Adsorption of Hexavalent Chromium from Aqueous Solution by Rice Husk-Based Adsorbent

By

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12066

Dissertation submitted in partial fulfilment of
the requirements for the
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CERTIFICATIONS

CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Civil Engineering Programme of
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
Bachelor of Engineering (Hons)
(Civil Engineering)

Approved by,

____

(Prof Dr Malay Chaudhuri)

Universiti Teknologi PETRONAS

Tronoh, Perak

Sept 2012

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.

Muhammad Haziq bin Rahim

ABSTRACT

Chromium exists in two stable oxidation states apart from its metal form that are the trivalent state and hexavalent state. Hexavalent chromium has been identified by academicians worldwide to be hazardous towards the human health in general as a result of ingestion, direct or indirect. Existing methods of treating Cr(VI)-contaminated water proves to be sophisticated and may be out of reach for developing countries until the near future. Hence the employment of a simple yet effective method of treatment is vital to counter this kind of contamination in places with limited capital and capabilities where it can be mobilized easily without the need for sophisticated machineries and equipment. Adsorption promises an effective way of removing hexavalent chromium from aqueous solutions based on researches done throughout the globe while still maintaining feasibility. Efforts are being made to come up with new materials to be used as adsorbent, preferably from low-cost materials produced as a waste product from other industries to further cut down the cost of treatment by studying the adsorptive capability of said materials. This project studied the adsorptive capabilities of rice husk-based adsorbent for use in decontaminating purposes. Preliminary experiment showed an adsorption percentage as high as 99.9% of 20 mg/L chromium solution using acid-treated rice husk-based adsorbent. Tests for other parameters such as pH value, contact time and adsorbent dosage resulted in positive results and pH 2 is found to be the optimum pH value for adsorption tests, two hours of shaking was the equilibrium time and adsorbent dosage of 8 g/L was the equilibrium dosage for testing purposes. In addition to that, adsorption of chromium(VI) by acid-treated rice husk-based adsorbent fitted well into pseudo first-order and pseudo second-order kinetic models, and it demonstrates a high adsorptive capacity of 47.62 mg/g in isotherm studies. The acid-treated RHA as well as exhausted acid-treated RHA were characterized by means of FTIR and SEM.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Chromium is a common pollutant, introduced into natural waters through the discharge of a wide range of industrial wastewaters. Various chemical processes employ the use of chromium for catalytic reactions, one of them being selective oxidation of hydrocarbons. Chromium is present in the environment in three common forms which are the chromium metal, trivalent chromium and hexavalent chromium.

While trivalent chromium or Cr(III) occurs naturally in the environment and is considered an essential nutrient, its hexavalent counterpart, Cr(VI) is highly toxic (Owlad et al., 2009). Recent studies by Kaats et al. (2011) have illustrated the beneficial effects of Cr(III) in helping insulin to regulate glucose levels. Hexavalent chromium or Cr(VI) however is generally produced by industrial processes which include chrome plating, leather tanning and the production of dyes.

According to a review by Costa (1997), exposure to Cr(VI) is capable of inducing a wider variety of cancers in addition to the lung cancer which had been known for at least a century to be caused by hexavalent chromium (Langard, 1990; Gibb et al., 2000). Recent work suggests that Cr(VI) may be carcinogenic if ingested (Sedman et al., 2006; Beaumont et al., 2008).

A notable event involving hexavalent chromium contamination occurred in the town of Hinkley in California where hexavalent chromium is added into cooling water to prevent rust in the machinery used to compress natural gas in the transmission pipelines between 1952 and 1966. Unfortunately the Cr(VI)-containing water was stored in unlined ponds which, in turn, contaminated the groundwater in the town. Investigations by Izbicki et al. (2012) shows that the contamination is widespread and the groundwater contains much higher Cr(VI) content compared to the maximum allowable content set forth by the World Health Organization that is 0.05 mg/L (WHO, 2011). This event was adapted into a movie entitled Erin Brockovich which was released in the year 2000.

1.2 Problem Statement

1.2.1 Problem Identification

Approximately 90% of the chromite ore mined throughout the world annually is used to produce stainless steels and other alloys. About 7% is used in manufacturing chemicals with a major portion being used to produce tanning agent for leather besides other chemical compounds such as pigments for paints and chrome plating (Assem and Zhu, 2007).

With the abundance of industries incorporating the usage of chromium in their processes, equal effort must be enforced to monitor the wastewater produced by said industries for their chromium content. The bio-accumulating property of toxic heavy metals, in this case being hexavalent chromium (Preetha and Viruthagiri, 2007; Koçberber and Dönmez, 2007), dictates industrial effluent to be treated prior to being released to the environment.

Various techniques are being employed to treat industrial effluents containing heavy metals. These include chemical precipitation, adsorption, electrolysis, and bioaccumulation by living cells (Üçer et al*.,* 2006; Barrera-Díaz et al., 2012). According to McKay (1995), adsorption seems to be among the most promising methods to treat waste stream contaminated by metal ions.

Huang (1978) stated in his review that activated carbon has the capability to adsorb metals such as chromium. However, commercial activated carbon is being produced from coal that is generally acknowledged to be a valuable, non-renewable source of energy in addition to its high production cost. Hence the need to produce adsorbent of similar or better adsorption capacities with lower production cost is gaining attention from researchers and academicians globally.

This paper focuses primarily on the adsorbent capacity and capability of rice husk-based adsorbent to be applied in the treatment of industrial wastewater containing hexavalent chromium.

1.2.2 Significance of the Project

Untreated industrial effluent can pose several adverse impacts towards the ecology, one of it being the negative effect towards human health in general. Sophisticated and complicated treatment methods may cost a fortune for small companies and developing countries like Nigeria (Uhegbu et al., 2012), Algeria (Leghouchi et al., 2009) and Bangladesh (Bhuiyan et al., 2011), to adhere to the effluent standards set forth by numerous organizations. Cheaper and easier alternatives with readily available materials are needed in order to achieve the aforementioned standards. Rice husk-based adsorbent is the focus of this research as it is a waste product obtained from paddy plantations and can be provided in a vast amount with a very low production cost. Also, an investigation by Roy et al. (1993) found that rice husk-based adsorbent possesses high adsorption capacities of heavy metals such as cadmium, lead and chromium.

1.3 Objectives of the Study

- To prepare and characterize the rice husk-based adsorbents.
- To assess the potential of rice husk-based adsorbents in adsorptive removal of hexavalent chromium from aqueous solution.
- To conduct detailed hexavalent chromium adsorption test with the selected rice husk-based adsorbent(s).
- To study desorption of hexavalent chromium from chromium-loaded rice husk-based adsorbent.
- To develop a simple procedure for removing hexavalent chromium by rice husk-based adsorbent from industrial wastewater and disposing off the used rice husk-based adsorbent.

1.4 Scope of the Study

- Preparations of the rice husk-based adsorbent.
- Feasibility of using rice husk-based adsorbent as a low cost adsorbent for the removal of hexavalent chromium from water.
- Characterization of the selected rice husk-based adsorbent by using scanning electron microscopy, infra-red spectroscopy, surface area and pore size analysis.
- Parameters that affect the adsorption process of hexavalent chromium.
- Comparison between removals of hexavalent chromium in water using rice husk-based adsorbent against other adsorbents.
- Desorption of hexavalent chromium from rice husk-based adsorbent.
- Development of a simple procedure for removing hexavalent chromium from industrial effluent by rice husk-based adsorbent and disposing off the used rice husk-based adsorbent.

1.5 Relevancy of the Project

This research paper pays attention on the human health factor involving hexavalent chromium contamination in wastewater effluent. The high concentration of toxic heavy metal pollutant in turn can be absorbed by various aquatic organisms such as fish and shellfish which is a source of food for the local population (Uhegbu et al., 2012). In addition to that, improper management of Cr(VI)-contaminated wastewater can result in the absorption of toxic heavy metals by the groundwater which the local population commonly harvest as a source of drinking water and for other domestic purposes. This was the scenario in Hinkley, California where a lawsuit was filed against Pacific Gas & Electric by Erin Brockovich and PG&E was ordered to pay a huge sum of money totalling up more than USD 300 million to affected residents. While a profitable company may afford the high cost of sophisticated treatment method, a cheaper and simpler alternative yet effective alternative is needed for parties unable to afford the high cost. This cheaper alternative is what this paper trying to achieve with rice husk-based adsorbent with the hope to reduce the fatality of hexavalent chromium contamination towards human health in the nearest future by reducing its content to a permissible level.

1.6 Feasibility of the Project within the Scope and Time Frame

This project is an extended study over two semesters for fulfilling the requirement of Final Year Project I and II courses prior to graduating. The following are the aims of the project for the FYP I course:

- Produce a literature review on the subject.
- Prepare rice husk-based adsorbents for experimental purposes.
- Perform preliminary experiments to confirm the ability of rice husk-based adsorbent to adsorb hexavalent chromium from industrial effluent.

Post-FYP I demands data analysis to be conducted within FYP II. More detailed experiments varying with the optimum parameters that can improve adsorption will be planned and carried out throughout FYP II period. Among the experiments planned for FYP II are:

- Optimum pH value test.
- Optimum contact time.
- Optimum adsorbent concentration.
- Adsorption isotherm experiment.
- Desorption of hexavalent chromium from rice husk.
- Simple procedure to remove hexavalent chromium from industrial wastewater by rice husk-based adsorbent and its disposal.

Estimated project cost will not be exceeding permissible budget by the university as all materials can be obtained at a small cost in addition to the availability of laboratory equipment for this research at Environmental Engineering Laboratory.

CHAPTER 2

LITERATURE REVIEW

2.1 Chromium Forms and Mobility

In 1798, a French chemist, N. L. Vauquelin discovered the element Chromium in Siberian red lead ore (Costa and Klein, 2006). Chromium is widely distributed in nature, occupying the 21st position in the index of most commonly occurring elements in the earth's crust. It occurs naturally in the compound of chromium, oxygen and iron that is known as chromite (Chandra and Kulshreshtha, 2004). Chromium exists in two stable oxidation states which are the trivalent chromium and hexavalent chromium besides its metal form. Trivalent chromium or Cr(III) is considered essential in a balanced diet as it stabilizes the metabolism of glucose and lipids (Anderson, 1997). However, Costa (1997) and Zhitkovich et al. (1996) suggested that ingestion of a large amount of trivalent chromium poses health problem such as lung cancer.

Hexavalent chromium or Cr(VI) is the term coined to demonstrate chemical compounds containing the element chromium in the +6 oxidation state. Chromium(VI) compounds are essentially anthropogenic and do not occur naturally in the environment. Large amount of this type of chromium are produced through multiple industrial processes that most commonly include material tanning, chrome pigment production and the production of stainless steel (Assem and Zhu, 2007). Inhalation and ingestion of hexavalent chromium is widely accepted to be disastrous towards the health aspect. Ingestion of high doses of Cr(VI) results in acute, potentially fatal and affects the respiratory, cardiovascular, gastrointestinal, hepatic, renal and neurological systems of the human body (IPCSb, 2006; ECB, 2005; ATSDR, 2000).

95% of chromium(III) is bound to large molecular mass proteins while a small proportion associates with low molecular mass oligopeptides in the blood (IPCSa, 2006). Chromium compounds are widely distributed in the human body, with a greater distribution reported following exposure to chromium(VI) compounds compared to its trivalent counterpart. This illustrates that chromium(VI) has the higher tendency to cross plasma membranes (IPCSb, 2006).

2.2 Chromium(VI) Contamination

Chromium(VI) does not occur naturally in the environment, unlike chromium(III). A wide range of industrial processes adopt the usage of chromium for various purposes such as the production of stainless steel and tannery (Zayed and Terry, 2003). Often wastes from such industries are used as a fill material at numerous locations to reclaim marshlands and backfill (Salunkhe et al., 1998). When these events occur and no specific attention is being given to this matter, leaching and seepage of Cr(VI) from the soils into the groundwater poses health hazard. According to Chandra et al. (1997), tanning industry is a major contributor of chromium contamination of water resources and estimated that in India alone, 2000-3200 tonnes of elemental chromium escape into the environment annually from the tanning industry with a concentration of 2000-5000 mg/L in the effluent.

Table 1.0 summarizes the concentration of chromium in the environmental samples based on findings by earlier researchers. Recommended guidelines for freshwater life are 0.01 mg/L for Cr(VI and 0.08 mg/L for Cr(III), for marine life 0.01 mg/L for Cr(VI) and 0.5 mg/L for Cr(III), for irrigation water 0.08 mg/L for Cr(VI) and 0.05 mg/L for Cr(III) and for drinking water is 0.05 mg/L for Cr(VI) (Krishnamurthy and Wilkens, 1994; Pawlisz, 1997).

Table 1: Chromium Concentration in the Environment (Zayed and Terry, 2003)

Sample Type	Concentration	Reference
Natural soils	5-1000 mg/kg	Adriano (1986)
	5-3000 mg/kg	Skeffington et al. (1976)
	5-1500 mg/kg	Verry and Vermette (1991)
	30-300 mg/kg	Katz and Salem (1994)
	Trace to 5.23%	NAS (1974)
Serpentine soils	634-125000 mg/kg	Adriano (1986)
World soils	200 mg/kg (mean)	Vinogradov (1959)
	100-300 mg/kg	Aubert and Pinta (1977)
	10-150 mg/kg (mean 40 mg/kg)	NAS (1974)
US soils	25-85 mg/kg (mean 37 mg/kg)	Shacklette et al. (1971)
	57 mg/kg (mean)	Smith et al. (1989)
Canadian soils	10-5000 mg/kg (mean 43 mg/kg)	Pawlisz (1997)
Japanese soils	87 mg/kg (mean)	Smith et al. (1989)
Swedish soils	74 mg/kg (mean)	Smith et al. (1989)
Sediments	0-31000 mg/kg	Pawlisz (1997)
Fresh water	0-117 µg/L (average 9.7 µg/L)	Pawlisz (1997)
Sea water	0-0.5 µg/L	Pawlisz (1997)
Air	1-545000 ng m^3	Pawlisz (1997)
	100 ng m^3	USEPA (1983)
Plants	0.006-18 mg/kg	Pawlisz (1997)
Animals	0.03-1.6 mg/kg	Pawlisz (1997)

2.3 Health Problems Associated with Hexavalent Chromium in Water

While the toxicity of chromium depends on its oxidation state, chromium(VI) is more toxic than chromium(III) although ingestion of chromium(III) may pose cancer threats too. As stated earlier, acute ingestion of chromium(VI) have the potential to cause mortal effects to the respiratory, cardiovascular, gastrointestinal, hepatic, renal, and neurological systems (Assem and Zhu, 2007). The corrosive nature of some chromium(VI) compounds also leads to similar effects. In a suicide attempt by a 17-year-old male, caustic burn in the stomach, duodenum and gastrointestinal haemorrhage were noted. The subject knowingly ingested potassium dichromate with a concentration of 29 mg/kg and caused respiratory distress with severe haemorrhage (ATSDR, 2000).

The International Agency for Research on Cancer (IARC) (1997) have classified chromium(VI) as carcinogenic to humans (Group 1) based on sufficient evidence in humans as encountered in the chromate production, chromate pigment production and chromium plating industries.

2.4 Removal of Hexavalent Chromium from Water

There exist several treatment methods for removing hexavalent chromium from water. Díaz et al. (2012) have listed several ways to achieve a tolerable chromium concentration.

2.4.1 Traditional Cr(VI) Reduction Treatment

Traditional Cr(VI) reduction treatment employs two different methods, using sulphur compounds to reduce hexavalent chromium to trivalent chromium and using iron salts to achieve similar purpose.

For the use of sulphur compounds, the typical procedure is to reduce chromium(VI) to chromium(III) followed by its precipitation as Cr(III) hydroxide (Díaz et al., 2012). The effluent is treated with sodium hydroxide solution or calcium hydroxide slurry to neutralize the acidity and precipitate the chromium. However, this method produces a large amount of residual sludge that presents difficulties in managing and disposal (Canning, 1982).

As for using iron salts to reduce hexavalent chromium, an acidic condition is a pre-requirement (Chen et al., 2007; Gheju and Iovi, 2006; Gheju et al., 2008; Welch et al., 2005) as Fe(II) and Fe(III) appear as free ions in aqueous solution at low pH values. Iron (II) chloride and iron (II) sulphate are commonly used in this process. This method also produces solid waste when ferrous sulphate is used as reducing agent, while sulphur dioxide is produced when sodium sulphite is used as a reducing agent.

2.4.2 Electrochemical Methods

There are many ways to implement the reduction of hexavalent chromium through electrochemical means. They depend on the pH of the aqueous solution, intensity of current density and the material of chosen electrodes (Barrera-Díaz et al., 2012).

Electrocoagulation is one type of electrochemical method employed in chromium reduction. It is the production of destabilizing agents that neutralize the electric charge of the pollutants present in a solution. Commonly consists of reservoir of solution with two electrodes; an anode and a cathode, it requires external sources to provide energy to dissolute sacrificial anode which is typically aluminium or iron (Emamjomech and Sivakumar, 2009).

2.4.3 Cr(VI) Reducing Bacteria

In this method of reducing hexavalent chromium, generally there exist common stages in its process. Firstly, it involves the binding of chromium to the cell surface. Then comes the translocation stage of chromium into the cell, followed by the reduction of chromium(VI) to chromium(III) (Singh et al., 2011). Common types of microorganisms utilized are aerobic Cr(VI) reducing bacteria (Singh et al., 2011), anaerobic Cr(VI) reducing bacteria (Lin et al., 2011) and fungi (Sharma and Adholeya, 2011).

2.5 Adsorptive Processes

Although there exists multiple methods of removing hexavalent chromium in an aqueous solution such as membrane separation (Chakravarti et al., 1995) and evaporation (Aksu and Kutsal, 1990) in addition to the three methods aforementioned, adsorption is recognized as an economical yet effective process for a wide range of application. Adsorption is also used widely to remove chromium metals from waters and industrial wastewater.

2.5.1 Commercial and Synthetic Activated Carbon

The most extensively studied adsorbent for chromium adsorption is found to be produced from various sources, natural and synthetic alike (Mohan and Pittman, 2007). It has an exceptionally high surface areas ranging from 500-1500 m^2/g, well-developed internal micro-porosity structure and a wide spectrum of surface functional groups like carboxylic group are present (Chingombe et al., 2005).

Commercial activated carbon is derived from natural resource that is coal. However, coal being non-renewable in nature, is a priceless source to be consumed for chromium adsorption. Hence there have been numerous studies on the effectiveness of synthetically-produced activated carbon from various natural materials available. Among the natural materials used are coconut shell (Chaudhuri and Azizan, 2012), wood and dust (Selomulya et al., 1999), *Terminalia arjuna* nuts (Mohanty et al., 2005) and hazelnut shell (Kobya, 2004). Synthetic activated carbons are produced by carbonization employing slow substrate heating in the absence of air below the temperature of 600^oC.

2.5.2 Low-Cost Adsorbents

The costly production of activated carbons has stimulated academicians and researchers to find a much cheaper alternative with equal or better adsorption capacities for chromium adsorption. Bailey et al. (1999) reviewed potentially low-cost sorbents for heavy metals and described “low cost” as requiring little processing, abundant in nature, or is a by-product or waste material from other industries. Some of the reported low-cost adsorbents include tree barks (Alves et al., 1993), chitosan (Hsien and Rorrer, 1995), dead biomass (Roy et al., 1993), clay (Khan et al., 1995), rice husk (Roy et al., 1993) and fly ash (Banerjee et al., 1997). Adsorptions of a wide range of heavy metals including chromium were tested. In addition to that, the effectiveness of native or chemically modified biomass for hexavalent chromium removal have been tested and proven by various researchers (Chen et al., 2012; Matin et al., 2012; Altun and Pehlivan, 2012).

2.6 Adsorption

In 1773, C.W. Scheele first observed adsorption for gases and subsequently, Lowitz has identified adsorption for solutions in 1785. Adsorption is now recognized as a significant phenomenon in most natural physical, biological, and chemical processes. Sorption on solids, particularly active carbon, has become a widely used operation for purification of waters and wastewaters (Weber, 1972).

Weber (1972) conversely described in his literature that adsorption is a process in which the molecules or atoms of one phase interpenetrate nearly uniformly among those of another phase to form a “solution” with the second phase that occurs at a surface interface. The term sorption, which includes both adsorption and absorption, is a general expression for a process in which a component moves from one phase to be accumulated in another, particularly for cases in which the second phase in solid. The process of adsorption can occur at an interface between any two phases, such as, liquid-liquid, gas-liquid, gas-solid, or liquid-solid interfaces. The material being concentrated or adsorbed is termed the adsorbate, and the adsorbing phase is termed the adsorbent (Weber, 1972).

The primary driving force for adsorption may be a consequence lyophobic (solvent disliking) character of the solute relative to the particular solvent or high affinity of the solute for the solid. In a majority of waters and wastewaters treatment processes, adsorption occurs as a combination of the two driving forces, which can be affected to varying degrees by a number of factors. The degree of solubility of a dissolved substance is by far the most significant factor in determining the intensity of the first of the two driving forces. In the present context, “degree” of solubility can be thought of as the extent of chemical compatibility between a solvent system and a solute (Weber, 1972).

According to Weber (1972), in adsorption in a solid liquid system, the distribution ratio of the solute between the liquid and the solid phases are the measurement of the position of equilibrium. One commonly preferred form of depicting this distribution is to express the quantity, q_e as a function of C_e at a fixed temperature, the quantity, q_e being the amount of solute adsorbed per unit weight of the solid adsorbent and C_e the concentration of the solute remaining in solution at equilibrium. An expression of this type is termed as adsorption isotherm. The Langmuir adsorption isotherm is given as:

$$q_e = \frac{(Q_0 b C_e)}{(1 + b C_e)} \qquad (1)$$

The Langmuir model was first used to describe the adsorption of gas molecules onto metal surface (Langmuir, 1918). However, this model has been used successfully in many other processes. The other two convenient forms of Langmuir Equation are:

$$\frac{C_e}{q_e} = \frac{1}{b Q_0} + \frac{C_e}{Q_0} \qquad (2)$$

or

$$\frac{1}{q_e} = \frac{1}{Q_0} + \left(\frac{1}{b Q_0}\right)\left(\frac{1}{C_e}\right) \qquad (3)$$

One can choose either of the forms to apply the linearization of data that accord with the Langmuir equation. The range and spread of the data and on the particular data to be emphasized typically predetermines the type of form of choice. Although the basic assumptions explicit in the development of the Langmuir isotherm are not met in most adsorption system concerning water and wastewater treatment, the Langmuir isotherm has been found particularly useful for description of equilibrium data for such systems providing parameters (Q_0 and b) with which to quantitatively compare adsorption behaviour in different adsorbate-adsorbent systems.

There exists another adsorption isotherm that is known as the Freundlich or van Bemmelen equation. This equation has been widely used for many years alongside with the Langmuir equation and is a special case for heterogeneous surface energies in which the energy term, b, in the Langmuir equation (Equation 1) varies as a function of surface coverage, q_e, due to variations in heat of adsorption. The Freundlich equation has the general form of:

$$q_e = K_F C^{1/n} \qquad (4)$$

Where K_F and n are constants, and n >1

The situation n <1 is the most common and corresponds to a normal L-type Langmuir isotherm, while n >1 is indicative of a cooperative sorption, which involves strong interactions between molecules of adsorbate (Khezami and Capart, 2005).

The Freundlich equation is empirical; but is often useful as a means of data description. Data are usually fitted to the logarithmic form of equation

$$\log q_e = \log K_F + \frac{1}{n} \log C \qquad (5)$$

which gives a straight line with a slope of 1/n and intercept equal to the value of the log K_F for C_e =1. The intercept specifies sorption capacity and the slope, 1/n, of adsorption intensity. The Freundlich equation generally agrees quite well with the Langmuir equation and experimental data over moderate ranges of the concentration, C_e. Unlike the Langmuir equation, however, it does not reduce to a linear adsorption expression at very low concentrations, nor does it agree well with the Langmuir equation at high temperatures, since n must reach some limit when the surface is fully covered.

In determining the mechanism of the adsorption process however, several kinetic models are incorporated. A simple pseudo-first-order equation due to Lagergen was used by Ho and Mckay (1998):

$$\frac{d_{qt}}{dt} = k_{ad}(q_e - q_t) \qquad (6)$$

where: q_e , q_t = the amount of adsorption at equilibrium and at time t

k_{ad} = rate constant of the pseudo first- order adsorption process

The integrated rate law after the application of the initial condition of q_t = 0 at t= 0, becomes:

$$\log(q_e - q_t) = log q_e - \frac{k_{ad}t}{2.303} \qquad (7)$$

Plot of log (q_e - q_t) versus t gives a straight line for the first order adsorption kinetics, which allow computation of the adsorption rate constant, k_{ad}.

This equation differs from a true first order equation in two ways:

(i) The parameter k_{ad} (q_e-q_t) does not represent the number of available sites

(ii) The parameter log (q_e) is an adjustable parameter and often it is found to be not equal to the intercept of the plot of log (q_e-q_t) versus t, whereas in a true first order log (q_e) should be equal to the intercept.

In such cases, applicability of the second order kinetics has to be tested with the rate equation (Ozturk & Kavak, 2005; Sharma & Bhattacharya, 2004).

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (8)$$

where k_2 = the second order rate constant in g/(mg)(min)

From the boundary conditions, t = 0 to t = t and qt = 0 to qt = qt, the integrated form of the equation becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \qquad (9)$$

which can be written in the linear form,

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e}\right)t \qquad (10)$$

where $h = k_2 q_e^2$ can be regarded as the initial sorption rate as t → 0. Under such circumstances, the plot of $\frac{t}{qt}$ vs t should give a linear relationship, which allows computation of q_e, k, and h.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

This chapter details on the steps in preparing experimental materials as well as their characterization and experimental procedure for adsorption.

3.1.1 Preparation of Rice Husk-Based Adsorbent

The preparation of the rice husk-based adsorbent will be based on the method applied by Daffalla et al. (2010). Rice husk will be obtained from a rice mill. Firstly, the rice husk will be washed thoroughly with distilled water to remove soil and clay. Then it will be dried in air at 105^oC in an oven for 24 hours.

Next, the rice husk will be subjected to thermal treatment where they will be burned at the temperature of 300, 400 and 600^oC to determine the optimum burning temperature. At these different temperatures, different materials will be produced. Considerable amount of carbon will be present after burning at 300^oC, while more silica will be present at 400^oC. High amorphous silica would be produced after burning at 600^oC. Two samples will be burned at 300^oC, one for one hour and the other for four hours. A sample for each 400^oC and 600^oC will be burned for four hours. Two samples will be treated chemically for this research. A sample will be treated with 13 M sulphuric acid (H_2SO_4) at the ratio of 100 mL of sulphuric acid for every 20 g of raw rice husk where it will be heated to $175\text{-}180^oC$ for 20 minutes with occasional stirrings. Another sample will be treated using 0.5 M sodium hydroxide solution (NaOH) for 4 hours.

Next, the produced rice husk-based adsorbent will be milled and sieved with openings of 250-500 μm.

3.1.2 Preparation of Chromium-Bearing Solution

A stock Cr(VI) solution (1000 mg/L) will be prepared in distilled water using potassium dichromate ($K_2Cr_2O_7$). All other working solutions will be prepared by diluting the stock solution by distilled water.

3.1.3 Preliminary Test

A preliminary adsorption test will be carried out to determine which of the burned rice and chemically treated husk-based adsorbent has the highest adsorption capability. The test will be conducted by preparing 100 ml aqueous solution of 20 mg/L in concentration and 0.2 g of the six different types of rice husk-based adsorbents at different pH value (2-6) in conical flasks placed on the orbital shaker. The orbital shaker will be set to 150 rpm for 24 hours. The remaining unadsorbed hexavalent chromium will be analysed by atomic adsorption spectrophotometer to determine the highest adsorption capability among the four.

3.1.4 Detailed Adsorption Test

There are a number of studies done by other researchers which detailed on several factors that can affect the adsorption of hexavalent chromium (Hu et al., 2009; Souundarrajan et al., 2012). These tests will be conducted in duplicate for each of the factor as follows.

3.1.4.1 Effect of pH Value

The pH value is one of the factors that can affect the adsorption of chromium(VI). Several studies on adsorption involving rice husk-based adsorbent and other types of low-cost adsorbents have proven that pH value to be a significant factor (Chen et al., 2012; Matin et al., 2012). 0.2 g of the rice husk-based adsorbent with the highest adsorption capability will be used in this experiment in a 20 mg/L Cr(VI) solution with varying pH values of 2.0, 3.0, 4.0, 5.0 and 6.0. This experiment will be conducted at a temperature of 22^{o}C with a contact time of 24 hours.

3.1.4.2 Effect of Contact Time

Contact time is another factor affecting the adsorption rate of chromium(VI) (Altun and Pehlivan, 2012). A fixed amount of rice husk based-adsorbent dosage will be added to flasks containing aqueous solution of chromium(VI) at optimum pH and agitated between 5 minutes to 3 hours.

3.1.4.3 Effect of Adsorbent Concentration

The effect of adsorbent concentration on the adsorption of chromium(VI) will be studied by applying different dosage into aqueous solution of chromium(VI). 100 mL of chromium(VI) bearing water will be added in different conical flasks containing 0.1-1.0 g of the rice husk based-adsorbent with the highest adsorption capacity.

3.1.5 Adsorption Isotherm

Isotherm studies need to be carried out in order to determine the adsorptive capacity of rice husk-based adsorbent for chromium(VI). The equilibrium adsorption data will be fitted into Freundlich and Langmuir isotherm models.

3.1.6 Desorption Test

The necessity to study the desorption of chromium(VI) from exhausted rice husk-based adsorbent rises with the need to understand the nature of the adsorption itself. Improper disposal of the exhausted may pose adverse impacts to the environment if the hexavalent chromium leaches out from the adsorbent. In the desorption test, dried rice husk-based adsorbent containing chromium(VI) will be subjected to elution by 1 M of solution of KOH, NaOH, HCl and H_2SO_4. The efficiency of the desorption will be calculated using the following expression (Genç et al., 2003):

$$Desorption\ (\%) = \frac{amount\ of\ chromium\ (VI)\ desorbed}{amount\ of\ chromium\ (VI)\ adsorbed}\ X\ 100$$

3.2 Apparatus and Chemicals

3.2.1 Apparatus

1. Pipettes.
2. Volumetric flasks.
3. Conical flasks.
4. Orbital shaker.
5. DR 2800™ Portable Spectrophotometer.
6. Oven.
7. Sieve.
8. Reagent bottles.
9. 0.45 µm membrane filter and filtration apparatus.
10. Analytical balance.

3.2.2 Chemicals and Materials

1. Potassium dichromate, ($K_2Cr_2O_7$).
2. Sodium hydroxide, ($NaOH$).
3. Potassium hydroxide, (KOH).
4. Hydrochloric acid, (HCl).
5. Sulphuric acid, (H_2SO_4).
6. Distilled water.
7. Rice husk.

3.3 Project Activities and Key Milestones

The activities and targets for both FYP I and FYP II have been planned out to complete the project smoothly. These are shown in Table 2 and 3 respectively.

Table 2: Project Activities and Key Milestones for FYP I

No.	**Detail/Week**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	▒	**8**	**9**	**10**	**11**	**12**	**13**	**14**
1	Selection of Project Topic	■							▒							
2	Literatures Review		■	■	■	■			▒							
3	Submission of Extended Proposal						★		▒							
4	Preparation of Rice Husk-Based Adsorbent							■	▒	■						
5	Proposal Defence								▒		★					
6	Preliminary Experiment								▒			■	■	■		
7	Submission of Interim Draft Report								▒						★	
8	Submission of Interim Report								▒							★

Legends:

■ Project Activity ★ Key Milestone ▒ Mid-Semester Break

Table 3: Project Activities and Key Milestones for FYP II

No.	Detail/Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Experiment Execution	■	■	■	■	■	■	■	░	■	■	■	■				
2	Submission of Progress Report								░	★							
3	Compare the Efficiency with other Adsorbents								░				■				
4	Pre-EDX								░				★				
5	Submission of Draft Report								░					★			
6	Submission of Dissertation (soft bound)								░						★		
7	Submission of Technical Paper								░						★		
8	Oral Presentation								░							★	
9	Submission of Project Dissertation (Hard Bound)								░								★

Legends:

■ Project Activity ★ Key Milestone ░ Mid-Semester Break

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Preliminary Results

A preliminary experiment was conducted to identify which of the prepared rice husk-based adsorbent has the highest adsorptive capabilities in different pH values as mentioned in part 3.1.3. The result of the test is presented as figures that follow.

Table 4: Preliminary Test Results

No.	Category	pH	Init. Conc. (mg/L)	Rdg 1	Rdg 2	Rdg 3	Avg	Adsorption %
1	RHA 300C, 1h	2	20.00	3.94	3.86	3.90	3.90	80.50
2	RHA 300C, 1h	3	20.00	10.50	10.60	11.00	10.70	46.50
3	RHA 300C, 1h	4	20.00	16.60	17.00	16.80	16.80	16.00
4	RHA 300C, 1h	5	20.00	17.20	17.00	17.20	17.13	14.30
5	RHA 300C, 1h	6	20.00	16.50	17.50	17.90	17.30	13.50
6	RHA 300C, 4h	2	20.00	13.75	14.00	13.82	13.86	30.70
7	RHA 300C, 4h	3	20.00	15.95	17.00	17.30	16.75	16.20
8	RHA 300C, 4h	4	20.00	16.60	16.60	16.60	16.60	17.00
9	RHA 300C, 4h	5	20.00	9.60	10.30	11.00	10.30	48.50
10	RHA 300C, 4h	6	20.00	12.60	16.55	12.60	13.92	30.40
11	RHA 400C, 4h	2	20.00	17.80	17.75	17.38	17.64	11.80
12	RHA 400C, 4h	3	20.00	18.70	19.55	19.65	19.30	3.50
13	RHA 400C, 4h	4	20.00	18.40	18.75	18.90	18.68	6.60
14	RHA 400C, 4h	5	20.00	18.35	18.35	18.55	18.42	8.00
15	RHA 400C, 4h	6	20.00	18.45	18.45	18.50	18.47	7.60
16	RHA 600C, 4h	2	20.00	19.15	19.10	19.35	19.20	4.00
17	RHA 600C, 4h	3	20.00	18.55	19.10	19.45	19.03	4.80
18	RHA 600C, 4h	4	20.00	17.40	18.25	18.65	18.10	9.50
19	RHA 600C, 4h	5	20.00	18.60	18.65	18.70	18.65	6.70
20	RHA 600C, 4h	6	20.00	18.35	18.85	18.95	18.72	6.40
21	Acid-Treated	2	20.00	0.03	0.02	0.02	0.02	99.90
22	Acid-Treated	3	20.00	0.02	0.02	0.02	0.02	99.90
23	Acid-Treated	4	20.00	0.02	0.02	0.02	0.02	99.90
24	Acid-Treated	5	20.00	0.03	0.03	0.04	0.03	99.80
25	Acid-Treated	6	20.00	0.05	0.05	0.05	0.05	99.70
26	Alkali Treated	2	20.00	17.65	17.95	18.10	17.90	10.50
27	Alkali Treated	3	20.00	17.70	17.85	18.25	17.93	10.30
28	Alkali Treated	4	20.00	17.65	17.95	18.10	17.90	10.50
29	Alkali Treated	5	20.00	19.60	19.75	19.80	19.72	1.40
30	Alkali Treated	6	20.00	20.00	20.40	19.50	19.97	0.00

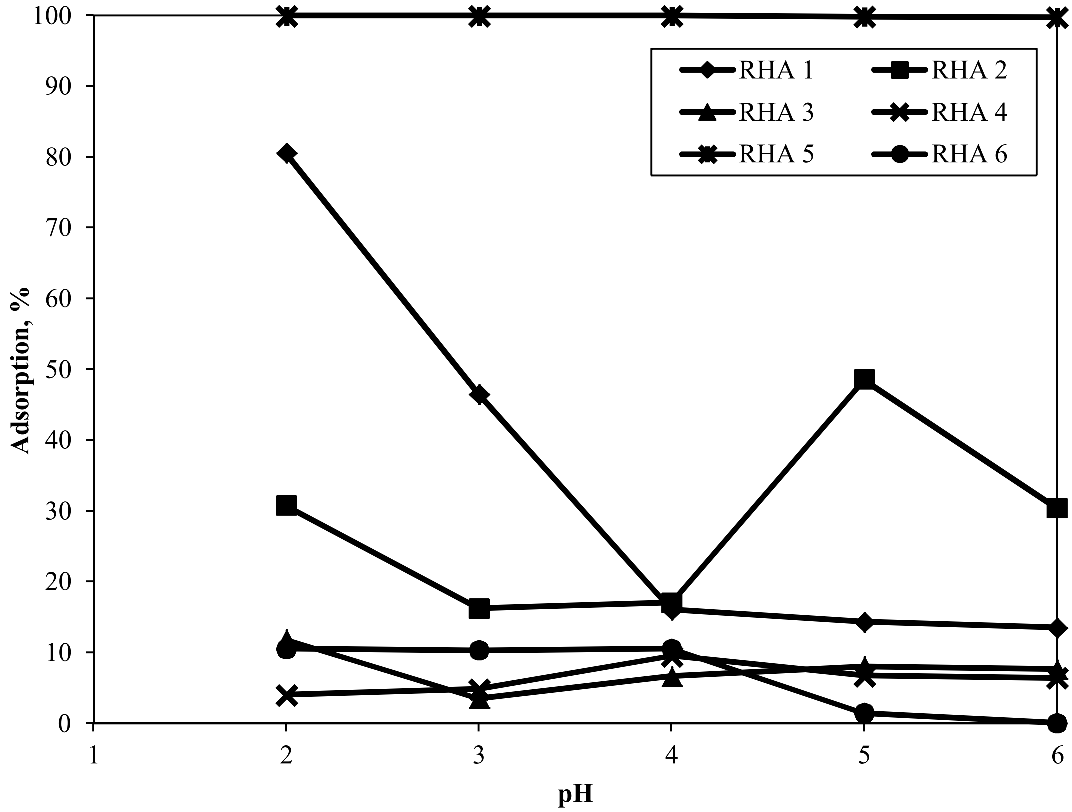

Figure 1: Rice Husk-based Adsorbents Adsorptive Capacity

From these data, more specific tests will be conducted on the subject as stated in part 3.1.4. Adsorbent 5 which was the acid-treated rice husk-based adsorbent demonstrated almost 100% of adsorption percentage for every pH value; hence the initial concentration of the chromium solution was increased from 20 mg/L to 60 mg/L to determine the optimum pH for this type of adsorbent. The following data was obtained from conducting same experiment but with 60 mg/L concentration and acid-treated rice husk-based adsorbent.

Table 5: Effect of pH on Acid-Treated RHA Adsorption

SL	Category	pH	Init. Conc. (mg/L)	Rdg 1	Rdg 2	Rdg 3	Avg	Adsorption %
1	Acid-Treated RHA	1	60.00	15.10	15.40	15.30	15.27	74.55
2	Acid-Treated RHA	2	60.00	19.30	20.80	19.00	19.70	67.10
3	Acid-Treated RHA	3	60.00	25.50	25.80	25.30	25.53	57.45
4	Acid-Treated RHA	4	60.00	26.70	27.20	26.40	26.77	55.38
5	Acid-Treated RHA	5	60.00	28.40	28.10	28.60	28.37	52.70
6	Acid-Treated RHA	6	60.00	27.60	28.50	28.42	28.17	53.00

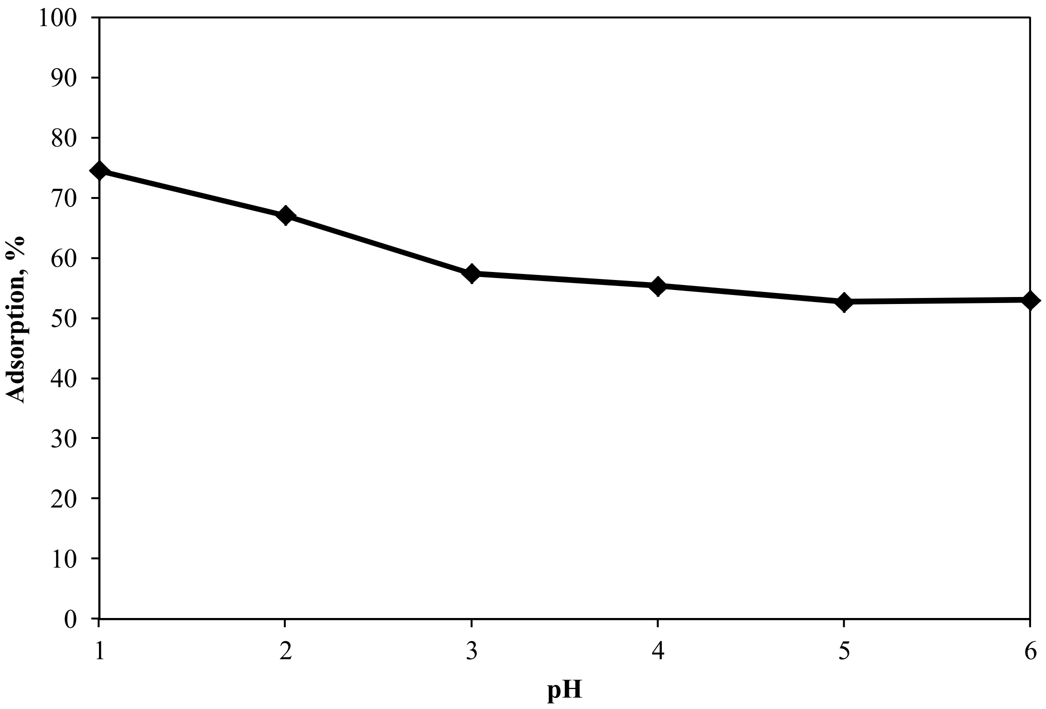

Figure 2: Effect of pH on Acid-Treated RHA Adsorption

It can be observed from the data obtained that adsorption percentage of chromium increases with the decrease in pH value. The percentage of adsorption at pH 1 is the highest and at pH 6 is the lowest. For the purpose of this research, pH 2 will be opted as the optimum pH value as the amount of hydrochloric acid needed to achieve pH 1 is much higher than it is to achieve pH 2. This may lead to increment in treatment cost in terms of chemicals used in a large scale treatment process. A similar study on chromium(VI) adsorption by Chaudhuri and Azizan in 2012, where they employed coconut coir activated carbon in their study, reported insignificant increase in adsorption percentage for pH values lower than 2. This also justifies the selection of pH value of 2 as the optimum pH for adsorption tests throughout this study.

Dichromate anion, $Cr_2O_7^{2-}$, present in potassium dichromate was the source of chromium(VI) of the aqueous solution. Chromate, CrO_4^{2-}, and dichromate, $Cr_2O_7^{2-}$, exist in a chemical equilibrium of $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$ in the aqueous solution, hence according to the predominance diagram, the position of the equilibrium depends on both pH and the analytical concentration of chromium. The dichromate ion can become the predominant ion in acidic solution and the chromate is the predominant species in alkaline solution. Maximum adsorption of chromium(VI) by the acid-treated rice husk-based adsorbent at low pH of 1 may be attributed to the presence of large amount of hydrogen ions (H^+) at such pH level.

4.2 Effect of Contact Time on Adsorption

Following up the preliminary experiment is the testing for contact time parameter in adsorption. In this experiment, four different concentrations, 60 mg/L, 80mg/L, 100 mg/L and 120 mg/L were prepared and the dosage of adsorbent was fixed to 0.2 g. The samples were then shaken using orbital shaker from 5 minutes to 3 hours. Presented in the following is the data for the test.

Table 6: Contact Time Experiment Results

No.	Init. Conc. (mg/L)	Contact Time (Min)	Rdg 1	Rdg 2	Rdg 3	Avg	Adsorption %
1	60.00	5.00	40.40	40.20	40.10	40.23	32.90
2	60.00	15.00	39.50	39.50	38.70	39.23	34.60
3	60.00	30.00	33.00	34.90	35.70	34.53	42.40
4	60.00	60.00	31.70	32.10	32.20	32.00	46.60
5	60.00	90.00	24.40	25.50	25.70	25.20	58.00
6	60.00	120.00	20.20	19.20	19.50	19.63	67.20
7	60.00	150.00	22.40	20.00	19.50	20.63	65.60
8	60.00	180.00	20.00	18.50	20.60	19.70	67.10
9	80.00	5.00	60.90	60.80	71.00	64.23	19.70
10	80.00	15.00	54.30	56.50	56.70	55.83	30.20
11	80.00	30.00	50.20	48.70	49.60	49.50	38.00
12	80.00	60.00	47.40	47.60	47.70	47.57	40.50
13	80.00	90.00	37.90	37.60	37.80	37.77	52.70
14	80.00	120.00	34.60	35.00	35.10	34.90	56.30
15	80.00	150.00	34.40	34.80	35.70	34.97	56.20
16	80.00	180.00	34.80	36.70	32.90	34.80	56.50
17	100.00	5.00	76.80	77.00	77.60	77.13	22.90
18	100.00	15.00	70.40	70.60	70.40	70.47	29.50
19	100.00	30.00	67.80	66.80	67.60	67.40	32.60
20	100.00	60.00	60.40	60.40	60.40	60.40	39.60
21	100.00	90.00	58.40	57.00	56.80	57.40	42.60
22	100.00	120.00	53.20	53.40	53.40	53.33	46.70
23	100.00	150.00	53.60	55.00	55.80	54.80	45.20
24	100.00	180.00	53.80	55.50	55.60	54.97	45.00
25	120.00	5.00	90.20	90.20	90.00	90.13	24.90
26	120.00	15.00	86.20	86.60	87.00	86.60	27.80
27	120.00	30.00	79.80	79.80	80.00	79.87	33.40
28	120.00	60.00	75.00	76.80	75.20	75.67	36.90
29	120.00	90.00	72.40	73.40	73.80	73.20	39.00
30	120.00	120.00	68.20	68.00	68.20	68.13	43.20
31	120.00	150.00	68.80	70.00	68.80	69.20	42.30
32	120.00	180.00	68.00	68.80	69.00	68.60	42.80

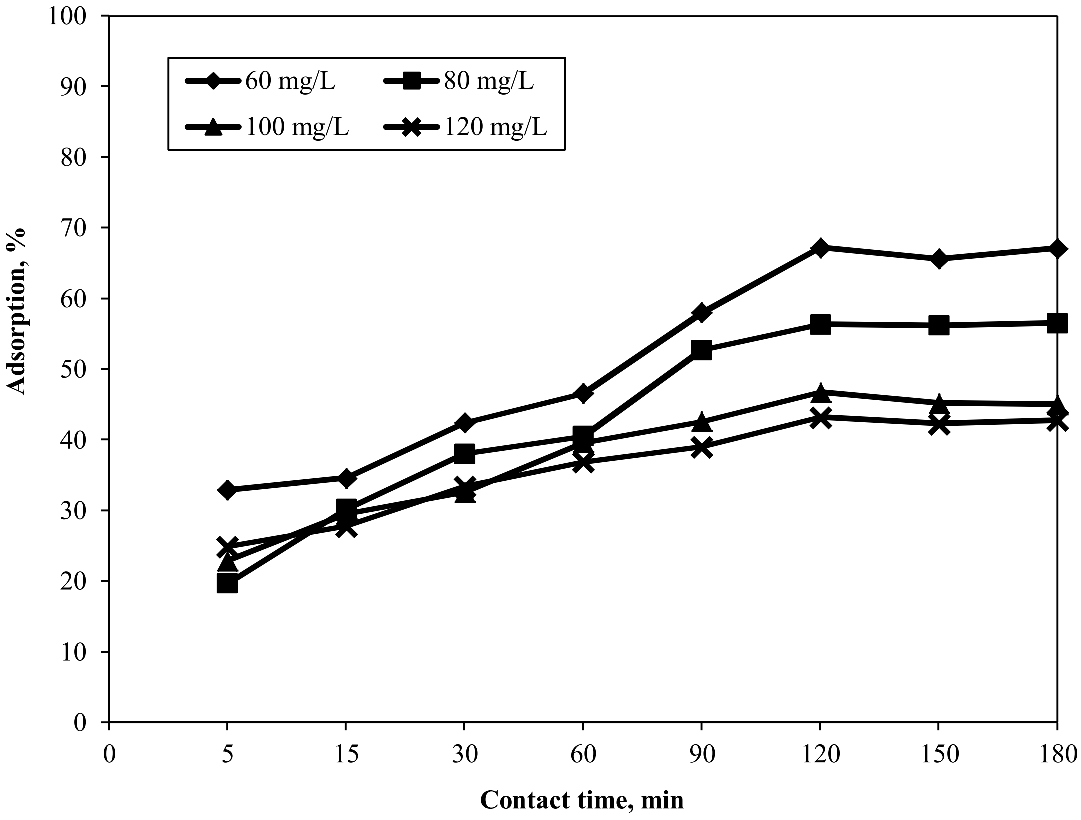

Figure 3: Graph of Adsorption Percentage against Contact Time

The pattern that can be understood from the results of this experiment is that adsorption percentage increases with the increase in contact time. However, when the contact time reaches the threshold of two hours, any increment in contact time then would not have significant improvement in adsorption ratio. Hence it can be deduced that the equilibrium time for adsorption within the same scenario is two hours, regardless of the concentration of chromium solution.

4.3 Effect of Adsorbent Dosage on Adsorption

The next parameter that was tested was how adsorbent dosage affects the adsorption percentage of chromium-bearing solution. For this experiment, six different adsorbent dosages that were 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 g were added into 100 mL of 80 mg/L chromium solution and shaken for two hours at the pH value of 2. The following was the data obtained from the test.

Table 7: Adsorbent Dosage Experiment Results

No.	Init. Conc. (mg/L)	Adsorbent Dose (g)	Rdg 1	Rdg 2	Rdg 3	Avg	Adsorption %
1	80.00	0.10	60.20	60.20	60.40	60.27	24.60
2	80.00	0.20	34.60	35.00	35.10	34.90	56.30
3	80.00	0.40	23.70	23.70	23.90	23.77	70.20
4	80.00	0.60	10.80	11.10	10.90	10.93	86.30
5	80.00	0.80	0.06	0.04	0.04	0.05	99.90
6	80.00	1.00	0.32	0.33	0.31	0.32	99.60

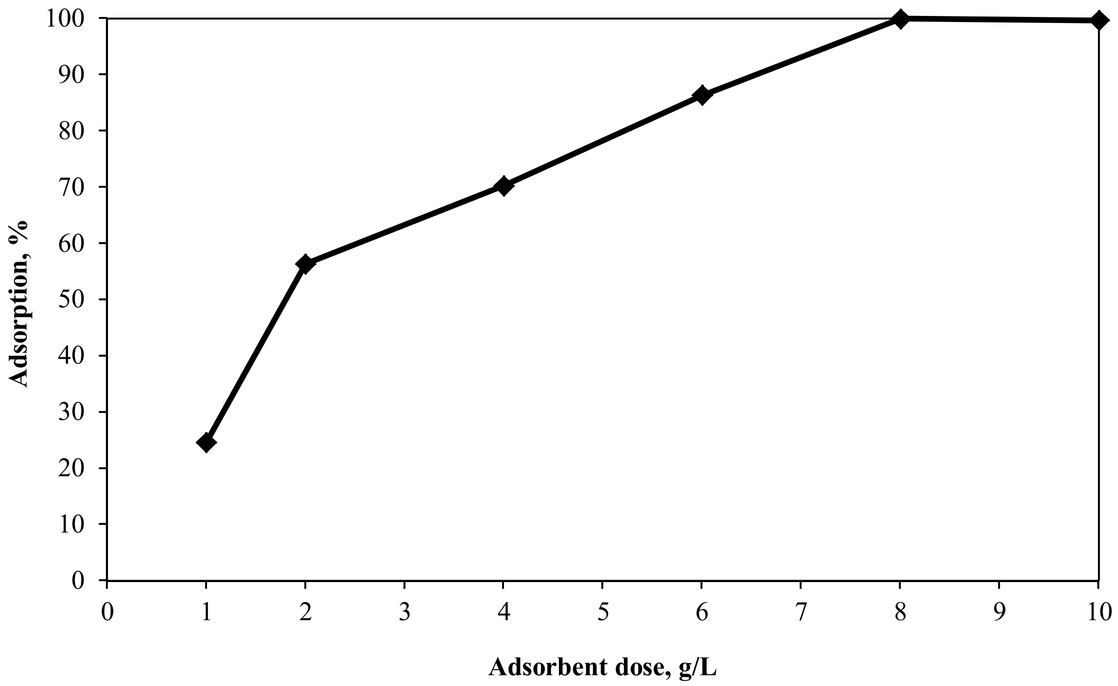

Figure 4: Graph of Adsorbent Dosage against Adsorption Percentage

From this experiment, the equilibrium adsorbent dosage was identified to be 8 g/L of chromium solution. With the increase in adsorbent dosage, adsorption percentage also shows and increment. However, no increment was identified at 10 g/L as the adsorption was already at 100%.

4.4 Adsorption Kinetics

In order to identify the kinetics of chromium(VI) adsorption by acid-treated rice husk-based adsorbent, two commonly used kinetic models, pseudo first-order (Lagergren, 1998) and pseudo second-order (Ho et al., 2000) were employed.

$$\frac{dq}{dt} = k_1(q_e - q_t) \qquad (1)$$

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \qquad (2)$$

q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), q_t is the amount of solute adsorbed at time *t* per unit weight of adsorbent (mg/g), and k_1 and k_2 are reaction rate constants. The following linearized time dependent functions were obtained by integrating and rearranging Equations 1 and 2 for the boundary conditions $t = 0 \text{ to} > 0$ and $q = 0 \text{ to} > 0$.

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \qquad (4)$$

Presented in the following are the data obtained for kinetic studies of chromium(VI) adsorption using acid-treated rice husk-based adsorbent.

Table 8: Pseudo First-Order Reaction Rate Constants for Chromium(VI) Adsorption by Acid-Treated RHA

Init. Conc. (mg/L)	q_e (exp) (mg/L)	k_1	q_e (calc.) (mg/L)	R^2
60.00	20.18	0.014	11.90	0.93
80.00	22.55	0.020	16.60	0.89
100.00	23.33	0.020	12.40	0.99
120.00	25.93	0.010	11.16	0.97

Table 9: Pseudo Second-Order Reaction Rate Constants for Chromium(VI) Adsorption by Acid-Treated RHA

Init. Conc. (mg/L)	q_e (exp) (mg/L)	k_2	q_e (calc) (mg/L)	R^2
60.00	20.18	0.0028	21.20	0.95
80.00	22.55	0.0023	24.70	0.97
100.00	23.33	0.0037	24.50	0.99
120.00	25.93	0.0044	26.60	0.99

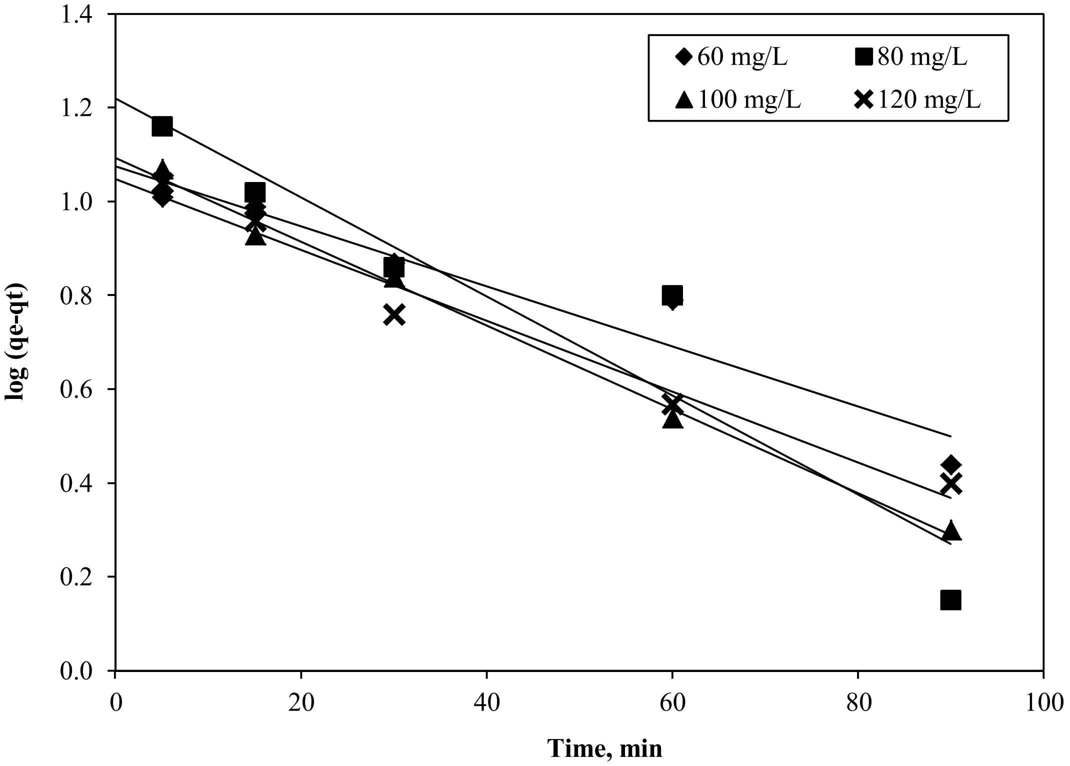

Figure 5: Pseudo First-Order Kinetic Plot for Chromium(VI) Adsorption by Acid-Treated RHA

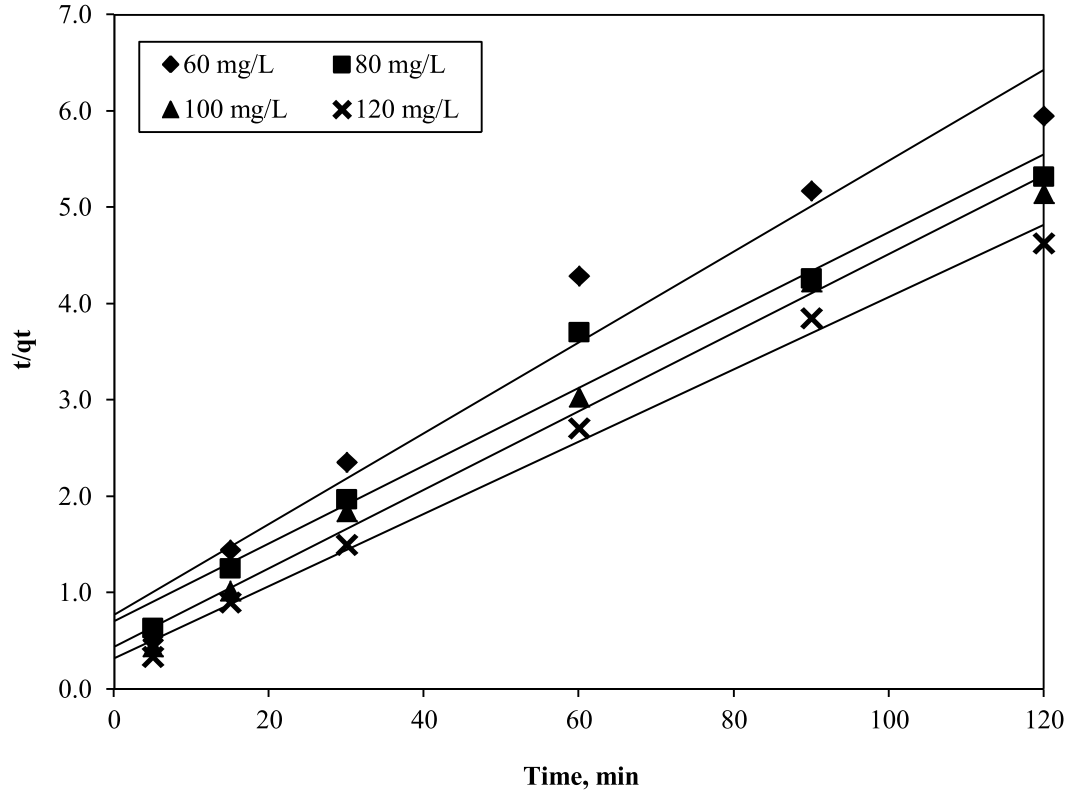

Figure 6: Pseudo Second-Order Kinetic Plot for Chromium(VI) Adsorption by Acid-Treated RHA

From the plots produced, we can notice that the R^2 values and the pattern of the plots indicate the adsorption of chromium(VI) by acid-treated rice husk-based adsorbent complied with the kinetic models well. This compliance with the pseudo second-order kinetic model strongly suggests that chemical adsorption exists between chromium(VI) and acid-treated rice husk-based adsorbent.

4.5 Adsorption Isotherm

Isotherms for chromium(VI) adsorption by acid-treated rice husk-based adsorbent were determined by batch equilibrium test using an optimum contact time of 2 hours and optimum pH value of 2. The isotherms were fitted into the linear form of the Langmuir equation and Freundlich equation as presented in the following plots.

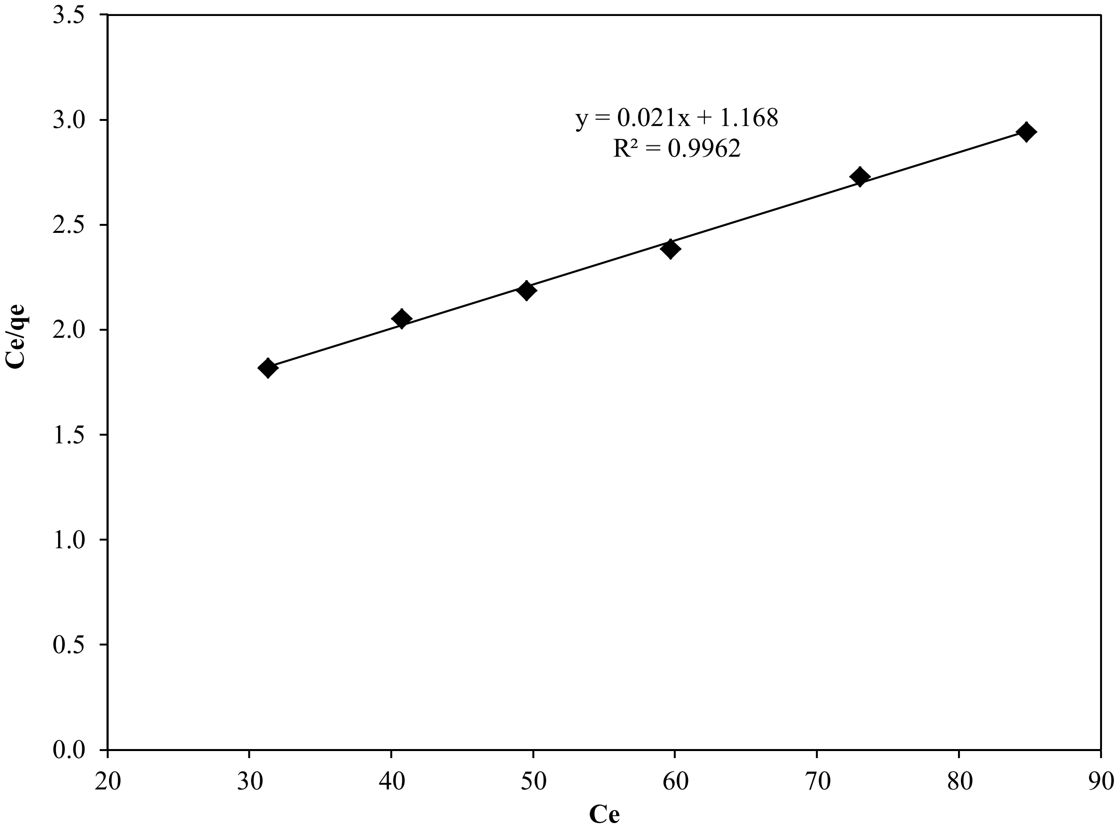

Figure 7: Langmuir Isotherm for Chromium(VI) Adsorption by Acid-Treated RHA

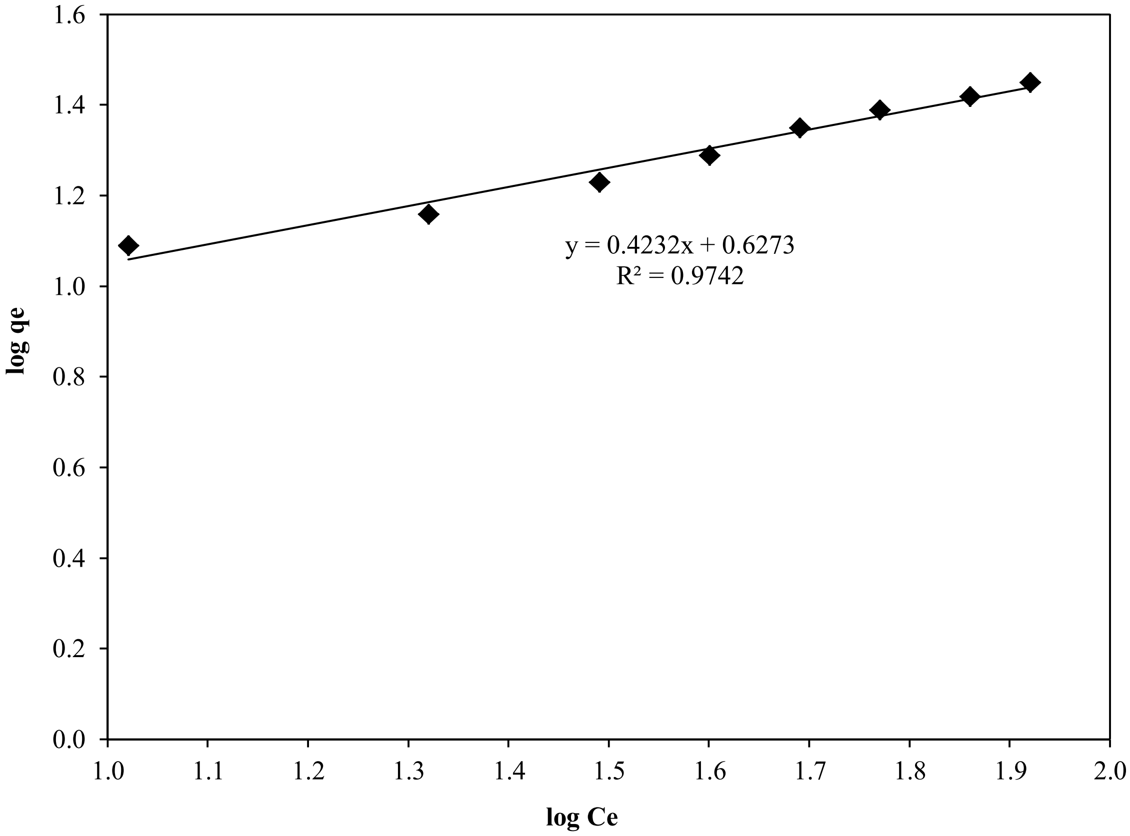

Figure 8: Freundlich Isotherm for Chromium(VI) Adsorption by Acid-Treated RHA

The values of Langmuir constants and Freundlich constants are shown in the following table.

Table 10: Langmuir and Freundlich Isotherm Constants for Chromium(VI) Adsorption by Acid-Treated RHA

Adsorbent	Langmuir Constant		Freundlich Constant	
	Q_o	b	K_f	$1/n$
Acid-Treated RHA	47.62	0.018	4.24	1.48

Based on these values of constants, it indicates that acid-treated rice husk-based adsorbent has a high adsorption capacity for chromium(VI). Some comparison of adsorption capacity between various materials used by researchers worldwide is presented in the following table.

Table 11: Chromium(VI) adsorption capacity of activated carbon prepared from different waste material and bituminous coal

Material	Adsorption Capacity (mg/g)	pH	Reference
Coconut shell	20.00	2.5	(Alaerts et al., 1989)
Coconut shell	6.00	3.0 - 4.0	(Selomulya et al., 1999)
Dust coal	4.40	3.0 - 4.0	(Selomulya et al., 1999)
Hazelnut shell	17.70	2.0	(Cimino et al., 2000)
Used tyre	48.10	2.0	(Hamadi et al., 2001)
Bituminous coal	44.40	2.0	(Hamadi et al., 2001)
Sawdust	1.90	2.0	(Hamadi et al., 2001)
Petroleum pitch	23.70	3.0	(Park et al., 2003)
Almond shell	20.00	1.0	(Demirbas et al., 2004)
Apricot stone	21.00	1.0	(Demirbas et al., 2004)
Hazelnut shell	170.00	1.0	(Kobya, 2004)
***Terminalia arjuna* nuts**	28.40	1.0	(Mohanty et al., 2005)
***Hevea brasiliensis* sawdust**	44.10	2.0	(Karthikeyan et al., 2005)
Palm shell	12.60	3.0 - 4.0	(Owlad et al., 2010)
Bituminous coal	27.80	1.5 - 2.0	(Chaudhuri & Azizan, 2012)
Coconut coir	38.50	1.5 - 2.0	(Chaudhuri & Azizan, 2012)
Acid-Treated RHA	47.62	2.0	(This study)

4.6 Desorption Study

A desorption test was conducted as stated on part 3.1.6 of this report to study the desorption capacity of exhausted acid-treated rice husk-based adsorbent. Obtained data were tabulated and plotted as follow.

Table 12: Desorption Capacity of Acid-Treated RHA

Chemical	Adsorbed Chromium (mg)	Reading 1	Reading 2	Reading 3	Average	Desorption %
NaOH	98.900	4.800	3.800	3.900	4.167	4.21
KOH	98.900	1.900	1.800	1.900	1.867	1.89
HCl	98.900	0.110	0.100	0.110	0.107	0.11
H_2SO_4	98.900	0.046	0.045	0.045	0.045	0.05

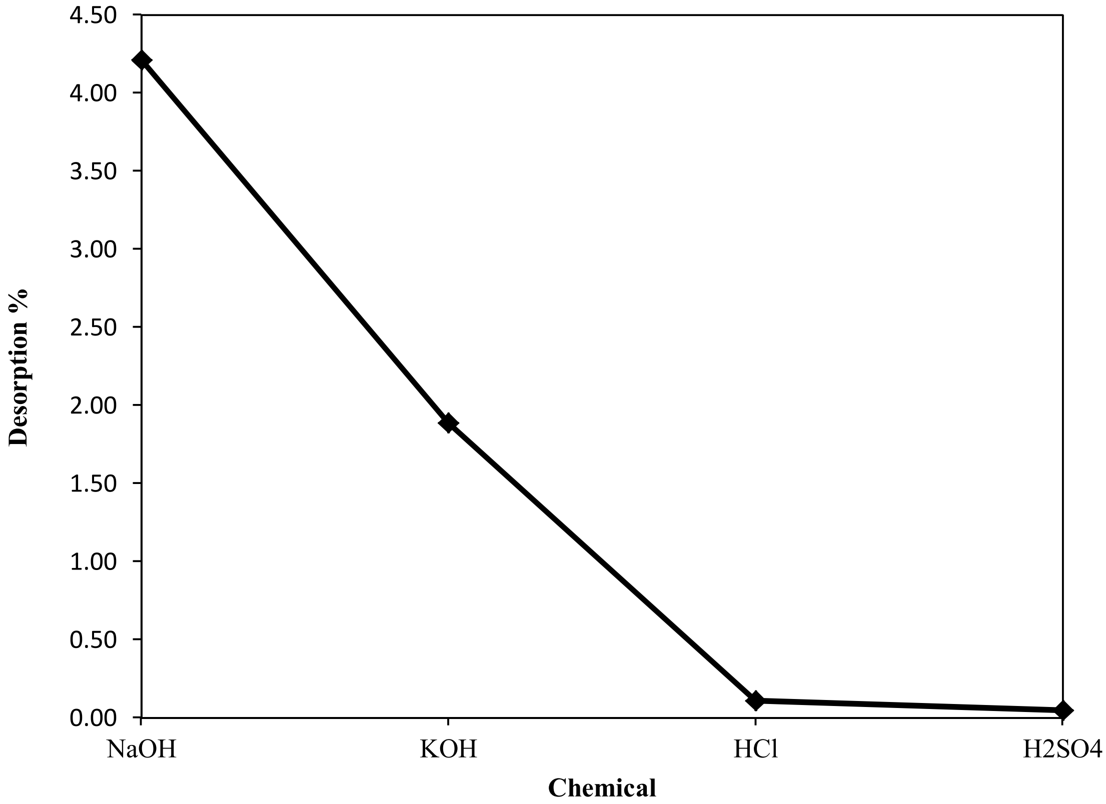

Figure 9: Desorption Percentage of Acid-Treated RHA

From these data presented, it can be deduced that the desorption capacity of acid-treated rice husk-based adsorbent is very low. The highest desorption percentage obtained was 4.21% using sodium hydroxide. Thus, exhausted acid-treated rice husk-based adsorbent is not suitable to be reused and must be disposed of properly to prevent leaching. Due to its strong chemical bonds as suggested in the pseudo second-order results, it is very unlikely for leaching to occur naturally in the environment. However, precautionary steps should be taken to prevent leaching from happening.

4.7 Characterization of Acid-Treated RHA

4.7.1 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy was conducted on acid-treated RHA as well as exhausted acid-treated RHA to identify which functional groups were responsible for the chemical adsorption of chromium(VI) onto the surface of acid-treated RHA. Presented in the following are the two plots obtained from FTIR test.

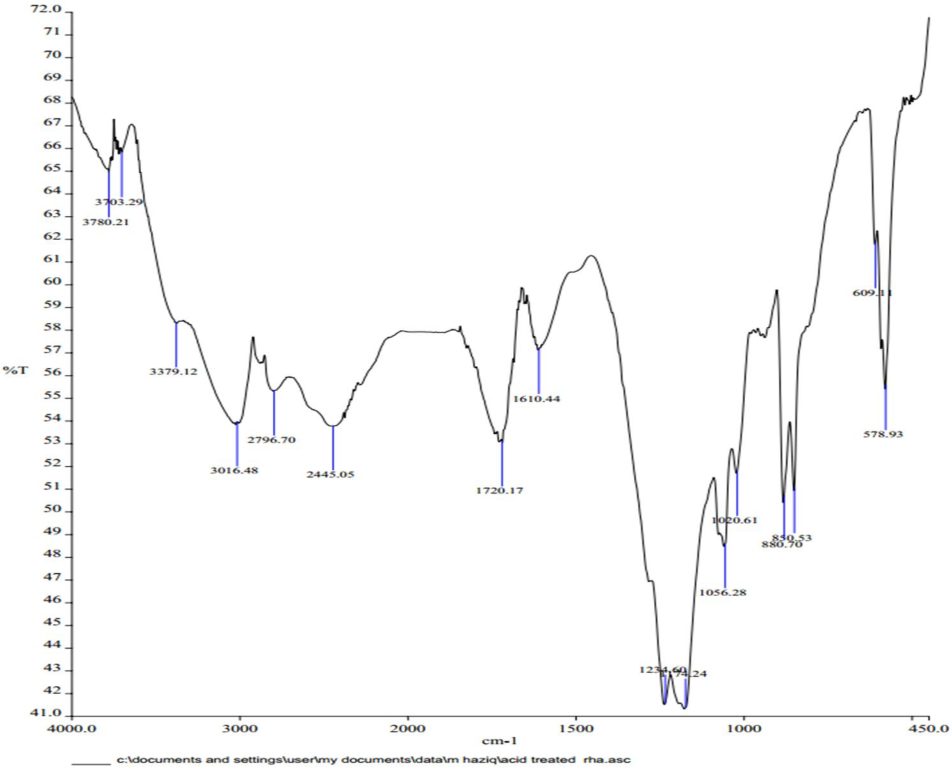

Figure 10: FTIR of Acid-Treated RHA

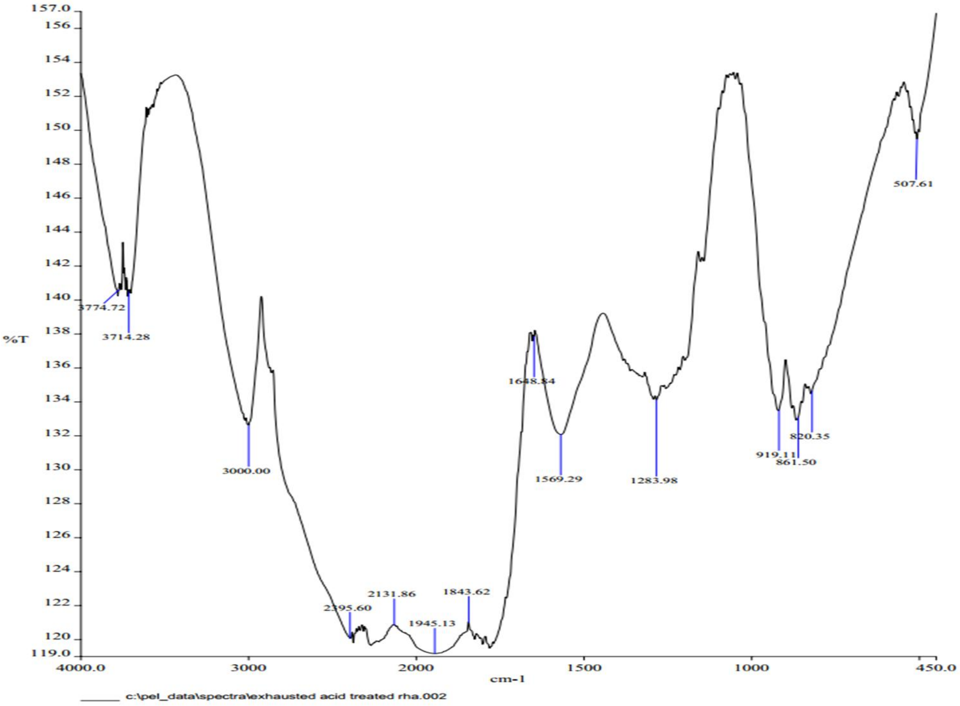

Figure 11: FTIR of Exhausted Acid-Treated RHA

From the plots presented, it was found out the functional groups responsible in the adsorption of chromium(VI) belong in the wavelength range of 2400 – 1700 cm^{-1}. Comparing this information with the table of IR Absorptions for Representative Functional Groups, it was identified that C=O stretches belonging to various functional groups such as aldehydes, ketones, carboxylic acids, esters and acid chlorides are responsible for this reaction as well as C,N triple bond stretch in nitriles, -N=C=O stretch in isocyanates and the –N=C=S stretch in isothiocyanates.

4.7.2 Scanning Electron Micrograph (SEM)

Scanning Electron Microscopy was conducted on acid-treated rice husk-based adsorbent to characterize the surface of the adsorbent. The following figure demonstrates the micrograph produced from the characterization.

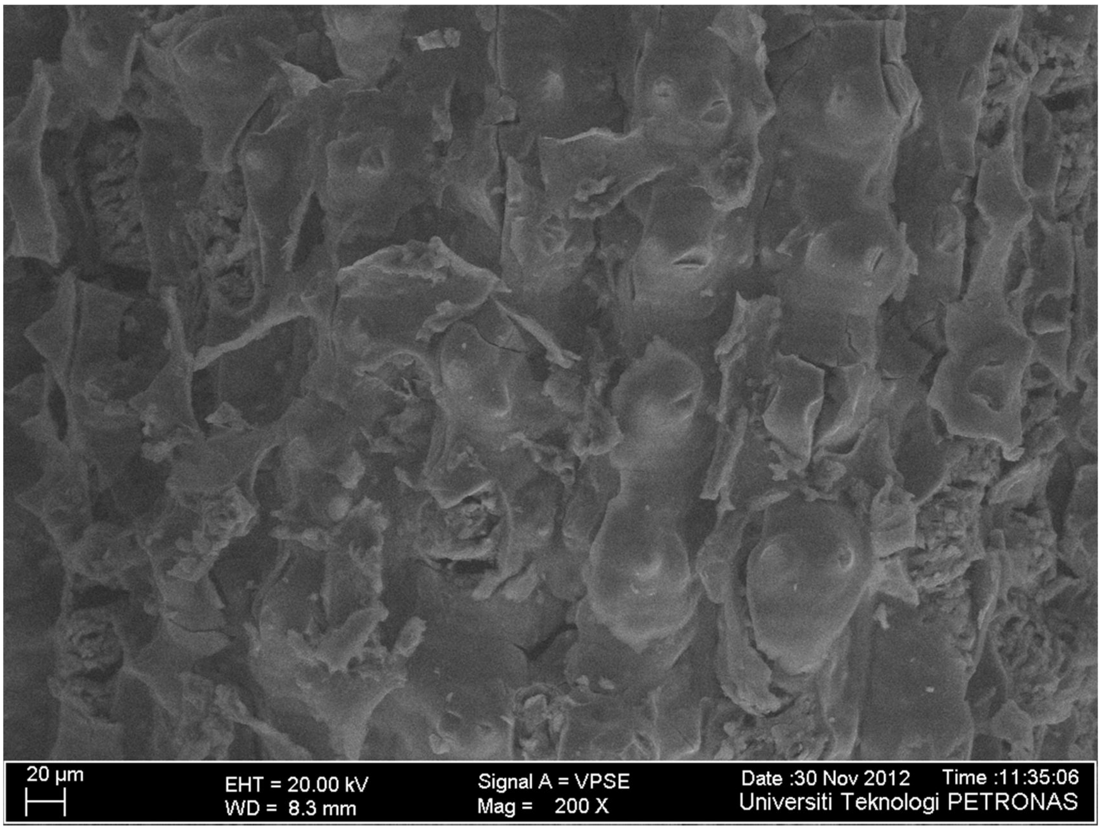

Figure 12: SEM of Acid-Treated RHA

The micrograph displayed uneven and rough surface on the acid-treated RHA. These provided a large surface area for chemical adsorption between chromium(VI) and acid-treated RHA to occur during contact.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

From the results recorded in the preliminary experiment, rice husk-based adsorbent has the capacity to replace commercial adsorbents used in the treatment of Cr(VI)-contaminated waters. All six of the samples had shown a significant number in adsorptive capabilities, with a value of as high as 99.90% in the adsorption of hexavalent chromium from aqueous solution where the chromium concentration was 20 mg/L. Detailed experiments conducted to further comprehend the adsorptive capacity and capability of rice husk-based adsorbents also had been showing positive results and relevant with the objectives of this research. Optimum pH for adsorption experiments involving rice husk-based adsorbents in general was found to be at pH 2 while the equilibrium contact time was identified to be 2 hours. Equilibrium dose had been tested and the result highlighted 8 g/L of chromium solution as the optimum dose. As for kinetic studies, adsorption of chromium(VI) by using acid-treated rice husk-based adsorbent fitted well into both pseudo first-order and pseudo second-order kinetic models and to top that, adsorption isotherm studies had determined its adsorptive capacity to be as high as 47.62 mg/g. Desorption study had shown that acid-treated rice husk-based adsorbent has very low desorption percentage, hence it is not suitable to be recovered and reused for treatment purposes as well as it requires a proper way of disposal after use. Its compliance to the pseudo second-order kinetic model suggested strong chemical bonds exist between adsorbents and chromium, thus the likelihood of leaching to occur is low. The acid-treated RHA as well as exhausted acid-treated RHA were characterized by means of FTIR and responsible functional groups were identified. SEM also demonstrated rough and uneven surface on acid-treated RHA, justifying a large surface area for chemical adsorption between chromium(VI) and the adsorbent to occur. Thus, it can be concluded that rice husk-based adsorbent has the ability to come as an alternative to conventional methods of treating waters that have been polluted with hexavalent chromium, especially the rice husk-based adsorbent that has been treated chemically with acid.

5.2 Recommendation

Due to the nature of the experimental work present in this research, I highly recommend that the real world scenario is adopted into this effort. A deeper understanding on the real, current situation of hexavalent chromium contamination in the local as well as global environment should aid this research. Considering the fact that the ideal conditions existing in the experimental procedures may be difficult to be reproduced in the actual chromium contamination treatment, I suggest that visits to industries producing this kind of pollutant be conducted to understand their treatment method to prevent said circumstance.

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