Removal of Zn(II), Cu(II), Chemical Oxygen Demand (COD) and Colour from Anaerobically Treated Palm Oil Mill Effluent (POME) using Microwave Incinerated Rice Husk Ash (MIRHA)

By

Khairil Asraf bin Che Amat (10236)

Supervisor: AP Dr Shamsul Rahman Mohamed Kutty

Dissertation submitted in partial fulfilment of

The requirement for the

Bachelor of Engineering (Hons)

(Civil Engineering)

JAN 2011

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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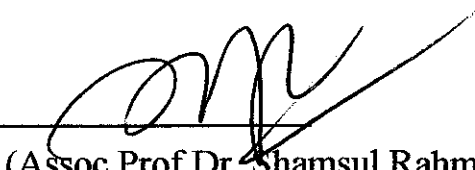A Project Dissertation submitted to the

Civil Engineering Programme

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Approved by,

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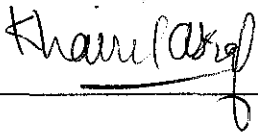
(Assoc Prof Dr. Shamsul Rahman Mohamed Kutty)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

JANUARY 2011

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the originality work contained herein have not been undertaken nor done unspecified sources or persons.

KHAIRILF ASRAF BIN CHE AMAT

ABSTRACT

Many have known and may have realized what heavy metals can cause to human bodies and the environment. The effect caused by heavy metals has become more severe day by day because of the rapid growth of technology which requires usage of these materials and low awareness upon minimizing their effect to human bodies. Nonetheless, research has been conducted in many parts of the world to remove or minimize the effect of heavy metals toward the environment. Therefore we have seen that many technologies have been introduced to attain its purpose. Effective coagulation technology, membrane filtration technology, ion exchange, electro dialysis, and reverse osmosis are some examples of removing heavy metals from the water. About 3 tonnes of POME was produced for every ton of oil extracted in an oil mill. The POME produced contains high concentration of Chemical Oxygen Demand (COD) and color. The objective of this paper was to use the microwave incinerated rice husk ash (MIRHA) as a recycled adsorbent in removing $Cu(II)$, $Zn(II)$, COD and color from treated POME wastewater. Rice husk were burned at 800°C temperature to produce MIRHA and it was then soaked overnight in H_2SO_4. The effect of various dosages of MIRHA and contact time on removal of $Zn(II)$, $Cu(II)$, COD and colour from POME were conducted by batch study. The highest $Cu(II)$ removal of 88% was achieved at 50000 mg/L dosage of MIRHA at 12 hr contact time. While for $Zn(II)$, 74% removal was achieved at 50000 mg/L dosage of MIRHA at 18 hr contact time. Optimum removal of COD (41%) and colour (88%) was achieved at 40000 mg/L and 50000 mg/L dosage of MIRHA at 6 hr contact time, respectively. MIRHA proved to be effective in removing $Zn(II)$, $Cu(II)$, COD and colour from POME wastewater.

ACKNOWLEDGEMENT

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

It is known that Malaysia is currently one of the largest producer and exporter of palm oil in the whole world. Based on index mundi statistic website, Malaysia produced a total distribution of 16.8 million tons in 2005 itself, making it as the biggest production in the world. This economic-generate activity however contributes to an enormous amount of effluent that could pollute the environment if they are not properly treated. For every ton of crude palm oil produced, it is estimated that about 2.5 – 3.5 tons of palm oil mill effluent (POME) is generated (Ahmad, et, al., 2005).

In Malaysia, although biological treatment processes are widely applied, they are still incapable of meeting with the Department of Environment's (DOE) standard requirement. Therefore, they still have the potential of polluting the environment as the treated effluent is still colored and contained high concentration of non-biodegradable organics (COD/BOD ratio) which require further treatment (Fadhli, 2008).

Heavy metals are found to be in excessive amount in the industry and its contamination is commonly discussed amongst the environmentalists as they can cause serious water pollution and threat to the environment. It is necessary to treat metal-contaminated wastewater before discharging into water bodies or natural streams. Heavy metal removal from inorganic effluent can be achieved by conventional treatment process such as chemical precipitation, ion exchange, and electrochemical removal. These processes have significant disadvantages which are for instance, incomplete removal, high-energy requirements, and production of toxic-sludge (Eccles, 1999).

Even though discharge of heavy metals into the environment has decreased in many countries due to stringent legislations, the demand for an economic and environmental

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friendly method for heavy metals removal still exists (M.H Isa et. al., 2004). Thus, adsorption may offer an alternative solution as it has been widely proven to remove heavy metals and residue organics.

1.2 Problem Statement

Copper (Cu) is commonly found in industrial discharges e.g. circuit boards, metal surface treatments, mining operations, etc. Cu is an essential micronutrient, but at high doses it can cause anemia, stomach & intestinal disorder and kidney & liver damage. Zinc (Zn) is also an essential micronutrient, but excess zinc is toxic and can cause nausea, anemia, stomach cramp and skin irritation (Al-Madhoun et. al., 2005).

Colored effluent may not be an immediate concern when discharge to the streams or drains but issues such as interference with sunlight transmission and photosynthetic activity in receiving water bodies, aesthetic and some dye stuff potential carcinogenicity would warrant an adequate address of the problem (Yap, J. et. al., 2008).

The organic pollutants of wastewater are generally measured in terms of chemical oxygen demand (COD), biochemical oxygen demand (BOD) and total organic carbon (TOC). In reducing COD level, studies have shown that adsorption characteristics of fly ash and brick kiln ash are of alternative solution and can be used for decentralized applications (Rani Devi, et. al., 2005).

In this study, treated POME has been used as the wastewater for the case study where the amount of discharged POME has contributed to environment pollution. Malaysian Environmental Quality Act 1974 stated that palm oil products require an efficient and environmental-friendly management system in order to treat, utilize and dispose in accordance to reduce all kinds of pollution and maintain the water quality. Table 1.1 shows the parameter limits for effluent discharge. The effluent discharge must comply with the Malaysian Environmental Quality Act 1974 and Environmental Quality (Prescribed Premises) set by the Department of Environment (DOE), Malaysia.

Table 1.1: Prevailing effluent discharge standards for treated palm oil mills (Industrial Processes and The Environment, 1999).

PARAMETER		PARAMETER LIMITS	REMARKS
pH		5 – 9	
Temperature	°C	45	
Oil and Grease	mg/L	50	
BOD; 3-day, 30°C	mg/L	100	
(COD)	mg/L	-	No discharge standard after 1984
Suspended Solid	mg/L	-	No discharge standard after 1984
Ammonical Nitrogen	mg/L	150	Value of filtered sample
Total Nitrogen	mg/L	200	Value of filtered sample

The challenge of converting POME into an environmental friendly waste needs an efficient and effective treatment method. A reliable and cost-effective process is therefore in much need as the demand of inexpensive treatment is rising.

The present study focuses on reducing the amount of heavy metals and residue organics from treated POME taken at a nearby palm oil plant using microwave incinerated rice husk ash (MIRHA) as the adsorbent in an adsorption process. Agricultural wastes have been widely used as an adsorbent because of its abundance availability, low-cost, and effective due to its respective characteristics. Some of the reported low-cost adsorbents include saw-dust, bark, and leaves (M.H Isa et. al., 2004). Therefore, this study would like to investigate upon rice husk ash's effectiveness as an alternative adsorbent.

1.3 Objective

In the present study, the effectiveness of MIRHA as adsorbent in removing heavy metals and residue organics from treated POME was examined and analyzed.

The objectives of this research were focused to:

- Study the feasibility of MIRHA as an adsorbent to remove and reduce the amount of heavy metals (Zn and Cu), COD and color on POME
- Study the minimum contact time taken to remove and reduce the amount of heavy metals (Zn and Cu), COD and color on POME
- Study the optimum dosage needed on MIRHA to remove and reduce the amount of heavy metals, COD and color on POME

1.4 Scope of Study

This study was comprised of experimental work at laboratory scale. Actual POME was used as stock solution and heavy metals of interest (Zn and Cu) were added to vary the parameters. MIRHA was burned at 800°C in order to produce more silica. Batch studies were conducted using orbital shaker and the experiments conducted are at different contact time using different dosages. Parameters used to assess the performance of MIRHA were Cu, Zn, COD and color.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metals

2.1.1 Copper

Copper (Cu) is a reddish brown nonferrous mineral which has been used for thousands of years for various purposes. It is closely related with silver and gold, where its applications are varied in the modern life, ranging from coins to pigments (WiseGeek, 2011). It is commonly found in industrial discharges such as circuit boards, metal surface treatments, mining operations and many more (Al-Madhoun W.A, et. al., 2005). Copper is also widely used in production of wire, brass, cooking utensils, boiler pipe, and feritilizers (Ching T.T et. al., 1987). Copper is an essential element in plants and animals (including humans), or in other words an essential micronutrients for us.

However, excess amount of copper in our bodies could cause anemia, stomach & intestinal disorder and kidney & liver damage (Al-Madhoun W.A, et. al., 2005). Victims of Wilson's disease will steadily accumulate copper in the liver, central nervous system and kidneys (Kawata, 1984).

Reaserches have been done to minimize the amount of copper discharged in the effluent. Al-Madhoun W.A et al reported that use of ash from palm oil factory could be an alternative solution against the dispersion of Copper and Zinc in the water bodies to a permissible level. A sharp increase was seen in the amount of Cu adsorbed during the first 20 minutes of agitation time whereas the rate of adsorption decreased thereafter and completed after 120 minutes. The behavior of Cu adsorption was best described by Freundlich isotherms as it showed highest value of R^2(Al-Madhoun W.A, et. al., 2005).

2.1.2 Zinc

Zinc (Zn) is a metallic chemical element found in reasonable abundance around the world. It is used in a variety of alloys and compounds which have a range of uses, from sunscreen to fine art (WiseGeek, 2011). Zn is also produced by electroplating industries, one of the oldest industries that deal with surface finishing and metal deposition. It is an essential element for enzyme activators in humans, but it is toxic at levels of 100-500 mg/day (Flaviane V. Pereira, et. al., 2008).

Although it is one of the micronutrients to our bodies, excess of Zn can cause health problems such as stomach cramps, skin irritation, nausea and anemia. Very high levels of Zn can damage pancreas, upset protein metabolism and cause arteriosclerosis (Al-Madhoun W.A, et. al., 2005). Therefore, with its widespread of discharges into the environment, it is necessary to develop an alternative that could curb and reduce the amount of Zn in the wastewater.

Flaviane V. Pereira et al in their journal evaluate Zn removal from aqueous single metal solution and real electroplating wastewater on both batch and continuous experiments using fixed-bed columns prepared in laboratorial scale. For batch studies of single aqueous solution, the adsorption of Zn in modified sugarcane bagasse (MB1) and modified wood sawdust (MS1) reached equilibrium after 20 and 30 minutes. The adsorption isotherm was described in Langmuir isotherm where the linear plot of MS1 showed a greater adsorption capacity (Flaviane V. Pereira, et. al., 2008).

In other studies, use of ash from palm oil factory as an adsorbent for removing Zn through adsorption process has proved to be successful. Al-Madhoun et al reported that Zn had a sharp increase of adsorption in the first 10 minutes of agitation where it ended after 90 minutes with removal up to 50%. In test of optimum pH, the removal increased rather abruptly from pH 7-8 and was suspected of precipitation. Hence, pH 7 was chosen as the optimum pH. The adsorption isotherm was represented by Freundlich isotherms as it yielded highest values of R^2 (Al-Madhoun, et. al., 2005).

2.2 Chemical Oxygen Demand (COD)

The main constituents of domestic wastewater are proteins, carbohydrates, detergents, tannins, lignin, humic acid, fulvic acid and many other dissolved organic compounds (Devi R. et. al., 2005). Chemical Oxygen Demand (COD) is a measure of the oxygen equivalent of the organic matter content of the waste that is susceptible to oxidation by a strong chemical oxidant. Some organic wastes become oxidized in water without the intervention of bacteria and these deplete the dissolved oxygen in water. This is represented by COD (Malay Chaudri, 2011). This phenomenon could cause disturbance to the aquatic lives as they depend on dissolved oxygen in the water to live.

In recent years, increasing concerns of water pollution has created awareness of reducing organic matter from polluting the water bodies. This has led to the introduction of more strict legislation to control water pollution. However, high concentration of non-biodegradable organics (COD/BOD ratio) still requires further treatment (Fadhli, 2008).

According to Rani Devi et al (2005), brick kiln ash and fly ash are of potential adsorbents in reducing COD in domestic wastewater. Fly ash and brick kiln ash could give a maximum reduction in COD of 66.92% and 72.29% respectively, indicating positive results of reducing COD for test of contact time. The equilibrium was attained at 250 min and 300 min respectively for fly ash and brick kiln ash. The comparison between fly ash and brick kiln ash is its surface area. It is cited that the larger surface area gives better performance for the adsorption (Rani Devi et. al., 2005).

Emmanuel O.A et al (2008) reported to have removed COD from industrial wastewater using activated carbon prepared from animal horns. Optimum dosage of adsorbent for COD was 90 g/L and removal achieved was 90.62% for adsorbent dosage. The COD removal was seen at pH 5 with 90% efficiency. This may be attributed to the larger number of H^+ ions present. Adsorption behavior of activated carbon prepared from animal horns was best fitted by linear, Langmuir and Freundlich as the coefficient of determination (R^2) yields high values indicating that adsorption of COD have succeeded (Emmanual O.A. et. al., 2008).

2.3 Adsorption

Adsorption is the adhesion of atoms, ions, biomolecules of gas, liquids, or dissolved solids to a surface. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. It differs from adbsorption, in which a fluid permeates or is dissolved by a liquid or solid. The term sorption encompasses both processes. Adsorption is also a transient process requiring regeneration of adsorbents when adsorption capacity is saturated (Suzuki, 1997). Both adsorption and precipitation are the common methods used in removing heavy metals from municipal wastewater. Drawback of precipitation has led to an intensive use of adsorption process from various types of adsorbents (Kutty S.R.M. et. al., 2010).

Solubility of a molecule is one of the parameters representing the hydrophilicity. Figure 2.1 shows the solubility range of metals in order to for adsorption to occur. It also occurs that during the extraction of the molecule from aqueous phase to the surface of an adsorbent, the surface area that is in contact with the water becomes smaller, which influences interaction forces between the molecules and the surrounding water. This interaction forces explains the affinity between a molecule in the water surface which is quantitized in part by solvophonic interaction approach that takes into account Van der Waals energy, static energy, energy for formation of the cavity for a solute molecule and the surface tension for the interface (Azura, 2008).
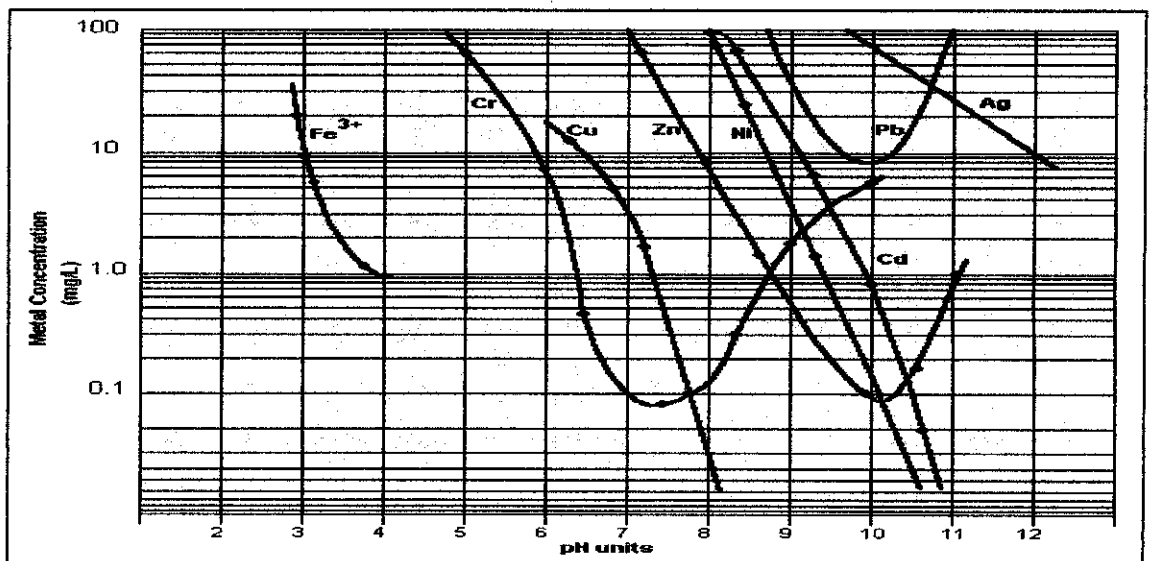
Figure 2.1: Solubility curve for heavy metals (Source: www.hoffland.net).

Adsorption processes for water treatment can be designed on the basis of equilibrium and rate information involved in transport and accumulation of specific components. The more hydrophobic the component is, the tendency to be extracted to the solid surface is higher. This is factual result especially hydrophobic solids such as carbon surfaces. Hydrophobicity of an organic molecule is judged from the balance of lipophilic groups such as paraffinic and aromatic groups and polar groups or hydrophilic groups such as hydroxyl and carboxyl groups (Suzuki, 1997).

2.3.1 Adsorption on Industrial By-Products

For many years now industrial by-products are being used or enhanced to become a new adsorbent as the wastes are abundantly available everywhere.Fly ashes were also investigated as adsorbents for removal of toxic metals. Exploration of bagasse, a solid waste from sugar industry for Cd(II) and Ni(II) removal was done by Gupta et al. (2003) with a pH ranging from 6 – 6.5. Alinnor (2007) used fly ash from coal – burning for removal of Cu(II) and Pb(II) ions. Barakat (2005) studied hydrous titanium oxide for adsorption of Cr(VI) and Cu(II) (Barakat M.A., 2005).

2.4 Rice Husk and Rice Husk Ash

Agricultural wastes, such as sawdust, coconut shell, bagasse, and rubber seed are often considered as solid wastes of agriculture, easily and widely available. These wastes materials are causing problems to dispose. Therefore, efforts have been made to recycle the materials as adsorbents in removing heavy metals or organic matters from the wastewater.

Current world production of rice paddy is 500 million tons and hence 100 million tons of rice husk are produced. Its characteristics of tough, woody, abrasive nature of hulls, low nutritive properties, resistance to weathering, the great bulk, and high ash content have made it difficult to be disposed. Apart of that, it also has a large dry volume due to its low bulk density and highly resistant to natural degradation. It is recognized that only the cement and concrete industries can consume such large quantities of solid pozzolanic wastes (Hwang C.L. et. al.,1996).

Rice husk ash (RHA) is typically generated in large amounts in rice-producing regions worldwide as a by-product during the burning of the rice husk, an agricultural waste. If burning occurs under controlled conditions, it results in good quality RHA containing 80 -95% silica and having a highly reactive pozzolanic nature (Fongsatitkul P. et. al., 2010).

Rice has ash has been proved to be an effective low-cost adsorbent in several studies. According to Uma R. Lakshmi, et al (2008), RHA had been an effective adsorbent for Indigo Carmine dye (use in textile industry for dyeing). For test of effect of initial pH, it can be inferred that the dye removal due is maximum and constant at pH greater than or equal to 4 and optimum dosage was found to be 10 g/L. In the test of contact time was seen at rapid adsorption during the first 15 min, thereafter, it decreases gradually until it reaches equilibrium in 8 hours. The adsorption behavior of RHA in removing indigo carmine dye was best fitted in the Freundlich isotherm models (Uma R. Lakshmi, et. al., 2008).

In other case, study done by Mahvi A.H et at (2004) have discovered potential use of rice husk and rice husk ash for removal of phenol in aqueous systems. The rate of adsorption decreases with increasing pH which can be attributed to the depending of phenol ionization on the pH value. At low pH values, the surface or sorbent would be surrounded by hydronium ions, which enhance phenol interaction with binding site of the sorbent by greater attractive forces. Equilibrium time required for the phenol to be adsorbed by rice husk ash was 3hours with minimum dosage of 0.3 g in 100ml of solution. Analysis of the isotherm data is important in order to develop an equation that accurately represents the results and which could be used for design purposes. Hence, linear regression of the experimental data showed that Freundlich equation best represented phenol adsorption data.

2.5 Adsorption Isotherms

Analysis of equilibrium data is important for developing an equation that can be used to compare different adsorbents under different operational conditions and to design and optimize an operating procedure. In order to obtain equilibrium adsorption data, batch experiments were therefore performed (Mondal M.K., 2009). It is important to establish the most appropriate correlation for the equilibrium curves in order to optimize the design of an adsorption system (Lakshmi Uma. R. et. al., 2008).

The equilibrium isotherm plays an important role in predictive modeling for analysis and design of adsorption systems. The ratio between the amount adsorbed and that remaining in the solution at a fixed temperature describes the relationship between adsorbent and adsorbate (EtciOzlem, et. al., 2009). Many researchers have used Freundlich and Langmuir isotherms equations to represent the equilibrium data for adsorption because of their validities for heterogeneous and homogenous surface respectively (Lakshmi Uma. R. et. al., 2008). The equations for the three types of adsorption isotherms are expressed by linear isotherm, Langmuir isotherm, Freundlich isotherm (Emmanual O.A. et. al., 2008).

2.5.1 Freundlich Isotherms

Freundlich equation explains adsorption into a heterogeneous surface with uniform energy (Zhou Y.F. et. al., 2010). This isotherm is widely used by many researchers to describe the adsorption characteristics of the adsorbent used in water and wastewater treatment (Metcalf & Eddy, 2004). The isotherm is expressed in equation below:

$$\frac{x}{m} = K_f C_e^{1/n}$$

Where;

$\frac{x}{m}$ = Mass of adsorbate adsorbed per unit mass of adsorbent, (mg/g)

K_f = Freundlich capacity factor, (mg/g)

C_e = Equilibrium concentration of adsorbate in solution after a dsorption, mg/L

$\frac{1}{n}$ = Freundlich intensity parameter

The constants can be determined by plotting ln (x/m) versus ln C_e using equation below:

$$\ln \left(\frac{x}{m}\right) = \ln K_f + 1/n \ln C_e$$

2.5.2 Langmuir Isotherms

Langmur equation is based on monolayer adsorption on active sites of the adsorbent (Zhou Y.F. et. al., 2010). It is the most commonly used isotherms in adsorption of a solute from a liquid solution. Whenever a gas is in contact with a solid there will be an equilibrium established between the molecules in the gas phase and the corresponding adsorbed species (molecules) which are bound to the surface of the solid. The isotherm is defined as:

$$q_e = \frac{Q_o B C_e}{1 + Q_o C_e}$$

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Where;

q_e	=	Mass of adsorbate adsorbed per unit mass of adsorbent
Q_o	=	The equilibrium sorption capacity for complete monolayer
B	=	The sorption equilibrium constant
C_e	=	Equilibrium concentration of adsorbate in solution after adsorption

The Langmuir isotherm was developed assuming:

i-   A fixed number of accessible sites are available on the adsorbent surfaces, all of which have the same energy.

ii-   Adsorption is reversible.

The linear form of Langmuir isotherm is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_o B} + \frac{1}{Q_o} C_e$$

2.6 Adsorption Kinetics

Adsorption kinetic models present relationship between the solute uptake rate and time (important in treatment process design) (Kutty, et. al., 2009). In order to evaluate the kinetic mechanisms that control the adsorption process, pseudo-first-order and pseudo-second-order models were employed to interpret the experimental data.

Pseudo-first-order kinetic model,

$$\frac{dq}{dt} = k_1(q_e - q)$$

$$ln(q_e - q) = ln\ q_e - k_1t$$

Pseudo-second-order kinetic model,

$$\frac{dq}{dt} = k_1(q_e - q)^2$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where q_e =   Amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g)

q =   Amount of solute adsorbed at time t per unit weight of adsorbent (mg/g)

k_1 & k_2 = Constants

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CHAPTER 3

METHODOLOGY

3.1 Introduction

Upon conducting the project, several experiments have been done to test the effectiveness of the adsorbent. As stated earlier in scope of study, the tests consist of varying adsorbent dosage and contact time. The experiments were done in reference with other final year project students and postgraduate students. This chapter explains about the materials, type of tests, and methods used during the experiment.

3.2 Health, Safety and Environment

While conducting laboratory works, safety were always put into measure. OSHA Guide of Chemical Hazard was referred to before entering the laboratory so that all possible hazards can be avoided. Laboratory briefing has been attended before entering the laboratory for every student in order to keep up with the latest news, learning the safety measure and ways of preventing, and knowing rules and regulations that must be obeyed while being in a laboratory.

3.3 Materials
3.3.1 Chemicals

All chemicals are of analytical reagent (RA) grade and were obtained from the Environmental Laboratory, Civil Engineering Department, UniversitiTeknologiPetronas. The chemicals are; Zinc Chloride ($ZnCl_2$), Copper Chloride (CuCl), hydrochloric acid, (HCl) and sodium hydroxide (NaOH). Stock solution was prepared by mixing $ZnCl_2$ and CuCl in POME.

3.3.2 Adsorbent

Rice husk were collected from BERNAS Rice Mill in Seberang Perak before being burned at controlled temperature of 800°C to become Microwave Incinerated Rice Husk Ash (MIRHA). Then the MIRHA will be immersed in sulfuric acid (H_2SO_4) 0.5N for 24 hours before washed with distilled water thoroughly to remove excessive acid until the water from the residue reach pH of 4. Finally the MIRHA will be oven-dried at 103 to 105°C for 24 hours.

3.4 Equipments

Tools	Description
pH meter	Calibrated with buffers of pH 4.0, 7.0 and 10.0 before being used
Orbital shaker	To agitate the solutions and adsorbent
Filter papers 0.45 μm	To separate fine solids from solution or air
Atomic Absorption Spectrophotometer (AAS)	Determine the concentration of a particular element (the analyte) in a sample to be analyzed.

3.5 Methodology

3.5.1 Preparation of MIRHA

Rice husk were collected from BERNAS Rice Mill in Seberang Perak before being burned at controlled temperature of 800°C to become Microwave Incinerated Rice Husk Ash (MIRHA). Then the MIRHA will be immersed in sulfuric acid (H_2SO_4) 0.5N for 24 hours before washed with distilled water thoroughly to remove excessive acid until the water from the residue reach pH of 4. Finally the MIRHA will be oven-dried at 103 to 105°C for 24 hours.
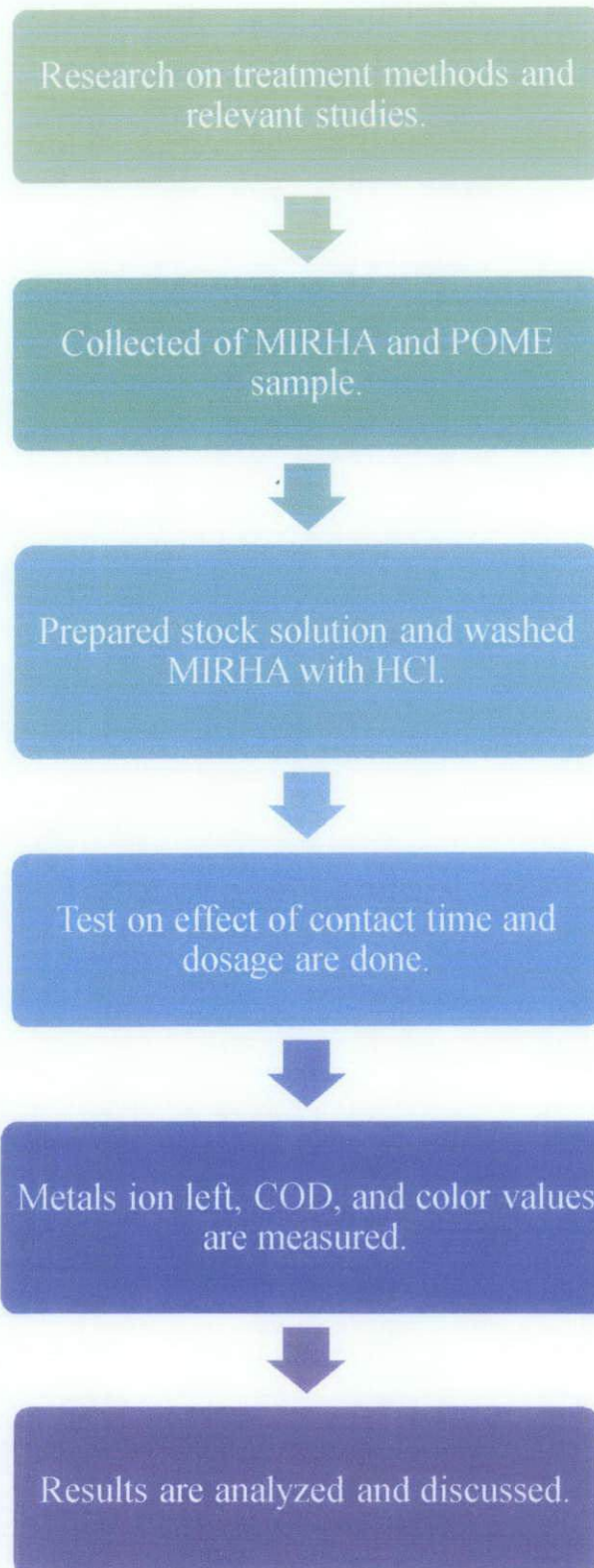
3.5.2 Preparation of Stock Solution

The stock solution of Zinc Chloride (ZnCl) and Copper Chloride (CuCl) was prepared using the binary mixture. 20 mg/L concentration of both Zinc and Copper Chloride were added in 10L of treated POME. The solution were then diluted with Hydrochloric Acid (HCl) 1M to lower down its pH until it reached a range between 4-5 in order to avoid metal hydroxide precipitation.

3.5.3 Batch Adsorption Studies

For batch experimental run, triplicate sets of conical flasks filled with 100mL of sample mixed with ZnCl and CuClwere used during the tests. MIRHA of dosage ranging from 10,000 – 50,000 mg/L were added to each set of conical flasks, followed by agitation using the orbital shaker. The time of agitation by orbital shaker was set to be 1, 2, 3, 4, 5, 6, 12 and 18 hours respectively. After shaking, the samples were all filtered and the supernatant liquid was analyzed for their residual concentration of metal ions using atomic absorption spectrophotometer, COD and color using spectrophotometer.

3.5.4 Flow Chart

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┌─────────────────────────────────┐
│  Research on treatment methods  │
│       and relevant studies.     │
└─────────────────────────────────┘
                │
                ▼
┌─────────────────────────────────┐
│    Collected of MIRHA and POME  │
│             sample.             │
└─────────────────────────────────┘
                │
                ▼
┌─────────────────────────────────┐
│   Prepared stock solution and   │
│       washed MIRHA with HCl.    │
└─────────────────────────────────┘
                │
                ▼
┌─────────────────────────────────┐
│   Test on effect of contact     │
│      time and dosage are done.  │
└─────────────────────────────────┘
                │
                ▼
┌─────────────────────────────────┐
│  Metals ion left, COD, and      │
│   color values are measured.    │
└─────────────────────────────────┘
                │
                ▼
┌─────────────────────────────────┐
│  Results are analyzed and       │
│           discussed.            │
└─────────────────────────────────┘
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CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

In this chapter, the result of adsorption experiments will be presented and discussed. It is to assess the MIRHA's efficiency in treating or reducing heavy metals and residual organics in the stock solution, here we used POME mixed with metal ions.

4.2 Characteristics of Treated POME

POME was collected at local palm oil mill, Bota, Perak. The samples were stored in a cold room at 4°C. This storage technique had no observable effect on its composition. Fresh POME is thick brownish slurry. Its temperature is around 80 to 90°C, alkalinitic with pH 8.0 – 9.0 and contains high concentration of organic matter (COD = 700-1000 mg/L, BOD = 1000 – 10,000 mg/L). The effluent is non-toxic as no chemical was added in the oil extraction process. A typical characteristic of POME is given in Table 1 below. The raw POME has a high content of degradable organic matter, which most probably caused by the presence of unrecovered palm oil. This highly polluting effluent can therefore cause severe pollution of water waste due to oxygen depletion. Furthermore, its thick and high value of color may disperse and affect the water bodies which then would cause unpleasant sight.

Table 4.1: Characteristics of treated POME and its respective standard discharge limit by the Department of the Environment Malaysia.

Parameters	Concentrations	Standard Limit
Temperature ($^{\circ}$C)	22-27	-
pH	8.63 ± 0.008	5.0 - 9.0
COD (mg/L)	700 - 800	100
sCOD (mg/L)	589 ± 2	-
sCOD (mg/L)	600 - 700	-
BOD (mg/L)	1000 - 10000	100
TKN (mg N/L)	186 ± 44	-
TSS (mg/L)	29 ± 7	400

4.3   Characteristics of MIRHA

The adsorbent used during the batch studies, were sent to the laboratory in Block P, University Teknologi Petronas to sort out its characteristics through Field Emission Scanning Electron Microscopy (FESEM). MIRHA burned at 800°C was magnified ranging from 200 – 10000 times. The pictures are shown below:

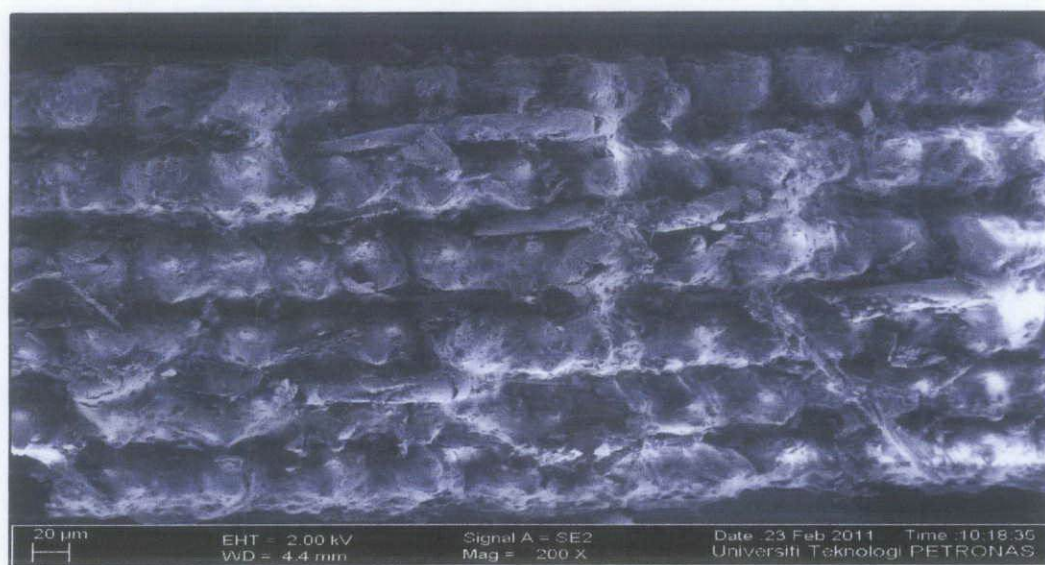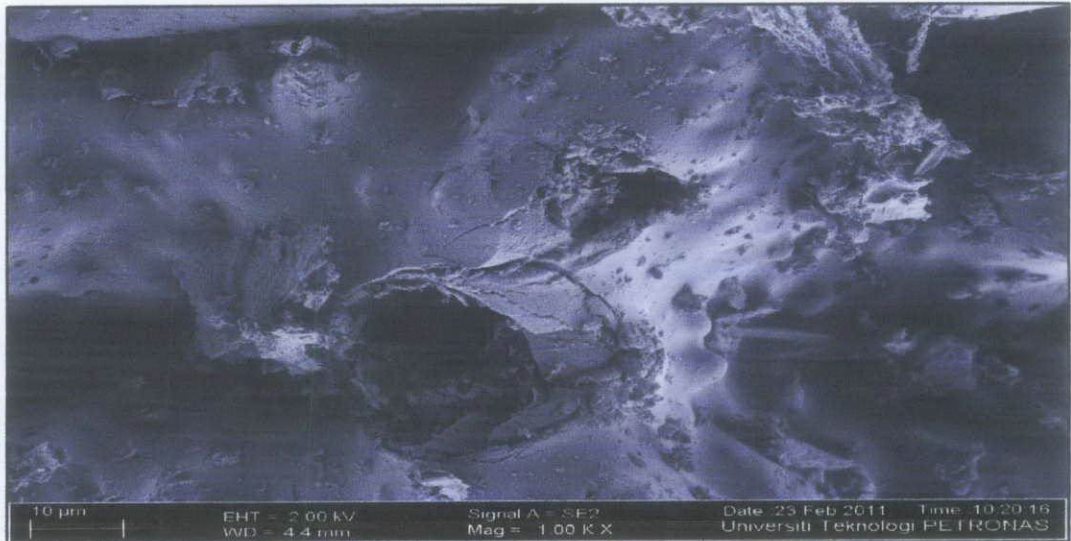Figure 4.1: The SEM micrographs of MIRHA 800°C at 200x.

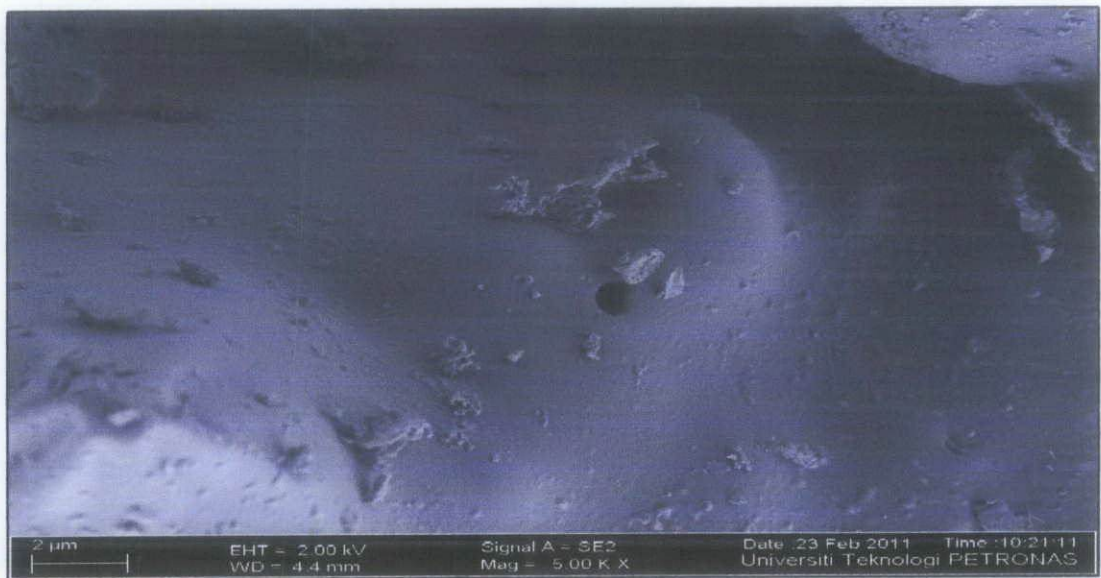Figure 4.2: The SEM micrographs of MIRHA 800°C at 1000x.

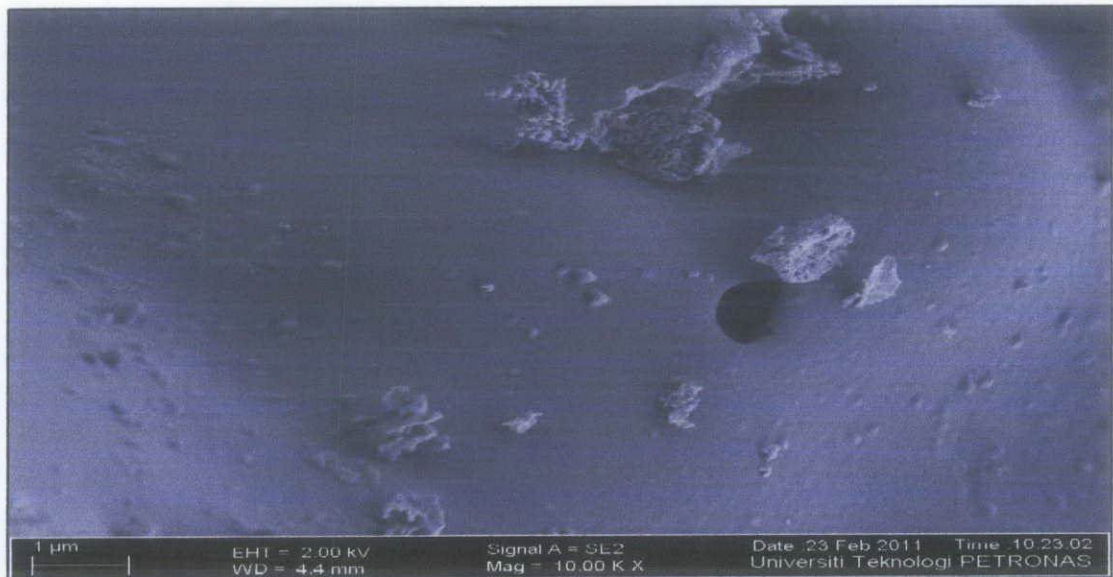
Figure 4.3: The SEM micrographs of MIRHA 800°C at 5000x.

Figure 4.4: The SEM micrographs of MIRHA 800°C at 10000x.

4.4 Batch Study Analysis on Adsorption of Copper (Cu)

Table 4.2 in Appendix A is the result of adsorption process of MIRHA on treated POME mixed with metal ions. Cu and Zn were added to test the effectiveness of MIRHA that is burned to 800°C. Based on the table, we can see that MIRHA has successfully reduced the amount of Cu inside the stock solution (which in this study was POME). The initial concentration of Cu added to treated POME was 20 mg/L. After several days, the amount of Cu has reduced to 17.9 mg/L due to metal hydroxide precipitation. So the initial Cu concentration before shaking was set to 17.9 mg/L with initial pH of 4.92.

The measurement of initial and final concentration of Cu was done using Automatic Adsorption Spectrophotometer (AAS). The batch experiment studies were done with triplicate samples in order to get the average value of Cu being reduced by the MIRHA of dosage varied from 10000 – 50000 mg/L. In addition, the contact time between MIRHA and treated POME were in range of 1 hour up to 18 hours to study its adsorption behavior.
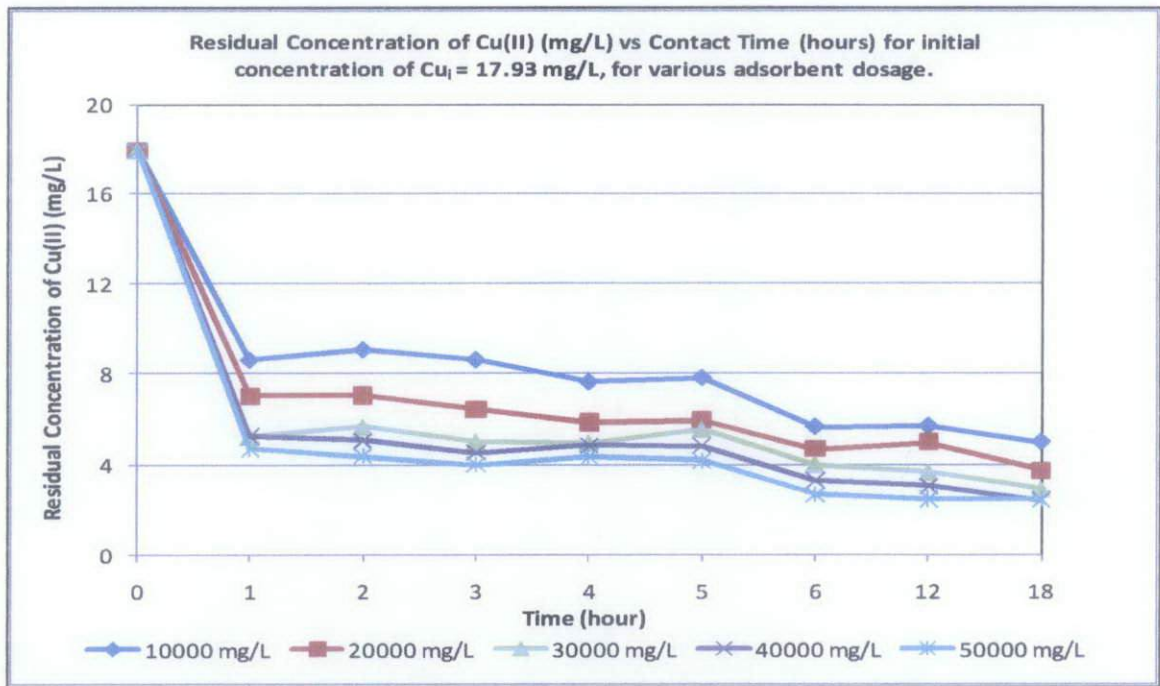
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Figure 4.5: Residual Cu concentration vs. Time (hours) with varied adsorbent dosage.

From figure 4.5, the residual concentration of Cu seems to be decreasing with increasing of contact time. A rapid decreased has been seen during the first hour of contact time between MIRHA and POME. Highest percentage removal was seen at 18 hours with adsorbent dosage of 50000 mg/L in 18 hours. The percentage removal was recorded at 86.13%.

Another graph of residual concentration against dosage were plotted to observe POME's highest efficiency on effect of dosage. In figure 4.6 below, it can be seen that at every variation of contact time, a drastic fall was recorded at adsorbent dosage of 10000 mg/L where after that, the increase of dosage gave little effect on adsorption though the lowest residual was seen at 50000 mg/L. Therefore, another batch experiment study is conducted with lower adsorbent dosage and contact time to test the adsorption behavior on POME.
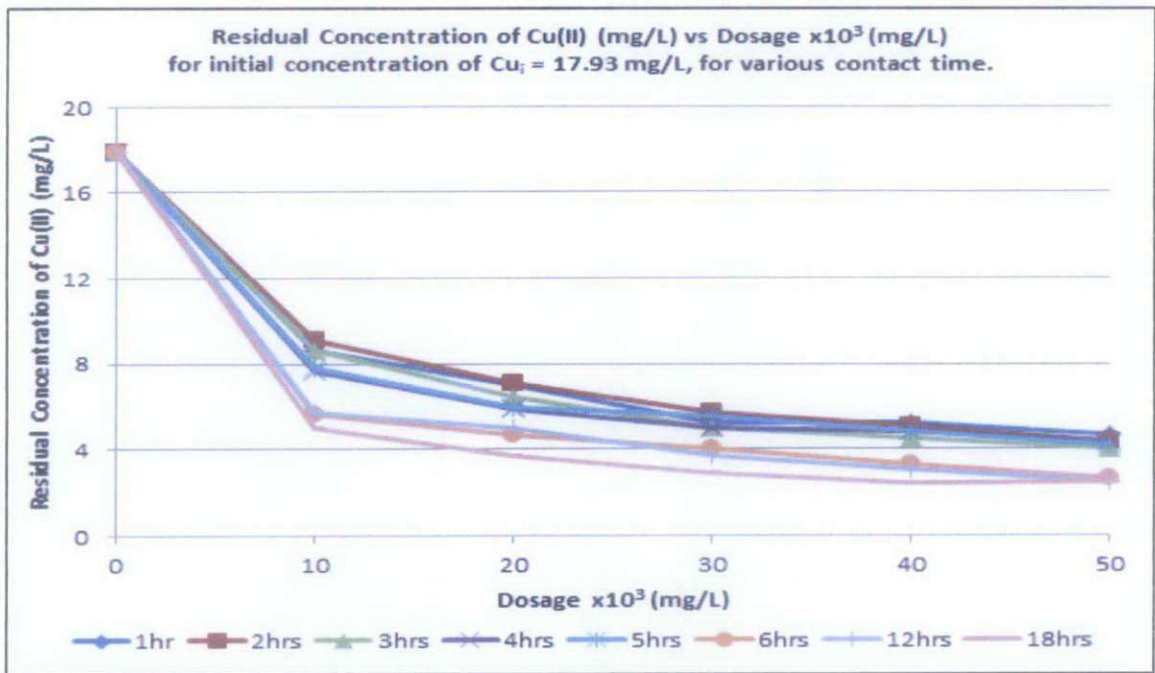
Figure 4.6: Residual Cu concentration (mg/L) vs. dosage (mg/L) with varied contact time.
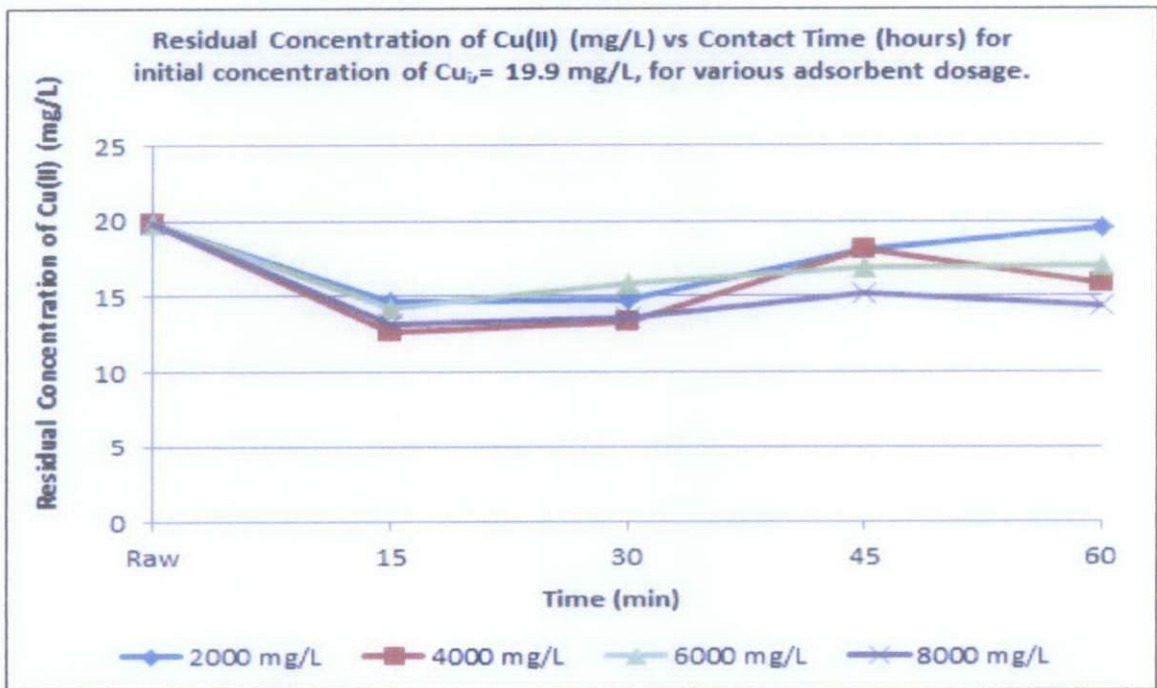

Figure 4.7: Residual concentration of Cu (mg/L) vs. time (min) with varied adsorbent dosage.

Figure 4.7 above shows the result of batch studies of MIRHA with low adsorbent dosages against time. The dosages were varied from 2000-8000 mg/L. The contact time

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was also reduced ranging from 15-60 minutes. This was done since in the previous batch studies, the residual concentration of Cu fell drastically in the first hour.

However, the result in the new batch studies does not seem to be as expected as we can see in figure 4.7, the concentration of Cu increased after 30 minutes of contact time. This situation might be due to saturation of Cu onto the adsorbent surface area. Nevertheless, the MIRHA did adsorb the amount of Cu even though in small dosages as what observed during the first 15 and 30 minutes of contact time where the residual was lowered to below than 15 mg/L. This has practically removed at least 25% of residual concentration even though in small surface area.

4.5   Batch Study Analysis on Adsorption of Zinc (Zn)

The second parameter tested on MIRHA is its capability in reducing the amount of Zn. Zn was tested from the same stock solution where Cu was added. The initial calculation of concentration of Zn was set to be 20 mg/L. However, believed to be metal hydroxide precipitation, the concentration of Zn has reduced to 17.49 mg/L. The batch experiments were thereby started with initial Zn concentration of 17.49 mg/L with initial pH value of 4.92.

From figure 4.8, highest percentage removal of Zn was seen 73.5% with adsorbent dosage of 5000 mg/L. The residual concentration of Zn is seen as gradually decreasing as the contact time increase. The fall on first hour did not occur as rapid as what happened to Cu. In the writer's opinion, this might be due to the availability of surface area of MIRHA where the Zn had to explore for free surface area in order to be adsorbed on MIRHA. That was why Zn was seen slowly decreasing with contact time.
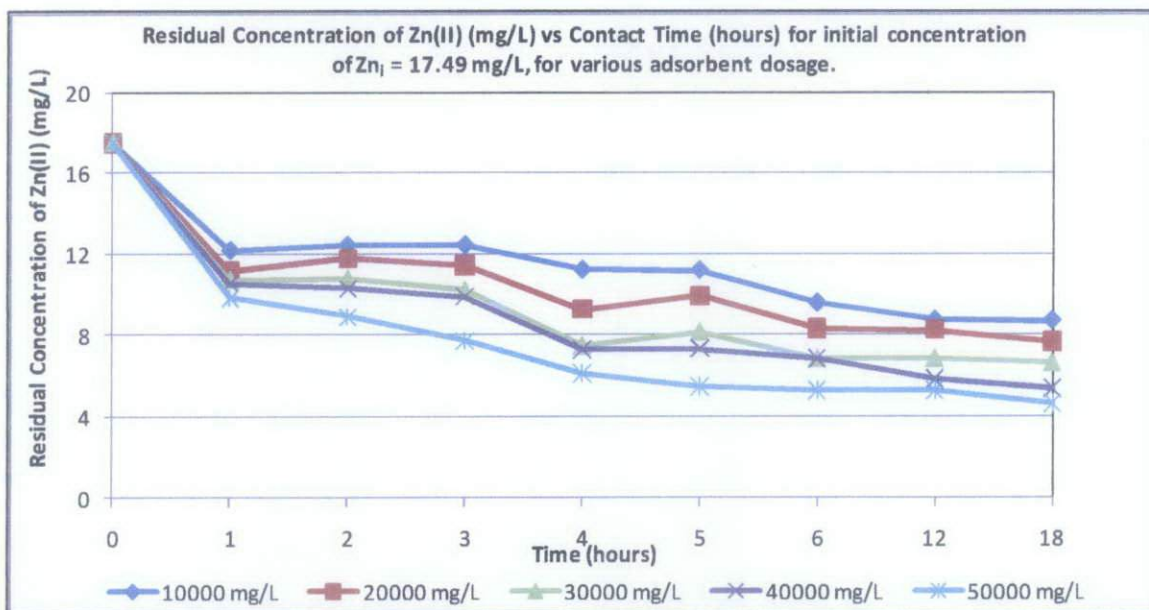
Figure 4.8: Residual Zn concentration vs. time (hour) with varied adsorbent dosage.

As to observe the adsorption behavior of MIRHA on Zn clearer, another graph is plotted for residual concentration of Zn against dosage. In figure 4.9, Zn was seen to be in rapid reduction in a dosage of 10000 mg/L. However, with increasing time, residual concentration of Zn was seen to be slowly decreased with lowest concentration was obtained after 18 hours of contact time in 50000 mg/L. The result was rather convincing as the objective of reducing heavy metals on POME using MIRHA has been achieved.
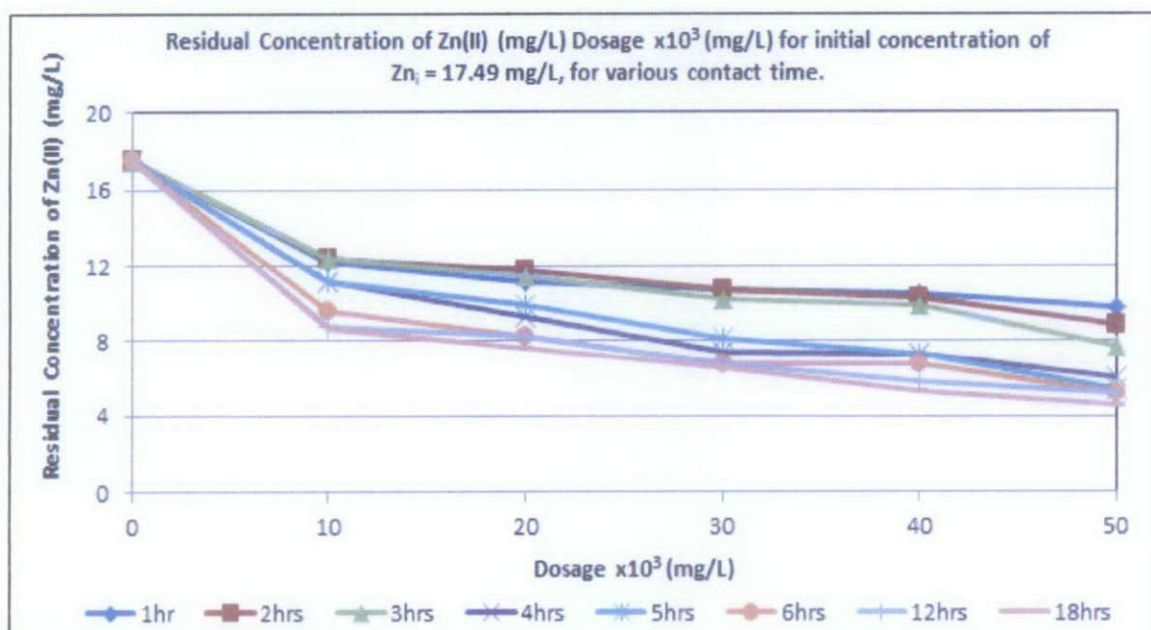

Figure 4.9: Residual Zn concentration vs. dosage (mg/L) with varied contact time.

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Another batch adsorption study was conducted to observe the minimum uptake rate of MIRHA onto Zn. Therefore, the amount of dosage reduced to 2000-8000 mg/L in contact time of 15-60 minutes. In figure 4.10, the pattern of the lines were seen to be similar than that of in Cu where the residual concentration of Zn increased after 30 minutes of reaction. This situation believed to be the saturation of Zn ions onto the surface of adsorbents.
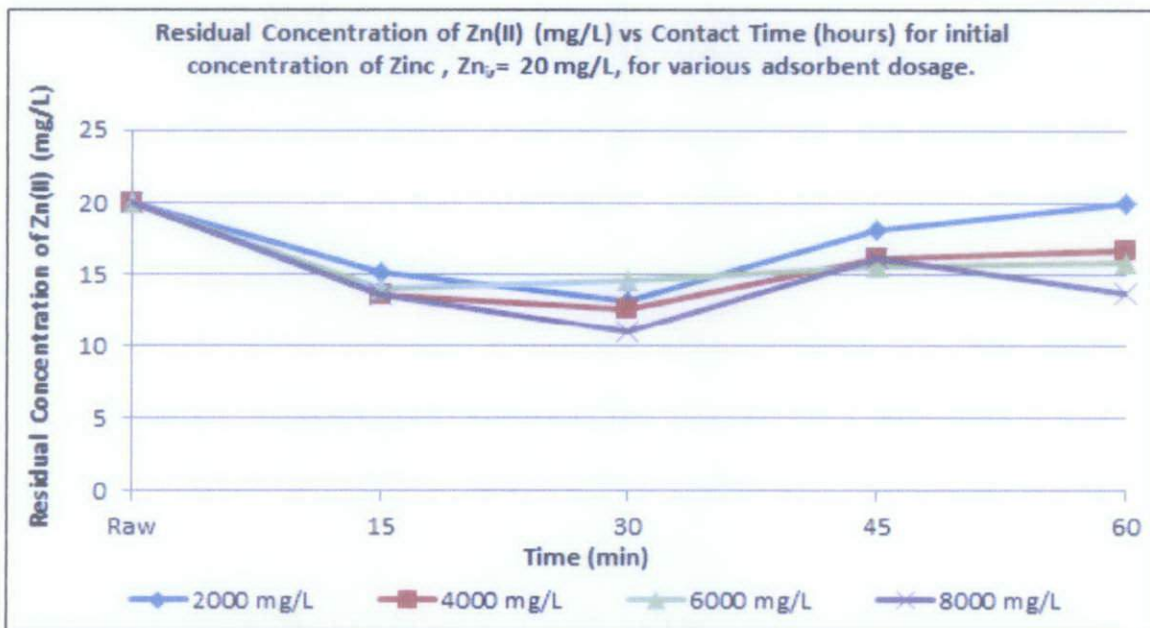

Figure 4.10: Residual concentration of Zn (mg/L) vs. time (min), with varied adsorbent dosage.

4.6 Batch Study Analysis on Removal of Chemical Oxygen Demand (COD)

COD is the third parameter being tested on effectiveness of MIRHA in adsorption. Based on table 3 in Appendix A, the concentrations of COD do not seem to reduce much. In figure 4.11 below, the residual concentration of COD fell from 773 mg/L to a level below 600 mg/L in the first hour. The concentration fell gradually with increasing time though at the end of the experiment there seem to be an unstable reading where the concentration spiked up. In this situation, mistakes and error did take place sometime as the experiment is considerably sensitive as it involved chemical that reacts fast with the environment. Even a small hit or shake on the vial after being taken out from the reactor and cooled down, could cause a big difference of concentration.
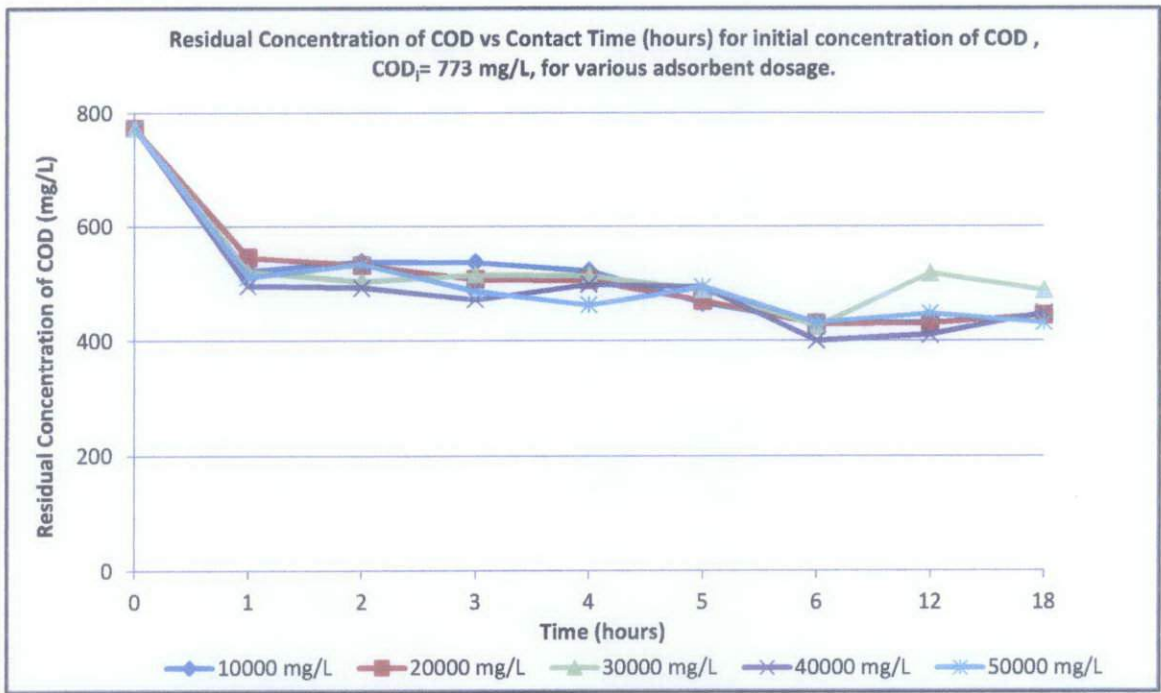
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Figure 4.11: Residual concentration of COD (mg/L) vs. time (hours), with varied adsorbent dosage.

Even though the rate of removal did not turn out as expected, MIRHA however did show its feasibility in reducing the amount of concentration with its highest percentage removal of 48.19%. The removal was seen at 6 hours of time agitation in 40000 mg/L of dosage. The figure 4.12 below shows the percentage removal of COD against time.
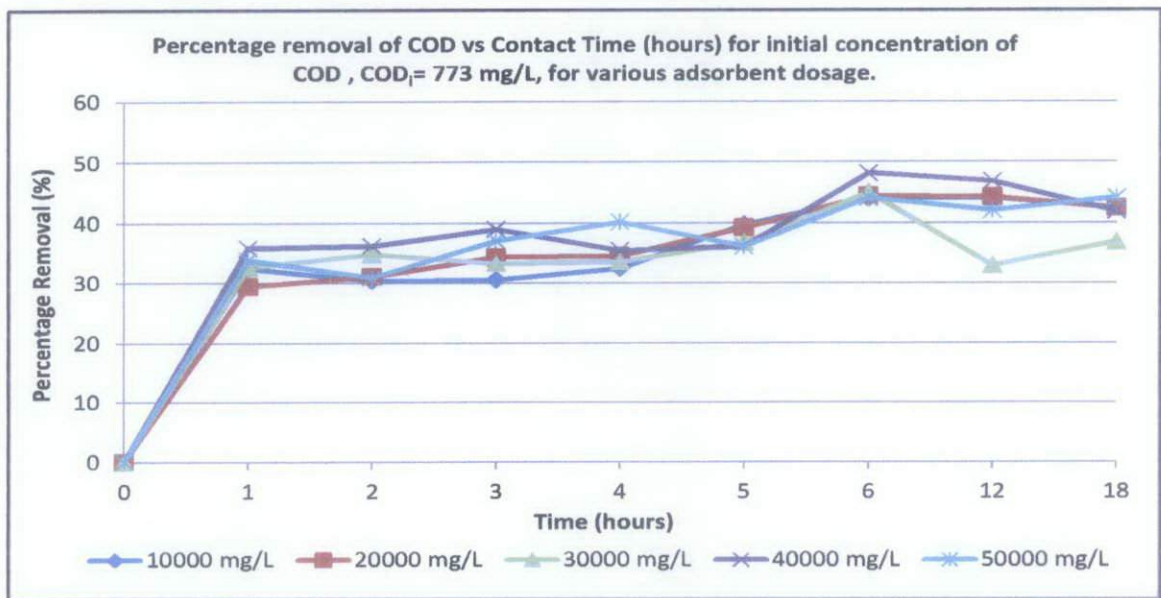

Figure 4.12: Percentage removal of COD (mg/L) vs. contact time (hours), with varied adsorbent dosage.

The capability of MIRHA in adsorbing concentration of COD was observed to be effective in dosage of 10000 mg/L. After that, the lines were seen to be equilibrium with slight removal. In figure 4.13, a graph of residual concentration was plotted against dosage to observe the effect of adsorbent dosage against adsorption.
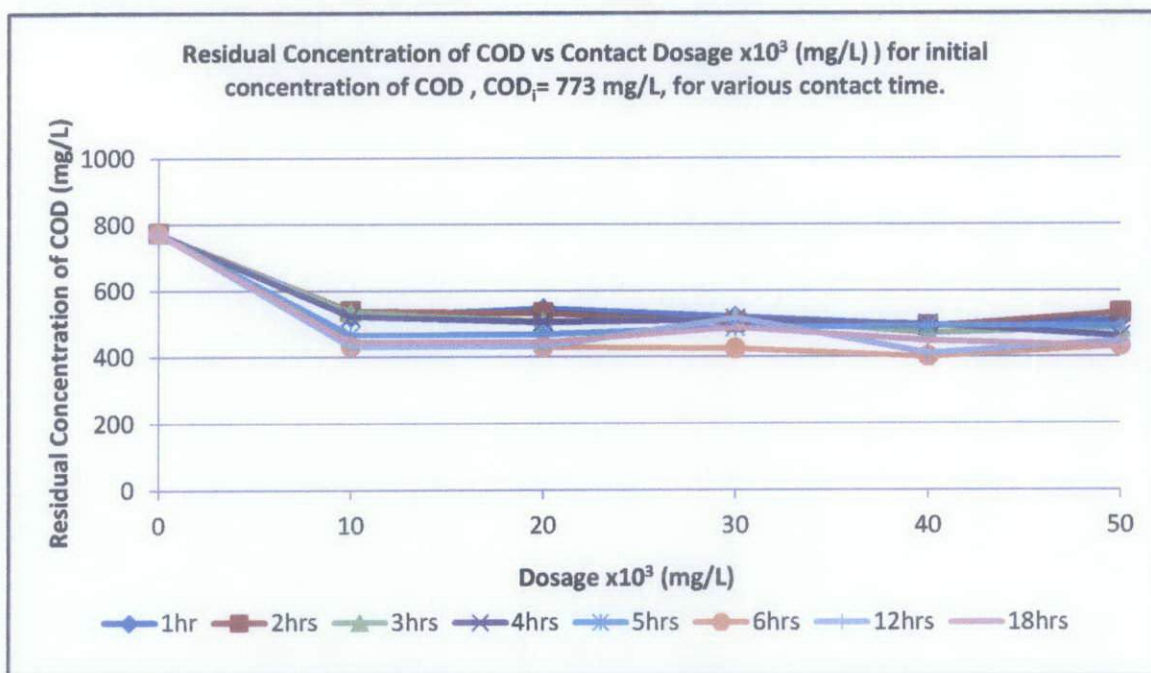

Residual Concentration of COD vs Contact Dosage x10³ (mg/L)) for initial concentration of COD , COD$_i$= 773 mg/L, for various contact time.

Figure 4.13: Residual concentration of COD (mg/L) vs. dosage (mg/L), with varied contact time.

Seeing that the efficiency of MIRHA in reducing the concentration of COD was at best in 10000 mg/L and during the first hour of the experiment, another batch study was conducted in order to find the curve of dosage needed by MIRHA in adsorbing this parameter. Therefore, figure 4.14 shows a result of residual concentration of COD plotted against time, lowered from 15-60 minutes and dosage varied from 2000-8000 mg/L.
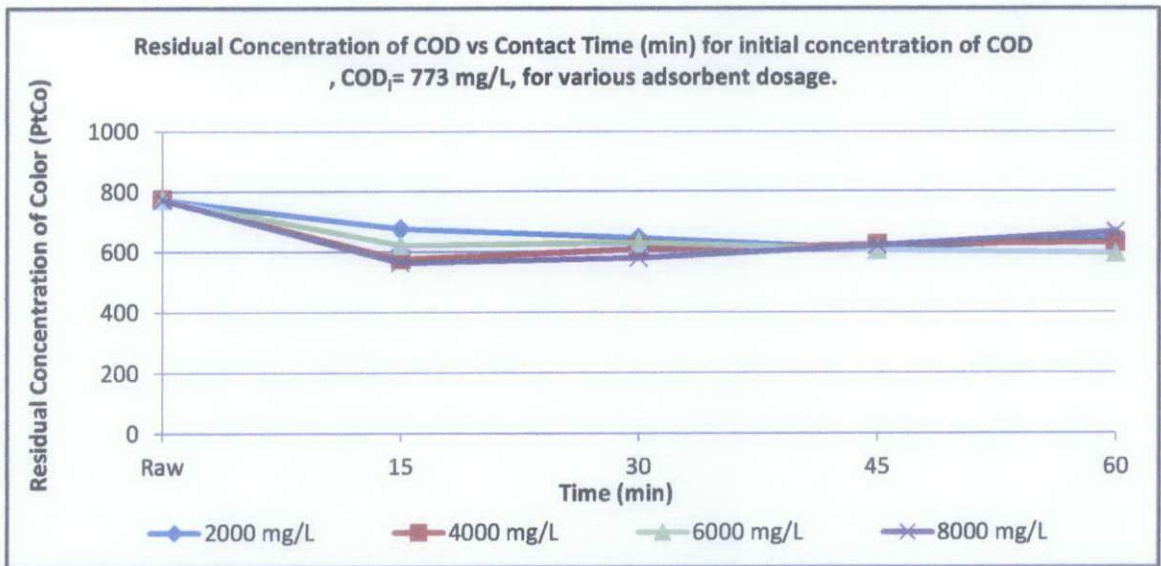
Figure 4.14: Residual concentration of COD (mg/L) vs. time (minute), with varied adsorbent dosage.

In this batch study, the adsorption process was seen to be a little bit slow relative to the increasing time as it barely reached equilibrium after 15 minutes of time agitation. With small surface area to be adsorbed to, the residual remain almost at the same reading until the end of the experiment. This may be due to the unavailability of surface to be adsorbed after the first 15minutes of contact time. However, still the MIRHA managed to show some removal during the experiment.

4.7   Batch Study Analysis on Adsorption of Color

The last parameter tested on MIRHA in adsorption was its efficiency in removing color. In many occasions rice husk ash has been proved to be effective in removing color from the water bodies. For example, Uma R. Lakshmi reported to have reduced the concentration of indigo carmine dye using rice husk ash obtained from a paper mill.

Based on the result achieved, figure 4.15 shows a positive outcome of adsorption. MIRHA observed to be effective in reducing the concentration of color on POME with highest percentage removal of 86.8% achieved in 6 hours of contact time. A drastic fall of residual concentration can be seen in the first hour where the initial color of 4700 PtCo dropped almost 50% of its concentration. Effect of different adsorbent dosage had not been giving much impact where the lines tended to be plotting the same pattern

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on the graph which then combined toward a similar percentage removal at the end of the experiment.
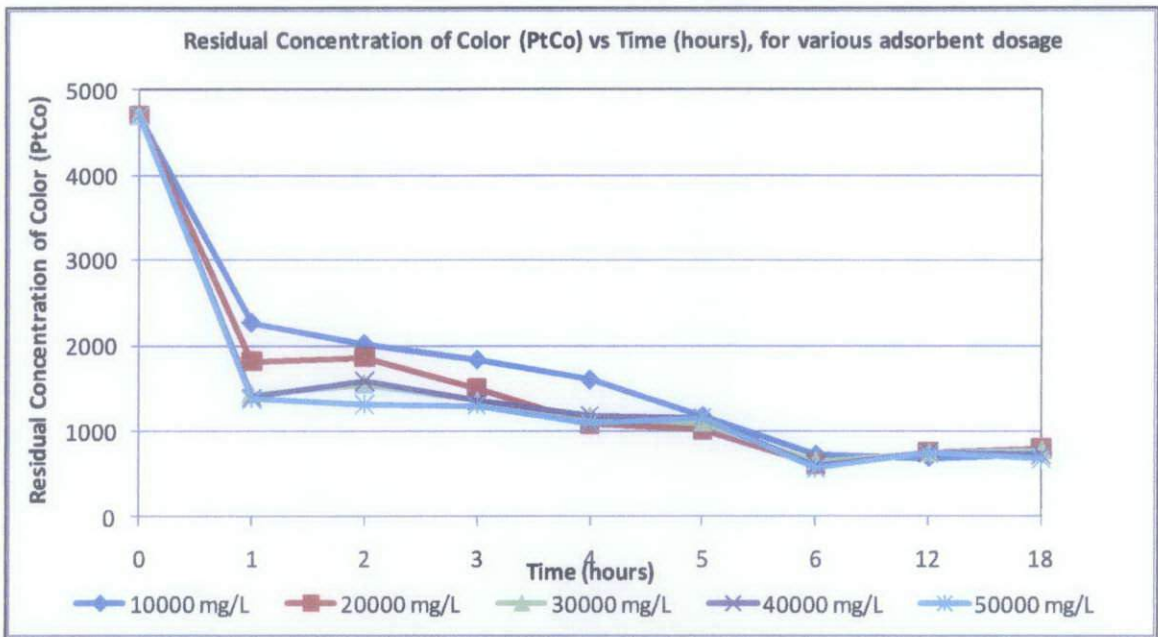

Figure 4.15: Residual concentration of color vs. time (hours), with varied adsorbent dosage.
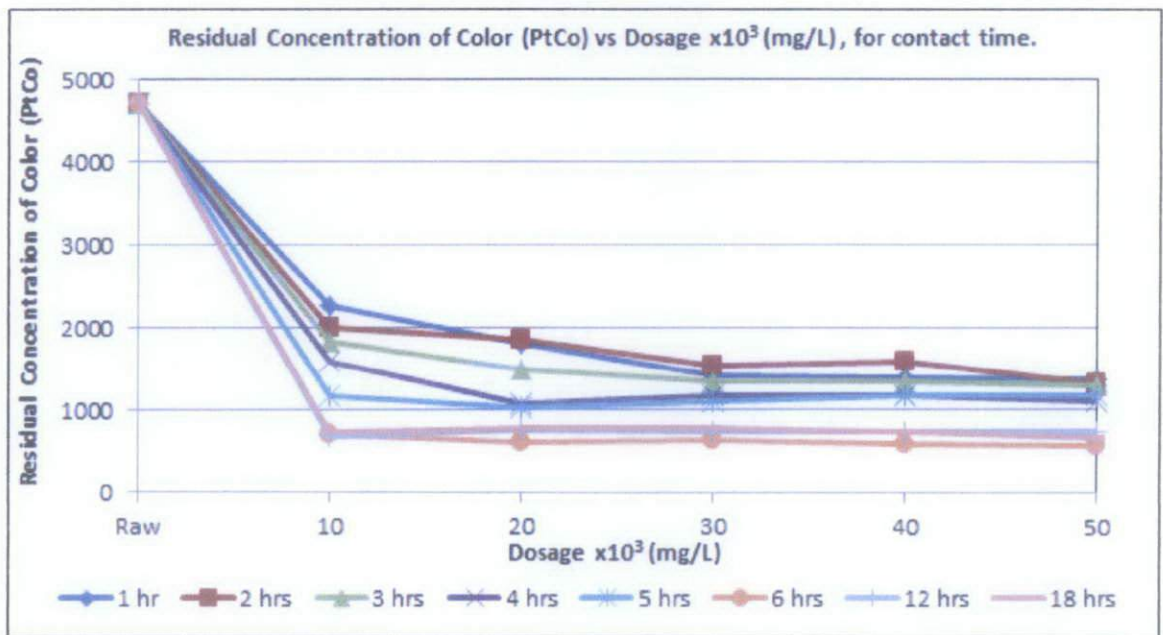

Figure 4.16: Residual concentration of color vs. dosage (mg/L), with varied contact time.

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In order to investigate the minimum uptake rate of MIRHA in reducing the concentration of color in POME, a graph of residual concentration against dosage is plotted in figure 4.16 above. With referred to the above graph, it can be seen that a minimum dosage of 10000 mg/L of MIRHA is needed to reduce the concentration of color in POME. Most of the lines began to show a constant rate of removal after a dosage of 30000 mg/L and above indicating that MIRHA has reached its limit of adsorption in that dosage. Further study is done with lowering the amount of adsorbent dosage to check if there is a lower amount of minimum uptake rate of MIRHA on color.

In figure 4.17 is the result of residual concentration of color against time with dosages below than 10000 mg/L. In this batch study, the dosage was varied from 2000-8000 mg/L with contact time differ 15-60 minutes. During the first 15 minutes of contact time, the concentration of color dropped from 4000 PtCO to as low as 2000 PtCo. However the increase of the concentration later showed that some mistake might occur during the batch experiments. This might be due to mixed up of samples during the reading taken, causing the concentration to increase after 15 minutes of contact time. Nevertheless, the residual maintain below 3000 PtCo after 60 minutes for all adsorbent dosages. This result indicates that even of dosage as low as 2000 mg/L, MIRHA is still capable of adsorbing color from POME.
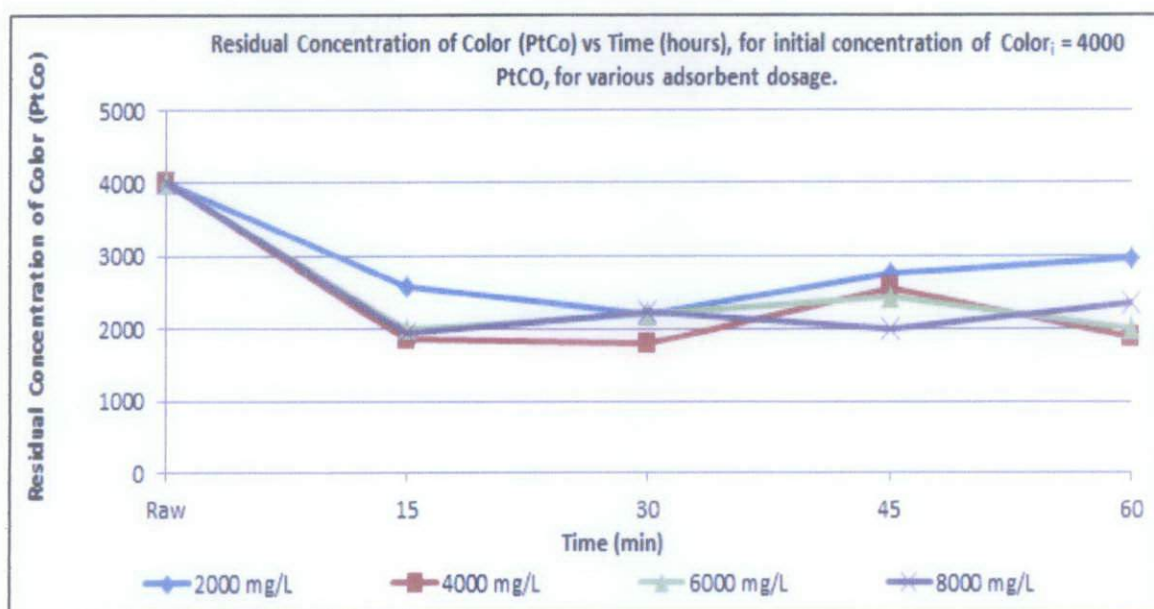

Figure 4.17: The residual concentration of color (PtCo) vs. time (min), with varied adsorbent dosage.

4.8   Adsorption Isotherms

As for the isotherms of the experiments, the results were presented in Freundlich and Langmuir. Most of the results seem to be following Freundlich isotherms where the R^2 values were higher than that of Langmuir. Summaries of all isotherms for each contact time are shown below. The complete isotherm plots are attached in Appendix C.

4.8.1   Adsorption Isotherms for Copper Adsorption

Table 4.2: Summary of isotherm coefficients for Cu, with time varied from 1-18 hours.

Time (hrs)	Freundlich				Langmuir					
	lnK_f	K_f	$1/n$	R^2	$1/Q_o$	Q_o	$1/Q_oB$	B	R^2	R_L
1	-4.223	0.015	1.904	0.931	1.904	0.525	24.950	0.076	0.722	0.567
2	-3.731	0.024	1.620	0.992	-1.255	-0.797	21.686	-0.058	0.971	2.374
3	-3.408	0.033	1.547	0.994	-1.025	-0.976	17.881	-0.057	0.902	2.342
4	-4.771	0.008	2.379	0.972	-2.501	-0.400	25.750	-0.097	0.827	34.657
5	-4.440	0.012	2.148	0.963	-2.192	-0.456	24.691	-0.089	0.888	8.911
6	-3.109	0.045	1.807	0.922	-1.439	-0.695	13.480	-0.107	0.827	-14.813
12	-2.637	0.072	1.506	0.909	-0.873	-1.146	10.730	-0.081	0.630	5.354
18	-2.695	0.068	1.821	0.967	-1.263	-0.792	10.059	-0.126	0.780	-3.916

Table 4.3: Summary of isotherm coefficients for Cu, with time varied from 15-60mins.

Time (min)	Freundlich				Langmuir					
	$\ln K_f$	K_f	$1/n$	R^2	$1/Q_o$	Q_o	$1/Q_oB$	B	R^2	R_L
15	-1.56	0.21	0.72	0.007	0.39	2.53	5.72	0.07	0.004	0.59
30	4.42	82.91	-1.58	0.043	3.26	0.31	-33.27	-0.10	0.227	47.94
45	-1.82	0.16	0.46	0.017	1.37	0.73	6.35	0.22	0.051	0.32
60	12.70	3.3×10^5	-4.77	0.732	16.99	0.06	-240.17	-0.07	0.840	3.42

Table 4.2 and 4.3 both show the results of isotherms for Copper. It was observed that the R^2 yielded were much higher in Freundlich following by their K values. This can be concluded that the adsorption behavior followed the Freundlich isotherm. However, in table 4.3, the R^2 values were unstable highs and lows due to inconsistency of the readings. The experiment should be re done to study MIRHA's exact behavior in a smaller contact time.

4.8.2 Adsorption Isotherms for Zn

Table 4.4: Summary of isotherm coefficients for Zn, with time varied from 1-18 hours.

Time (hrs)	Freundlich				Langmuir					
	$\ln K_f$	K_f	$1/n$	R^2	$1/Q_o$	Q_o	$1/Q_oB$	B	R^2	R_L
1	-16.39	7.62×10^{-8}	6.29	0.948	-19.42	-0.05	257.58	-0.08	0.915	4.06
2	-8.53	1.97×10^{-4}	3.01	0.766	-7.62	-0.13	127.11	-0.06	0.664	2.50
3	-5.53	3.96×10^{-3}	1.82	0.671	-3.07	-0.33	70.80	-0.04	0.308	1.76
4	-5.53	3.96×10^{-3}	1.82	0.671	-3.07	-0.33	70.80	-0.04	0.308	1.76
5	-3.67	0.03	1.24	0.793	-0.08	-12.77	30.92	0.00	0.169	1.03
6	-4.79	0.01	1.9×10^4	0.855	-2.35	-0.43	36.60	-0.06	0.601	2.79
12	-4.98	0.01	2.11	0.849	-2.54	-0.39	35.53	-0.07	0.711	3.53
18	-4.17	0.02	1.77	0.883	-1.75	-0.57	27.44	-0.06	0.692	2.77

Table 4.5: Summary of isotherm coefficients for Zn, with time varied from 15-60mins.

Time (min)	Freundlich				Langmuir					
	$\ln K_f$	K_f	$1/n$	R^2	$1/Q_o$	Q_o	$1/Q_oB$	B	R^2	R_L
15	-17.71	0.00	6.81	0.544	-4.04	-0.25	68.18	-0.06	0.404	2.45
30	0.99	2.70	-0.21	0.002	1.62	0.62	-11.65	-0.14	0.210	-2.54
45	-4.89	0.01	1.64	0.124	-1.10	-0.91	41.06	-0.03	0.030	1.36
60	3.00	20.01	-0.01	0.541	-3.11	-0.32	66.75	-0.05	0.603	1.87

Table 4.4 and 4.5 both show the results of isotherms for Zinc. It was observed that the R^2 yielded were much higher in Freundlich following by their K values. This can be concluded that the adsorption behavior followed the Freundlich isotherm. However, in table 4.3, the R^2 values were unstable highs and lows due to inconsistency of the readings. The experiment should be re done to study MIRHA's exact behavior in a smaller contact time.

4.8.3   Adsorption Isotherms for COD

Table 4.6: Summary of isotherm coefficients for COD, with time varied from 1-18 hours.

Time (hrs)	Freundlich				Langmuir					
	InK_f	K_f	$1/n$	R^2	$1/Q_o$	Q_o	$1/Q_oB$	B	R^2	R_L
1	-44.80	3.5×10^{-20}	7.53	0.190	-0.73	-1.36	441.61	0.00	0.218	1.02
2	-34.66	8.86×10^{-16}	7.53	0.156	-0.24	-4.22	184.61	0.00	0.022	1.01
3	-53.65	5.01×10^{-24}	9.00	0.666	-0.71	-1.40	413.35	0.00	0.565	1.02
4	-52.40	1.75×10^{-23}	8.81	0.512	-0.73	-1.36	421.05	0.00	0.518	1.02
5	143.56	2.2×10^{50}	-22.84	0.901	2.05	0.49	-936.06	0.00	0.884	1.02
6	-42.26	4.43×10^{-19}	7.41	0.147	-0.31	-3.24	167.16	0.00	0.046	1.02
12	17.52	4.07×10^7	-2.46	0.106	0.29	3.49	-85.86	0.00	0.251	1.03
18	9.83	1.86×10^4	-1.20	0.007	0.10	10.40	-1.27	-0.08	0.010	4.11

Table 4.7: Summary of isotherm coefficients for COD, with time varied from 15-60 mins.

Time (min)	Freundlich				Langmuir					
	$In K_f$	K_f	$1/n$	R^2	$1/Q_o$	Q_o	$1/Q_oB$	B	R^2	R_L
15	-6.08	0.00	1.50	0.110	-0.02	-56.18	28.83	0.00	0.022	1.01
30	-36.65	1.2×10^{-16}	6.26	0.383	-0.13	-7.63	99.64	0.00	0.238	1.01
45	107.25	3.78×10^{46}	-16.15	0.140	0.45	2.20	-259.87	0.00	0.146	1.02
60	26.70	3.92×10^{11}	-3.61	0.071	0.30	3.34	-165.68	0.00	0.268	1.02

Table 4.6 and 4.7 both show the results of isotherms for COD. It was observed that the R^2 yielded were much higher in Freundlich following by their K values. This can be concluded that the adsorption behavior followed the Freundlich isotherm. However, in table 4.3, the R^2 values were unstable highs and lows due to inconsistency of the readings. The experiment should be re done to study MIRHA's exact behavior in a smaller contact time.

4.8.4 Adsorption Isotherms for Color

Table 4.8: Summary of isotherm coefficients for color, with time varied from 1-18 hours.

Time (hrs)	Freundlich				Langmuir					
	$\ln K_f$	K_f	$1/n$	R^2	$1/Q_o$	Q_o	$1/Q_oB$	B	R^2	R_L
1	-11.77	7.73×10^{-6}	2.23	0.920	-0.01	-107.53	30.05	0.00	0.677	1.00
2	-17.55	2.4×10^{-8}	3.01	0.845	-0.02	-61.73	42.10	0.00	0.749	1.00
3	-23.69	5.15×10^{-11}	3.92	0.928	-0.02	-50.00	42.02	0.00	0.736	1.00
4	-14.39	5.6×10^{-7}	2.71	0.543	-0.01	-88.50	23.78	0.00	0.291	1.00
5	16.87	2.13×10^{7}	-1.70	0.024	0.03	30.77	-27.02	0.00	0.150	1.01
6	-36.32	1.68×10^{-16}	6.42	0.831	-0.03	-32.26	24.16	0.00	0.735	1.01
12	91.07	3.6×10^{39}	-13.02	0.542	0.07	14.71	-44.76	0.00	0.346	1.02
18	-23.25	8×10^{-11}	4.28	0.194	0.07	-0.03	26.92	-1.29	0.276	-0.08

. Table 4.9: Summary of isotherm coefficients for color, with time varied from 15-60 mins.

Time (min)	Freundlich				Langmuir					
	$\ln K_f$	K_f	$1/n$	R^2	$1/Q_o$	Q_o	$1/Q_oB$	B	R^2	R_L
15	-7.86	0.00	1.82	0.371	0.00	-454.55	9.73	0.00	0.137	1.00
30	21.63	2.5×10^{9}	-2.04	0.114	0.01	105.26	-14.14	0.00	0.294	1.01
45	-13.27	0.00	2.45	0.617	0.00	-250.00	17.04	0.00	0.357	1.00
60	4.44	84.99	0.19	0.007	0.00	714.29	3.34	0.00	0.042	1.00

Table 4.2 and 4.3 both show the results of isotherms for Color. It was observed that the R^2 yielded were much higher in Freundlich following by their K values. This can be concluded that the adsorption behavior followed the Freundlich isotherm. However, in table 4.3, the R^2 values were unstable highs and lows due to inconsistency of the readings. The experiment should be re done to study MIRHA's exact behavior in a smaller contact time

4.9   Kinetics Study

Based on the results of all the parameters, it can be concluded that since the R value for second order is higher than the latter, the kinetics behavior on adsorption are best fitted in the pseudo-kinetic-second order which is the chemisorptions. Chemisorption is a sub-class of adsorption, driven by a chemical reaction occurring at the exposed surface. A new chemical species is generated at the adsorbent surface (e.g. corrosion, metallic oxidation). The strong interaction between the adsorbate and the substrate surface creates new types of electronic bonds - ionic or covalent, depending on the reactive chemical species involved. Shown below are the graphs and table for all tested parameters, first and second order.

4.9.1 Pseudo-first Order Kinetics for Copper, Zinc, COD and Color

Figure 4.18 to 4.21 show the linear plot of the pseudo-first order models, respectively while table 4.10 through 4.13 are the tables showing the value of K1 and R^2. It was observed that the adsorption for all parameters; Cu, Zn, COD and Color did not follow the monomolecular reaction as they all yielded low R^2 and K1 values where all the lines were inconsistent showing the sign of instability. Hence, the pseudo-second order graphs are plotted.
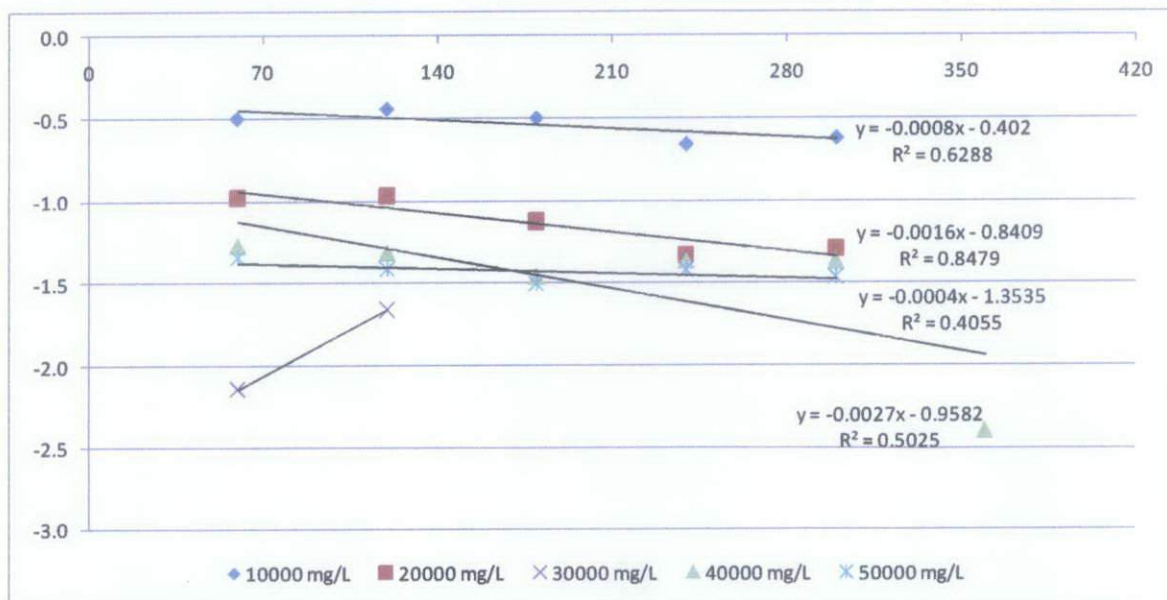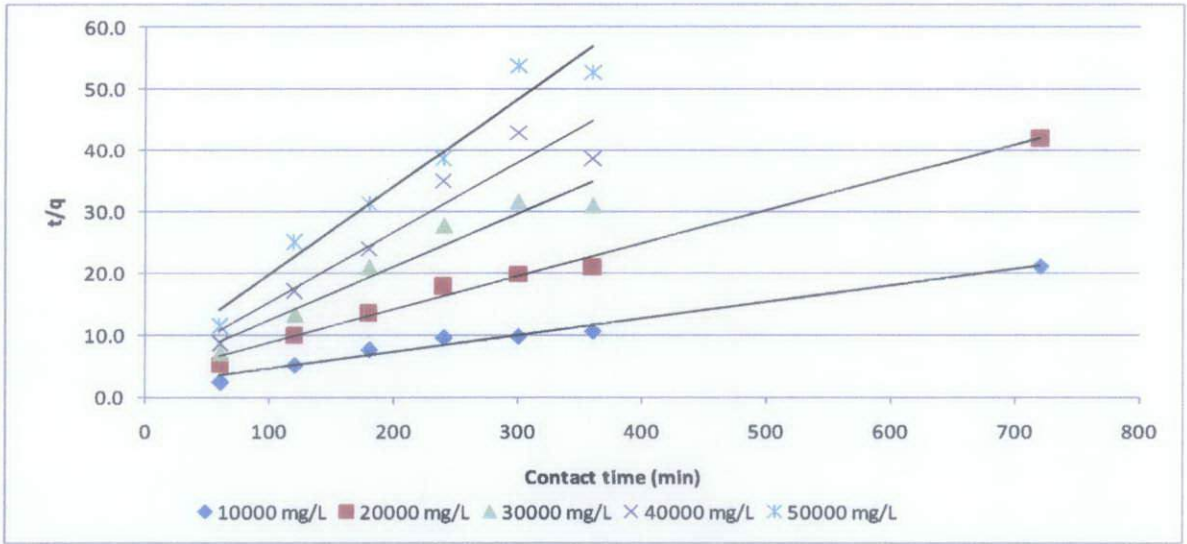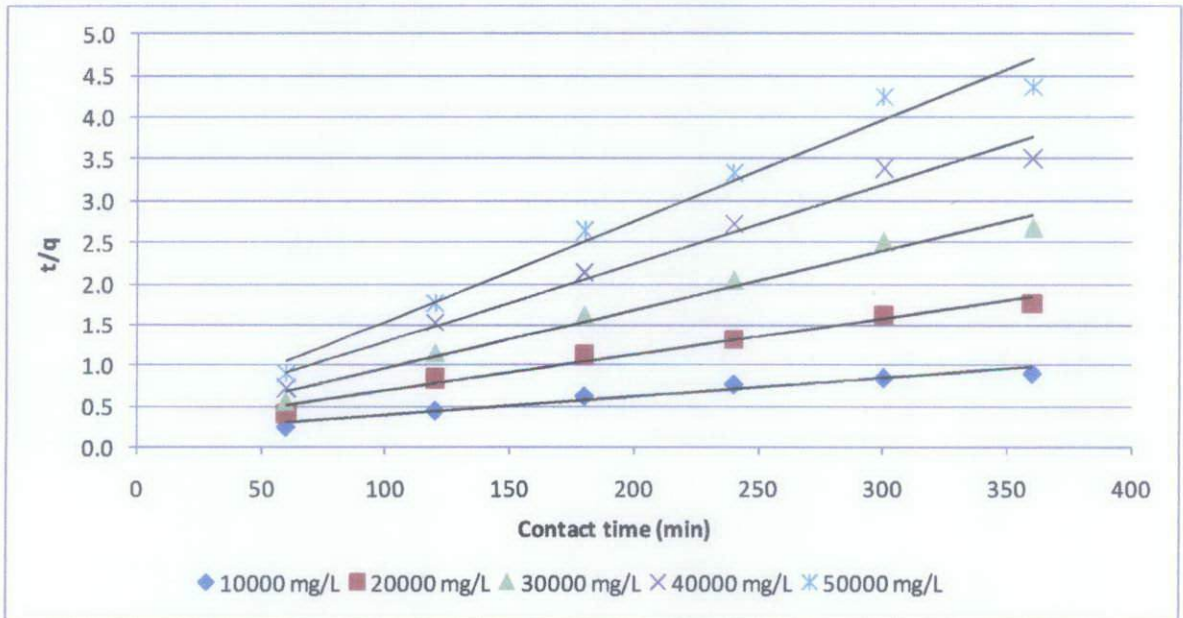

Figure 4.18: Linear plot lines of pseudo-first order kinetics for Copper at various dosages.

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Table 4.10: K1 and R^2 values for Copper at various dosages.

MIRHA Conc (mg/L)	k1	R2	Equation
10000	0.0008	0.6288	y = -0.0008x - 0.402
20000	0.0016	0.8479	y = -0.0016x - 0.8409
30000	0.008	1	y = - 0.008x - 2.6118
40000	0.0027	0.5025	y = - 0.0027 - 0.9582
50000	0.0004	0.4055	y = - 0.0004 - 1.3535
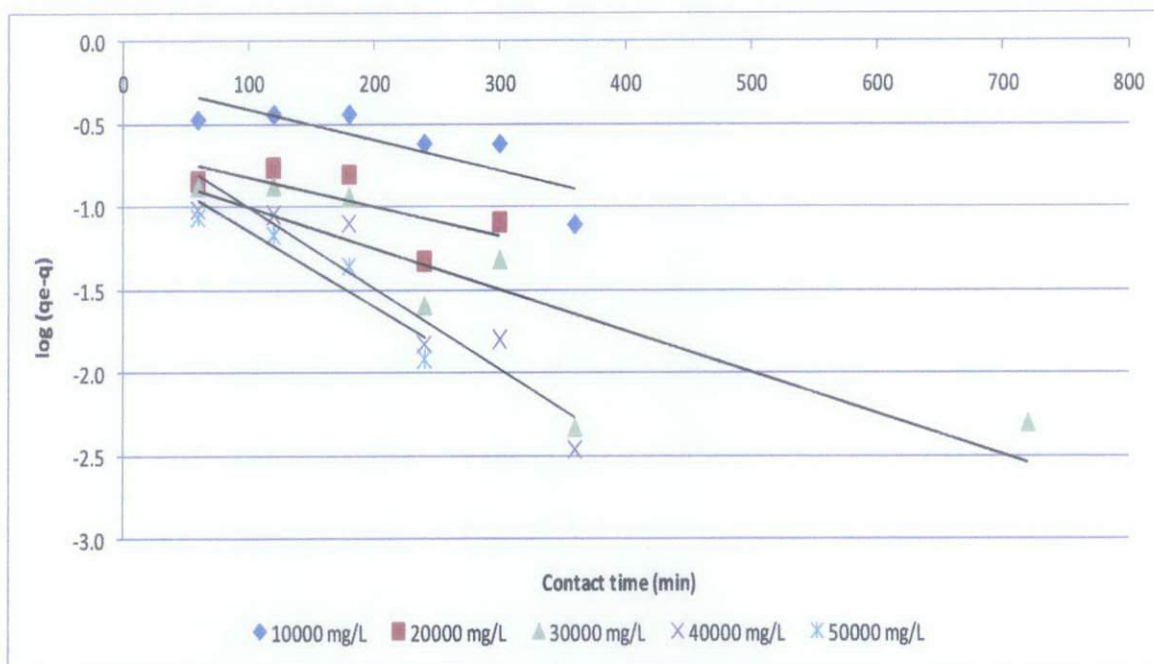
Figure 4.19: Linear plot lines of pseudo-first order kinetics for Zinc at various dosages.

Table 4.11: K1 and R^2 values for Zinc at various dosages.

MIRHA Conc (mg/L)	k1	R2	Equations
10000	0.0018	0.668	0.0018x - 0.2277
20000	-0.0018	0.4892	0.0018x - 0.6484
30000	0.0025	0.7083	0.0025x - 0.7577
40000	0.0048	0.8701	0.0048x - 0.5206
50000	0.0046	0.8708	0.0046x - 0.6851

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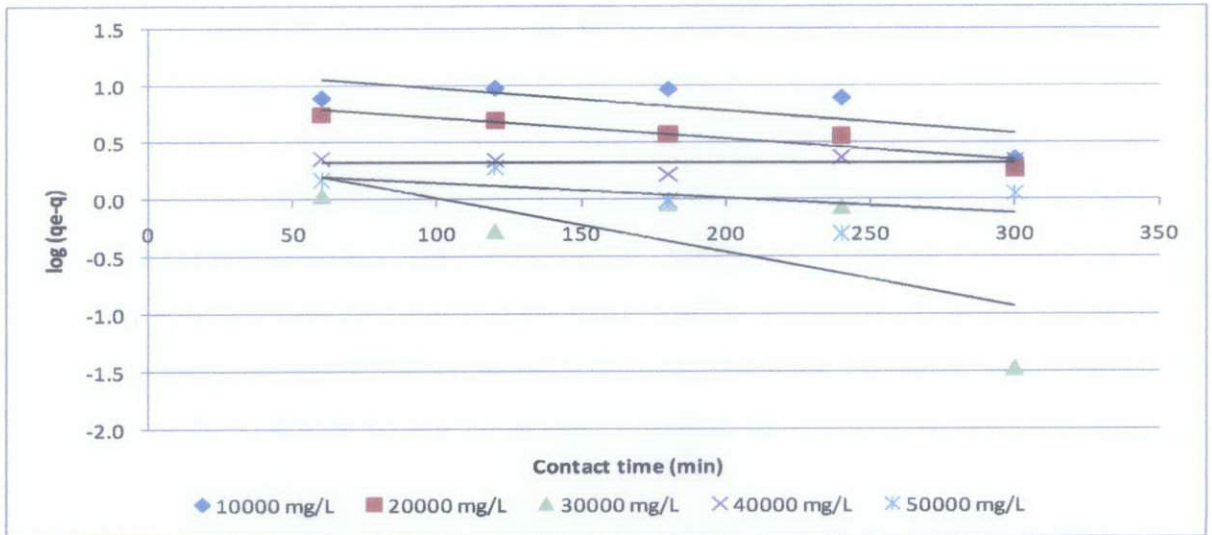
Figure 4.20: Linear plot lines of pseudo-first order kinetics for COD at various dosages.

Table 4.12: K1 and R^2 values for COD at various dosages.

MIRHA Conc (mg/L)	k1	R2	Equations
10000	0.0019	0.492	0.0019x + 1.1694
20000	0.0018	0.8648	0.0018x + 0.9028
30000	0.0047	0.4948	0.0047x + 0.4877
40000	2.00E-05	0.0006	2E-05x + 0.3256
50000	0.0014	0.3504	0.0014x + 0.2865
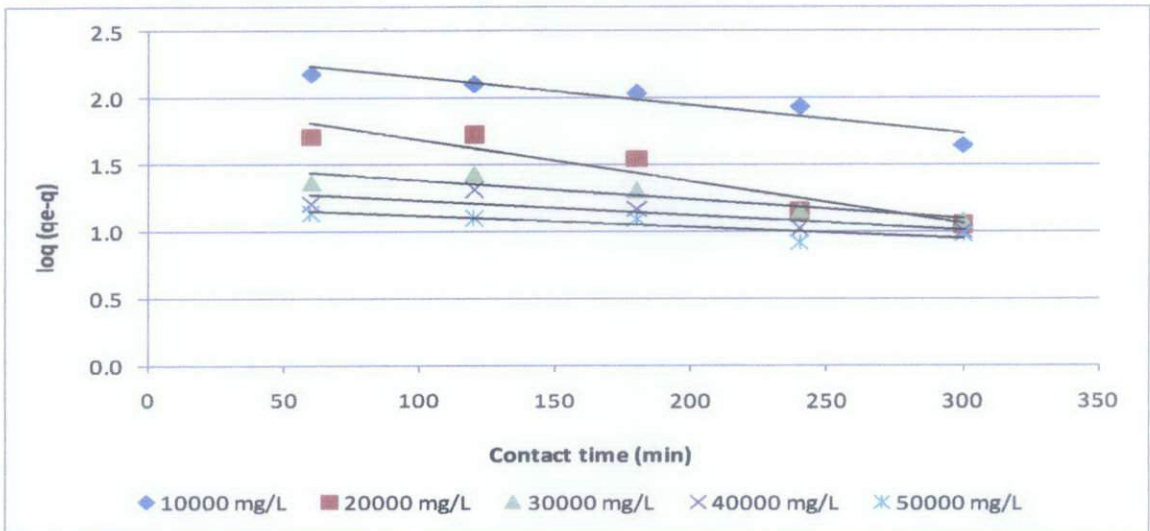
Figure 4.21: Linear plot lines of pseudo-first order kinetics for Color at various dosages.

Table 4.13: K1 and R^2 values for Color at various dosages.

MIRHA Conc (mg/L)	k1	R2	Equation
10000	0.0021	0.8885	0.0021x + 2.3593
20000	0.0031	0.8923	0.0031x + 2.0017
30000	0.0014	0.8319	0.0014x + 1.5214
40000	0.0011	0.707	0.0011x + 1.3485
50000	0.0008	0.7238	0.0008x + 1.1952

4.9.2 Pseudo-second-order Kinetics for Copper, Zinc, COD and Color

Figure 4.22 to 4.25 are the linear plots of pseudo-second order models of all the parameters while table 4.14 through 4.17 are the K1 and R^2 values, respectively. It can be well described that all the parameters are compliance to the pseudo-second order kinetic as they strongly showed high values of K1 and R^2. This suggests chemical adsorption or chemisorptions between the adsorbent and the adsorbate. A similar phenomenon was observed in the adsorption of color from textile wastewater using oil palm ash (Isa et al., 2008).
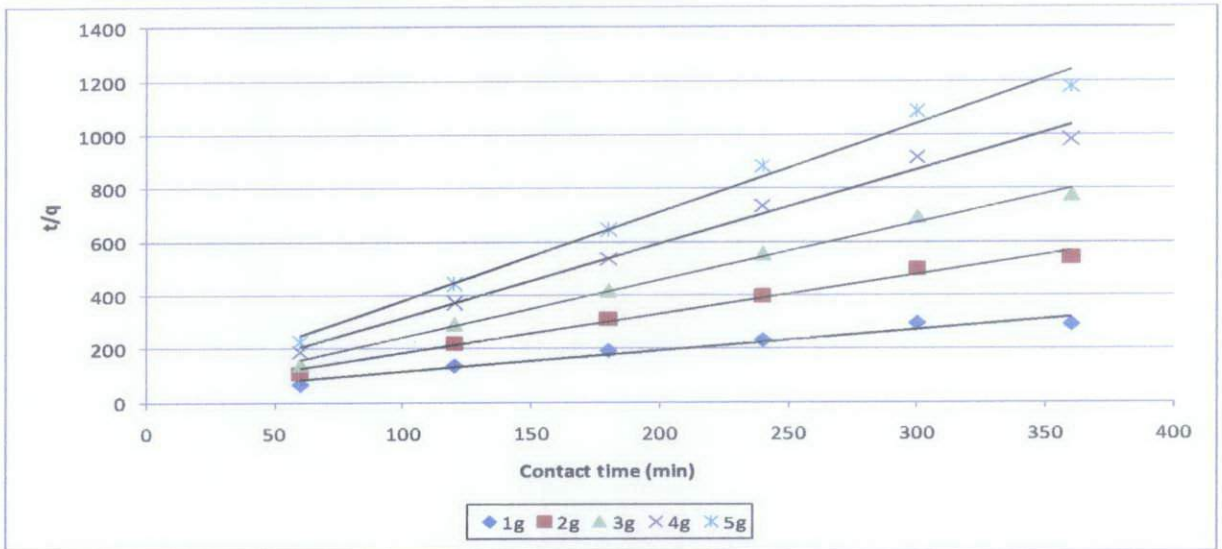
Figure 4.22: Linear plot lines of pseudo-second order kinetics for Copper at various dosages.

Table 4.14: K1 and R^2 values for Copper at various dosages.

MIRHA Conc (mg/L)	k1	R2	Equation
10000	0.7951	0.9254	0.7951x + 35.961
20000	1.4727	0.9892	1.4727x + 38.62
30000	2.147	0.9948	2.147x + 29.229
40000	2.7606	0.9874	2.7606x + 42.746
50000	3.3081	0.9885	3.3081x + 50.308
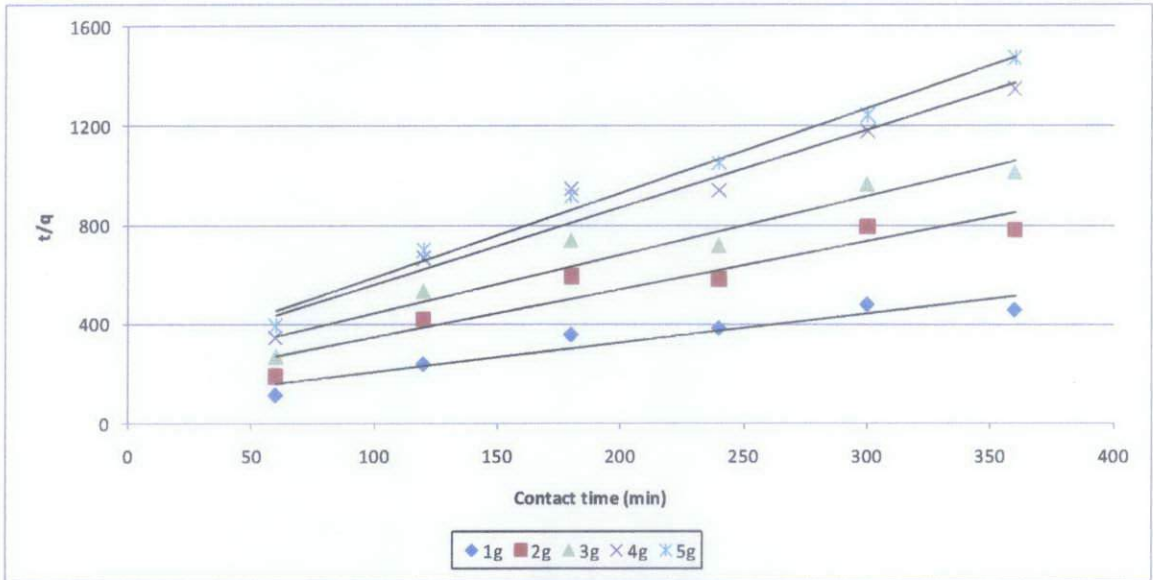
Figure 4.23: Linear plot lines of pseudo-second order kinetics for Zinc at various dosages.

Table 4.15: K1 and R^2 values for Zinc at various dosages.

MIRHA Conc (mg/L)	k1	R2	Equations
10000	1.1709	0.8973	1.1709x + 90.681
20000	1.9398	0.9032	1.9398x + 152.64
30000	2.3818	0.9288	2.3818x + 205.43
40000	3.4165	0.9871	3.4165x + 246.64
50000	3.1234	0.9495	3.1234x + 249.81

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Figure 4.24: Linear plot lines of pseudo-second order kinetics for COD at various dosages.

Table 4.16: K1 and R^2 values for COD at various dosages.

MIRHA Conc (mg/L)	k1	R2	Equations
10000	0.0268	0.9784	0.0268x + 1.885
20000	0.0538	0.9904	0.0538x + 3.311
30000	0.0863	0.9283	0.0863x + 3.8935
40000	1.14E-01	0.9088	0.1138x + 3.8527
50000	0.1427	0.9551	0.1427x + 5.5868

Figure 4.25: Linear plot lines of pseudo-second order kinetics for Color at various dosages.

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Table 4.17: K1 and R^2 values for Color at various dosages.

MIRHA Conc (mg/L)	k1	R2	Equation
10000	0.0022	0.9511	0.0022x + 0.1769
20000	0.0044	0.9767	0.0044x + 0.2553
30000	0.0072	0.9805	0.0072x + 0.2445
40000	0.0096	0.9727	0.0096x + 0.3347
50000	0.0121	0.9747	0.0121x + 0.3372

CHAPTER 5

CONCLUSION AND RECOMMENDATIOS

5.1 Conclusion

Rice husk ash is an abundance source that can be obtained in many places around the world, exclusively in Malaysia itself. Their method of disposal was said to be conventional and not enviromental friendly to the world nowadays. With recycling rice husk, it can be made use on so many things which one of them is as an adsorbent for the adsorption process.

Adsorption capacity is strongly dependant on contact time, pH, and adsorbent dosage. The experimental data were fitted in Langmuir and Freundlich equation, which the adsorption behavior was seen to be fitted well in the Freundlich isotherms as the values of R^2 yielded were higher. Increase of dosage seemed to be more effective in most of the experiments where the minimum dosage to remove all parameters was seen at 10000 mg/L. In the effect contact time, the minimum time taken for MIRHA to be adsorbed was seen at as low as 1 hour.

With all the results presented, MIRHA proved to be useful in adsorbing Cu, Zn, COD and Color in POME to an acceptable level set by the Department of Environment, (DOE). However, further studies need to be put on the effect of MIRHA in reducing the amount of COD concentration in POME. The highest percentage removal achieved was only at 48%. Nevertherless, MIRHA managed to remove other parameters successfully and therefore proved to be use as an alterative adsorbent for the adsroption tehcnology.

5.2 Recommendations

For further research in in completing this topic, there are some some recommendations the author would like to highlight. They are:

1. To use the real wastewater that contain heavy metals instead of using real wastewater that does not contain heavy metals.

2. To further the effect of contact time in order to see the equilibrium of the graphs, as to determine the optimum dosage of MIRHA.

3. To sychronize the dosage with the time contact as to monitor its process on each of the dosages.

4. To investigate further on removing COD using MIRHA, as the present study produced were unstable and did not fulfill the expectation.

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Appendix A.1

Dosage x10^3 (mg/L)		0.0	10.0	20.0	30.0	40.0	50.0
Parameter		Conc (mg/L)					
	Raw	Cu (II)	Cu (II)	Cu (II)	Cu (II)	Cu (II)	Cu (II)
Time	0.00	17.93	17.93	17.93	17.93	17.93	17.93
(hours)		0	0	0	0	0	0
1	1	15.38	8.82	7.52	4.56	5.21	4.56
	2	15.07	8.45	6.64	5.83	5.06	4.83
	3	15.08	8.60	6.98	5.38	5.52	4.75
	ave	15.18	8.62	7.05	5.25	5.27	4.71
	%	15.36	51.90	60.70	70.70	70.63	73.71
2	1	14.94	9.08	7.35	5.59	5.22	4.52
	2	15.22	9.23	6.75	5.63	5.38	4.47
	3	15.03	8.94	7.11	5.84	4.66	4.13
	ave	15.06	9.08	7.07	5.69	5.08	4.37
	%	16.01	49.35	60.58	68.28	71.65	75.61
3	1	16.12	8.43	6.64	5.55	4.41	4.15
	2	15.65	8.58	6.62	4.80	4.40	4.02
	3	15.25	8.87	6.06	4.73	4.76	3.86
	ave	15.67	8.63	6.44	5.03	4.52	4.01
	%	12.59	51.89	64.09	71.96	74.77	77.64
4	1	16.29	7.64	5.88	5.15	4.68	4.11
	2	16.52	7.86	5.86	4.56	5.04	4.60
	3	16.96	7.43	5.83	5.20	4.87	4.32
	ave	16.59	7.64	5.86	4.97	4.86	4.35
	%	7.47	57.37	67.34	72.28	72.88	75.76
5	1	16.72	8.05	5.94	5.41	4.85	4.22
	2	17.20	7.68	5.97	5.72	4.93	4.03
	3	17.30	7.79	5.98	5.60	4.74	4.27
	ave	17.07	7.84	5.96	5.58	4.84	4.17
	%	4.77	56.29	66.74	68.91	73.01	76.73
6	1	13.06	5.74	5.13	4.37	3.55	2.68
	2	11.85	5.02	4.38	3.77	3.18	2.68
	3	14.41	6.23	4.57	3.91	3.15	3.66
	ave	13.11	5.66	4.69	4.02	3.29	2.68
	%	26.89	68.41	73.84	77.60	81.64	85.07
12	1	13.33	6.52	5.05	4.07	3.62	1.71
	2	11.01	5.26	4.75	3.68	2.97	2.56
	3	11.71	5.32	5.13	3.27	2.56	2.40
	ave	12.02	5.70	4.97	3.68	3.05	2.48
	%	32.97	68.21	72.27	79.50	82.99	86.17
18	1	11.79	5.45	3.88	3.03	2.20	3.06
	2	13.64	5.10	3.44	3.21	1.95	2.52
	3	12.86	4.43	3.90	2.57	2.66	2.46
	ave	12.76	4.99	3.74	2.94	2.43	2.49
	%	28.81	72.15	79.13	83.62	86.45	86.13

Table 1: Results on residual Cu concentration and percentage removal using MIRHA as adsorbent.

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Appendix A.2

Dosage x10^3 (mg/L)		0.0	10.0	20.0	30.0	40.0	50.0
Parameter		Conc (mg/L)					
	Raw	Zn (II)	Zn (II)	Zn (II)	Zn (II)	Zn (II)	Zn (II)
Time (hours)	0.00	17.49	17.49	17.49	17.49	17.49	17.49
		0	0	0	0	0	0
1	1	14.79	10.57	11.65	10.53	10.98	9.00
	2	14.68	12.14	11.52	11.11	10.65	10.80
	3	14.61	12.20	10.29	10.55	10.00	9.74
	ave	14.69	12.17	11.15	10.73	10.54	9.85
	%	15.98	30.41	36.22	38.67	39.72	43.71
2	1	14.25	12.33	12.00	10.75	9.62	8.13
	2	14.82	12.75	11.66	10.81	10.70	8.67
	3	15.09	12.51	11.65	10.71	10.60	9.93
	ave	14.67	12.42	11.77	10.75	10.31	8.91
	%	16.12	28.98	32.70	38.51	41.06	49.06
3	1	14.00	12.35	11.72	11.00	10.00	7.35
	2	15.04	12.60	10.96	10.38	9.67	7.27
	3	14.72	12.34	11.63	10.00	10.00	8.52
	ave	14.36	12.43	11.43	10.19	9.89	7.71
	%	17.90	28.94	34.62	41.74	43.46	55.91
4	1	15.11	11.60	8.53	7.08	7.40	5.58
	2	14.98	10.49	9.29	6.72	7.18	6.19
	3	15.29	11.53	9.20	7.85	5.62	6.51
	ave	15.12	11.21	9.24	7.46	7.29	6.10
	%	13.53	35.93	47.14	57.32	58.31	65.14
5	1	14.91	11.40	10.43	9.22	6.55	5.64
	2	15.27	10.93	9.92	9.18	7.81	5.23
	3	15.05	11.26	10.02	8.15	7.64	5.49
	ave	15.08	11.20	9.92	8.15	7.33	5.45
	%	13.79	35.98	43.28	53.40	58.08	68.84
6	1	12.83	6.68	10.13	8.26	6.87	4.84
	2	14.55	9.00	6.04	6.61	6.73	5.70
	3	14.67	10.15	8.70	5.62	6.89	3.86
	ave	14.61	9.58	8.29	6.83	6.83	5.27
	%	16.48	45.25	52.60	60.95	60.96	69.88
12	1	15.33	9.84	9.18	7.12	5.20	4.29
	2	12.19	7.67	8.25	6.84	6.26	5.71
	3	10.16	6.92	9.37	7.17	6.01	5.82
	ave	12.56	8.75	8.25	6.84	5.82	5.28
	%	28.20	49.96	52.83	60.89	66.70	69.83
18	1	11.64	10.99	9.30	8.03	3.79	4.90
	2	15.65	8.39	7.66	6.54	6.49	4.54
	3	14.19	9.04	9.01	6.69	5.79	4.44
	ave	13.82	8.71	7.66	6.61	5.36	4.63
	%	20.96	50.18	56.20	62.19	69.36	73.54

Table 2: Results on residual Zn concentration and percentage removal using MIRHA as adsorbent.

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Appendix A.3

Dosage x10³ (mg/L)		0		10		20		30		40		50	
Parameter		COD (mg/L)	%	COD (mg/L)	%	COD (mg/L)	%	COD (mg/L)	%	COD (mg/L)	%	COD (mg/L)	%
Raw		773	0	773	0	773	0	773	0	773	0	773	0
1	1	599		509		494		442		480		556	
	2	613	19.45	522	32.47	542	29.43	521	32.60	496	35.83	467	33.83
	3	656		461		549		440		446		467	
	ave	623		522		546		521		496		512	
2	1	657		546		550		492		526		560	
	2	631	19.19	531	30.34	515	31.11	504	34.80	493	36.22	534	30.92
	3	586		519		544		488		426		583	
	ave	625		539		533		504		493		534	
3	1	632		557		484		457		478		675	
	2	657	17.81	537	30.53	514	34.35	612	33.29	469	38.94	491	37.06
	3	617		547		501		478		469		482	
	ave	635		537		508		516		472		487	
4	1	618		577		552		490		558		455	
	2	646	18.28	499	32.47	506	34.54	540	33.55	499	35.45	470	40.17
	3	631		522		520		511		514		477	
	ave	632		522		506		514		499		463	
5	1	662		468		456		509		494		500	
	2	614	16.77	464	39.72	486	39.24	469	36.74	532	36.09	504	36.09
	3	654		451		467		462		494		494	
	ave	643		466		470		489		494		494	
6	1	617		435		352		425		401		432	
	2	503	34.80	430	44.05	433	44.4	482	45.02	400	48.19	493	44.11
	3	505		449		426		455		390		503	
	ave	504		433		430		425		401		432	
12	1	499		753		452		523		595		452	
	2	564	31.22	592	44.11	446	44.24	523	32.99	411	46.83	444	42.04
	3	532		432		431		518		546		473	
	ave	532		432		431		518		411		448	
18	1	710		622		649		561		526		459	
	2	613	20.83	445	42.43	510	42.43	561	36.87	449	41.91	488	44.11
	3	611		578		445		488		451		432	
	ave	612		445		445		488		449		432	

Table 3: Results on residual COD concentration and percentage removal using MIRHA as adsorbent.

Dosage x10³ (mg/L)		0		10		20		30		40		50	
Parameter		Color (PtCo)	%	Color (PtCo)	%	Color (PtCo)	%	Color (PtCo)	%	Color (PtCo)	%	Color (PtCo)	%
Raw		4700	0.0	4700	0.0	4700	0.0	4700	0.0	4700	0.0	4700	0.0
1	1	3900		2150		1950		1550		1450		1500	
	2	3100	0.0	2550	51.8	1600	61.3	1300	69.5	1300	70.2	1700	70.7
	3	4700		2100		1900		1450		1450		1250	
	ave	3900		2267		1817		1433		1400		1375	
2	1	350		1950		2050		1700		1600		1400	
	2	3450	0.0	2200	57.1	1700	60.3	1550	67.0	1650	66.3	1300	72.0
	3	3550		1900		1850		1400		1500		1250	
	ave	2450		2017		1867		1550		1583		1317	
3	1	3600		1750		1700		1250		1350		1300	
	2	3500	0.0	1900	61.0	1550	68.1	1250	71.3	1350	71.3	1400	72.3
	3	2800		1850		1250		1550		1350		1500	
	ave	3300		1833		1500		1350		1350		1300	
4	1	4350		1650		1050		1200		1250		1050	
	2	4100	0.0	1550	66.0	1100	77.0	1100	75.2	1100	74.8	1200	76.6
	3	4150		1250		1100		1200		1200		1050	
	ave	4200		1600		1083		1167		1183		1100	
5	1	3650		1250		850		1050		1100		1150	
	2	3600	0.0	1100	75.0	1000	78.2	1200	76.7	1200	75.2	1150	75.2
	3	3650		1200		1050		1050		1200		1200	
	ave	3633		1175		1025		1100		1167		1167	
6	1	2650		1600		1150		1600		1250		1050	
	2	2600	0.0	1400	84.6	1350	86.8	1300	86.2	1100	87.2	1200	87.8
	3	2550		1450		1150		1250		1200		1150	
	ave	2600		724		620		649		602		573	
12	1	3650		1400		1800		1550		1400		1450	
	2	3550	0.0	1400	85.2	1450	83.8	1450	84.0	1450	84.0	1400	84.7
	3	3550		1300		1550		1450		1600		1550	
	ave	3583		696		761		752		752		747	
18	1	5050		1500		1600		1350		1400		1400	
	2	4950	0.0	1400	84.3	1750	83.0	1550	83.4	1400	84.5	1400	85.6
	3	5000		1450		1550		1700		1500		1350	
	ave	5000		738		799		780		729		677	

Table 4: Results on residual color concentration and percentage removal using MIRHA as adsorbent.

Appendix A.5

Dosage x10^3 (mg/L)	Parameter		Time (min)	15	%	30	%	45	%	60	%
			Raw	Ave			Ave		Ave		Ave	
0	Conc (mg/L)	Cu (II)	19.9		0.0		0.0		0.0		0.0
		Zn (II)	20.0		0.0		0.0		0.0		0.0
	COD (mg/L)		773		0.0		0.0		0.0		0.0
	Colour (PtCo)		4000		0.0		0.0		0.0		0.0
	pH		4.96								
2	Conc (mg/L)	Cu (II)	19.9	14.6	26.56	14.8	25.55	18.1	8.85	19.5	1.81
		Zn (II)	20.0	15.2	24.05	13.1	34.27	18.2	8.82	20.0	-0.20
	COD (mg/L)		773	676	12.55	646	16.43	609	21.22	646	16.43
	Colour (PtCo)		4000	2600	35.00	2200	45.00	2750	31.25	2950	26.25
	pH		4.96	5.78		5.94		5.85		5.92	
4	Conc (mg/L)	Cu (II)	19.9	12.6	36.62	13.3	33.20	18.1	9.05	15.9	20.12
		Zn (II)	20.0	13.6	32.06	12.5	37.27	16.2	19.04	16.7	16.23
	COD (mg/L)		773	576	25.49	610	21.09	624	19.28	631	18.37
	Colour (PtCo)		4000	1850	53.75	1800	55.00	2550	36.25	1900	52.50
	pH		4.96	5.77		5.76		5.83		5.83	
6	Conc (mg/L)	Cu (II)	19.9	14.3	28.17	15.8	20.52	16.9	15.09	17.1	14.08
		Zn (II)	20.0	14.0	29.66	14.6	26.65	15.6	22.04	15.9	20.44
	COD (mg/L)		773	622	19.53	630	18.50	606	21.60	595	23.03
	Colour (PtCo)		4000	2000	50.00	2200	45.00	2450	38.75	2000	50.00
	pH		4.96	5.75		5.77		5.90		5.80	
8	Conc (mg/L)	Cu (II)	19.9	13.2	33.40	13.5	31.99	15.1	23.94	14.4	27.57
		Zn (II)	20.0	13.5	32.26	11.0	45.09	16.2	19.04	13.7	31.26
	COD (mg/L)		773	564	27.04	580	24.97	621	19.66	665	13.97
	Colour (PtCo)		4000	1950	51.25	2250	43.75	2000	50.00	2350	41.25
	pH		4.96	5.76		5.80		5.81		`	
100	Conc (mg/L)	Cu (II)								4.8	76.06
		Zn (II)								5.1	74.35
	COD (mg/L)									532	31.18
	Colour (PtCo)									1100	72.50
	pH									5.82	
200	Conc (mg/L)	Cu (II)								2.5	87.53
		Zn (II)								3.5	82.36
	COD (mg/L)									560	27.55
	Colour (PtCo)									900	77.50
	pH									5.62	

Table 5: Results on residual Cu, Zn, COD and Color and percentage removal using MIRHA, with time varied from 15-60 mins.

Appendix B.1

Calculation of weight required in preparation of Copper Chloride ($CuCl_2$) and Zinc Chloride ($ZnCl_2$) solution to be added into POME.

$Cu = 63.55$ g/mol $Cl_2 = 71$ g/mol

$CuCl_2 = 134.55$ g/mol

Mole ratio $= CuCl_2 / Cu$

$$= 2.117 \cong 2.12$$

As to prepare 20 mg/L of Cu concentration

$2.12 \times (20 \text{ mg/L}) = 42.4$ mg/L

For 10 L of solution

42.4 mg/L x 10 L = 424 mg of Cu.

$Zn = 65.39$ g/mol $Cl_2 = 71$ g/mol

$ZnCl_2 = 136.39$ g/mol

Mole ratio $= ZnCl_2 / Zn$

$$= 2.146 \cong 2.15$$

As to prepare 20 mg/L of Zn concentration

$2.15 \times (20 \text{ mg/L}) = 43$ mg/L

For 10 L of solution

43 mg/L x 10 L = 430 mg of Zn.
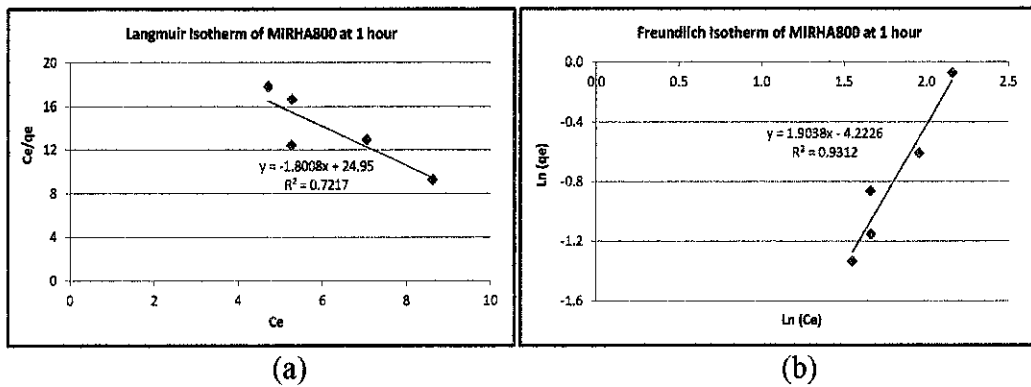
Figure C.1: Langmuir (a) and Freundlich (b) isotherms at 1 hr contact time for Cu.
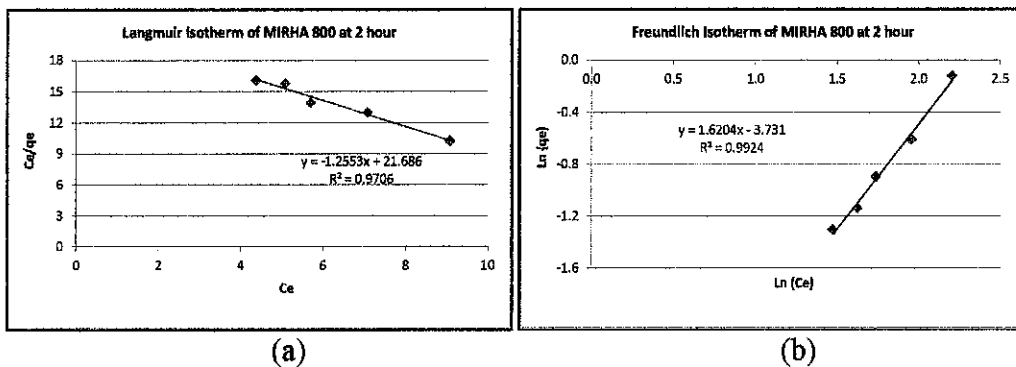
Figure C.2: Langmuir (a) and Freundlich (b) isotherms at 2 hr contact time for Cu.
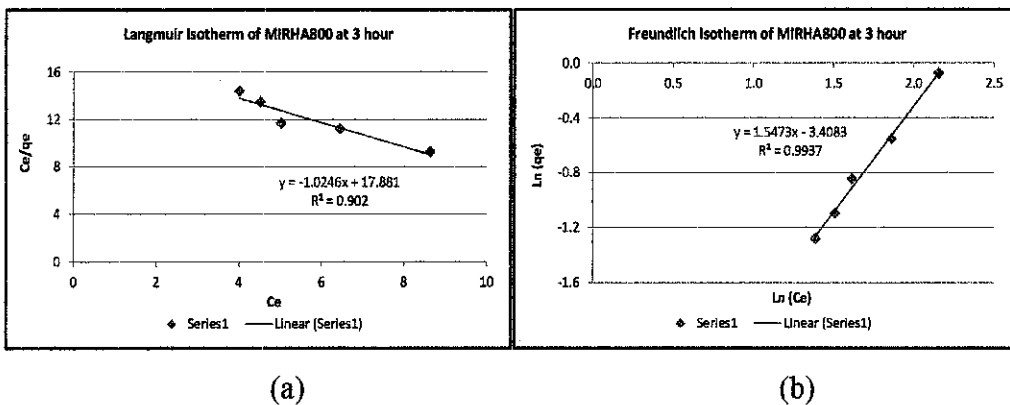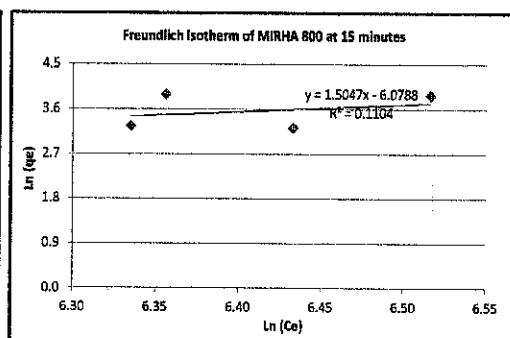

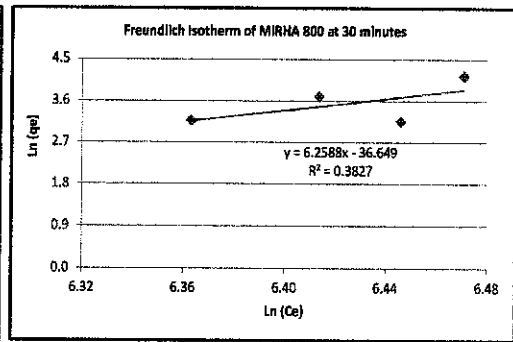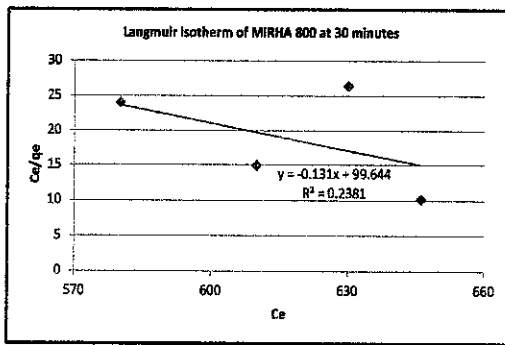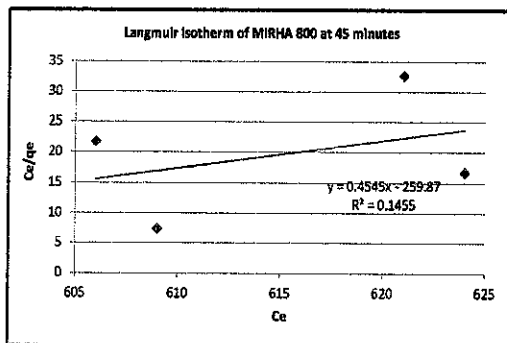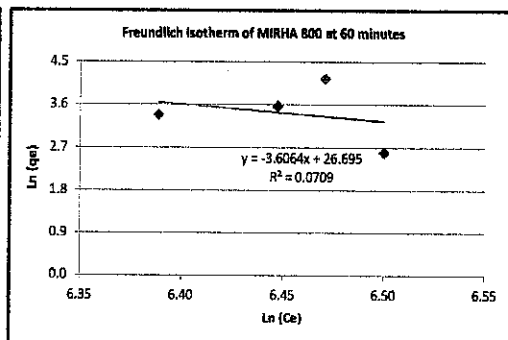Figure C.3: Langmuir (a) and Freundlich (b) isotherms at 3 hr contact time for Cu.
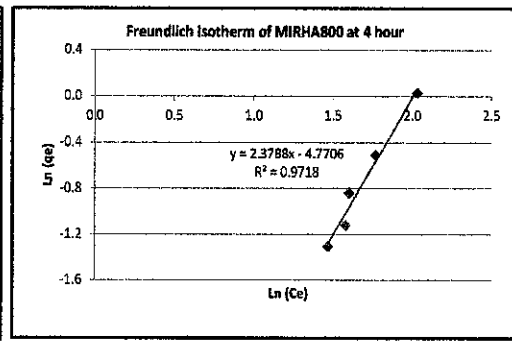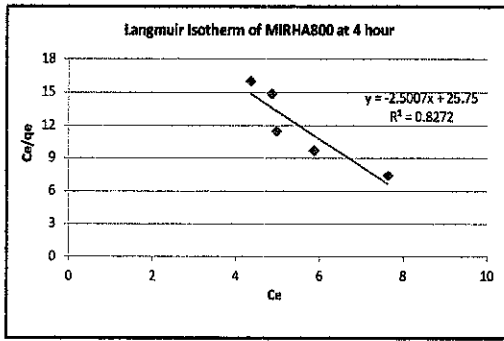
Figure C.4: Langmuir (a) and Freundlich (b) isotherms at 4 hr contact time for Cu.
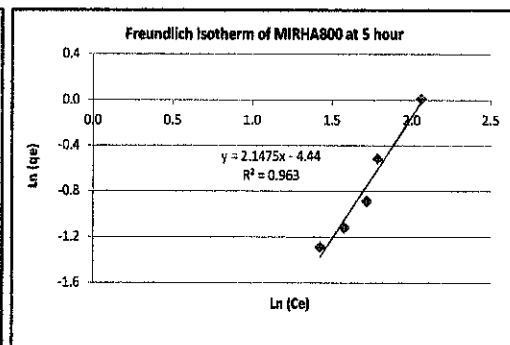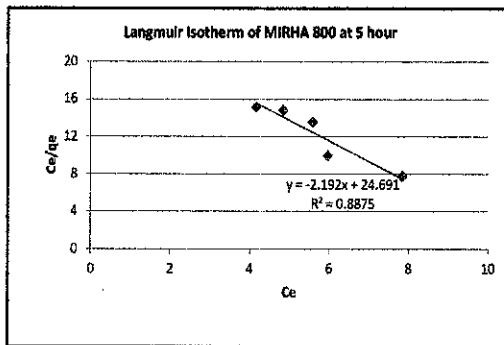
Figure C.5: Langmuir (a) and Freundlich (b) isotherms at 5 hr contact time for Cu.
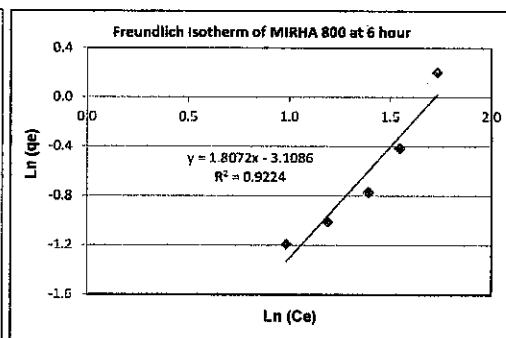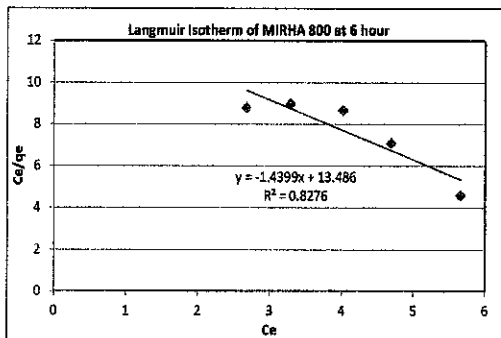
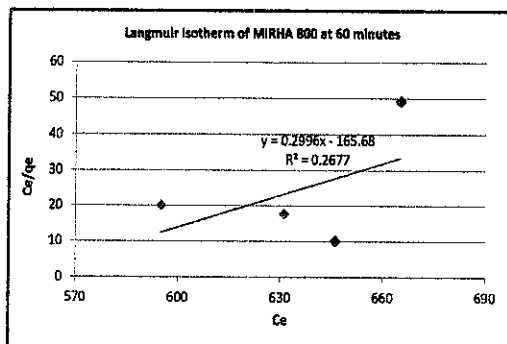
Figure C.6: Langmuir (a) and Freundlich (b) isotherms at 6 hr contact time for Cu.
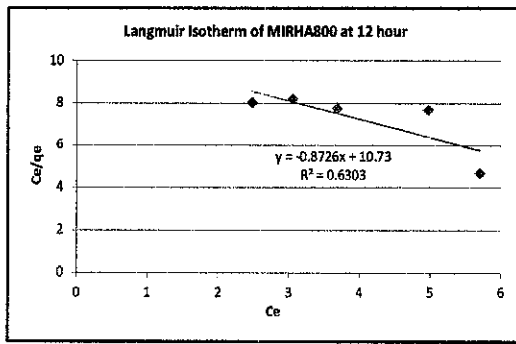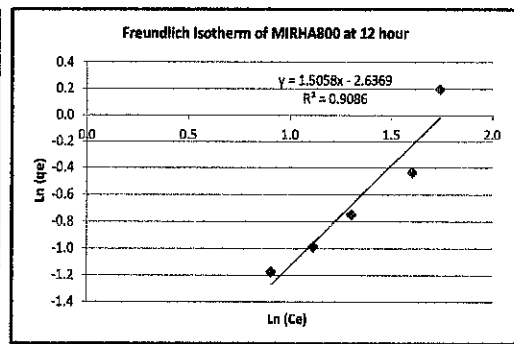
Figure C.7: Langmuir (a) and Freundlich (b) isotherms at 12 hr contact time for Cu.
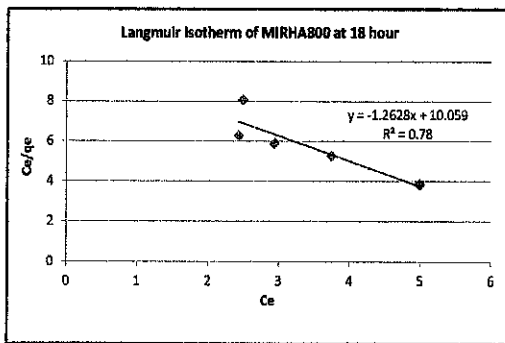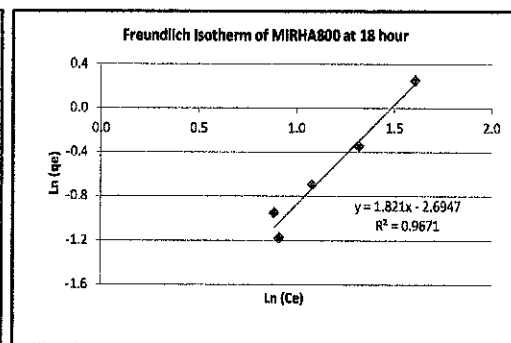
Figure C.8: Langmuir (a) and Freundlich (b) isotherms at 18 hr contact time for Cu.
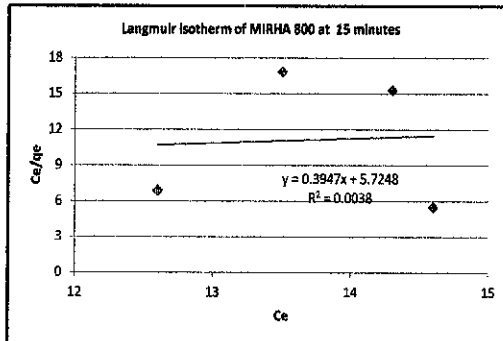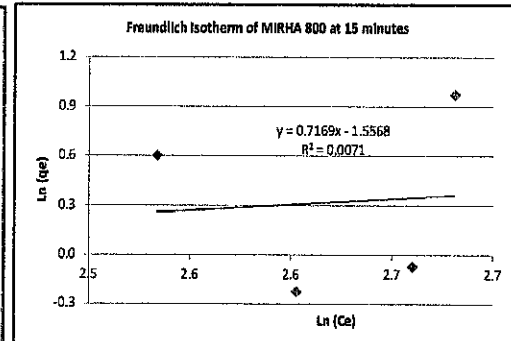
Figure C.9: Langmuir (a) and Freundlich (b) isotherms at 15 min contact time for Cu.
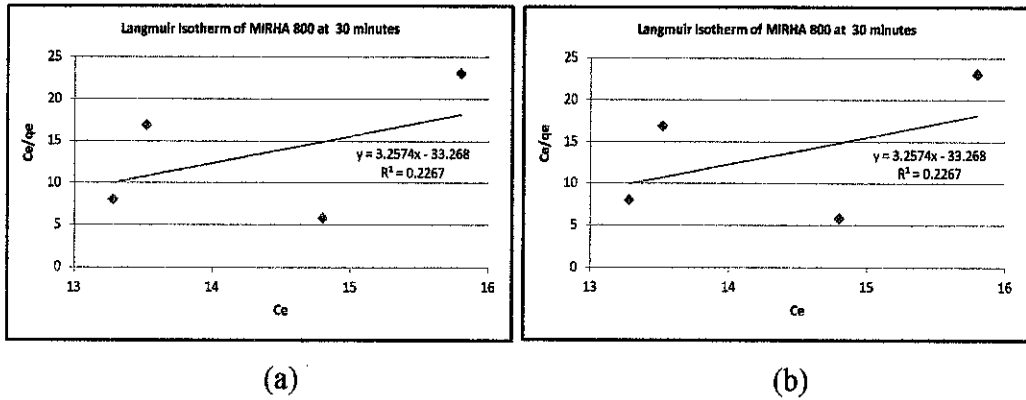
Figure C.10: Langmuir (a) and Freundlich (b) isotherms at 30 min contact time for Cu.
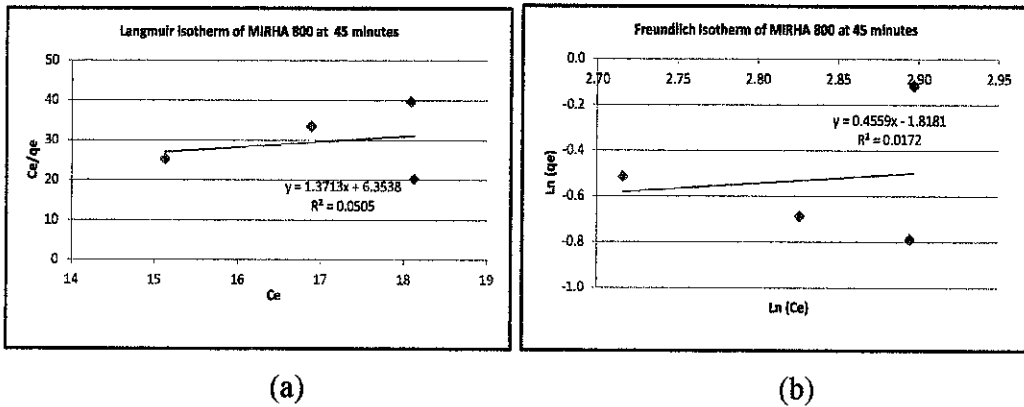
Figure C.11: Langmuir (a) and Freundlich (b) isotherms at 45 min contact time for Cu.
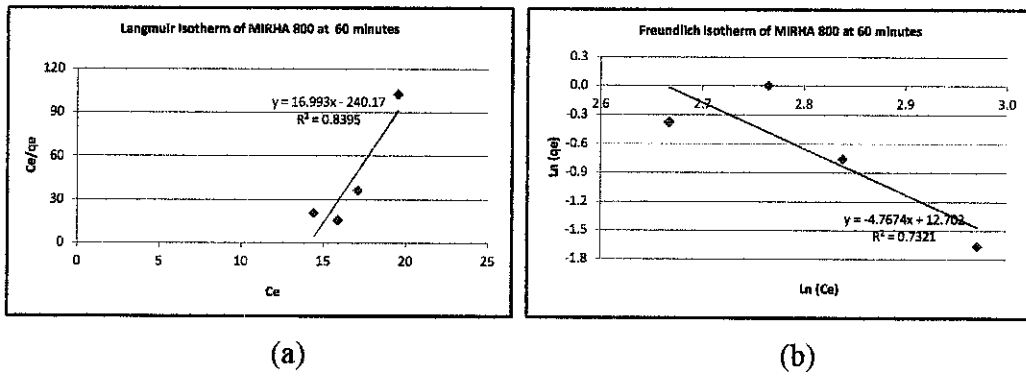
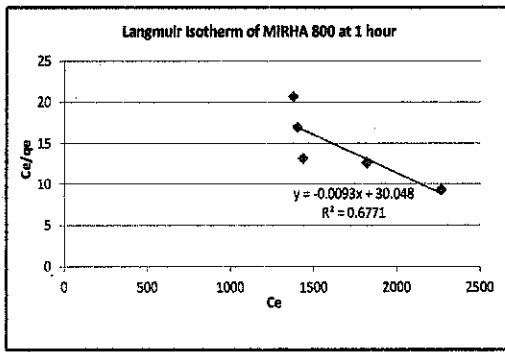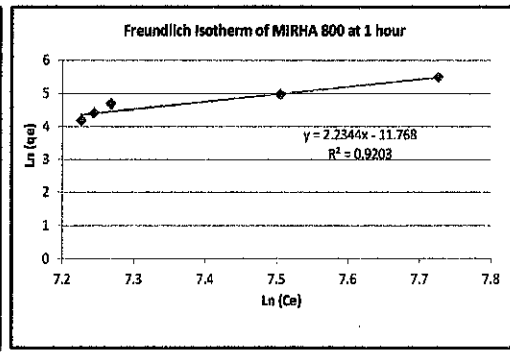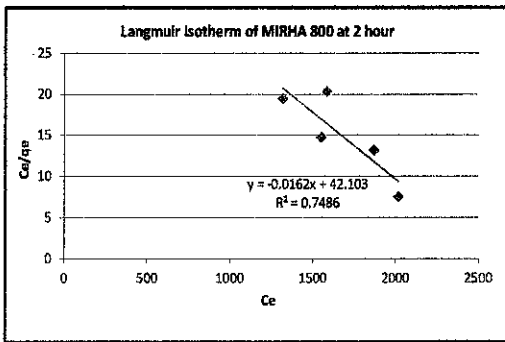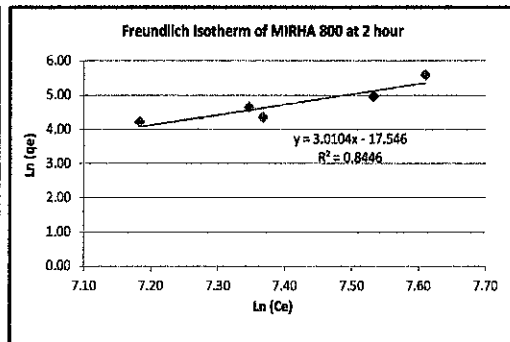Figure C.12: Langmuir (a) and Freundlich (b) isotherms at 60 min contact time for Cu.
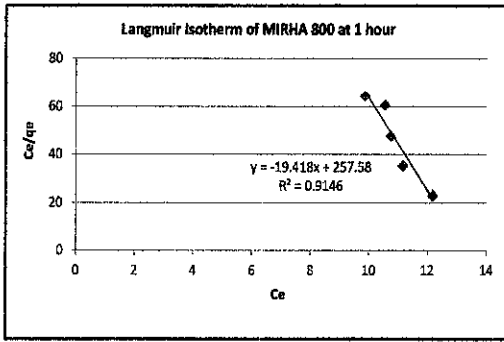
(a)
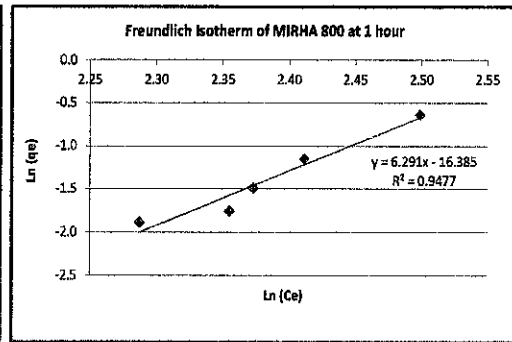
(b)

Figure C.13: Langmuir (a) and Freundlich (b) isotherms at 1 hr contact time for Zn.
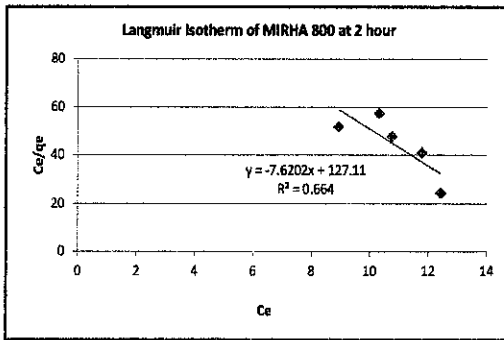
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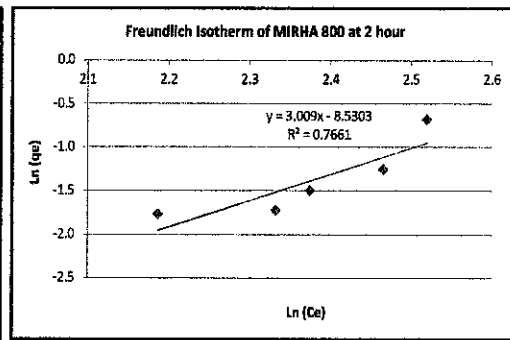
(b)

Figure C.14: Langmuir (a) and Freundlich (b) isotherms at 2 hr contact time for Zn.
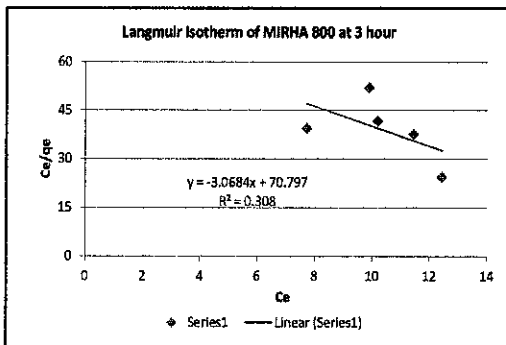
(a)
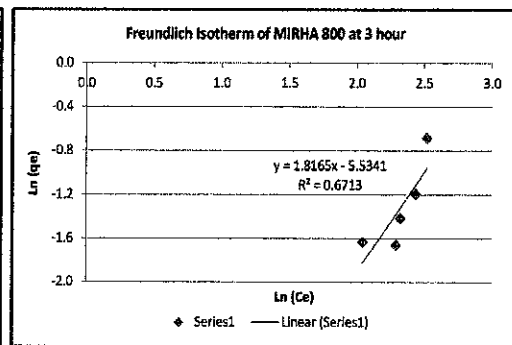
(b)

Figure C.15: Langmuir (a) and Freundlich (b) isotherms at 3 hr contact time for Zn.
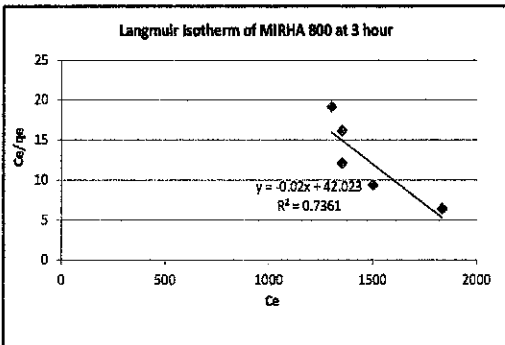
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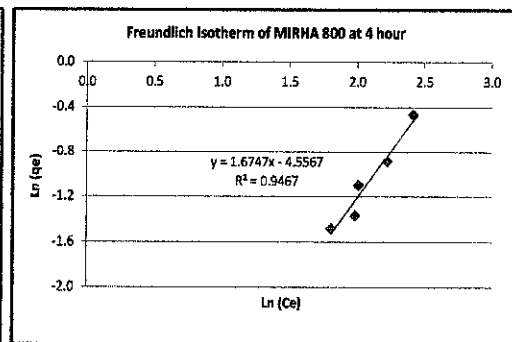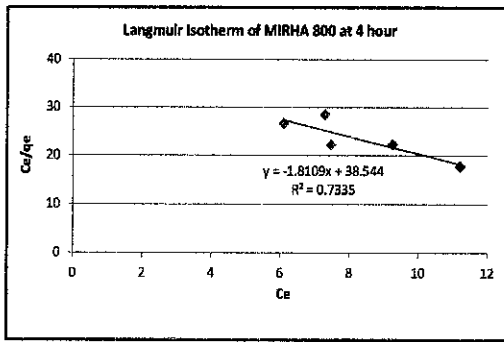
(a)　　　　　　　　　　　　(b)

Figure C.16: Langmuir (a) and Freundlich (b) isotherms at 4 hr contact time for Zn.
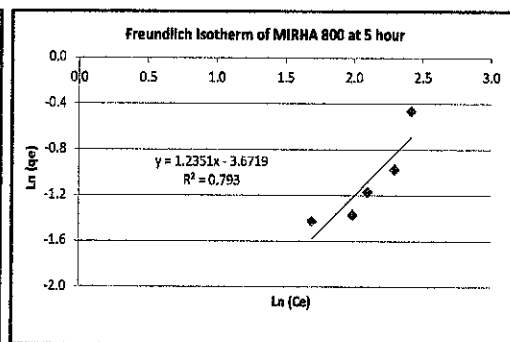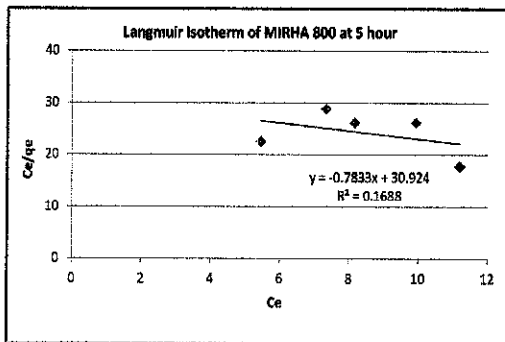
(a)　　　　　　　　　　　　(b)

Figure C.17: Langmuir (a) and Freundlich (b) isotherms at 5 hr contact time for Zn.
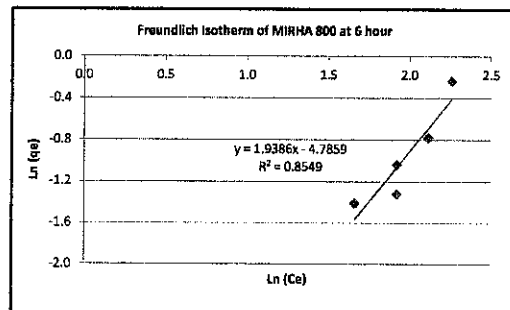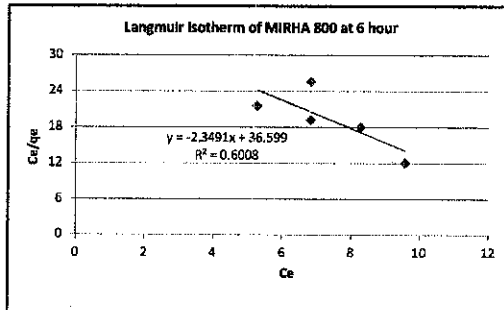
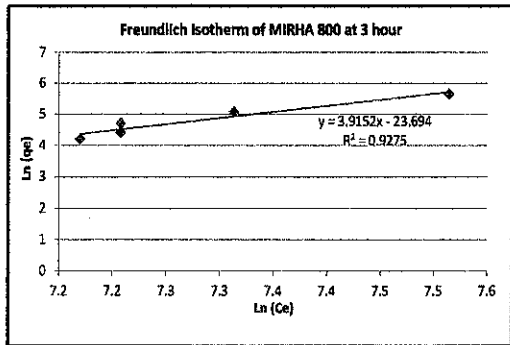(a)　　　　　　　　　　　　(b)

Figure C.18: Langmuir (a) and Freundlich (b) isotherms at 6 hr contact time for Zn.
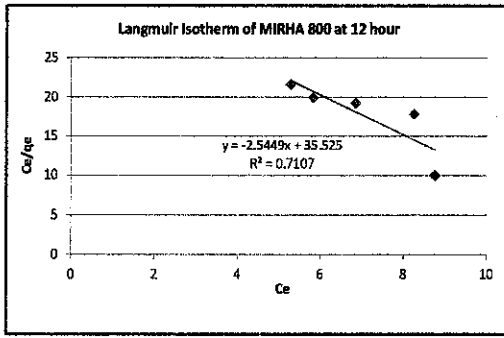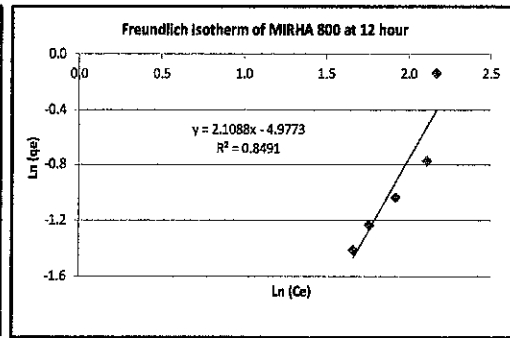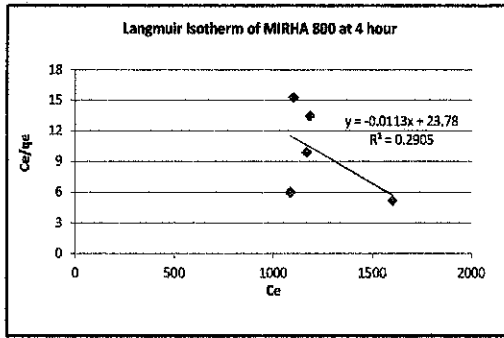
(a)   (b)

Figure C.19: Langmuir (a) and Freundlich (b) isotherms at 12 hr contact time for Zn.
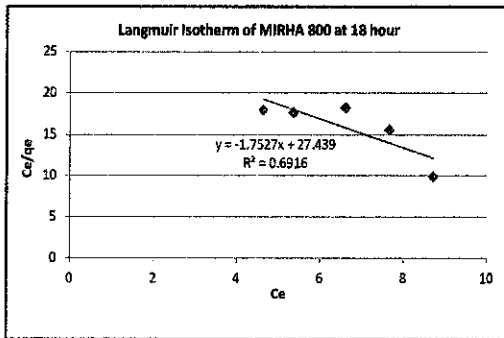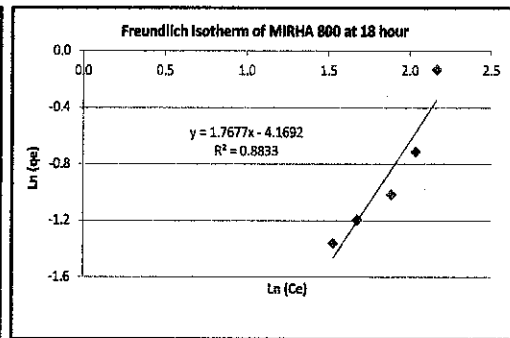
(a)   (b)

Figure C.20: Langmuir (a) and Freundlich (b) isotherms at 18 hr contact time for Zn.
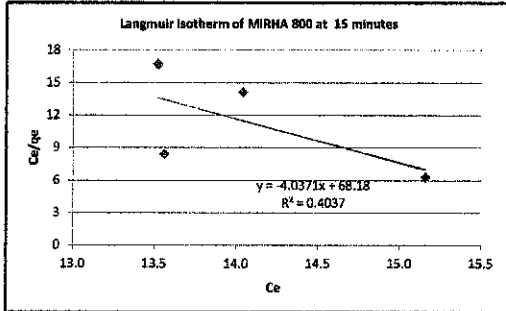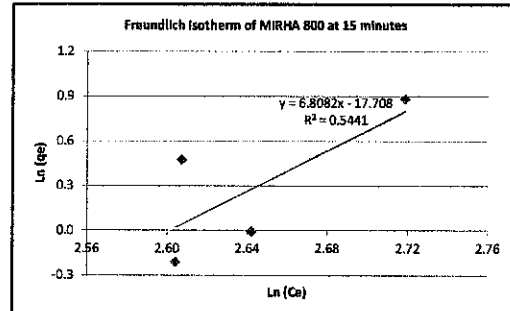
(a)   (b)
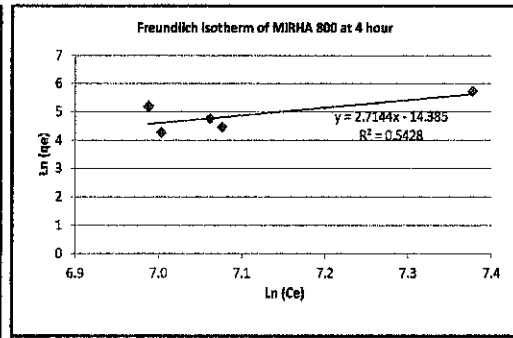
Figure C.21: Langmuir (a) and Freundlich (b) isotherms at 15 min contact time for Zn.
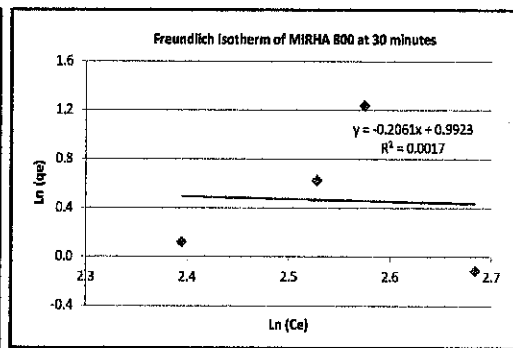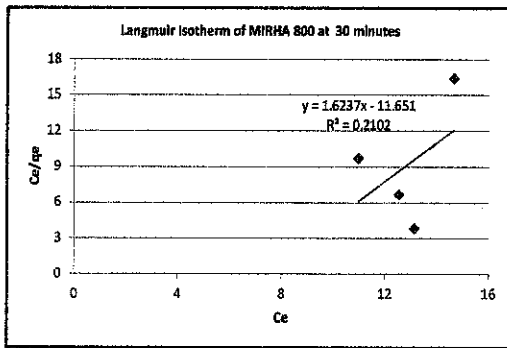
(a)   (b)

Figure C.22: Langmuir (a) and Freundlich (b) isotherms at 30 min contact time for
Zn.
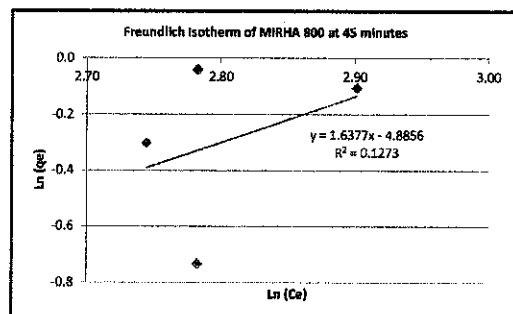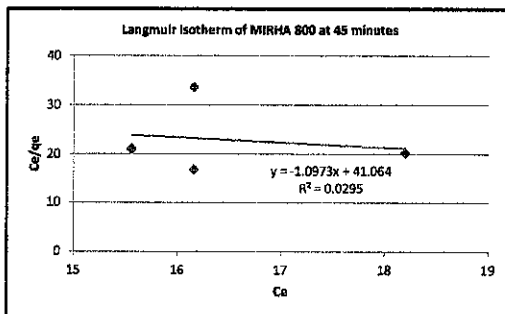
(a)   (b)

Figure C.23: Langmuir (a) and Freundlich (b) isotherms at 45 min contact time for
Zn.
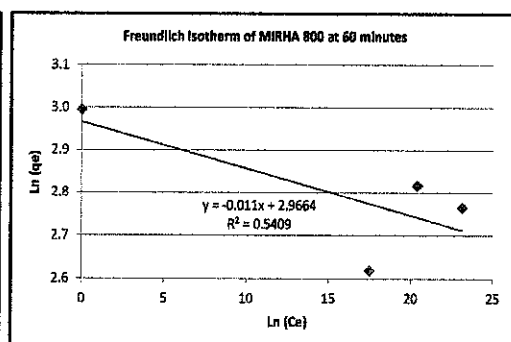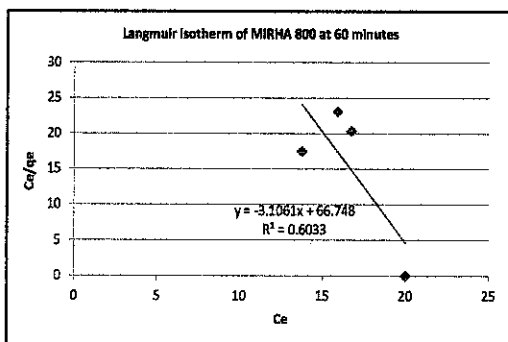
(a)   (b)

Figure C.24: Langmuir (a) and Freundlich (b) isotherms at 60 min contact time for
Zn.
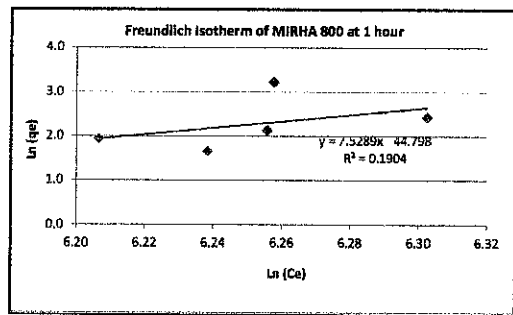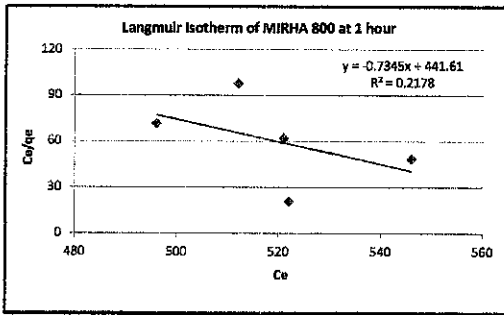
(a)   (b)

Figure C.25: Langmuir (a) and Freundlich (b) isotherms at 1 hr contact time for
COD.
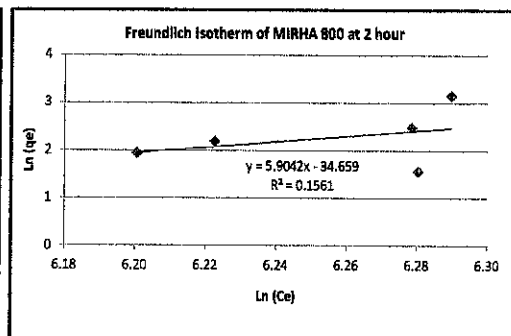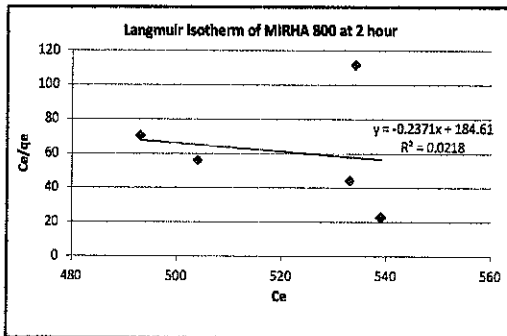
(a)   (b)

Figure C.26: Langmuir (a) and Freundlich (b) isotherms at 2 hr contact time for
COD.
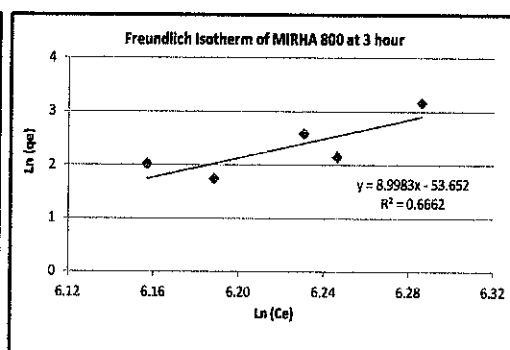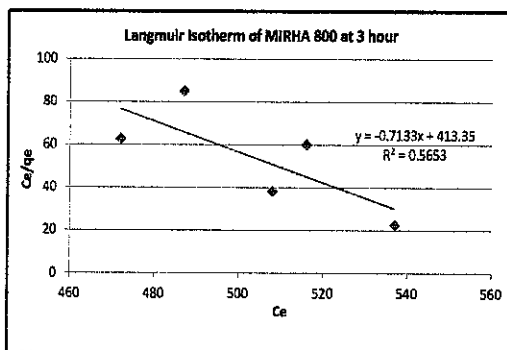
(a)   (b)

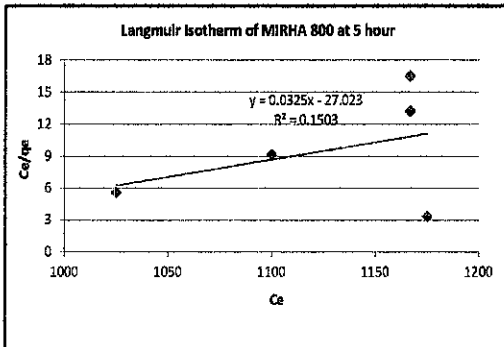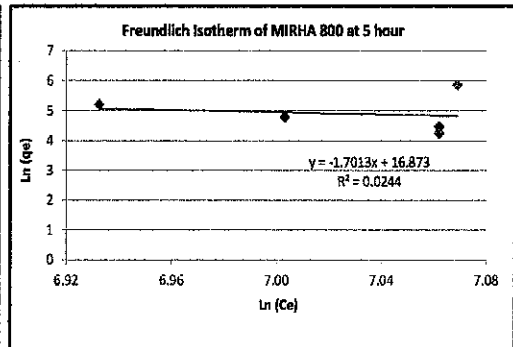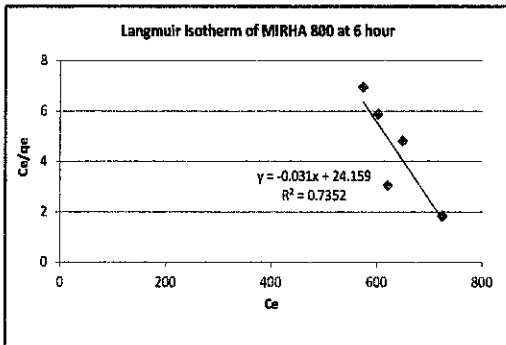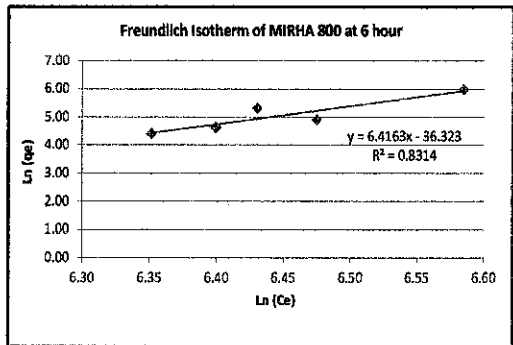Figure C.27: Langmuir (a) and Freundlich (b) isotherms at 3 hr contact time for
COD.

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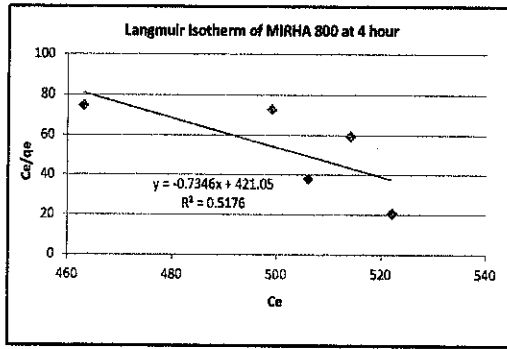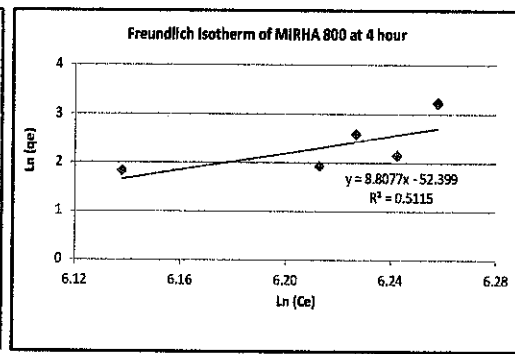
(a)   (b)

Figure C.28: Langmuir (a) and Freundlich (b) isotherms at 4 hr contact time for COD.
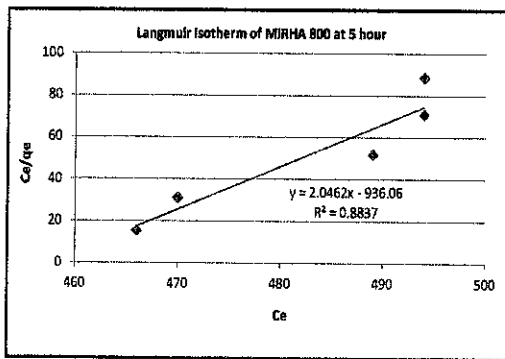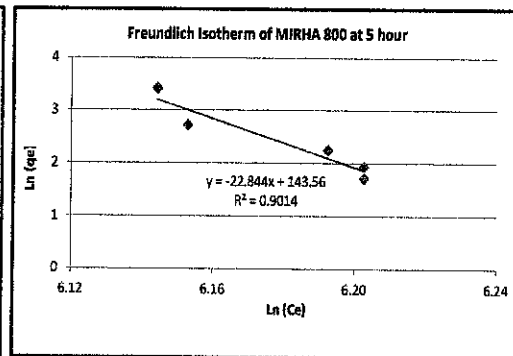
(a)   (b)

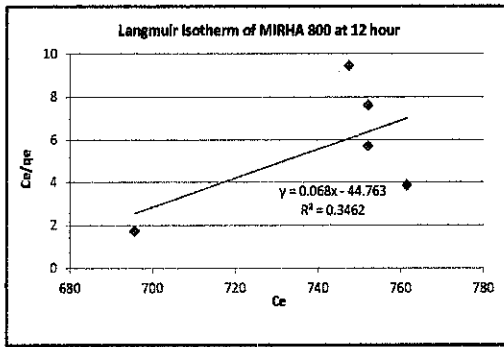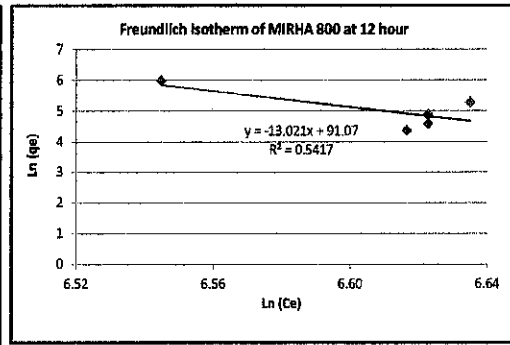Figure C.29: Langmuir (a) and Freundlich (b) isotherms at 5 hr contact time for COD.
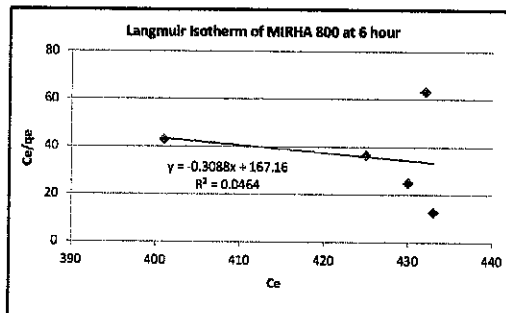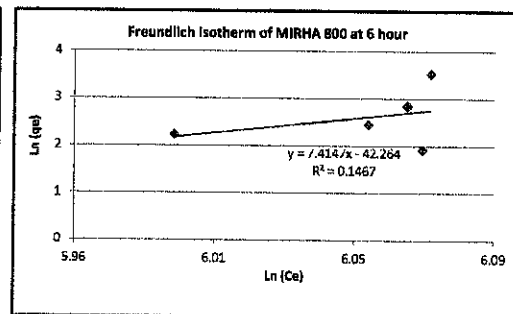
(a)   (b)

Figure C.30: Langmuir (a) and Freundlich (b) isotherms at 6 hr contact time for COD.
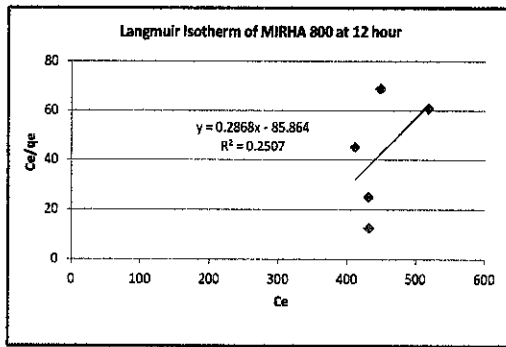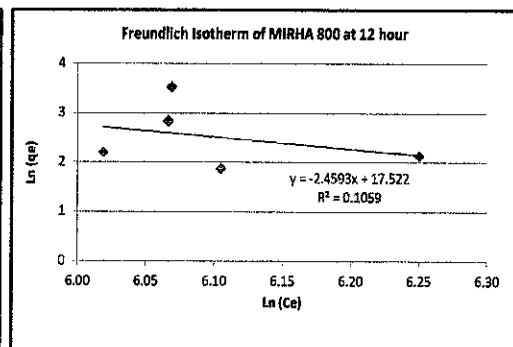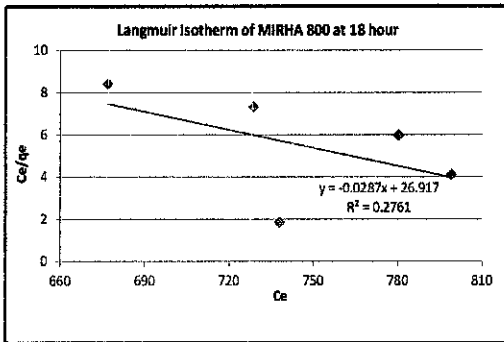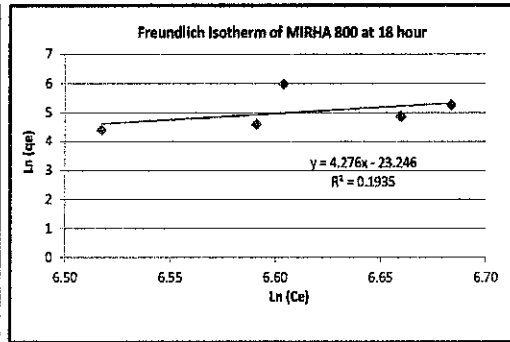
(a)   (b)

Figure C.31: Langmuir (a) and Freundlich (b) isotherms at 12 hr contact time for COD.
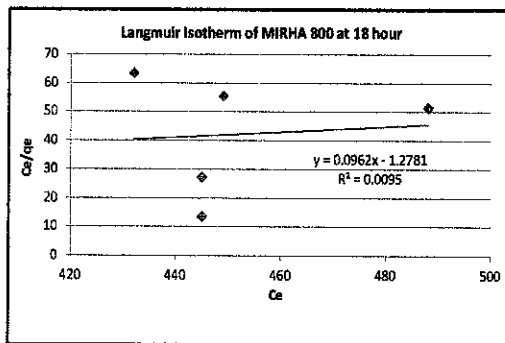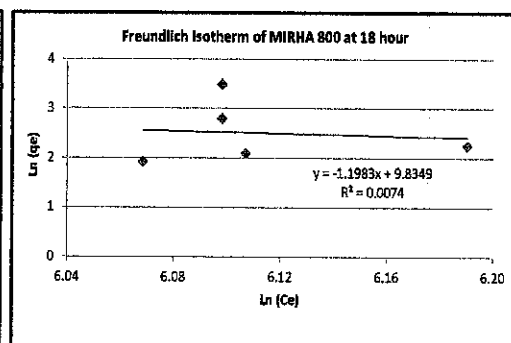
(a)   (b)

Figure C.32: Langmuir (a) and Freundlich (b) isotherms at 18 hr contact time for COD.
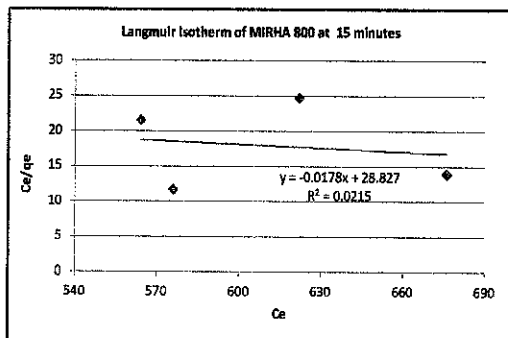
(a)   (b)

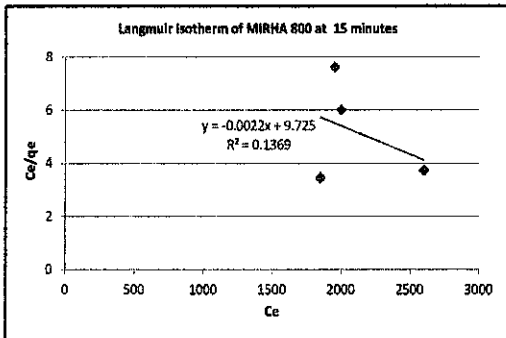Figure C.33: Langmuir (a) and Freundlich (b) isotherms at 15 min contact time for COD.

Figure C.34: Langmuir (a) and Freundlich (b) isotherms at 30 min contact time for COD.
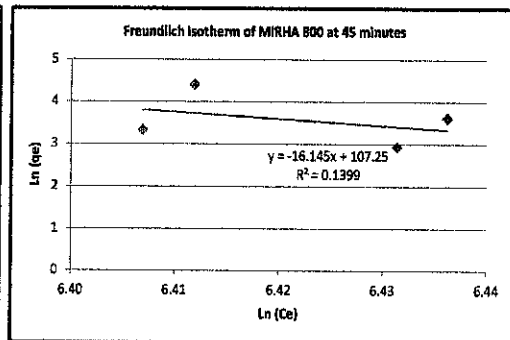
Figure C.35: Langmuir (a) and Freundlich (b) isotherms at 45 min contact time for COD.

Figure C.36: Langmuir (a) and Freundlich (b) isotherms at 60 min contact time for COD.

Figure C.37: Langmuir (a) and Freundlich (b) isotherms at 1 hr contact time for Color.

Figure C.38: Langmuir (a) and Freundlich (b) isotherms at 2 hr contact time for Color.

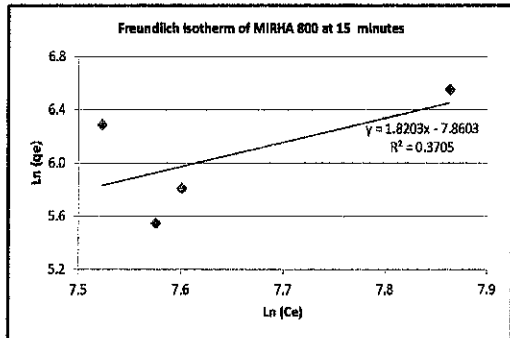Figure C.39: Langmuir (a) and Freundlich (b) isotherms at 3 hr contact time for Color.

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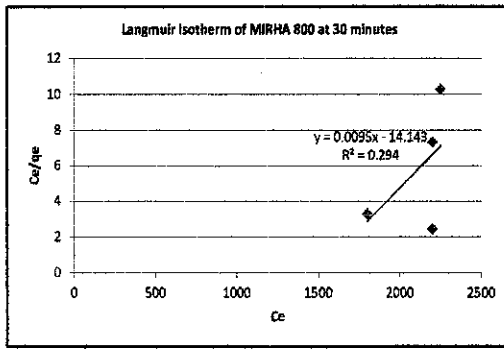Figure C.40: Langmuir (a) and Freundlich (b) isotherms at 4 hr contact time for Color.

Figure C.41: Langmuir (a) and Freundlich (b) isotherms at 5 hr contact time for Color.

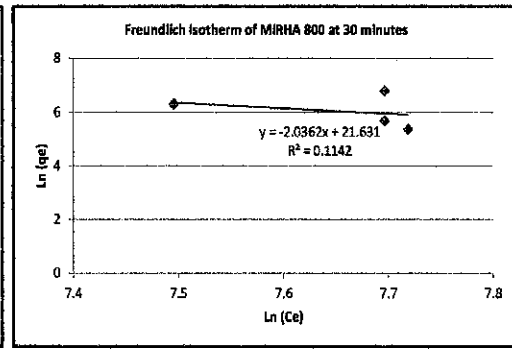Figure C.42: Langmuir (a) and Freundlich (b) isotherms at 6 hr contact time for Color.

Figure C.43: Langmuir (a) and Freundlich (b) isotherms at 12 hr contact time for Color.

Figure C.44: Langmuir (a) and Freundlich (b) isotherms at 18 hr contact time for Color.

Figure C.45: Langmuir (a) and Freundlich (b) isotherms at 15 min contact time for Color.

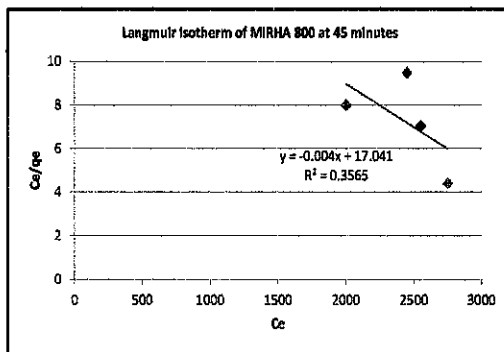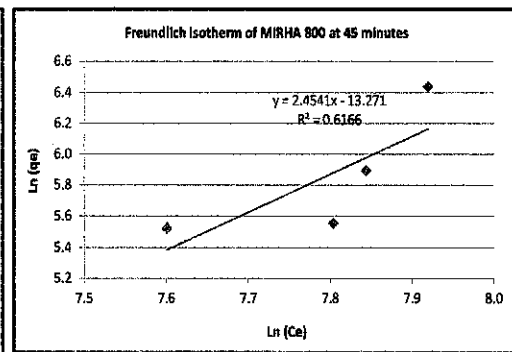(a)   (b)

Figure C.46: Langmuir (a) and Freundlich (b) isotherms at 30 min contact time for
Color.

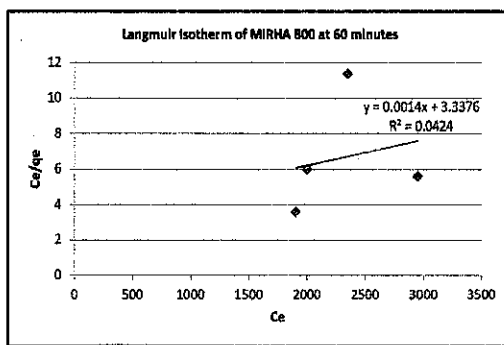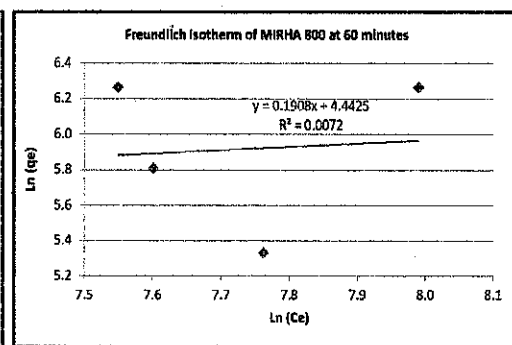(a)   (b)

Figure C.47: Langmuir (a) and Freundlich (b) isotherms at 45 min contact time for
Color.

(a)   (b)

Figure C.48: Langmuir (a) and Freundlich (b) isotherms at 60 min contact time for
Color.