfide precipitation is that the sludge does not thicken well and sulphides are a potential odor and health hazard. Co-precipitation is another process where many metals are adsorbed on alum or iron flocs but it has disadvantage of generating large quantities of sludge. For conclusion, chemical precipitation produces a large amount of sludge.

2.2.2 Solvent Extraction

Liquid-liquid extraction (also frequently referred to as solvent extraction) of metals from solutions on a large scale has experienced a phenomenal growth in recent years due to the introduction of selective complexing agents. In addition to hydrometallurgical applications, solvent extraction has gained widespread usage for waste reprocessing and effluent treatment. Solvent extraction involves an organic and an aqueous phase. The aqueous solution containing metal or metals of interest is mixed intimately with the appropriate organic solvent and metal passes into the organic phase. In order to recover the extracted metal, the organic solvent is contacted with an aqueous solution whose composition is such that metal is stripped from the organic phase and is reextracted into stripping solution. The concentration of the metal in the strip liquor may be increased, often 10 to 100 times over that of the original feed solution. Once the metal of interest has been removed, the organic solvent is recycled either directly or after a fraction of it has been treated to remove impurities (Lewinsky, 2006).

2.2.3 Membrane Process

Reverse osmosis is pressure driven membrane process in which a feed stream under pressure is separated into a purified permeate stream and a concentrated stream by selective permeation of water through a semi permeable membrane. Reverse osmosis enjoys wide spread popularity in the treatment of numerous diverse wastewaters. For example in the metal finishing industry, it is used for the recovery of plating chemicals from rinse water as well as purification of mixed wastewater to allow its reuse. Reverse osmosis has also been successfully demonstrated for the removal of Cr, Pb, Fe, Ni, Cu, and Zn from vehicle wash rack water (Lewinsky, 2006).

Electro dialysis is accomplished by placing cation and anion selective membranes alternatively across the path of an electric current. When the current is applied, the electrically attracted cations will pass through the cation exchanging membranes in one direction. The result is that salinity decreases between one pair of membranes increases between the next pair etc. Water can then pass through several such membranes until the required salinity is achieved. Dialysis involves the separation of solids by making use of unequal diffusion through membranes. The rate of diffusion is related to the concentration gradient, across the membranes (Lewinsky, 2006). The most common problem of membrane process is fouling and lesser durability of membranes.

2.2.4 Ion Exchange

Ion exchange is a process in which ions on the surface of the solid are exchanged for ions of a similar charge in a solution with which the solid is in contact. Ion exchange can be used to remove undesirable ions from wastewater. Cations are exchanged for hydrogen or sodium and anions for hydroxide or chloride ions (Lewinsky, 2006).

2.2.5 Adsorption

Adsorption involves, in general, the accumulation (or depletion) of solute molecules at an interface (including gas-liquid interfaces, as in foam fractionation, and liquid-liquid interfaces, as in detergency). Adsorbent surfaces are often physically and/or chemically heterogeneous and bonding energies may vary widely from one site to another. Adsorption involves accumulation of substance at an interface, which can either be liquid-liquid, gas-liquid, gas-solid or liquid-solid. The material being adsorbed is termed the adsorbate and the adsorbing phase, the adsorbent (Lewinsky, 2006). Major disadvantages for adsorption process is high cost for adsorbent. But, the solution is by using low cost adsorbent such as palm shell activated carbon.

2.3 Adsorption Process

Adsorption is the accumulation of atoms or molecules on the surface of a material. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the adsorbent's surface. It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term *sorption* encompasses both processes, while desorption is the reverse process. Adsorption refers to the binding of molecules on the surface of solid material, i.e. an adsorption process involves the transfer of dissolved solutes from a liquid phase to the surface of an added solid phase which is also called adsorbent (Ghosh, 2006). The accumulation and concentration of pollutants from aqueous solutions by the use of biological materials, such as chitin, chitosan, yeasts, fungi or bacterial biomass, as adsorbent is termed biosorption (Crini, 2006).

Chemical adsorption results in the formation of a monomolecular layer of the adsorbate on the surface through forces of residual valence of the surface molecules. Physical adsorption results from molecular condensation in the capillaries of the solid. In discussing the fundamentals of adsorption it is useful to distinguish between physical adsorption, involving only relatively weak intermolecular forces, and

chemisorptions, which involves, essentially, the formation of a chemical bond between the sorbate molecule and the surface of the adsorbent (Lewinsky, 2006). The general features, which distinguish physical adsorption, chemisorptions have been encapsulated in Table 2.3.

Table 2.3: Distinction between physical adsorption and chemisorptions (Lewinsky, 2006)

Physical Adsorption	Chemical Adsorption
Low heat of adsorption (< 2 or 3 times latent heat of evaporation)	High heat of adsorption ($>$ or 3 times latent heat of evaporation)
Non-specific	Highly specific
Monolayer or multilayer. No dissociation of adsorbed species. Only significant at relatively low temperatures.	Monolayer only May involve dissociation. Possible over a wide range of temperature.
Rapid, non-activated, reversible	Activated, may be slow and irreversible
No electron transfers although polarization of sorbate may occur	Electron transfer leading to bond formation between sorbate and surface

2.4 Adsorbents

Adsorbents are used usually in the form of spherical pellets, rods, moldings, or monoliths with hydrodynamic diameters between 0.5 and 10 mm. They must have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high surface capacity for adsorption. The adsorbents must also have a distinct pore structure which enables fast transport of the gaseous vapours. Most industrial adsorbents fall into one of three classes:

- a) Oxygen-containing compounds – Are typically hydrophilic and polar, including materials such as silica gel and zeolites.

Silica gel is a chemically inert, nontoxic, polar and dimensionally stable (< 400 °C) amorphous form of SiO_2 . It is prepared by the reaction between sodium silicate and sulfuric acid, which is followed by a series of after-

treatment processes such as aging, pickling, etc. These after treatment methods results in various pore size distributions. Silica is used for drying of process air (e.g. oxygen, natural gas) and adsorption of heavy (polar) hydrocarbons from natural gas.

Zeolites are natural or synthetic crystalline aluminosilicates which have a repeating pore network and release water at high temperature. Zeolites are polar in nature. They are manufactured by hydrothermal synthesis of sodium aluminosilicate or another silica source in an autoclave followed by ion exchange with certain cations (Na^+ , Li^+ , Ca^{2+} , K^+ , NH_4^+). The ion exchange process is followed by drying of the crystals, which can be pelletized with a binder to form macroporous pellets. Zeolites are applied in drying of process air, CO_2 removal from natural gas, CO removal from reforming gas, air separation, catalytic cracking, and catalytic synthesis and reforming. Non-polar (siliceous) zeolites are synthesized from aluminum-free silica sources or by dealumination of aluminum-containing zeolites. The dealumination process is done by treating the zeolite with steam at elevated temperatures, typically greater than $500\text{ }^\circ\text{C}$ ($1000\text{ }^\circ\text{F}$). This high temperature heat treatment breaks the aluminum-oxygen bonds and the aluminum atom is expelled from the zeolite framework.

- b) Carbon-based compounds – Are typically hydrophobic and non-polar, including materials such as activated carbon and graphite.
- c) Polymer-based compounds - Are polar or non-polar functional groups in a porous polymer matrix.

Large number of adsorbents has been developed so far for the removal of inorganic. These include primarily activated carbon prepared from variety of materials of biological origin, industrial wastes, dead-biomass and organic wastes etc. Besides that several low cost adsorbents such as chitin, chitosan, clay, fly ash, peat, moss, zeolites, xanthates, seaweed/ algae/ alginate, lignin, bark/tannin rich material have also been explored for heavy metal containing wastewater (Lewinsky,

2006). Table 2.4 present some of the highest adsorption capacity reported for various low-cost adsorbents.

Table 2.4: Summary Table of Maximum Reported Adsorption Capacities (mg/g) (Lewinsky, 2006)

Sorbent	Source	Cd (II)	Cr (III)	Cr (VI)	Hg (II)	Pb (II)
Bark	Randell <i>et al.</i> 1974a; Teles de Vasconcelos and Gonzalez Beca 1993; Masri <i>et al.</i> , 1974 Randell <i>et al.</i> , 1974a ⁹¹⁻⁹⁴	32	19.45		400	182
CPEI cotton	Roberst and Rowland 1973 ⁹⁵				1000	
Chitin	Masri <i>et al.</i> 1974 (Cd, Cr, Hg, Pb) ⁹⁶	558	92		100	796
Chitosan	Pradas <i>et al.</i> 1994; Cadena <i>et al.</i> 1990 ^{97, 98}	16.50		57	1123	58
Clay	Matis and Zouboulis, 1994; Niu <i>et al.</i> 1993 ^{99,100}	28				116
Dead biomass	Sharma and Foster, 1994 ¹⁰¹			43.0		
Leaf mould	Masri <i>et al.</i> 1974; Srivastava <i>et al.</i> 1994 ^{96,102}				150	1587
Lignin	Masri and Friedman, 1974(Cd, Cr, Hg and Pb) ⁹⁶	87	17		632	1587
Modified wool	Low and Lee, 1991 ¹⁰²	46.65				
Moss	Tummavuori and Aho, 1980a; Kertman <i>et al.</i> 1993 ^{103,104}	5.058	76	43.9	16.2	135
Peat	Tummavuori and Aho, 1980b; Kertman <i>et al.</i> 1993 ^{103,104}					
Sawdust	Dikshit, 1989 ¹⁰⁵			16.05		230
Seaweed	Holan <i>et al.</i> 1993; Leusch <i>et al.</i> 1995 ^{106,107}	215				344
Xanthate	Bricka and Hill 1989; Flynn <i>et al.</i> 1980 ^{108,109}	33.27	19.67		1.149	18
Coir pith carbon	Kadirvelu and Namasivayam 2000, Kadirvelu <i>et al.</i> ¹¹⁰	94.0			154.0	264.0
Fly ash	Apak <i>et al.</i> 1998 ¹¹¹	198			.073	444.0
Red mud	Suemitsu <i>et al.</i> ¹¹²	67.0			7.1	165.0
Peanut hull carbon	Periasamy, 1993 ¹¹³	89.0			220.0	210.0
Furnace Sludge	Lopez-Delgado <i>et al.</i> , 1998 ¹¹⁴	7.4				68.0

2.5 Activated Carbon

Activated carbon, also called activated charcoal or activated coal, is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions (CPL Caron Link, 2008). The word *activated* in the name is sometimes substituted by *active*.

Activated carbon has the strongest physical adsorption forces of the highest volume of adsorbing porosity of any material known to mankind. It is a black, solid substance resembling granular or powdered charcoal and extremely porous with a very large surface area. Its surface area can reach up to more than 1000 m²/g. In other words, five grams of activated carbon can have the surface area of football field. Substances with high carbon content such coal, wood, and coconut shell can be used in the production of activated carbon. The raw material has a very large influence on the characteristics and performance of activated carbon. Activation refers to the development of the adsorption properties of carbon. Raw materials such as coal and charcoal do have some adsorption capacity, but this is greatly enhanced by activation process (Wan Nik *et al.*, 2006)

There are three main forms of activated carbon:

a) Granular Activated Carbon (GAC)

Irregular shaped particles sizes ranging from 0.2 to 5mm. This type of activated carbon is used in both liquid and gas phase applications.

b) Powder Activated Carbon (PAC)

Pulverized carbon with a size predominantly less than 0.18 mm (US mess 80). These are mainly used in liquid phase applications and for flue gas treatment.

c) Pellet Activated Carbon

Extruded and cylindrical shaped with diameters from 0.8 to 5mm. They are mainly used for gas phase applications because of their low pressure drop, high mechanical strength and low dust content.

Activated carbon consists mainly of carbon (87 to 97%) and other elements such as hydrogen, oxygen, sulfur and nitrogen. Various compounds are also present either originating from the material or generated during its preparation. Activated carbon also can absorb various substances both from gas and liquid phases. This ability justifies it as an adsorbent (Halena *et al.*, 1991)

In general, characteristics of activated carbon are controlled by the manufacturing process. Depending on the nature of the raw materials, the nature of activating agent and the condition of the activation process, the properties of activated carbon can be varied. The surface of activated carbon can contain protonated (C-OH₂⁺), neutral (COH) or ionized (CO⁻) groups. Activated carbon with protonated surfaces are also known as H-type carbons while activated carbons with ionized surfaces are known as L-type carbons (Huang *et al.*, 1977).

Certain contaminants accumulated on the surface of the activated carbon. This is called adsorption. The two main reasons why chemicals adsorb onto activated carbon are:

- a) a “dislike” of the water
- b) Attraction to the activated carbon.

Adsorption of most contaminants results from both reasons. There are many organic compounds, such as chlorinated and non chlorinated solvents, gasoline, pesticides and trihalomethanes. Activated carbon is also effective for removal of some of chlorine and moderately effective for removal of some heavy metals (Huang *et al.*, 1977)

Figure 2.2 show the schematically porous structure of activated carbon. Activated carbons are non-hazardous, processed, carbonaceous products, having a porous structure and a large internal surface area. These materials can adsorb a wide variety of substances. All activated carbons are characterized by their ramified pore system. Activated carbon is used as an inert porous carrier material for distributing chemicals on the large internal surface, thus making them accessible to reactants (K.D Henning *et al.*, 1987).

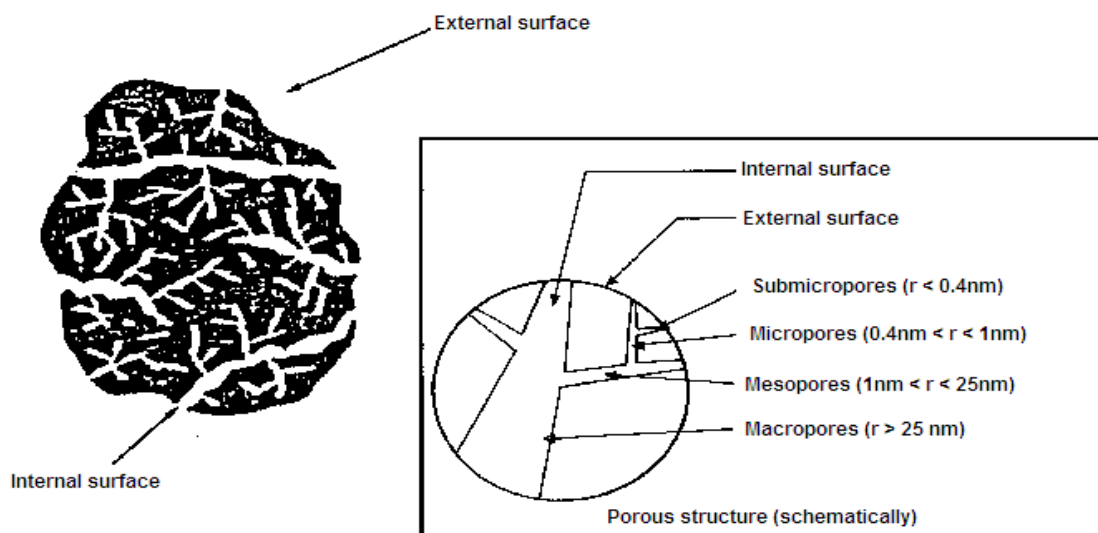


Figure 2.2: Schematic activated carbon model (K.D Henning *et al.*, 1987).

2.6 Palm shell Activated Carbon

Malaysia is having a lot of Palm Oil industries. Oil Palm shell is a good raw material for preparation and production of activated carbon. Palm shell (also known as *endocarp*) is a cheap and abundant agricultural by-product in tropical countries like Malaysia and Indonesia. Palm shell has been successfully converted into a well-developed activated carbon by thermal activation (physical activation) and chemical activation using with carbon dioxide (CO_2) and H_2PO_3 . Oil palm shell is a suitable raw material for making high quality activated carbon because of their inherent high densities and carbon contents, especially after pyrolysis (Guo and Lua, 1998, 2000 and 2002). In Malaysia, oil palm is the most important commercial crop. The explosive expansion of oil palm plantation has generated enormous amounts of vegetable waste. It was reported that Malaysia currently produces about 30 million tonnes annually of oil palm biomass, including trunks, fronds, fruit waste and empty fruit bunches. Of these, about two million tonnes of fruit shell (or endocarp) is generated annually (Chan, 1999). Preliminary studies have shown that it is feasible to prepare chars with sufficient densities and high porosity from oil palm fruit waste. The exchange/sorption properties of palm oil shell are due to the presence of some functional groups, such as carboxylic, hydroxyl, and lactone, which have a high affinity for metal ions (Tan *et al.*, 1993).

In recent years, development of surface modified activated carbon has generated a diversity of activated carbon with far superior adsorption capacity. The use of palm oil shell with surface modification to improve its metal removal performance would add its economic value, help reduce the cost of waste disposal, and most importantly, provide a potentially inexpensive alternative to existing commercial activated carbon. Oil palm shell has been successfully used to produce high quality activated carbon because of their inherent high densities and carbon content (Normah *et al.*, 1995; Hussein *et al.*, 1996). Table 2.5 gives the solid and apparent densities and porosities of both the shell and its char.

Table 2.5: Characteristics of oil palm shell and derived char (Guo and Lua, 2000).

	Solid density r_s (g/cm^3)	Apparent density r_a (g/cm^3)	Porosity $e[r_s - r_a] / r_s \times$ 100%
Oil palm shell	1.53	1.47	3.9
Shell char	1.62	1.31	19.1

2.7 Activated Carbon Treatment Methods

Activated carbon has been oxidized by treatment with various acidic or basic oxidizing agents. These treatments produced high degrees of oxidation and high concentrations of acidic oxides which resulted in reduced adsorption of aromatic compounds such as phenols (Coughlin *et al.*, *Envir. Sci. and Technol.* 2, 291, 1968). The oxidative treatment of PSAC with sulphuric acid will introduce more acidic C=O groups on the surface of PSAC (Mostafa, 1997; Toles *et al.*, 1999). This enhanced the electrostatic interaction between chitosan and the more negatively charged PSACC and this prevents any tendency of chitosan to agglomerate. This helped to increase the availability of active binding sites on the chitosan for adsorption of Cr VI at low pH conditions. It has also been suggested that formation of more acidic surface oxides on the carbon surface enhances its hydrophilic character and hence improve the hydrodynamic flow (Olin *et al.*, 1996).

2.8 Chitosan

Among the many other low cost absorbents identified (Olin *et al.*, 1996; Bailey *et al.*, 1999, Bailey *et al.*, 1997) chitosan has the highest sorption capacity for several metal ions (Deshpande, 1986). Chitin (2-acetamido-2-deoxy- β -D-glucose-(N-acetylglucan)) is the main structural component of molluscs, insects, crustaceans, fungi, algae and marine invertebrates like crabs and shrimps (Deshpande, 1986; Chen and Chang, 1994; Ilyina *et al.*, 1995). Worldwide, the solid waste from processing of shellfish, crabs, shrimps and krill constitutes large amount of chitinaceous waste. Chitosan (2-acetamido-2-deoxy- β -D-glucose-(Nacetylglucosamine)) is a partially deacetylated polymer of chitin and is usually prepared from chitin by deacetylation with a strong alkaline solution as shown in Figure 2.3.

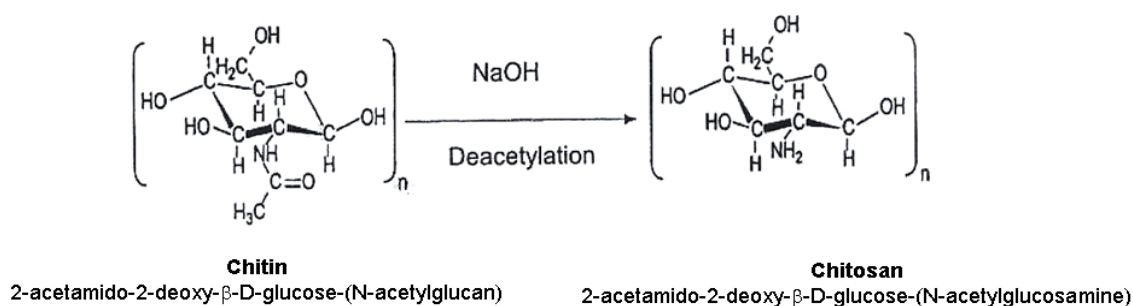


Figure 2.3: Conversion of chitin to chitosan by deacetylation

Chitosan chelates five to six times greater amounts of metals than chitin. This is attributed to the free amino groups exposed in chitosan because of deacetylation of chitin (Yang and Zall, 1984). The biosorbent material, chitosan, is slightly soluble at low pHs and poses problems for developing commercial applications. It is also soft and has a tendency to agglomerate or form a gel in aqueous solutions. In addition, the active binding sites of chitosan are not readily available for sorption. Transport of the metal contaminants to the binding sites plays a very important role in process design. Therefore, it is necessary to provide physical support and increase the accessibility of the metal binding sites for process applications. In the present investigation an attempt was made to overcome these mass transfer limitations by synthesizing a biosorbent by coating chitosan on the surface of palm oil shell charcoal and evaluating its equilibrium adsorption properties. The combination of the useful

properties of oil palm shell char and that of natural chitosan, could introduce a composite matrix with many application and superior adsorption capabilities.

2.9 Adsorption Isotherm

To examine the relationship between sorbed (q_e) and aqueous concentration C_e at equilibrium, sorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are most widely used.

2.9.1 Langmuir Model

The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. To get the equilibrium data, initial chromium concentration were varied while the adsorbent mass in each sample was kept constant. 3 hrs of equilibrium periods for sorption experiments were used to ensure equilibrium conditions. The Langmuir model takes the form:

$$q_e = \frac{K_L C_e}{1 + \alpha_L C_e}$$

where q_e (mg/g) is the amount of metal ions adsorbed onto the unit mass of the adsorbent to form a complete monolayer on the surface. K_L is the Langmuir equilibrium constant which is related to the affinity of binding sites; C_e the solution phase metal ion concentration, and α_L is the Langmuir constant (Aksu, 2001). The constants K_L and α_L are the characteristics of the Langmuir equation and can be determined from a linerized form of the Langmuir equation, represented

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{\alpha_L}{K_L} C_e$$

Therefore, a plot of C_e / q_e versus C_e , gives a straight line of slope α_L / K_L and intercept $1/K_L$. The constant K_L is the Langmuir equilibrium constant and the ratio α_L / K_L gives the theoretical monolayer saturation capacity.

2.9.2 Freundlich Model

On the other hand, the Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. The equation is commonly represented by

$$q_e = a C_e^b$$

where a and b are the Freundlich constants characteristics of the system, indicating the adsorption capacity and the adsorption intensity, respectively. To simplify the derivation of a and b , above equation can be linearized as

$$\ln q_e = b \ln C_e + \ln a$$

Therefore, a plot of $\ln q_e$ versus $\ln C_e$ enables the constant a and exponent b to be determined.

The Langmuir and Freundlich equations were used to describe the data derived from the adsorption of Cr by each adsorbent over the entire concentration range studied. The plot of C_e / q_e versus C_e showed that the experimental data reasonably well fitted the linearized equation of the Langmuir isotherm over the whole Cr concentration range studied. Linear plots of $\ln q_e$ versus $\ln C_e$ showed that the Freundlich isotherm was also representative for the Cr adsorption by all types of adsorbent tested.

CHAPTER 3

METHODOLOGY

Research methodology is a set of procedures or methods used to conduct research. This chapter describes the research methods used to study the simultaneous removal of chromium from an aqueous solution using two types of adsorbent which is Palm Shell Activated Carbon (PSAC) and Palm Shell Activated Carbon coated with Chitosan (PSACC).

3.1 Overall Methodology

Figure 3.1 shows overall methodology chart of this research. It starts from literature review followed by preparation of activated carbon from palm shell. Then the treatment of activated carbon was carried out by oxidising with sulphuric acid followed by surface coating with chitosan. Then the procedures for preparation of samples to study the effect of various parameters on adsorption of chromium were discussed. Finally the experimental procedures to study the adsorption isotherms were explained.

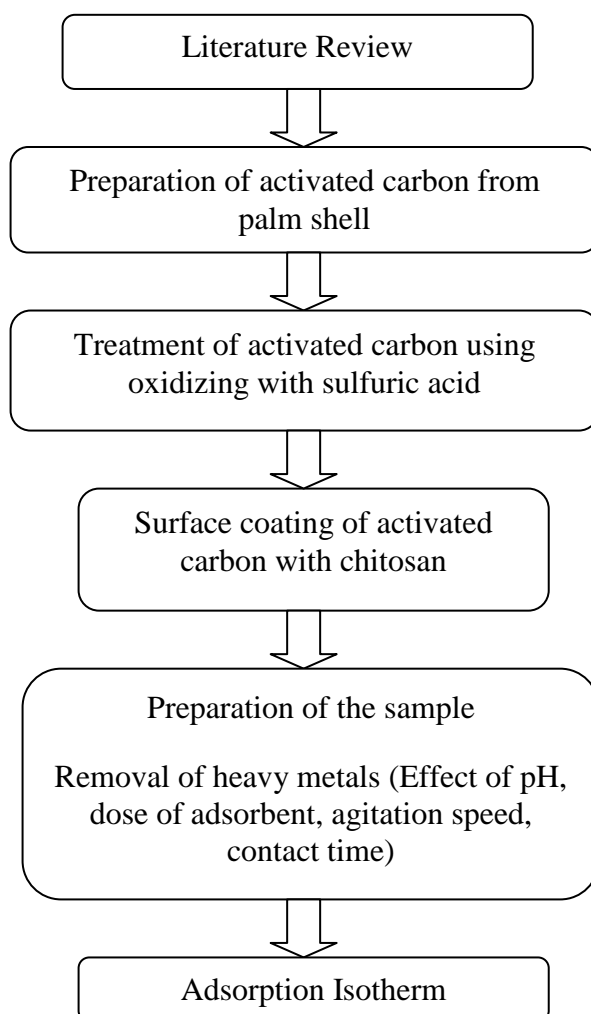


Figure 3.1: Flowchart of overall methodology

3.2 Materials

All the materials using in this research including oil palm shell, gas nitrogen, chitosan, oxalic acid, deionized water, sulphuric acid (H_2SO_4), Sodium bicarbonate ($NaHCO_3$), hydrochloric acid (HCL), sodium hydroxide (NaOH), potassium dichromate ($K_2Cr_2O_7$). AAS Standard solution, 1000 mg/L chromium were purchased from Merck (M) Sdn Bhd.

3.3 Experimental work

This section deals about the experimental procedure for the preparation of palm shell activated carbon, preparation of chitosan gel and oxidizing activated carbon using sulphuric acid. Then, the method was followed by surface coating of activated carbon with chitosan. Lastly, preparation of the sample using different types of parameter such as pH of solution, adsorbent dosage, agitation speed and contact time was studied. Then, run the sample using AAS.

3.3.1 Activated carbon preparation from oil palm shell

Oil palm shell was obtained from Kilang Sawit Lepar Hilir, Pahang, Malaysia. Oil palm shell is a suitable raw material for making high quality activated carbon because of their inherent high densities and carbon contents, especially after pyrolysis (Gua and Lua, 2000). As received oil palm shell was first dried at $110^\circ C$ for 24 hrs to reduce the moisture content. The dried shell was cut, ground and sieved. Size fractions of 2.0-2.8 mm were used. Pyrolysis was carried out in a horizontal controlled atmosphere furnace (Carbolite, CTE 12/75). About 15 g of the sample was placed in an alumina boat, and pushed into the hot zone of the furnace. During pyrolysis, nitrogen at a flow rate of $150\text{ cm}^3/\text{min}$ was used as purge gas. The furnace temperature was increased at a rate of $10^\circ C/\text{min}$ from room temperature to $600^\circ C$ and was held at this temperature for 2 hrs. The weight lost was obtained from the weight before and after pyrolysis. The pyrolysed sample was crushed into powder form.

3.3.2 Preparation of chitosan gel

About 50 g of chitosan was slowly added to 1000 ml of 10 wt% oxalic acid with constant stirring. The mixture was heated to 40-50°C to facilitate mixing. At room temperature, the chitosan-oxalic acid mixture formed a whitish viscous gel.

3.3.3 Oxidizing activated carbon with sulfuric acid

Activated carbon was washed with deionized water until any leachable impurities due to free acid and adherent powder were removed. The samples were then treated with 2% H₂SO₄ (v/v) in an incubator at 110°C for 24 hrs and soaked with deionized water until the solution pH was stable. Then, the adsorbent was soaked in 2% NaHCO₃ (w/v) till any residual acid left was removed. Finally, the samples (hereafter called acid treated oil palm shell char -PSAC) were dried overnight in an oven at 110°C, cooled at room temperature, and stored in a desiccator until use (Kadirvelu et al. 2001).

3.3.4 Surface coating of AC with chitosan

About 500 ml, of the chitosan gel was diluted with water (~500 ml) and heated to 40-50°C. About 500 g of the PSAC (from section 3.4.3 above) was slowly added to the diluted gel and mechanically agitated using a rotary shaker at 150 rpm for 24 hrs. The gel coated PSAC was then washed with deionized water and dried. The process was repeated for three times to form a thick coating of chitosan on the PSAC surface. The amount of chitosan coated was determined to be about 26% by weight. The chitosan coated PSAC (now called Palm Shell Activated Carbon coated with Chitosan, PSACC) were removed and neutralized by putting them in 0.5% NaOH solution for 3 hrs. The PSACC were then extensively rinsed with deionized water and dried (Babel and Kurniawan, 2004).

3.3.5 Preparation of the samples

Batch equilibrium experiments were carried out using PSAC and PSACC as adsorbents. Potassium dichromate ($K_2Cr_2O_7$) (Fluka, Switzerland) was used as the source of Cr (VI) in the synthetic wastewater. The Cr stock solution (500 mg/l) was prepared by dissolving 0.707 g of $K_2Cr_2O_7$ in 500 ml of deionized water. A series of flasks containing chromium solutions of varying concentrations from 5 to 40 mg/l prepared from the stock solution. Adjustment of pH was carried out using 0.1M NaOH and 0.1M HCL. Agitation of the system under investigation was carried out on a rotary shaker (Daiki Science Co. Ltd. South Korea). To maximize chromium removal by the adsorbent, batch experiments were conducted at ambient temperature using the optimum conditions of all pertinent factors, such as dose, pH, agitation speed, contact time and initial concentration (Chakravarty *et al.* 2002). Subsequent adsorption experiments were carried out with only optimized parameters. To ensure the accuracy, reliability, and reproducibility of the collected data, all the batch experiments were carried out in duplicate and the mean values of two data sets are presented. When the relative error exceeded the relative standard deviation by more than 1.0%, the data were disregarded and a third experiment was conducted until the relative error fell within an acceptable range. The concentration of the sample measured using AAS.

Figure 4.1 show the process using AAS. The reading was in concentration (mg/L). Before insert the sample into the tube, standard solution should be prepared. The standard solutions that be prepared were 2mg/L, 4mg/L, 6mg/L, 8mg/L, 10mg/L.

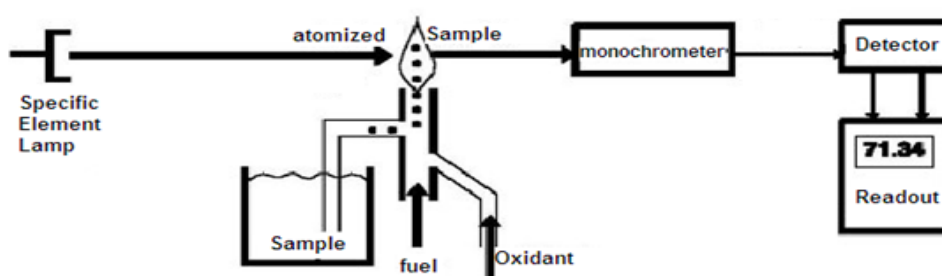


Figure 3.2: Flow Chart for Atomic Absorption Spectrometer

3.3.5.1 Effect of pH

pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the of the adsorbate during reaction. To examine the effect of pH on the chromium removal efficiency, the pH was varied from 1.0 to 8.0.

The constant parameter that be controlled was initial chromium concentration, agitation speed, contact time, amount of adsorbent dosage and temperature. Initial chromium concentration was 20mg/L, agitation speed and contact time was constant at 200 rpm and 3 hours. Amount of adsorbent for PSAC was 0.08g and 0.13g for PSACC. The sample of 50mL solution was prepared at 25°C. The pH was controlled using hydrochloric acid (HCl) and sodium hydroxide (NaOH).

3.3.5.2 Effect of Adsorbent Dosage

The dependence of chromium sorption on dose was studied by varying the amount of adsorbents from 0.02 to 0.16 g, while keeping other parameters (pH, agitation speed, and contact time) constant.

Initial chromium concentration, agitation speed, contact time, pH of solution, and temperature were the parameter that should be controlled to be constant. Initial chromium concentration was 20mg/L, agitation speed and contact time was controlled at 200 rpm and 3 hours. pH of solution was maintained at 4 using HCL and NaOH. Temperature was maintained at 25°C. The sample was prepared in 50 mL chromium solution.

3.3.5.3 Effect of Agitation Speed

The effect of agitation speed on removal efficiency of chromium was studied by varying the speed of agitation from 100 to 400 rpm, while keeping the optimum dose of adsorbents and optimum pH as constant.

The constant parameter that be controlled was initial chromium concentration, contact time, pH of solution, amount of adsorbent dosage and temperature. Initial chromium concentration was 20mg/L, contact time was constant at 3 hours. pH was controlled at 4 using HCL and NaOH. Amount of adsorbent for PSAC was 0.08g and 0.13g for PSACC. The sample was prepared in 50mL chromium solution. Temperature was maintained at 25°C.

3.3.5.4 Effect of Contact Time

Initial chromium concentration, pH of solution, amount of adsorbents, agitation speed and temperature were the parameter that should be controlled to be constant. Initial chromium concentration was 20mg/L. pH of solution was maintained at 4 using HCL and NaOH. Amount of adsorbent for PSAC was 0.08g and adsorbent for PSACC was 0.13g. The sample was prepared in 50 mL chromium solution. Agitation speed was controlled at 200 rpm and temperature was maintained at 25°C.

CHAPTER 4

RESULT AND DISCUSSION

For result and discussion, the factors that influence adsorption process will be studied. By using pH, dose of adsorbent, agitation speed and contact time as parameter, the optimum value will be determined for removal efficiency and chromium sorbed. In this chapter, discussion also based on production of activated carbon and the result which is the effect of parameters to adsorption process. Lastly, run the experiment using Atomic Absorption Spectrometer (AAS) with different parameter. The adsorption isotherm also discussed in this chapter which is using Freundlich and Langmuir model. It also was including effect of initial concentration. All of this will be discuss in result and discussion.

4.1 Palm Shell Activated Carbon

Oil palm shell has been successfully used to produce high quality activated carbon because of their inherent high densities and carbon content (Normah *et al.* 1995; Hussein *et al.* 1996; Guo and Lua, 2000). In this work, activated carbon from palm shell was prepared according to the method described at Chapter 3. Pyrolysis occurs during preparation of palm shell activated carbon. Nitrogen will be applied during pyrolysis to remove air inside the furnace. Preparation of palm shell was under vacuum. The weight lost will be calculated by taking the weight before and after pyrolysis. The result was shown in the Table 4.1. From the result, the weight will decrease after pyrolysis. The resulting kinetic parameters can be used to predict volatilization rates of palm shell as a function of temperature in a vacuum.

Table 4.1: Weight Loss during Pyrolysis

Palm Shell Char	Before Pyrolysis (g)	After Pyrolysis(g)	Weight Loss(g)
1	15	0.54	14.46
2	15	0.59	14.41
3	15	0.47	14.53

4.2 Preparation of Surface Coating Activated Carbon with Chitosan

The practical problems of chitosan solubility at low pH aqueous systems, gel forming behaviour and mass transfer limitations were overcome by coating it on other adsorbents like alumina, charcoal or interacting it with other adsorbents like alginate to form a rigid matrix structure of better mechanical strength (Babel and Kurniawan, 2004; Gotoh *et al.* 2004). In this study these problems were overcome by coating chitosan on palm shell activated carbon and the coating process yielded a stable granular composite adsorbent that was stable under acidic conditions. The cationic nature of chitosan and the anionic nature of oil palm shell charcoal yielded stable, granular composite matrix due to interaction between the two oppositely charged materials. Chitosan binds with both anionic and cationic species. Chromium (VI) and some other metals such as arsenic, depending on the pH, are known to exist as anions. Chromium (VI) forms dichromate anion at pH around 4. The amine groups of chitosan are largely responsible for the absorption of Cr (VI) ions from the solution (Fu *et al.* 1997; Dambies *et al.* 2001). At low pH, the amine group on chitosan is protonated. This leads to the interaction between NH_3^+ functional groups in chitosan and $\text{Cr}_2\text{O}_7^{2-}$ and the interaction is chiefly electrostatic attraction in nature (Fu *et al.* 1997).

4.3 Factor influencing the adsorption of Chromium ions

The influence of several operational parameters such as initial pH, dose of adsorbent, agitation speed, and contact time was investigated. The result were expressed as the removal efficiency (E) of the adsorbent on chromium, which was defined as

$$E (\%) = [(C_0 - C_1) / C_0] \times 100, \text{ where}$$

C_0 and C_1 are the initial and equilibrium concentration of chromium solution (mg/l), respectively.

The results also were expressed as the amount of chromium adsorbs (q). The heavy metals adsorbed (q) was defined using:

$$q (\text{mg/g}) = (C_0 - C_1)V/W$$

V is the volume of solution prepared which is 50ml, and W is the weight of adsorbent which is 0.13g for palm shell activated carbon (PSAC) and 0.08g for palm shell activated carbon coated with chitosan (PSACC).

The Cr (VI) ion concentration was determined by using Atomic Absorption Spectrometer (AAS).

4.3.1 Effect of pH

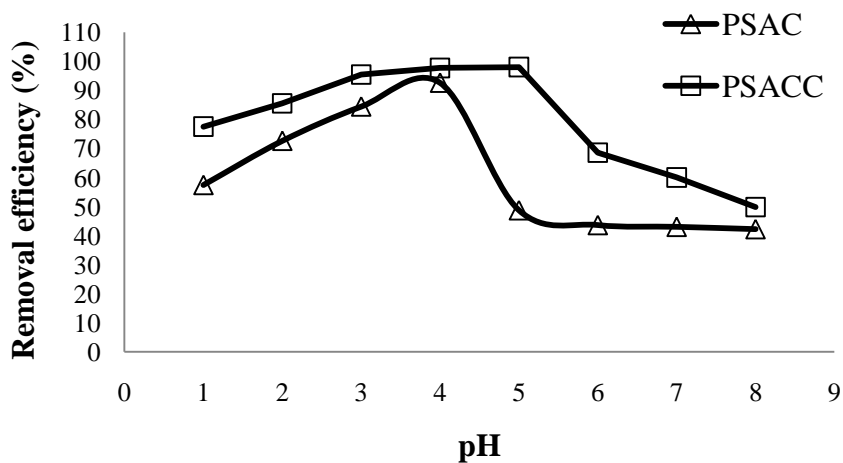


Figure 4.1: Effect of pH on the adsorption of Chromium ions on PSAC and PSACC

As shown in Figure 4.1 the uptake of free ionic chromium depends on pH, where optimal metal removal efficiency occurs at pH 5 for PSACC and then declining at higher pH. Removal efficiency for PSACC increased from 77% to 98% over pH range from 1.0 to 5.0. Another adsorbents which is palm shell activated carbon showed similar trends but with much lower removal efficiency and slight different optimum pH value. It can be concluded that oxidization of oil palm shell charcoal with sulphuric acid yielded acidic surface since pH values of point of zero charge for these materials are at a lower pH range compared to the value reported for most chemically untreated commercial activated carbon (Menendez et al. 1996). The surface acidity was due to the introduction of several oxygen-containing functional groups (Faria et al. 2004). With increase in pH from 5 to 9, the degree of protonation of the adsorbent functional group decreased gradually and hence removal was decreased.

The oxidative treatment of activated carbon with sulphuric acid will introduce more acidic C=O groups on the surface of activated carbon (Mostafa, 1997; Toles et al. 1999). This enhanced the electrostatic interaction between chitosan and the more negatively charged PSAC and this prevents any tendency of chitosan to agglomerate. This helped to increase the availability of active binding sites on the chitosan for adsorption of chromium at low pH conditions. It has also been suggested that formation of more acidic surface oxides on the carbon surface enhances its

hydrophilic character and hence improve the hydrodynamic flow (Olin et al. 1996). The interaction may not be very strong and the chitosan may agglomerate to a certain degree and become more soluble at low pH and hence reduces the availability of active binding sites on the chitosan for adsorption of chromium. Activated carbons are species with amphoteric character, thus depending on the pH of the solution their surfaces might be positively charged or negatively charged. The optimum value for PSAC occurs at pH 4 with removal efficiency increase from 57% to 92%. The removal efficiency reduced drastically from pH 4 to 8. At higher pH, the presence of oxygen containing functional groups makes the adsorbent surface negatively charged and hence there is repulsive electrostatic interaction between the adsorbent and the anions (Radovic et al. 1997; Faria *et al.* 2004). At pH greater than 8.5, insoluble chromium hydroxide starts precipitating from the solution, making true sorption studies impossible.

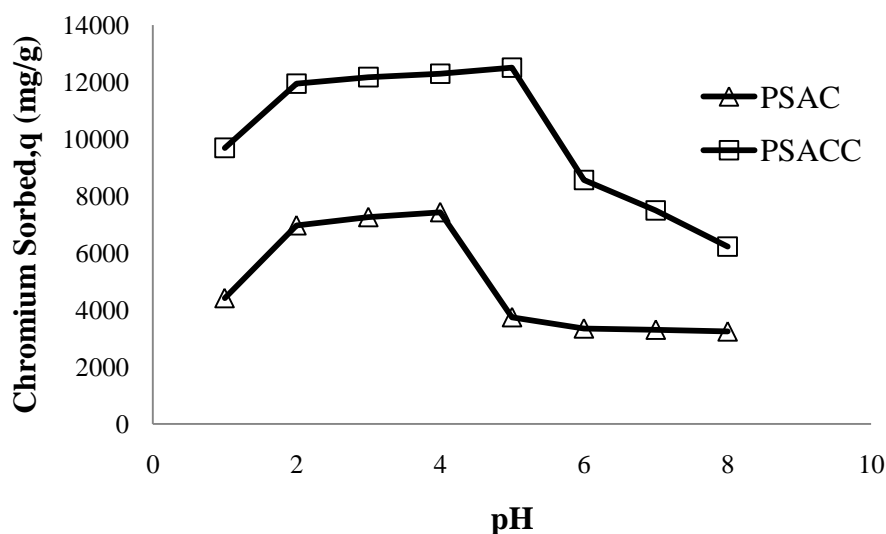


Figure 4.2: Chromium sorbed for effect of pH on the adsorption of Chromium ions on PSAC and PSACC

Chromium sorbed by PSAC and PSACC shown in Figure 4.2. The graph was similar like removal efficiency for effect of pH. Chromium sorbed for PSACC was higher than PSAC. The optimum value for PSACC occurs at pH 5 and chromium sorbed increase from 9687.5mg/g to 12500mg/g and then declining at higher pH. For PSAC, optimum value occurs at pH 4. The chromium sorbed will increase at low pH which is increase from 4415.4mg/g to 12287.5mg/g and then decrease at higher pH.

4.3.2 Effect of adsorbents dosage

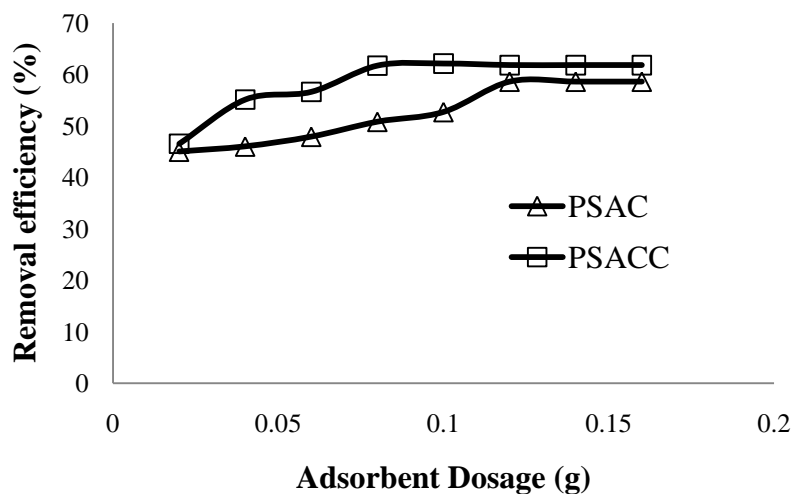


Figure 4.3: Effect of dose on the adsorption of Chromium ions using PSAC and PSACC

Figure 4.3 presents the chromium removal efficiency for two types of adsorbents used. From the Figure 4.3, it can be observed that removal efficiency of the adsorbent generally improved with increasing dose. This is expected due to the fact that the higher dose of adsorbents in the solution, the greater availability of exchangeable sites for the ions. Both of them showed no further increase in adsorption after a certain amount of adsorbent was added (0.08-0.12 g). At 20 mg/L concentration of chromium, the maximum chromium removal efficiency was about 62% for a PSACC at the dosage of 0.08 g, while for PSAC it was 59% at the dosage of 0.12 g.

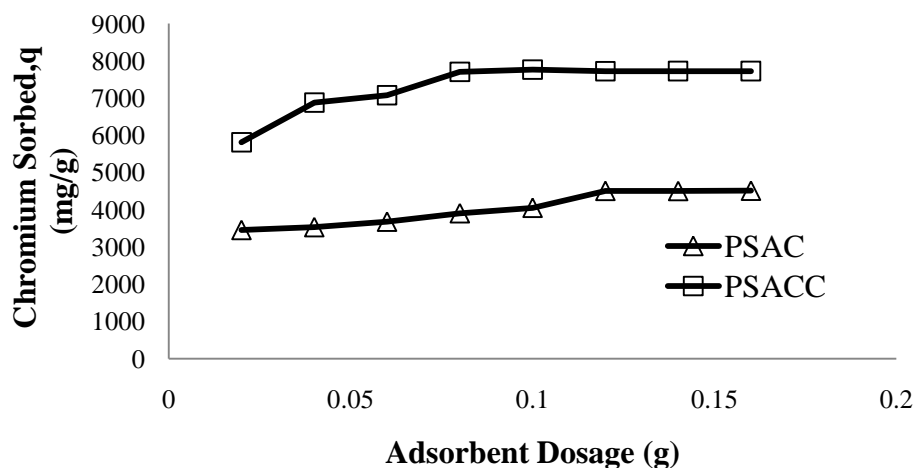


Figure 4.4: Chromium sorbed for effect of dose on the adsorption of Chromium ions using PSAC and PSACC

Chromium sorbed for PSACC higher than PSAC as shown in Figure 4.4. Both PSAC and PSACC were increased as increasing of adsorption dosage. Optimum value was similar like removal efficiency which is for PSAC was 0.12g and 0.08 for PSACC. The value of PSAC was increase from 3457.7mg/g to 4511.5mg/g and the value of PSACC was increase from 5812.5mg/g to 7725mg/g.

This suggests that after a certain dose of adsorbent, the maximum adsorption sets in and hence the amount of ions bound to the adsorbent and the amount of free ions remains constant even with further addition of the dose of adsorbent. It is interesting to note that the saturated values of chromium removal efficiency of the two types of adsorbents are different from one to another due to the extent of surface modification. Activated carbon, showed lower adsorption capacity, probably due to not coating of chitosan, which has lesser acidic surface oxides. The interaction may not be very strong. PSAC showed poorer adsorption capability for chromium as compared with the PSACC. This is consistent with the previous result (section Effect of pH) obtained on effect of pH. A close relationship between the surface basicity of the adsorbents and the anions is evident. This is similar to the findings of others, where the interaction between oxygen-free Lewis basic sites and the free electrons of the anions, as well as the electrostatic interactions between the anions and the protonated sites of the adsorbent are the main adsorption mechanism (Leon y Leon et al. 1992; Radovic et al. 1997; Faria et al. 2004).

4.3.3 Effect of agitation speed

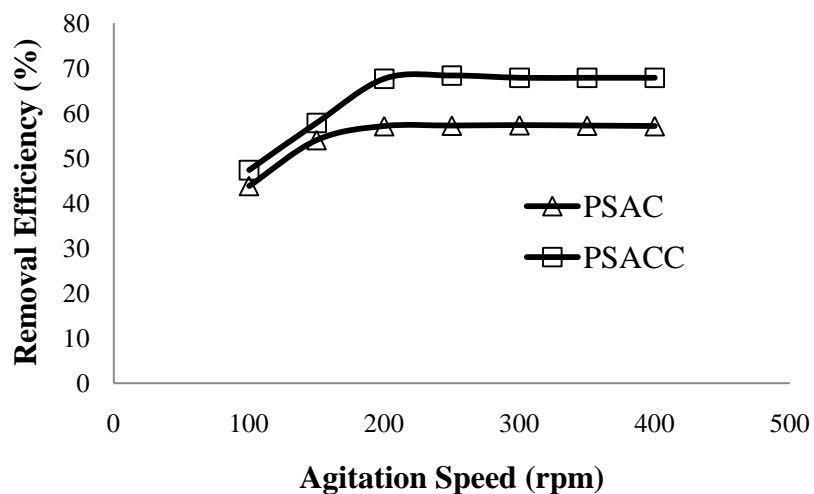


Figure 4.5: Effect of agitation on the adsorption of Chromium ions using PSAC and PSACC

As can be seen from Figure 4.5, the chromium removal efficient generally increased with increasing agitation speed. Removal efficiency for PSAC was increase from 43% to 57%. Then, the chromium removal efficiency of PSACC adsorbent increased from 47% to 67% when agitation speed increased from 100 rpm to 300 rpm and the adsorption capacity remained constant for agitation rates greater than 200 rpm.

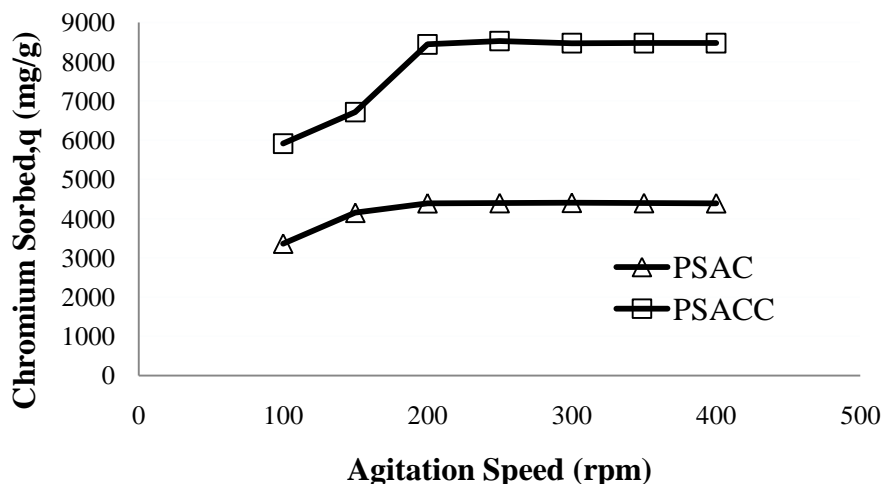


Figure 4.6: Chromium sorbed for effect of agitation on the adsorption of Chromium ions using PSAC and PSACC

Figure 4.6 shown chromium sorbed for PSACC was higher than PSAC. The optimum value for both adsorbents was at 200 rpm. The chromium sorbed will increase as increasing of agitation speed and then remained constant at higher speed. The chromium sorbed for PSAC was increase from 3365.4mg/g to 4392.3mg/g and chromium sorbed for PSACC also increase from 5912.5mg/g to 8475mg/g.

These results can be associated to the fact that the increase of the agitation speed, improves the diffusion of chromium ions towards the surface of the adsorbents. This also indicates that a shaking rate in the range 200-400 rpm is sufficient to assure that all the surface binding sites are made readily available for chromium uptake. Then, the effect of external film diffusion on adsorption rate can be assumed not significant. For convenience, agitation speed of 200 rpm was selected as the optimum speed for both the adsorbents.

4.3.4 Effect of contact time

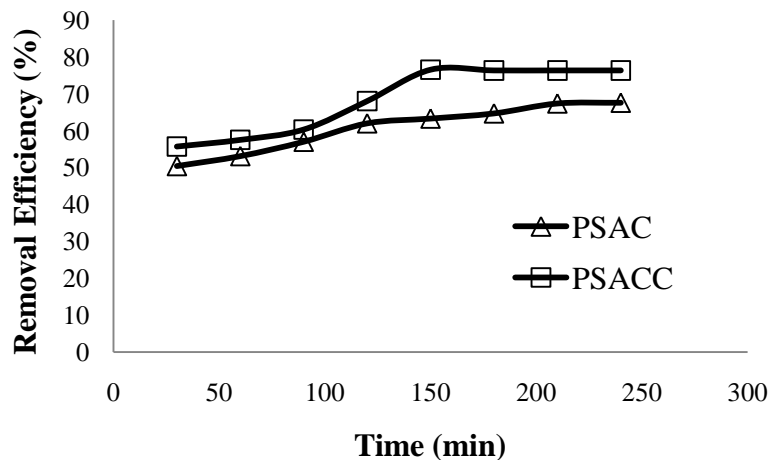


Figure 4.7: Effect of contact time on removal of chromium ions using PSAC and PSACC

Results from Figure 4.7 indicated that removal efficiency increased with an increase in contact time before equilibrium is reached. Other parameters such as dose of adsorbent, pH of solution and agitation speed was kept optimum, while temperature was kept at 25°C. It can be seen that chromium removal efficiency of PSACC increased from 55% to 76% when contact time was increased from 30 to 240 min. Removal efficiency for PSAC was also increase but lower efficiency compare from PSACC which is increased from 50% to 67%. Optimum contact time for PSACC adsorbents was found to be 150 min, compared to that of PSAC which was 210 min. Hence the chitosan coated beads require a shorter contact time.

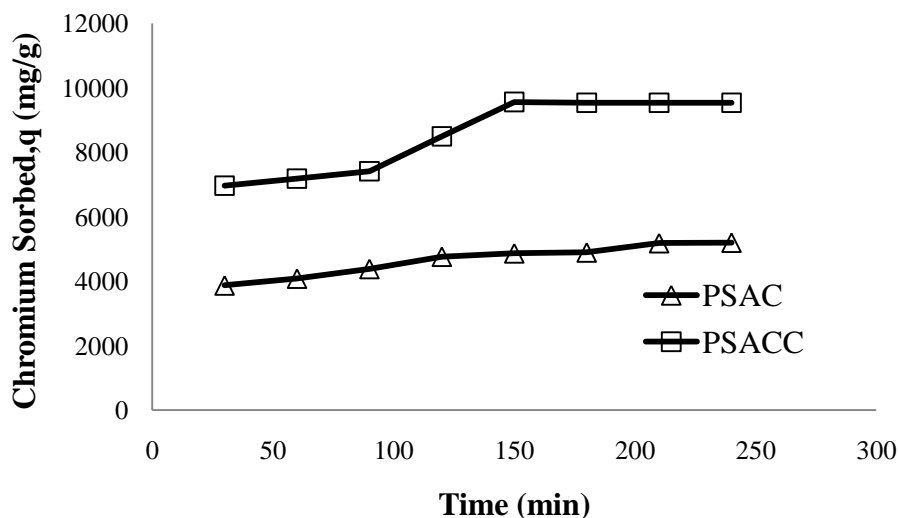


Figure 4.8: Chromium sorbed for effect of contact time on removal of chromium ions using PSAC and PSACC

Figure 4.8 mostly same like Figure 4.7 which is the optimum value for PSAC and PSACC were 210 min and 150 min. The PSACC was higher than PSAC and chromium value was increased when time increase. The value of chromium sorbed for PSAC and PSACC was increase from 3873.1mg/g to 5200m/g and 6962.5mg/g to 9537.5mg/g. The chromium sorbed remained constant after achieved the optimum value even increasing time.

Greater availability of various functional groups on the surface of chitosan, which are required for interaction with anions and cations, significantly improved the binding capacity and the process proceeded rapidly. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system.

4.4 Adsorption isotherm

To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves. Various isotherm equations have been used to describe the equilibrium nature of adsorption. Some of these equations are Freundlich, Langmuir, RedlichePeterson, Dubinin and Radushkevich, Tempkin, RadkoePraunitz and Toth equations. The topic of adsorption isotherm will recover removal efficiency and chromium adsorbed for the effect of initial concentration. Then, the study of sorption isotherm models using Freundlich and Langmuir.

4.4.1 Effect of initial concentration

The constant parameter that be controlled was pH of solution, agitation speed, contact time, amount of adsorbent dosage and temperature. pH of solution was 4, agitation speed and contact time was constant at 200 rpm and 3 hours. Amount of adsorbent for activated carbon was 0.08g and 0.13g for activated carbon coating chitosan. The sample was prepared in 50mL solution. Temperature was maintained at 25°C. The pH was controlled using acid hydrochloric (HCL) and sodium hydroxide (NaOH).

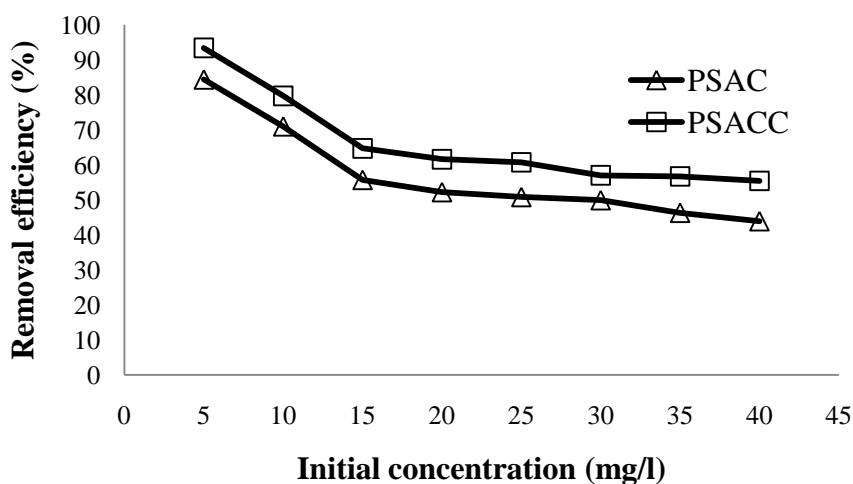


Figure 4.9: Effect of initial concentration on removal of chromium ions using PSAC and PSACC

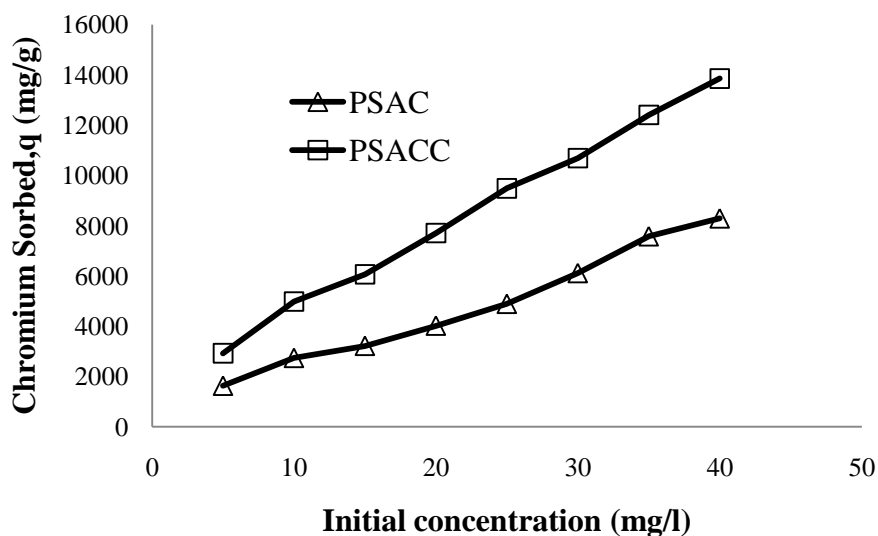


Figure 4.10: Chromium sorbed for effect of initial concentration on removal of chromium ions using PSAC and PSACC

The influence of initial concentration on removal efficiency and chromium sorbed of heavy metals was estimated. As shown in Figure 4.9, when the initial concentration was increased from 5 to 40 mg/l, the removal efficiency of heavy metals for PSAC was decreased from 84.4% to 43.9% and removal efficiency for PSACC was also decrease from 93.4% to 55.4%. Figure 4.10 showed, chromium sorbed increased as increasing of initial concentration. Chromium sorbed for PSAC and PSACC was increase from 1623.1mg/g to 8284.6mg/g and 2918.75mg/g to 13850mg/g.

4.4.2 Freundlich and Langmuir isotherms

Freundlich (Freundlich HMF, 1906) studied the sorption of a material onto charcoal and demonstrated that the ratio of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of the solute in the solution was not a constant at different solution concentrations. The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. The linearised Freundlich isotherms are represented by the following equation:

$$\text{Freundlich isotherm } \ln q_e = \ln K_F + 1/n \ln C_e,$$

where q_e (mg/g) is the amount of heavy metals sorbed, C_e (mg/l) is the initial concentration of Cr solution, K_F is Freundlich constant (l/mg), $1/n$ is the heterogeneity factor.

Langmuir (Langmuir I, 1918) proposed a theory to describe the adsorption of gas molecules onto metal surfaces. The Langmuir adsorption isotherm has been successfully applied to many other real sorption processes and it has been used to explain the sorption of heavy metals onto various adsorbents. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a heavy metals molecule occupies a site, no further adsorption can take place at that site. Theoretically, therefore, a saturation value is reached beyond which no further sorption can take place. The linearised Langmuir isotherms are represented by the following equations:

$$\text{Langmuir isotherm } C_e/q_e = C_e/q_m + 1/K_L q_m$$

where q_e (mg/g) is the amount of heavy metals sorbed, C_e (mg/l) is the initial concentration of chromium solution, K_L is the Langmuir adsorption constant (l/mg) related to energy of adsorption and q_m signifies adsorption capacity (mg/g). (Mall I.D *et al.*, 2006)

Figure 4.11 and 4.12 show the Freundlich ($\ln q_e$ versus $\ln C_e$) and Langmuir (C_e/q_e versus C_e) plot, respectively, for the AC and ACC adsorbents. The data have been analysed by two correlation coefficients. The linear R^2 coefficient for the linearised plots shown in Figure 4.11 (Freundlich) was higher than Figure 4.12 (Langmuir).

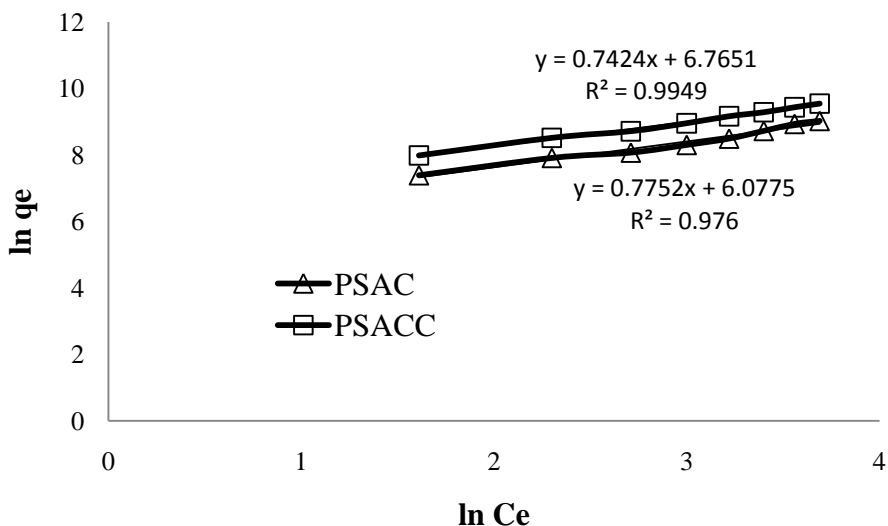


Figure 4.11: Freundlich isotherm plots for removal of Cr by PSAC and PSACC

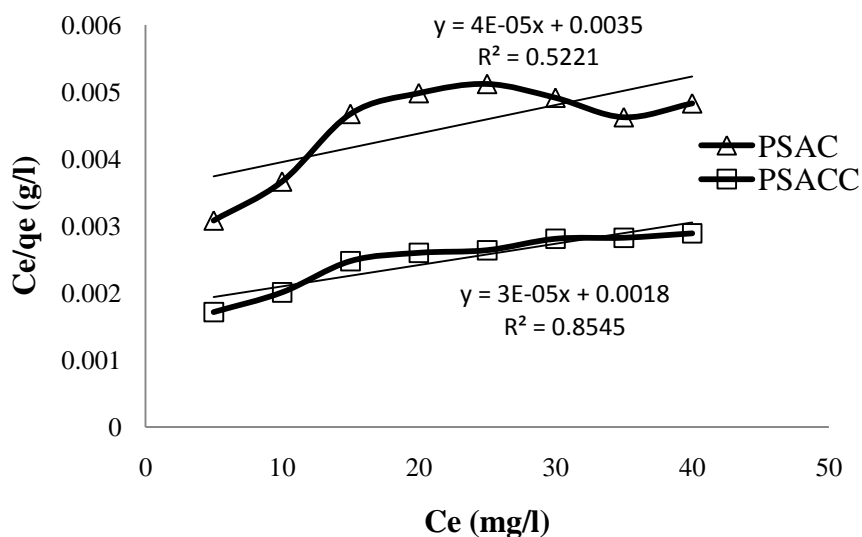


Figure 4.12: Langmuir isotherm plots for removal of Cr by PSAC and PSACC

The constants and correlation coefficients for the Freundlich and Langmuir isotherm analyses are shown in Table 4.2. In all cases the Freundlich equation represents a better fit of experimental data than the Langmuir equation, indicating to the applicability of monolayer coverage of the chromium on the surface of adsorbent. This can be explained due to the fact that activated carbon has a small surface area for metal adsorption. Therefore, only monolayer adsorption occurred on its surface, in spite of any surface modification. Comparison of Langmuir and Freundlich

isotherm constants obtained from other studies using other adsorbents shows that the values obtained in this study are comparable (Schmuhl et al. 2001).

Table 4.2: Isotherm model constants and correlation coefficients for adsorption of chromium ions from aqueous solution using PSAC and PSACC

Type of adsorbent	Freundlich			Langmuir		
	K_F (mg/mg)/(mg/l) ^{1/n}	1/n	R ²	K _L (l/mg)	q _m (mg/g)	R ²
Palm Shell Activated Carbon (PSAC)	435.9380	0.7752	0.976	0.0114	25000	0.8545
Palm Shell Activated Carbon coated with Chitosan (PSACC)	867.0529	0.7424	0.9949	0.0167	33333	0.5221

4.5 Conclusion for Result and Discussion

From the result, the weight loss during preparation of activated carbon can be measured. Weight before pyrolysis should be higher than after pyrolysis. The two adsorbent were prepared which are PSAC and PSACC. Before using AAS, the sample must be filter using vacuum filter to avoid plugging inside the tube of AAS. AAS measured the value of chromium concentration. This research studied four parameter which is pH, adsorbent dosage, agitation speed and contact time. The result showed optimum value for each parameter which is study of removal efficiency and chromium sorbed. The PSACC adsorbent was higher than PSAC for all parameter. This proved that chitosan can improve adsorption capacity. Then, the study of adsorption isotherm will be discussed. This is including effect of initial concentration to removal efficiency and chromium sorbed. From the result of initial concentration, adsorption isotherm was discussed which were including Freundlich and Langmuir isotherm. The Freundlich was chosen for the better fitting model than Langmuir as the former have higher correlation regression coefficient.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Activated carbon was prepared from palm shell using pyrolysis at 600°C by furnace. The treatment of activated carbon was carried out by oxidizing it with sulphuric acid and coating with chitosan. Two adsorbents namely Palm Shell Activated Carbon (PSAC) and Palm Shell Activated Carbon coated with Chitosan (PSACC) were used to remove chromium from aqueous solution. The effects of pH of the solution, adsorbent dosage, agitation speed, and contact time on adsorption of chromium were studied.

The effect of pH on the removal of chromium from an aqueous solution was studied. The results shown that maximum removal of chromium on PSAC is at pH = 4 whereas for PSACC is at pH = 5. The optimum value for the effect of adsorbent dosage is 0.08g for PSACC and 0.13g for PSAC. The effect of agitation speed remained constant after achieved optimum value which is 200 rpm for PSAC and PSACC. Equilibrium was reached for the effect of contact time whereas the optimum time for PSAC is 210 min and PSACC is 150 min. The PSACC adsorbent was higher than PSAC for all parameter. This proved that chitosan can improve adsorption capacity.

Freundlich and Langmuir isotherm were used to analyze the adsorption of Cr from aqueous solution. The results shown that Freundlich isotherm captured the adsorption of Cr better compared to Langmuir isotherm as the former have higher correlation regression coefficient.

5.2 Recommendation

In this research, there is using only two adsorbent which is Palm Shell Activated Carbon (PSAC) and Palm Shell Activated Carbon coated with Chitosan (PSACC). This research can be improved to be more success by using or add various types of adsorbent. So, removal efficiency of several types of adsorbent can be compared.

Palm shell activated carbon also can be coat with some other material. Adsorbents that we prepared in this were can also being used to remove other heavy metals such as copper, lead and so on. So that, the removal efficiency with the other metals can be compared. To improve the study of adsorption isotherm, various isotherms should be added which were using RedlichePeterson, Dubinin and Radushkevich, Tempkin, RadkoePraunitz and Toth equations. So, the understanding of adsorption isotherm can be improved.

5.3 Research Schedule

Figure 5.1 shows the Gantt chart used for Undergraduate Research Project 2 in doing the experimental and fabrication work for this project. The Gantt chart is important in managing the work schedule in order to ensure that the Undergraduate Research Project 2 can be completed on time.

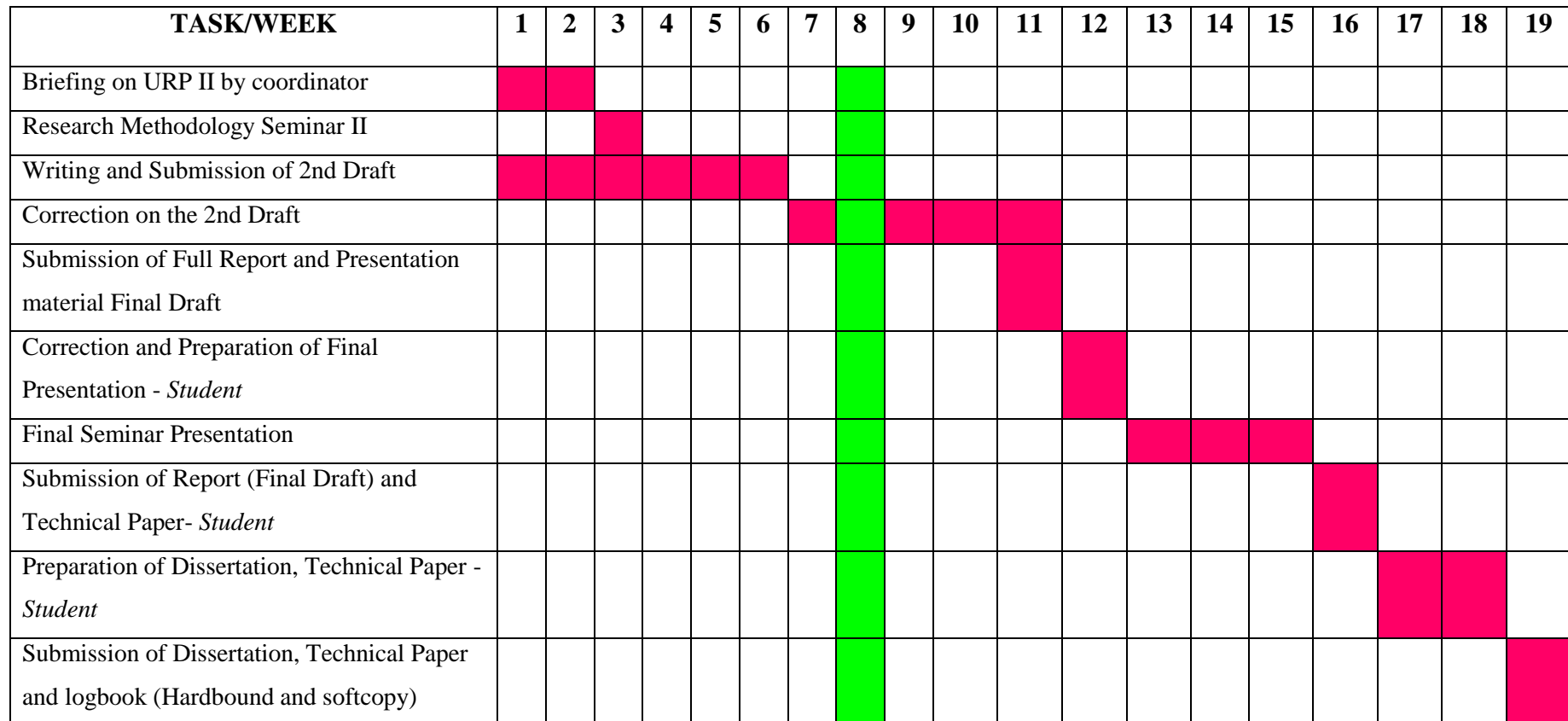


Figure 5.1: Gantt Chart for URP

Mid Semester Break	Mid Semester Break
Work in Progress	Work in Progress

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APPENDICES A: TABLES

A.1 Removal efficiency for the effect of pH

pH	Removal efficiency (%)	
	PSAC	PSACC
1	57.4	77.5
2	72.6	85.5
3	84.4	95.4
4	92.6	97.7
5	48.7	98
6	43.6	68.5
7	43	60
8	42.2	49.8

A.2 Chromium sorbed for the effect of pH

pH	q (mg/g)	
	PSAC	PSACC
1	4415.4	9687.5
2	6969.2	11937.5
3	7257.7	12168.8
4	7430.8	12287.5
5	3746.2	12500
6	3350	8562.5
7	3307.7	7493.75
8	3246.2	6225

A.3 Removal efficiency for the effect of adsorbent dosage

Dose (g)	Removal efficiency (%)	
	PSAC	PSACC
0.02	45	46.5
0.04	46	55.1
0.06	47.9	56.6
0.08	50.8	61.7
0.1	52.7	62.1
0.12	58.6	61.8
0.14	58.6	61.8
0.16	58.6	61.8

A.4 Chromium sorbed for the effect of adsorbent dosage

Dose (g)	q (mg/g)	
	PSAC	PSACC
0.02	3457.7	5812.5
0.04	3534.6	6881.3
0.06	3680.8	7075
0.08	3907.7	7706.3
0.1	4053.8	7762.5
0.12	4507.7	7725
0.14	4503.8	7726
0.16	4511.5	7726

A.5 Removal efficiency for the effect of agitation speed

Speed (rpm)	Removal efficiency (%)	
	PSAC	PSACC
100	43.8	47.3
150	54	57.8
200	57.1	67.6
250	57.2	68.3
300	57.3	67.8
350	57.2	67.8
400	57.1	67.8

A.6 Chromium sorbed for the effect of agitation speed

Speed (rpm)	q (mg/g)	
	PSAC	PSACC
100	3365.4	5912.5
150	4150	6718.8
200	4392.3	8443.8
250	4396.2	8531.3
300	4403.8	8475
350	4396.2	8476
400	4392.3	8476

A.7 Removal efficiency for the effect of contact time

Time (min)	Removal efficiency (%)	
	PSAC	PSACC
30	50.4	55.7
60	53.1	57.5
90	57	60.3
120	62	68
150	63.3	76.5
180	64.7	76.3
210	67.4	76.3
240	67.6	76.3

A.8 Chromium sorbed for the effect of contact time

Time (min)	q (mg/g)	
	PSAC	PSACC
30	3873.1	6962.5
60	4084.6	7187.5
90	4384.6	7412.5
120	4765.4	8493.8
150	4869.2	9562.5
180	4896.2	9537.5
210	5184.6	9537.4
240	5200	9537.4

A.9 Removal efficiency for the effect of initial concentration

Initial Concentration (mg/l)	Removal efficiency (%)	
	PSAC	PSACC
5	84.4	93.4
10	71	79.7
15	55.7	64.7
20	52.2	61.6
25	50.8	60.7
30	49.9	57
35	46.3	56.7
40	43.9	55.4

A.10 Chromium sorbed for the effect of initial concentration

Initial Concentration (mg/l)	q (mg/g)	
	PSAC	PSACC
5	1623.1	2918.75
10	2730.8	4981.3
15	3211.5	6062.5
20	4015.4	7700
25	4884.6	9481.3
30	6107.7	10687.5
35	7573.1	12400
40	8284.6	13850

A.11 Result for Freundlich Isotherm

ln Ce	q PSAC	ln q PSAC	q PSACC	ln q PSACC
1.61	1623.1	7.39	2918.75	7.98
2.3	2730.8	7.91	4981.3	8.51
2.71	3211.5	8.07	6062.5	8.71
3	4015.4	8.3	7700	8.95
3.22	4884.6	8.49	9481.3	9.16
3.4	6107.7	8.72	10687.5	9.28
3.56	7573.1	8.93	12400	9.43
3.69	8284.6	9.02	13850	9.54

A.12 Result for Langmuir Isotherm

Ce	q PSAC	Ce/qe PSAC	q PSACC	Ce/qe PSACC
5	1623.1	0.003080525	2918.75	0.0017131
10	2730.8	0.003661931	4981.3	0.0020075
15	3211.5	0.004670715	6062.5	0.0024742
20	4015.4	0.004980824	7700	0.0025974
25	4884.6	0.005118126	9481.3	0.0026368
30	6107.7	0.004911833	10687.5	0.002807
35	7573.1	0.004621621	12400	0.0028226
40	8284.6	0.004828236	13850	0.0028881

APPENDICES B: PICTURES



B.1: Palm shell



B.2: Palm shell before pyrolysis



B.3: Palm shell after pyrolysis



B.4: Palm shell activated carbon



B.5: Chitosan gel



B.6: Samples

