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Optimization of Heavy Metal Removal from Leachate Using Maize Leaves and Papaya Barks As Bio-sorbent

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F15A0041

A Thesis Submitted In Fulfilment of the Requirements for the Degree of Bachelor of Applied Science (Bio Industrial Technology) With Honours

Faculty of Bioengineering and Technology

Universiti Malaysia Kelantan

2018

DECLARATION

I hereby that the work included in this report was the result of the original research and was not submitted to any universities or institution for higher degree.

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ACKNOWLEDGEMENT

Bismillah-ir-Rahman-ir-Rahim,

I am deeply grateful to Allah Almighty for the chances and opportunity given by Him that has lead for the completion of this final year project.

My first thanks go to my supervisor, Dr Siti Roshayu Binti Hassan, for all the guidance, support, supervision, advice and time given from the starting of this project until the end of my project. I couldn’t be more be more grateful to have my supervisor. Although she was pregnant during this project, she still has a commitment to her work. Thank you so much.

Secondly, my beloved family (father, mother, brothers and sister) who stand next to me to give all the support and encouragement that is necessary. They are the people who constantly keep me going. They’ve always be with me since the beginning of my life.

Furthermore, my thanks to my beloved friends for being bear with me all the time and always give a helping hands when I asked for. The good and bad times during the project was occurred are always in my minds as the sweet memories. I really hope, our bonding will last for infinity.

Finally, is to where I am studying and successful do my final year project, Universiti Malaysia Kelantan. Thanks to the lab assistant who always help, understanding, and kind to me during that time. This place will always in my mind and I will never forget.

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LIST OF ABBREVIATIONS AND SYMBOLS

		Pages
ANOVA	Analysis of Variance	22
BOD	Biological Oxygen Demand	8
CCD	Central Composite Design	5
Cd	Cadmium	1
CH_2O	Formaldehyde	17
COD	Chemical Oxygen Demand	8
Cr	Chromium	1
DOE	Design of Experiment	22
FTIR	Fourier Transform Infrared Spectrometer	5
H_2SO_4	Sulphuric Acid	17
HNO_3	Nitric Acid	18
RPM	Rotation Per Minute	19
RSM	Response Surface Methodology	2
XRD	X-ray Diffraction	5

OPTIMIZATION OF HEAVY METAL REMOVAL FROM LEACHATE USING MAIZE LEAVES AND PAPAYA BARK AS BIOSORBENT

ABSTRACT

Adsorption process was used to replace the conventional method in removing the heavy metals from leachate. This research was conducted to study the efficiency removal of heavy metals in leachate using treated and untreated of maize leaves and papaya barks. Fourier Transform Infrared Spectrometer (FTIR) was used to observe the functional groups of adsorbent and for the crystallinity of the adsorbent were characterised using X-ray Diffraction (XRD). The batch studies were optimised: pH, agitation rate, adsorbent dosage, and contact period by using Response Surface Methodology (RSM). The optimum conditions predicted by RSM for treated adsorbent were found at pH 6.67, agitation rate (279.71 rpm), contact period (52.25 min) and adsorbent dosage (6.93 g) that indicated about 99.6236% removal efficiency of heavy metals. Contrarily, optimum parameter for untreated adsorbent are pH (5.50), adsorbent dosage (3.08 g), agitation rate (162.40 rpm), and contact period (52.14 min) which represented 92.322% removal efficiency. Adsorption isotherm was employed to study the adsorption capacity and behaviour of the adsorption. Result showed that for treated adsorbent correlation coefficient, R^2 is 0.9981 leads to Freundlich model. Untreated adsorbent followed the Langmuir model with R^2 of 0.9969.

Keywords: Adsorption, leachate, FTIR, XRD, adsorption isotherm

OPTIMISASI PENYIKIRAN LOGAM BERAT DARIPADA BAHAN LARUT RESAP DENGAN MENGGUNAKAN DAUN JAGUNG DAN BATANG BETIK SEBAGAI PENJERAPAN

ABSTRAK

Proses penjerapan telah digunakan untuk menggantikan kaedah konvensional dalam menyingkirkan logam berat dari bahan larut resap. Kajian ini telah dijalankan untuk mengkaji kecekapan penyingkiran logam berat dalam bahan larut resap dengan menggunakan daun jagung dan batang betik yang dirawat dan tidak dirawat. Spektrum Inframerah Transformasi Fourier (FTIR) telah digunakan untuk memerhatikan kumpulan berfungsi bahan penjerap dan keristalan bahan penjerap telah dicirikan menggunakan Pembelauan Sinar X-ray (XRD). Kajian kumpulan telah dioptimumkan: pH, kadar agitasi, dos bahan penjerap, dan tempoh masa dengan menggunakan 'Response Surface Methodology' (RSM). Keadaan optimum diramalkan untuk rawatan penyerap oleh RSM telah didapati pada, pH 6.67, kadar agitasi (279.71 rpm), tempoh masa (52.25 min) dan dos bahan penjerap (6.93 g) yang menunjukkan kecekapan penyingkiran logam berat iaitu 99.63%. Paras optimum bagi penyerap yang tidak dirawat adalah pH (5.50), dos bahan penjerap (3.08 g), kadar agitasi (162.40 rpm), dan tempoh masa (52.14 min) yang mewakili kecekapan penyingkiran iaitu pada 92.32%. Isotherm penjerapan digunakan untuk mengkaji keupayaan penjerapan dan sifat penjerapan. Keputusan menunjukkan bahawa untuk pekali korelasi penjerapan yang dirawat, R^2 adalah 0.9981 membawa kepada model Freundlich. Penjerapan yang tidak dirawat telah mengikuti model Langmuir kerana R^2 0.9969.

Katakunci: Penjerapan, bahan larut resap, FTIR, XRD, isotherm penjerapan.

CHAPTER 1

INTRODUCTION

1.1 Research Background

In era of globalization, increasing population and rapid development led to increase the amounts of waste disposal. Commonly, the waste is produced from industrial, municipal, agricultural and domestic waste. Water percolating through deposited waste had undergo aerobic and anaerobic microbial decomposition will produce landfill leachate (Kulikowska & Klimiuk, 2008). Leachate contained variety of toxic materials such as heavy metals, dyes, surfactant and phenols need to be treated. This is because, the presence of toxic material will give negative impacts and deterioration to the environment and also ecosystem (Brennan *et al*., 2017).

Heavy metals are natural components comprising Cadmium (Cd), Chromium (Cr), Lead (Pb), and Nickel (Ni). They do not affect mankind at low concentration, but at high concentration they affect by accumulating in living tissues and ultimately causing various disease and disorders (Raouf Ms & Raheim Arm, 2016). Several treatment are available in removal of heavy metals from leachate.

Heavy metals removal from wastewater had been before that accomplished through different methods such as coagulation, ion exchanges, oxidation, evaporation and membrane methods. Although those technologies can give higher efficiency in removal of heavy metal, however those methods required high reagents and high operational costs. To overcome this problem, adsorption process one of the efficient methods for treatment wastewater due to the effectiveness, economical and eco-friendly techniques were been applied.

According to the Fu & Wang (2011), adsorption is the process of removal solute from the liquid phase through contact with a solid adsorbent. Besides, it is fundamentally as mass exchange process by which metal ions are exchanged from the solution to the surface of adsorbent and progresses toward becoming bound by physical as well as synthetic connection. Effective adsorbent is a major factor in removal of heavy metals.

For instance, agricultural wastes are chosen because it have variety compositions such as lignin, cellulose, starch and hemicellulose. Those are available in low-cost and give larger availability of adsorption capability which will contribute high hydroxyl and phenolic groups which can give higher efficiency removal heavy metals. There are numerous agricultural waste such as rice husk, sawdust of walnut, coconut shells, ground wheat stems and peanut hulls can be used as effective adsorbent.

Response Surface Methodology (RSM) can used to optimize an experimental design in order to reduce the cost of expensive analysis. RSM is recovery statistical and useful mathematical techniques for process development, improvement, and optimization. RSM has been used in numerous chemical and biochemical processes to optimize and evaluate the interactive effects of independent factors (Sugashini & Begum, 2013).

1.2 Problem Statement

Deposited waste and the presence of the water will cause formation of leachate. Leachate will cause serious environmental problems such as soil and water pollution. To reduce the environmental pollution, the heavy metals content in leachate must be removed before released into the environment. Removal of heavy metals from leachate has been practiced in several decades by the conventional Physio-chemical removal methods. For example, ion exchange, neutralization and precipitation. However, those methods are usually found to be high-cost, by-product pollution and ineffective, particularly in leachate treatment with low concentration of heavy metals.

Adsorption process was used in the previous studies in order to reduce the cost, to decrease by-product pollution and to enhance the effectiveness of removing the heavy metals. This is because, this process used low cost materials such as maize leave and papaya barks as the adsorbent. This treatment can reduce the concentration of heavy metals even at lower concentration. Several factors can be achieved in removing heavy metals depend on molecular size and polarity of the adsorbate and types of adsorbent (activated carbon, treated, and untreated with chemical).

Commonly, treatment of wastewater used activated carbon due to an effective adsorbent. High cost was required during the production and operations to activate the adsorbent and certain complexion agents were needed to improve the efficiency removal for inorganic matter in removing the heavy metals.

Heavy metal removal in wastewater using agriculture waste as an adsorbent, have been investigated by the previous research. There were a lot of adsorbent used such as maize leaves, papaya barks, tea waste, and many more. Although maize leaves and papaya barks had been used from previous research, but the research was done without the chemical treatment. So, maize leaves and papaya barks were treated with chemical treatment have been selected to be used in this research.

Besides, excess wastes from maize leaves and papaya barks are thrown out as they have no potential used. By using those waste as an adsorbent, it will able to remove the heavy metals in leachate, thus reducing the wastes.

1.3 Objectives

The objectives of this research are:

1. To determine the efficiency of treated and untreated maize leaves and papaya bark as adsorbent in removal of heavy metal.
2. To optimize the adsorption of heavy metals by using Response Surface Methodology (RSM).
3. To assess the adsorption isotherm of treated and untreated maize leaves and papaya barks

1.4 Scope of Study

The research was conducted to determine the efficiency of untreated and treated maize leaves and papaya bark as an adsorbent in removal heavy metals from leachate which are cadmium and chromium. The raw materials were collected from Tanah Merah and Kuala Balah, Kelantan. Physical and chemical treatment was applied on the leachate before the adsorption studies. The optimization of parameters (i.e. pH, contact time, agitation rate, and adsorbent dosage) was achieved by using central composite design (CCD) from response surface methodology (RSM) to observe the adsorption efficiency.

The characteristics of functional groups of adsorbent were characterized by Fourier transform infrared spectrometer (FTIR). The phase structure of adsorbent was determined by X-ray Diffraction (R). Atomic Absorption Spectrophotometer (AAS) was used to determine the concentration of heavy metals in leachate. Lastly, adsorption isotherm, which were Langmuir and Freundlich model was used to assess the equilibrium efficiency of adsorption.

1.5 Significance of Study

The significance of this research is to find out the ability of agricultural waste (i.e. maize leaves and papaya barks) as adsorbent in removing heavy metals of leachate (cadmium and chromium). The capability of natural materials has proven considerably by the previous researchers. The study output is gained through the economical method used. This research was started with treated the adsorbent with acid, and the balanced adsorbent was used for untreated. The samples were continued to grind into small pieces to obtained powder. Batch studies experiment proceeded with RSM software and give the result for the effect of the pH, agitation rate, adsorbent dosage and contact period for efficiency removal percentages.

Adsorption isotherm was used to indicate variation in the target concentration of solute at the surface of adsorbent at equilibrium. Those isotherms in this research is Langmuir and Freundlich isotherm. This is due to commonly used and easy to make the comparison from the previous study.

CHAPTER 2

LITERATURE REVIEW

2.1 Adsorption

The conventional method to remove heavy metal had been widely practiced to treat the wastewater (leachate). For instance, chemical precipitation (Ku & Jung, 2001), ion exchanges (Alyüz & Veli, 2009), membrane filtration and solvent extraction. Although, those methods are efficient, but the limitation that requires high consumption of reagent and energy, higher operational cost and slow metal precipitation.

In order to overcome those limitations, adsorption process can be used as an alternative method to remove heavy metals in wastewater. Adsorption is a film of gas molecules accumulates on the surface when a solid is allowed to remain in contact with a gas. Unbalanced forces also have on the surface of a solid like liquids, molecules or ions. Therefore, solid surface tends to satisfy their unbalanced forces by attracting and accumulating on their surface other molecules. This process differs from absorption, the substances are not only retained on the surface but are distributed through the surface throughout the solid's body (Vennilamani *et al*., 2005).

2.1.1 Chemisorption

Adsorption is divided into two types, physical adsorption and chemisorption. Physical adsorption involved intermolecular forces between molecules of the adsorbent and adsorbate (Seetha *et al*., 2012). Besides, chemisorption or activated adsorption involved in chemical interaction between solid and adsorbed substances. Comparison between treated and untreated with chemical give a different effect. This is because, the untreated adsorbent can give lower removal efficiency heavy metals, higher Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD) and Total Oxygen Carbon (TOC), and causing soluble organic compound to be released (De Gisi *et al.*, 2016). The higher reading of COD, BOD and TOC will deplete the oxygen content in water.

According to Wan Ngah & Hanafiah (2008), acid treatment was used to reduce the organic content of adsorbent and increasing the porosity. Besides, Kumar & Bandyopadhyay (2006) had investigated that the rice husk was treated with Hydrochloric acid (HCl). The efficiency of removing the heavy metals was lowed. This is due to the surface of the rice husk were became protonated. So, heavy metals ions were left in phased of aqueous rather than on the adsorbent surface.

Wan Ngah & Hanafiah (2008) were also studied about the treatment with bases can attract the negative charge of hydroxyl ions of adsorbent. Example bases are Sodium Hydroxide (NaOH) and Potassium Hydroxide (KOH). Besides, the organic solvent can also be used as the chemical treatment to make the modification of the adsorbent. Example organic solvents that usually used are acetone, ethanol, chloroform, formaldehyde and glycol. Those solvent give effect based on the intermolecular forces such as hydrogen bonding, ion-dipole forces, electron pair donor-electron pair and etc. (Emin Argun & Dursun, 2006).

Adsorbent that was chemically modified provide efficient functioning for removing the organic compounds, rid of the colour of the adsorbate, and enhanced the metals adsorption.

2.1.2 Bio sorption

Research of Hlihor & Gavrilescu (2009) stated that adsorbent from agricultural waste has higher efficiency to remove the heavy metal from the wastewater. As a matter of fact, those waste can be good adsorbent due to having adsorption availability to remove the heavy metals. The mechanism of the adsorbent in adsorption process is when the leachate is mixed with the adsorbent (agriculture waste), internal mass transfer by pore diffusion from the outer surface of adsorbent to the inner surface of a porous structure will occur. After that, adsorption of adsorbate will occur on the active site of the pores of leachate (Raouf Ms & Raheim Arm, 2016).

Agriculture wastes such as peanut hull, grape stalk waste, tea waste, and teak leaf powder was used to treat the wastewater. Advantages of using agriculture waste are a simple method to treat the wastewater, superior adsorption ability, easy regeneration and easy viability. Agriculture materials contain cellulose, hemicellulose, lignin and starch. Cellulose and starch most effective to receive the functional groups from the heavy metals in wastewater (Guangqun Tan & Xiao, 2009).

According to the Arm (2017), cellulose is the first abundant biopolymer in the plant. Sources of cellulose can be established from the cotton stalk, bamboo, wheat straw, rice husk and flax. As studied by Hegazi, (2013), the efficiency of removal the cadmium and lead by using rice husk in the wastewater treatment are higher. This is because, dried rice husk have higher organic matter, 70-85%. At the same time, they discovered that the fly ash from the coal-burning power plant has higher efficiency in the removal of heavy metals (i.e. copper, nickel and iron).

In the adsorption process, parameters are the main consideration especially in the removal of heavy metals. Particularly, parameters were required to analyse which are affected by the removal efficiency of heavy metals. Table 2.1 listed the common parameters that were used during the removal of heavy metals.

Table 2.1: Common parameter were used

Parameters	Description
pH	Fundamental in the adsorption process The pH is depending on below factors: 1) Persuade changes of the adsorbent surface 2) Degree of ionization 3) Designation of adsorbate According to the Abbaszadeh *et al.* (2014), increasing of the pH (2 to 6) resulted in the higher percentage removal of Pb (II) from aqueous solution. Here, the ability of ion Pb (II) to displace ion H^+ connected on the surface of adsorbent and at the same time, it can attach the surface functional groups.

	Increasing the percentage removal of heavy metals due increasing the pH. This happened because of reducing challenges between protons and metals ions that have the same functional groups (Saeed *et al.*, 2005)
Initial concentration of adsorbate	Increment the initial concentration of Pb (II) affected the reducing removal percentages of Pb (II). Increasing of the adsorbate were facing limited accessibility of active sites on the surface of the adsorbent. Besides, ions Pb (II) are not adsorbed in that solution because of not enough accommodation of binding site (Abbaszadeh *et al.*, 2014). Mahmoud *et al*. (2015) analysed that initial concentration of Pb (II) was increased, showed that decreasing of the removal Nickel oxide. In this respect, lower initial concentration inhibits the sufficient adsorption site.
Temperature	Most of the researcher concluded that temperature were not affect the adsorption process (Mohd Ariff bin KamalI, 2010).
Contact time	Based on the Adib *et al*. (2017), starting from the 10 min early, an increase of the dye removal is been showed. But when it comes to the equilibrium points, the reading was slowed. That is because methylene blue dye and activated carbon of corn cobs and orange peel have strong interaction force. According to the Aravind *et al*. (2015), increasing of the percentage removal of Nickel (II) caused by increasing of the contact time. It results indicated there were rapidly increase the removal of Nickel (II), here maybe due to bigger surface area of

the pigeon pea pod at the beginning.

2.2 Wastewater

Wastewater is the water discharged from the industries, domestic municipal, communities and institutions. In specific, domestic municipal wastewater is defined as flows of water that used and discharged from municipal sources such as laundry, cleaning, and personal hygiene. For the industrial wastewater is came from printing, mining manufacturing and ceramic glass industries (Brennan *et al.*, (2017).

In fact, every person contributes of wastewater by using 200 to 500 litres per day. According to Norkhadijah *et al.* (2013),the production of municipal waste are from 48% to 68% that will generate to the leachate and it higher percentage compare to other country (i.e. Kanada and Korea).

2.2.1 Leachate

Leachate is the example of wastewater that contains higher toxicity such as heavy metals. It comes from percolating of the waste deposits that have been undergone aerobic and anaerobic microbial decomposition (Brennan *et al.,* 2017). In the process to treat the leachate, it involved two methods that include biological, and physical/chemical. Method for biological whereby, using the bacteria or microorganisms to enhance the removal percentage of heavy metals in leachate. For example, aerobic biological, anaerobic biological and reverse osmosis.

Indeed, rotating biological contactor (RBC) was one of the methods for biological treatment. RBC was needed a large disk with radial and concentric passages slowly rotating in a concrete tank. To form the thin layer of biomass, the rotation is needed. To multiple the organisms, it required to expose the oxygen into it. In fact, using the RBC is needed a huge amount of cost to running the treatment and need higher maintenances of workers (Raghab *et al.*, 2013).

Furthermore, physical/chemical treatment can be applied by using various treatment such as chemical precipitation, coagulation, ion exchange and membrane filtration. This treatment was applied to combine together the process of physical and chemical methods. For instance, the adsorption process is the physical treatment, whiles chemical treatment was applied by using the chemical.

Xiaoli *et al.* (2007) explained the presence of the toxic materials in residues of landfills is mostly a restriction for its reclamation. In fact, maximum natural chemical materials will the last be degraded, via biochemical reaction in the landfill leachate. Besides, those materials leached out from the landfill with water movement. However, most of the heavy metal will stay within the landfills due to the fact heavy metals migration is very constrained as compared to the amounts of metals accumulated in the landfills.

Heavy metal is the group of elements that have a specific weight higher than 5 g/cm^3. Those metals are able to divide into 2 types of classes which are Iron (Fe), Manganese (Mn), Nickel (Ni), and Copper (Cu) that are the essential micronutrient needed for normal growth and metabolic process in the plant. In contrast, cadmium

(Cd), Lead (Pb), and Chromium (Cr) are non-essential and highly toxic for the plant and human (Guangqun. Tan & Xiao, 2009). Heavy metal can give negative impact to plant, retarded the growth of plant by inhibiting the physiological processes such as respiration, photosynthesis and cell elongation.

2.3 Adsorption Isotherm

Adsorption isotherm can be defined as an expression of the relationship between the adsorbed solute quantity and the solute concentration in the fluid phase (Abdel Salam *et al*., 2011). Those models describe the behaviours of the adsorbate ions interact on the surface of the adsorbent. Furthermore, those models are used to explain in term of quantity adsorbed equilibrium and concentration of adsorbates remain in the bulk solution during the equilibrium (Nur et al., 2013).

Langmuir model has been effectively applied in the adsorption approaches and has been the maximum broadly used. Fundamental assumptions of the Langmuir concept is that adsorption takes region at particular homogeneous sites within the adsorbent.

Langmuir model is a calculation of adsorption of molecules at a fixed number of active site. Active sites are homogenously distributed over the surface of the adsorbent. The assumption is assumed that after a metal ions occupies a site, no in addition adsorption can take region at the sites (Srinivasa Rao *et al*., 2010).

On the other hand, Freundlich isotherm has been assumed heterogeneous surface energies, in which the energy term within the Langmuir equation varies as a characteristic of the surface coverage.

2.4 Bio-sorbent Characterization

In order to detect the surface functional groups of the adsorbent for the best efficient removing the heavy metals by Fourier Transform Infrared Spectrometer (FTIR). From the research of Tan *et al*. (2008) were detected functional groups for activated oil palm shells. At the 3400 cm^{-1} showed that O-H stretching vibrations bonds and 1086 cm^{-1} indicated C-OH stretching vibrations.

Next, X-ray Diffraction (XRD) is to observe crystalline phases of various material and the quantitative phase analyses subsequent to the identification at the wavelength 0.15406 nm (Tang *et al.,* 2017).

Adesola Babarinde et al (2006) had been discovered in determination concentration of heavy metal, by adding the raw material into the concentration of metal ion solution and had been left in the water bath. By used the Atomic Adsorption Spectrometer (AAS) measure the concentration of the residual ions in the solution after the adsorption process are occurred. By the result that had been obtained, she can reveal the adsorption isotherm and knows the best model to be conclude (Babarinde, Babalola, & Sanni, 2006).

CHAPTER 3

MATERIALS AND METHODS

3.1 Overall flow chart

Overview for overall process research activities is shown in Figure 3.1.

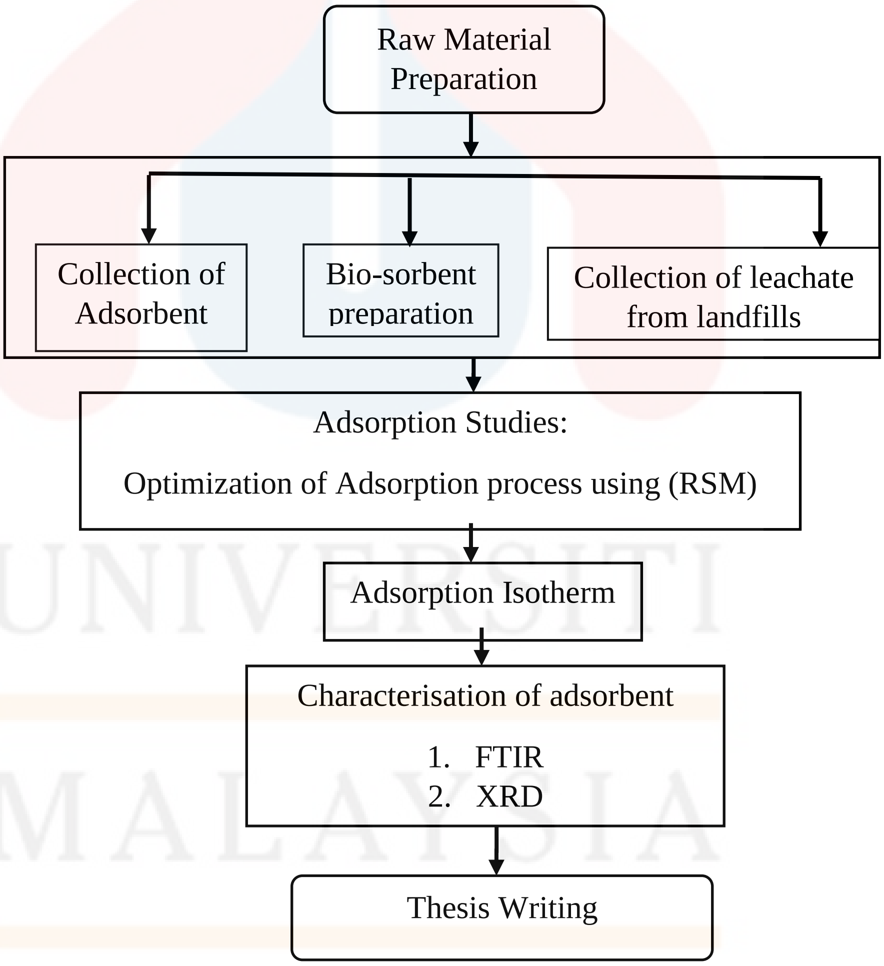


Figure 3.1: Overall flow charts of removal heavy metals

3.2 Materials and Chemical

The materials that were used include leachate, maize leaves, papaya bark, tap water, distilled water. Whereas, the chemical that were used, Nitric Acid (HNO_3), 0.1M of Sulphuric acid (H_2SO_4), and 39% of formaldehyde (CH_2O).

3.2.1 Preparation of raw materials

2 kg of each sample, maize leaves and papaya barks were collected from a farm in Tanah Merah and Kuala Balah, Kelantan, respectively. For this study, 1 kg of each sample was further treated with acid and the remaining used for untreated.

For the treated maize leaves, they were cut into small pieces, rinsed with distilled water and continued immersed with 0. 1M Sulphuric acid (H_2SO_4) solution. In contrast, for untreated sample, they were rinsed only with distilled water. Then, both samples were dried in the oven at 70℃ for 24 hours. The dried samples were grinded by using grinder machines. Those samples were transferred into sieving machines to obtain a fine powder and was kept in a zipper bag until further usage.

Meanwhile, for the papaya bark, the samples were cut into small size (4 cm by 4 cm), rinsed with tap water and continually immersed with 60 mL of 39% of Formaldehyde (H-CHO) within 2 or 3 hour. This is because to polymerized and insolubilize the tannin and pectin of the bark. After that, the barks were treated with 60 mL of 0.1 M H_2SO_4. Contrarily, the untreated papaya bark was rinsed only with tap water and immersed with distilled water. Those papaya barks were filtered and dried in the oven under the same condition. Continually, samples were grinded and sieving to obtain fine powder and was put in zipper bag for further usage. Lastly, both samples (maize leaves and papaya barks) were being combine as treated and untreated adsorbent by followed the ratio (1:1).

3.2.2 Collection of Leachate Sample

1 L of leachate was collected from Machang, Kelantan. The leachate were filtered and recorded for Physio-chemical properties which are pH, temperature, initial concentration of heavy metal, Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD), colour and turbidity. The samples were then mixed with 10mL of Nitric Acid (HNO_3) and kept in refrigerator at 5℃ for further usage.

3.3 Batch adsorption studies

In order to determine the efficient removal of heavy metal in leachate, constant variables were carried out such as temperature (37℃), the volume of leachate (100 mL), and initial concentration of leachate (217.74 g/mL). The independent parameters in this study were pH, agitation rate, adsorbent dosage and contact period.

The range of is between pH 5 to 7. For contact period, minimum values were 20 min while the maximum was 100 min. The agitation rate was between 150.00 rpm to 300.00 rpm. Last but not least, the adsorbent dosage was varied from 3.00 g to 7.00 g.

To figure out the dependent variables, the removal efficiency of heavy metals was calculated. This variable was intended to make the comparison between treated and untreated adsorbent which are more efficient. Adsorption studies to observe the efficiency of removal heavy metal were calculated by using Equation 3.1.

$$\text{Removal efficiency (\%)} = \frac{\text{Co-Ce}}{\text{Co}} \times 100$$

(Equation 3.1)

Where, Co and Ce: liquid-phase concentration at initial and equilibrium states (g/mL).

3.4 Optimization using Response Surface Methodology (RSM)

Those parameters were inserted in the Design Expert Software. Response Surface Methodology (RSM) was optimized for the experimental design by using the Central Composite Design (CCD). Table 3.1 shows the experimental design using a CCD.

Table 3.1: The experimental design for adsorption studies

Variable	Units	Low (-1)	High (+1)
1) pH	-	5.00	7.00
2) Contact period	min	20.00	100.00
3) Agitation rate	rpm	150.00	300.00
4) Adsorbent dosage	g	3.00	7.00

For this experimental design, the response is the percentage removal efficiency of heavy metal were shown. Table 3.2 indicated experimental run from the different condition were operated. 30 runs are generated by Central Composite Design (CCD) model. The experiments were done in triplicate to obtain an accurate reading for optimize percentage removal efficiency.

Table 3.2**:** Experimental runs using CCD model.

Bil	pH	Contact Period (min)	Agitation Rate (rpm)	Adsorbent Dosage (g)
1.	6.0	20.00`	225.00	5.0
2.	6.0	100.00	225.00	5.0
3.	7.0	100.00	150.00	3.0
4.	6.0	60.00	225.00	5.0
5.	6.0	60.00	300.00	5.0

6.	6.0	60.00	225.00	5.0
7.	7.0	100.00	150.00	7.0
8.	6.0	60.00	150.00	5.0
9.	5.0	20.00	150.00	7.0
10.	6.0	60.00	225.00	5.0
11.	7.0	20.00	300.00	3.0
12.	6.0	60.00	225.00	5.0
13.	5.0	20.00	150.00	3.0
14.	5.0	100.00	300.00	7.0
15.	6.0	60.00	225.00	7.0
16.	7.0	20.00	150.00	7.0
17.	7.0	60.00	225.00	5.0
18.	5.0	100.00	150.00	7.0
19.	6.0	60.00	225.00	3.0
20.	5.0	100.00	150.00	3.0
21.	5.0	100.00	300.00	3.0
22.	7.0	20.00	150.00	3.0
23.	5.0	20.00	300.00	7.0
24.	7.0	100.00	300.00	3.0
25.	7.0	20.00	300.00	7.0
26.	6.0	60.00	225.00	5.0
27.	7.0	100.00	300.00	7.0
28.	5.0	20.00	300.00	3.0
29.	5.0	60.00	225.00	5.0
30.	6.0	60.00	225.00	5.0

Design for Experiment (DOE) is encouragement tool for technique characterization, the strength of the DOE tool can discover full-size variation factors, and their interaction(s), that effect techniques overall performance, product overall performance and high-quality (Kamsonlian & Shukla, 2013). Besides, DOE is used for evaluating the parameter which has most influenced effect on response and to optimize parameters.

Optimization process involved three major steps which are performing the statistically designed experiments, estimating the coefficient in a mathematical model and predicting the response and checking the adequacy of the model *(Sahu et al.*, (2016). An empirical model that formed indicate the response to the adsorption process as shown in Equation 3.2.

$$Y=f\ \{ X_1, X_3, X_3, X_4 \ldots . X_n \}$$

(Equation 3.2)

Where Y is the response in the experiment, X_1 is the factor. The objectives are to optimise the response variable (Y). Interaction between Y and X showed an approximately by quadratic or polynomial model.

$$Y = b_o + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{44}X_4^2$$

(Equation 3.3)

Where b_o is constant, b_1, b_2, b_3, and b_4 the linear coefficient, b_{12}, b_{13}, b_{14}, b_{23}, b_{24} and b_{34} the cross product coefficient, and b_{11}, b_{22}, b_{33} and b_{24} are the quadratic coefficient. Analyses of variance (ANOVA) were obtained to get the quadratic model that establishes the statistical significance at 5% level of significance. 95% of confidence levels have explained the range that can be 95% of true mean the population. 3D-contour are been derived to related the response variables to predictor variables (Sahu *et al*., 2016).

3.5 Adsorption Isotherm

Adsorption isotherm was employed to study the adsorption efficiency using Langmuir models and Freundlich model. Freundlich model (Equation 3.4) can indicate as for non-ideal adsorption that involves heterogeneous adsorption. While, Langmuir isotherm in (Equation 3.5) is revealed the assumptions for maximum adsorption that corresponds to a saturated monolayer of adsorbate molecule on the adsorbent surface, the energy of adsorption is constant and no transmigration of the adsorbate in the plane of the surface.

Freundlich Isotherm:

$$\text{Log } q_e = \text{Log } K_f + \frac{1}{n} \text{Log } C_e$$

(Equation 3.4)

Where, Q_e is mass of adsorbed (mg/g), C_e is equilibrium concentration of the adsorbate (mg/L) and K_f and n in the Freundlich constants related to adsorption capacity and adsorption intensity respectively.

Langmuir Isotherm:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_o} + \frac{1}{Q_o}\,b$$

(Equation 3.5)

Where, the C_e is equilibrium concentration (mg/L), q_e is the amount adsorbed at equilibrium (mg/g) and b is Langmuir constant (L/mg).

3.6 Chemical Analysis and Characteristically.

3.6.1 Characterise Functional Group of Adsorbent

The functional group exist in treated and untreated maize leaves and papaya barks were analysed by using the machine of Fourier Transform Infrared Spectrometer (FTIR). 2 mg of adsorbent are squeezed to form a transparent pallets and the pallet are measured directly.

3.6.2 Observe the crystalline phase of adsorbent

In powder or polycrystalline diffraction, it is vital to have a sample with a smooth plane surface. If viable, the sample were grinded down to particle of approximately zero. 0.002 m to 0.1/2 mm cross section. The proper sample is homogenous and the crystallites were randomly dispensed. The sample were pressed tight into a sample holder in order to have flat surface.

3.4.3 Analysis of Heavy Metal Concentration in Leachate

100mL of leachate were filtered using the vacuum pump. Then, 15mL of sample was further filtered using the 20 mm syringe filter and was put in the falcon tube as the stock sample. To make the dilution, 1.5 mL from stock solution was initiated with 10^{-1} until 10^{-4}. Atomic Absorption Spectrometer (AAS) machines was used to determine the concentration of heavy metal such as cadmium and chromium that were located in leachate.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Raw Materials Preparation

4.1.1 Physiochemical properties of leachate

Landfill leachate can be described as any polluted liquid discharge percolating through the sediment waste within a dump site or landfill. In order to observed the heavy metals in leachate, Atomic Absorption Spectrophotometer (AAS), Cadmium and Chromium selected in the leachate. The AAS result were showed in Appendix (Table A).

To undergo the experiment, some information of leachate physiochemical composition was determined using PSI multiparameter as shown in Table 4.1.

Table 4.1 : Reading of PSI-multiparameter

Characteristics	Values
pH	2.9
Temperature	36.5 ℃
Dissolved Oxygen	• 26.1 %

	• 1.77 mg/L • 1.77 ppm
Conductivity Standard	954 µS/-cm
Conductivity (specific conductance)	783 µS/-cm
Total Dissolved Solid (TDS)	507.00mg/L
Chemical Oxygen Demand (COD)	12,000mg/L
Biochemical Oxygen Demand (BOD)	13,000mg/L
BOD_5/COD	0.28

Table 4.1 showed the physiochemical characteristics of leachate. The pH value are 2.9 indicated acidity of leachate are in strong acid. Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) are 12,000 mg/L and 13,000 mg/L respectively.

Based on Table 4.2, leachate that was collected at Tanah Merah, Kelantan within in range of young landfills. It can be concluded, age of leachates are less than 5 years and heavy metals in the leachate are in the range of low to medium.

Table 4.2: General characteristics of leachate at different age (source: Raghab *et al*., 2013)

Parameters	Young	Intermediate	Old
Age (years)	< 5	5-10	> 10
pH	< 6.5	6.5-7.5	> 7.5
COD (mg/L)	> 10,000	4,000-10,000	< 4,000
BOD_5/COD	> 0.3	0.1-0.3	<0.3
Heavy metals	Low-medium	Low	Low
Biodegradability	Important	Medium	Low

4.2 Adsorption studies

In the adsorption studies, constant variables used to create the appropriate condition of the adsorption of removing heavy metal in leachate. Those parameters are temperature (37℃), initial concentration of leachate (217.74 g/mL) and volume of leachate (100 mL).

Theoretically, the ability to remove heavy metals increase with the temperature increase. This is because of the increased mobility of molecules with sufficient energy to interact with the surface active sites. Besides, the temperature increase resulted in the swelling of the adsorbent's internal structure, which promotes the movement of large ion molecules of heavy metals (Ghafar, 2013). Even so, the adsorbent structure could be damaged at high temperature and perhaps even lead to failure of the adsorbent properties (Nasiruddin Khan *et al*., 2007).

The volume of leachate is constant, because it depends on the amount of the adsorbent use. High leachate volume is used, it contains large quantities of adsorbent to be adsorbed, it may require more adsorbent to remove the adsorbate from solution in order to have an effective adsorption (Ching *et al*., 2011).

Figure 4.1 shows the interaction of pH on the removal heavy metal of leachate. Increasing of the pH (3 to 7) will enhance the increment of heavy metals. This is because, increasing of the pH, will increased the adsorbent's surface become negatively charged. Hence, repulsion of the heavy metals ions in leachate and adsorbent were occurred (Song & Gao, 2013).

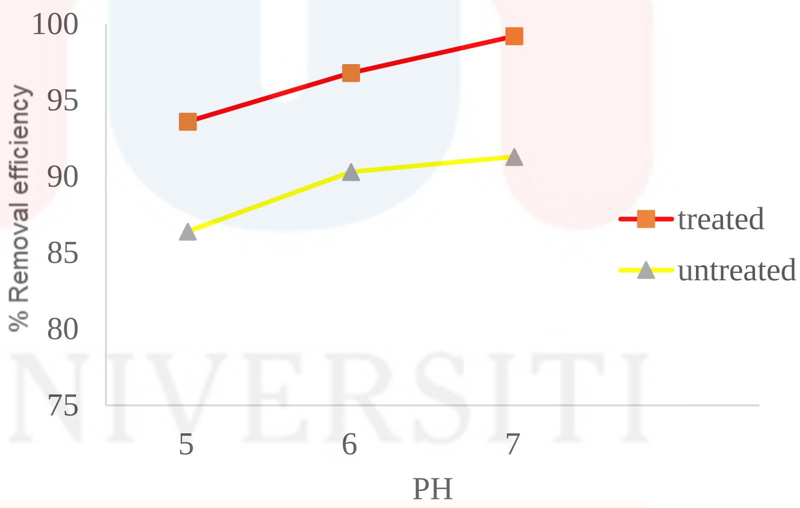


Figure 4.1: Effect of pH on the percentage for removal efficiency of heavy metal

Figure 4.2 indicated the removal of heavy metals were increased because increasing of the adsorbent dosage. In fact, the increment of the adsorbent dosage, will enhance the removal efficiency of heavy metal by existing a lot of active site.

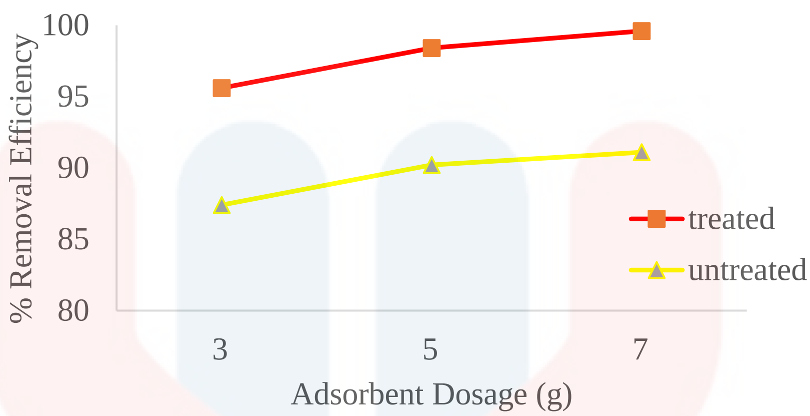


Figure 4.2: Effect of the adsorbent dosage on the percentage for the removal efficiency of heavy metal

Figure 4.3 shows the interaction of the percentage of the removal efficiency of heavy metals based on the agitation rate. The result were indicate, the faster the agitation rate will lower the % removal efficiency of the heavy metal. This is because, when the faster the agitation rate, the adsorption site not effective to adsorb the heavy metals of leachate.

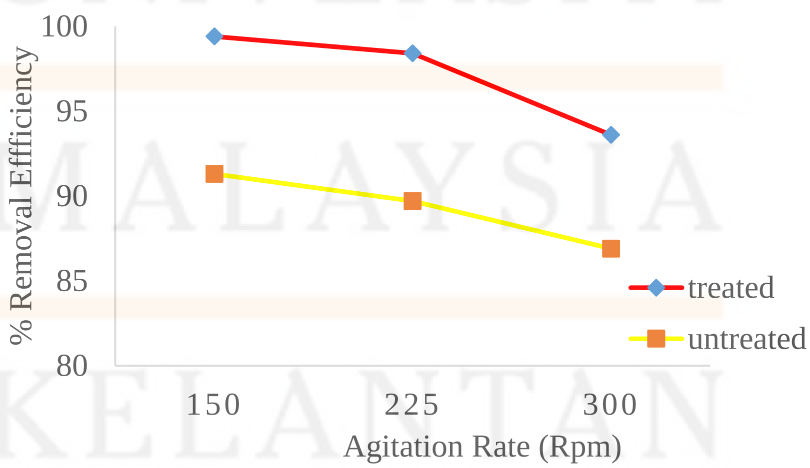


Figure 4.3: Removal efficiency of heavy metal by using agitation rate

Batch adsorption studies were done on treated and untreated maize leaves and papaya barks of removing heavy metals in leachate. The ratio 1:1 were been selected in other to combine both of the biosorbent. Optimization process shows removal efficiency as targeted response or dependent variable. From the Table 4.3, at the pH 7 indicated the higher removal efficiency. This is because, pH can affect the solubility of the metals ions and degree of ionization adsorbent during adsorption process. According to the Babarinde *et al*, (2006) increasing pH of natural maize leaves will adsorb 96.8% removal of cadmium.

Furthermore, the higher adsorbent dosage will indicated the highest removal efficiency of heavy metals. Theoretically, increasing adsorbent dosage is affecting the adsorptive surface and more availability of higher active adsorption sites. Research from (De Gisi et al. 2016), adsorbent dosage is one of the factor that can contribute the removal efficiency heavy metals. Adsorbent dosage is chosen because can affect the active site in adsorbing the heavy metals. Increasing adsorbent dosage enhances efficiency of removing heavy metals.

Contact period used due to increasing of the adsorption rate. The longer the contact period, the higher the adsorption heavy metals rate. From the result, treated are shows 100 min will increase the removal efficiency. Agitation rate affected by the interaction of adsorbent dosage-adsorbate. According to the Brahmaiah *et al*, (2013), increasing the contact period will enhance the effective collision between adsorbate and adsorbent.

4.3 Experimental Design Using Response Surface Methodology (RSM)

pH, contact period, agitation rate and adsorbent dosage were selected as independent variables and the removal efficiency (%) as the dependent response variables. Types of Central Composite Design were selected on Face Centre Design. This is because, the star points are at the centre of each face of the factorial space. So, $\alpha = \pm 1$. The running were made in triplicates due to obtain the accurate result.

Table 4.3 shows the experimental design of RSM for treated and untreated adsorbent. The highest removal efficiency for treated adsorbent are 99.6% contrarily to untreated adsorbent are 92.1%. Lowest removal efficiency for treated adsorbent are 93.6% and untreated are 86.2%.

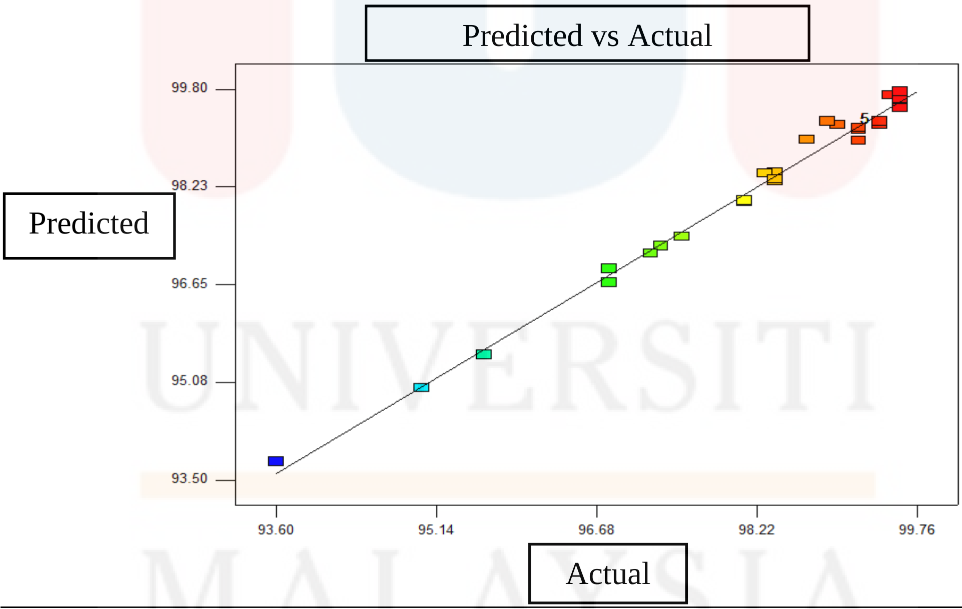
Table 4.3: Experimental Response of RSM for treated and untreated adsorbent

No	pH	Contact Period (min)	Agitation Rate (rpm)	Adsorbent Dosage (g)	Removal Efficiency (%)	
					Treated	**Untreated**
1.	6.0	20.00	225.00	5.0	98.4	88.8
2.	6.0	100.00	225.00	5.0	96.8	87.9
3.	7.0	100.00	150.00	3.0	97.2	90.3
4.	6.0	60.00	225.00	5.0	99.4	90.3
5.	6.0	60.00	300.00	5.0	99.2	90.2
6.	6.0	60.00	225.00	5.0	99.4	90.3
7.	7.0	100.00	150.00	7.0	98.1	88.0

8.	6.0	60.00	150.00	5.0	98.7	91.1
9.	5.0	20.00	150.00	7.0	99.6	90.2
10.	6.0	60.00	225.00	5.0	99.4	90.3
11.	7.0	20.00	300.00	3.0	96.8	87.4
12.	6.0	60.00	225.00	5.0	99.4	90.3
13.	5.0	20.00	150.00	3.0	99.4	90.7
14.	5.0	100.00	300.00	7.0	93.6	88.4
15.	6.0	60.00	225.00	7.0	99.6	91.0
16.	7.0	20.00	150.00	7.0	99.2	90.3
17.	7.0	60.00	225.00	5.0	99.0	89.7
18.	5.0	100.00	150.00	7.0	95.0	86.2
19.	6.0	60.00	225.00	3.0	99.6	92.1
20.	5.0	100.00	150.00	3.0	97.3	88.3
21.	5.0	100.00	300.00	3.0	98.1	89.2
22.	7.0	20.00	150.00	3.0	95.6	91.3
23.	5.0	20.00	300.00	7.0	98.4	89.0
24.	7.0	100.00	300.00	3.0	98.4	89.0
25.	7.0	20.00	300.00	7.0	98.3	86.9
26.	6.0	60.00	225.00	5.0	99.4	90.2
27.	7.0	100.00	300.00	7.0	97.5	87.6
28.	5.0	20.00	300.00	3.0	99.5	89.4
29.	5.0	60.00	225.00	5.0	99.4	90.2
30.	6.0	60.00	225.00	5.0	98.9	90.8

4.3.1 Diagnostic model

Predicted versus actual values for treated and untreated of adsorbent are shown in Figure 4.4. Analysis of the data to illustrate the interaction between actual and predicted removal efficiency. Actual values were obtained from the experiment, while predicted value gained through calculation quadratic equation. The figure describes the data that has been plotted were approximately to the straight line, and can describe it is a good relationship between actual and predicted values of response. It can be conclude that, the quadratic model is chosen in predicting the response variables for the experimental data.



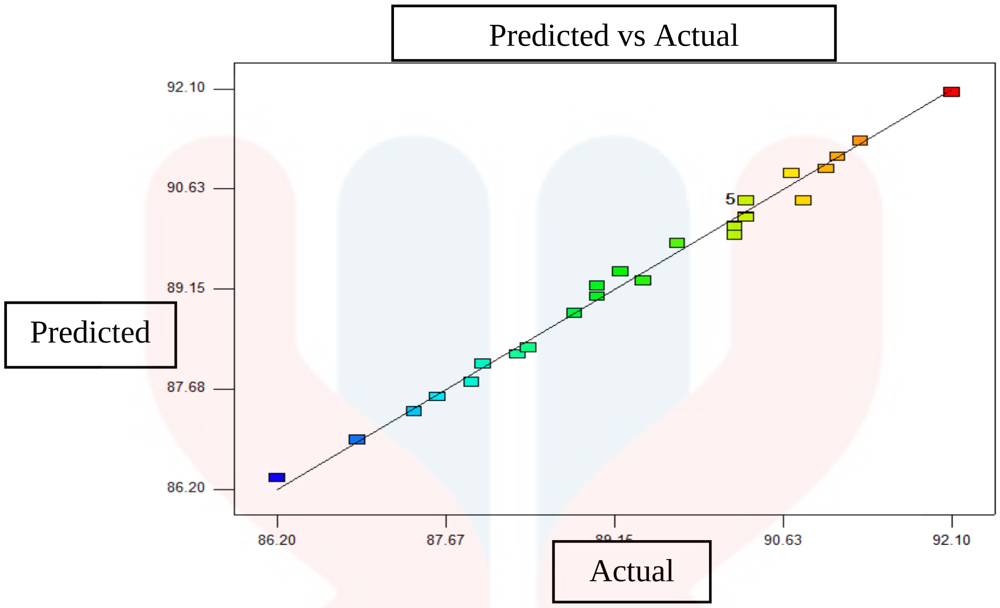


Figure 4.4: Predicted versus Actual value treated (upper) and untreated (lower)

In particular, treated adsorbent indicated the higher actual value (99.60%), approximately with predicted (99.763%). Contrarily, untreated value for actual (92.1%) and predicted is 92.046%.

4.3.2 Statistical of heavy metal adsorption

Probability (*p* value) > F value indicate sufficiency of the model. The model with *p* values > F value less than 0.0001 will accurately fit the obtained data. *p* value > F value below 0.0001 means that the experimental data collected can be experimentally explained by the model created by RSM with 99% accuracy. To identify the ability of the models about removal efficiency of heavy metal by using treated and untreated adsorbent, three different tests, such as sequential model sum of squares, lack of fit tests and the model summary statistics are been carried out. Table

4.4 and Table 4.5 show that the selections of a satisfactory model for treated and untreated adsorbent of removal heavy metal. Those result were indicated that quadratic model vs 2FI are been selected due to *p* value > F value less than 0.0001.

Table 4.4 Selection of a satisfactory model for treated of adsorbent removal efficiency (%) based on sequential model sum of squares

Sources	Sum of squares	*df*	Mean square	F values	*p* value prob. > F
Means vs Total	2.898E+005	1	2.898E+005		
Linear vs Mean	9.71	4	2.43	1.10	0.3788
2FI vs Linear	34.01	6	5.67	5.08	0.0029
Quadratic vs 2FI	20.56	4	5.14	118.81	<0.0001 suggested
Cubic vs Quadratic	0.37	8	0.046	1.13	0.4433
Residual	0.28	7	0.041		

Table 4.5: Selection of a satisfactory model for untreated adsorbent removal efficiency (%) based on sequential model sum of squares

Sources	Sum of squares	*df*	Mean square	F values	*p* value prob. > F
Means vs Total	2.404E+005	1	2.404E+005		
Linear vs Mean	15.14	4	3.79	2.20	0.0980
2FI vs Linear	17.72	6	2.95	2.22	0.0862
Quadratic vs 2FI	24.72	4	6.18	163.07	< 0.0001 suggested
Cubic vs Quadratic	0.26	8	0.032	0.74	0.6624
Residual	0.31	7	0.044		

The model summary statistics show that the "Predicted R^2" value of 0.9581 for the treated adsorbent was in reasonably agreement with the "Adjusted R^2" 0.9807 for the quadratic model. Meanwhile, for the untreated of adsorbent, "Predicted R^2" was 0.9556 and "Adjusted R^2" are 0.9811. Moreover, both of quadratic model had maximum values of "Predicted R^2" and "Adjusted R^2". The result indicated that the quadratic model is excellent explanation interaction between the independent variables and dependent variables in Table 4.6 and Table 4.7 respectively.

Table 4.6: Model Summary Statistics for treated of adsorbent

Sources	Standard Deviation	R^2	Adjusted R^2	Predicted R^2
Linear	1.49	0.1495	0.01335	-0.3923
2FI	1.06	0.6733	0.5013	-0.0680
Quadratic	0.21	0.9900	0.9807	0.9581
Cubic	0.20	0.9956	0.9819	0.7349

Table 4.7: Model Summary Statistics for untreated of adsorbent

Sources	Standard Deviation	R^2	Adjusted R^2	Predicted R^2
Linear	1.31	0.2604	0.1421	-0.1304
2FI	1.15	0.5651	0.3362	-0.2023
Quadratic	0.19	0.9902	0.9811	0.9556
Cubic	0.21	0.9947	0.9780	0.7028

The ability of the models was further explained through analysis of variance (ANOVA). ANOVA preferred that the equation and the real relationship between the response and the significant variable supported by the equation were appropriate.

ANOVA justified the importance and how adequate the models are been selected. From Table 4.8, dividing the sum of the squares of each of the variation sources, the model and the error variance by the respective degrees of freedom gives the mean square values. The model terms with value of Probability > F less than 0.05 are considered as significant. With the respect of removal efficiency as showed in Table 4.8, the model value is 106.11 and Probability > F value of 0.0001 that justified the model's significance. In accordance with the confirmation, B, D, AB, AC, AD, BD, CD, B^2, C^2, D^2 are the significant model terms. Other than that, the values are not significant.

Besides that, Lack of Fit F-value of 1.06 indicated that the Lack of Fit is not significant relative to the pure errors. There is a 50.71% chance that a “Lack of Fit-value” this large could occur due to the noise. Non-significant lack of fit is good to obtain that models to fit.

Table 4.8: ANOVA for response surface quadratic model of treated of adsorbent.

Sources	Sum of squares	Degree of freedom	Mean square	F values	Prob. > F
Model	64.28	14	4.59	106.11	< 0.0001
A-pH	0.000	1	0.000	0.000	1.0000
B-contact period	9.39	1	9.39	216.98	< 0.0001
C-agitation rate	5.556E-004	1	5.556E-004	0.013	0.9113
D-adsorbent dosage	0.32	1	0.32	7.40	0.0158
AB	12.25	1	12.25	283.10	< 0.0001
AC	0.36	1	0.36	8.32	0.0113
AD	9.92	1	9.92	229.10	< 0.0001
BC	0.022	1	0.022	0.52	0.2819
BD	7.84	1	7.84	181.18	< 0.0001
CD	3.61	1	3.61	83.43	< 0.0001
A^2	8.423E-003	1	8.423E-003	0.19	0.6654
B^2	7.11	1	7.11	164.40	< 0.0001
C^2	0.24	1	0.24	5.64	0.0313
D^2	0.30	1	0.30	7.04	0.0180
Residual	0.65	15	0.043		

Lack of Fit	0.44	10	0.044	1.06	0.5071
Pure Error	0.21	5	0.042		

Comparison with untreated of adsorbent in Table 4.9, the model values is 108.53. Lack of Fit F-value of 0.86 also can indicated the Lack of Fit is not insignificant relative to the pure errors. There is a 60.86% chance that a “Lack of Fit-value”.

Table 4.9: ANOVA for response surface quadratic model of untreated of adsorbent

Sources	Sum of squares	Degree of freedom	Mean square	F values	Prob. > F
Model	57.57	14	4.11	108.53	< 0.0001
A-pH	0.067	1	0.067	1.77	0.2028
B-contact period	4.60	1	4.60	121.41	< 0.0001
C-agitation rate	4.81	1	4.81	126.81	< 0.0001
D-adsorbent dosage	5.67	1	5.67	149.56	< 0.0001
AB	2.40	1	2.40	63.40	< 0.0001
AC	5.76	1	5.76	152.10	< 0.0001
AD	0.12	1	0.12	3.23	0.0923
BC	7.84	1	7.84	206.90	< 0.0001
BD	1.10	1	1.10	29.10	< 0.0001
CD	0.49	1	0.49	12.93	0.0026
A^2	0.82	1	0.82	21.68	0.0003
B^2	12.12	1	12.12	319.95	< 0.0001
C^2	0.049	1	0.049	1.28	0.2756
D^2	2.79	1	2.79	73.51	< 0.0001
Residual	0.57	15	0.038		
Lack of Fit	0.36	10	0.036	0.86	0.6068
Pure Error	0.21	5	0.042		

4.3.3 Development of regression model using Central Composite Design (CCD)

CCD model was designated to make the comparison and interaction of response. This is because to aims formed polynomial regression equation for expression quadratic model. Besides, through polynomial's highest order, sequential model sum of square can be express the model. Percentage efficiency removal of heavy metals can be obtained from final empirical for treated and untreated adsorbent as given in Equation. 4.1 and Equation 4.2 respectively.

$$\text{Removal efficiency (\%)} = 99.29 + 0.0000A - 0.72B - 5.556E\text{-}003C - 0.13D + 0.88AB + 0.15AC + 0.79AD + 0.037BC - 0.70BD - 0.48CD - 0.057A^2 - 1.66B^2 - 0.31C^2 + 0.34D^2$$

(Equation 4.1)

$$\text{Removal efficiency (\%)} = 90.45 - 0.061A - 0.51B - 0.52C - 0.56D + 0.39AB - 0.60AC - 0.087AD + 0.70BC - 0.26BD + 0.18CD - 0.56A^2 - 2.16B^2 + 0.14C^2 + 1.04D^2$$

(Equation 4.2)

This equation explains the way of individual variables or double interaction affected different types of adsorbent from leachate. Negatives value show that treated and untreated of adsorbent is negatively affected by individual or double interaction factors. In other words, it indicated the removal efficiency were decrease. Whereas, positive coefficient values point out that factors are increase the removal of heavy metal in the tested range.

4.3.4 Response surface contour plot

The contour plot represent the response to selected factors in two dimensions which easily determine the effect of the independent variables on the dependent variables. The response surface contour plots of removal efficiency of heavy metal versus the interaction effect of pH, contact period, agitation rate and adsorbent dosage for the treated and untreated of adsorbent are shown in Figure 4.5 until Figure 4.6 respectively.

Each contour plots represent a number of combinations between two variables and the other variable kept constant. The maximum percentage of removal efficiency is point out by the surface confined in the smallest curve of the contour plot. The optimum values of variables factors could be analysed by the saddle point or by justified the maximum values formed by the x and y-coordinates in the surface of contour plots.

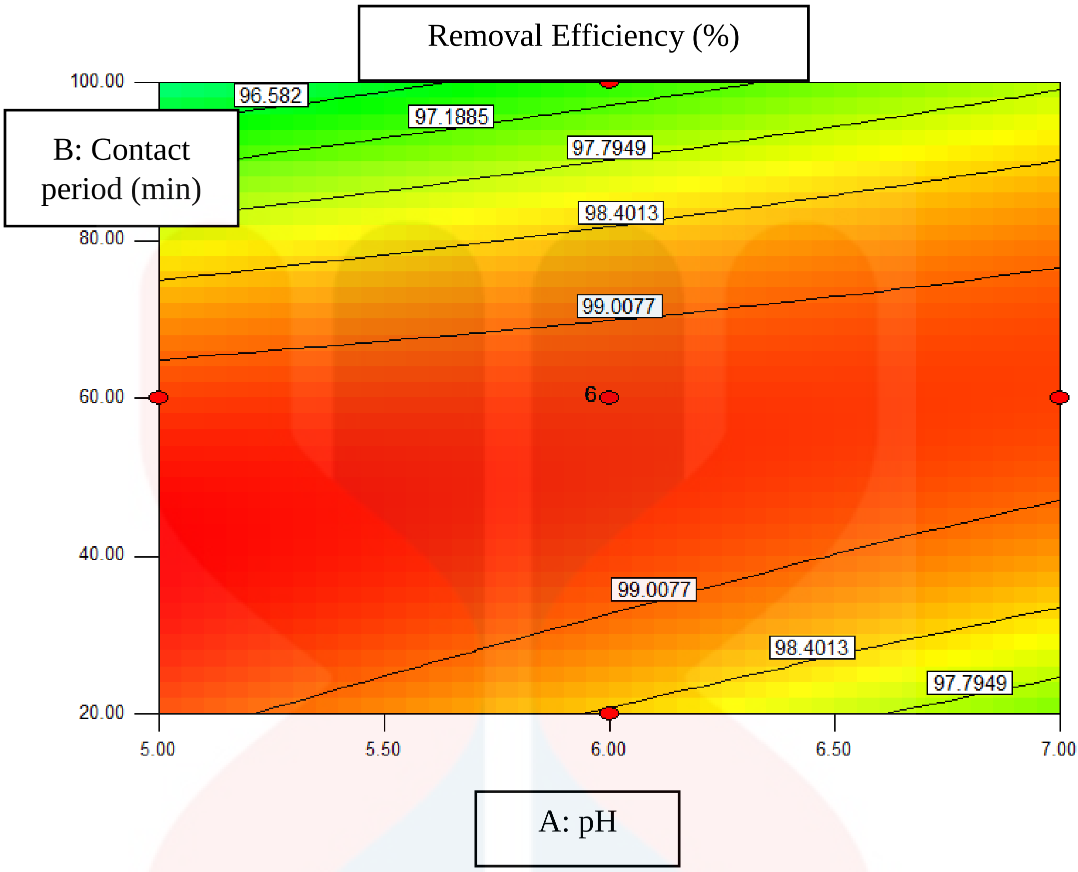


Figure 4.5 : Contact period vs pH that been treated with acid (2D-contour)

Based on the Figure 4.5, interaction of pH and contact period effect the removal efficiency of heavy metals. Increasing of the contact period (20 min until 60 min) and increment of the pH will obtain higher removal, due to double hydroxide layers in the metals ions was diffused at high pH (5-7). The darker regions (red) in treated adsorbent was determined the higher removal 99.077%. Whereas, for the untreated adsorbent in Figure 4.7, there is no darker region that can be manipulated.

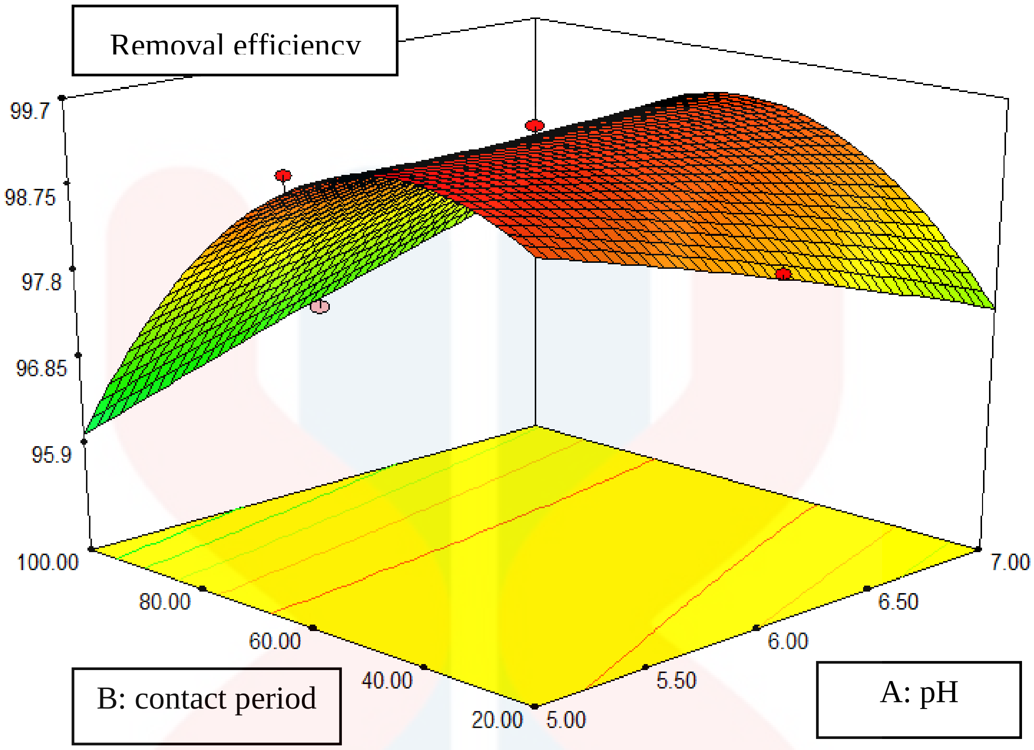


Figure 4.6: Contact period vs pH that been treated with acid (3D-contour)

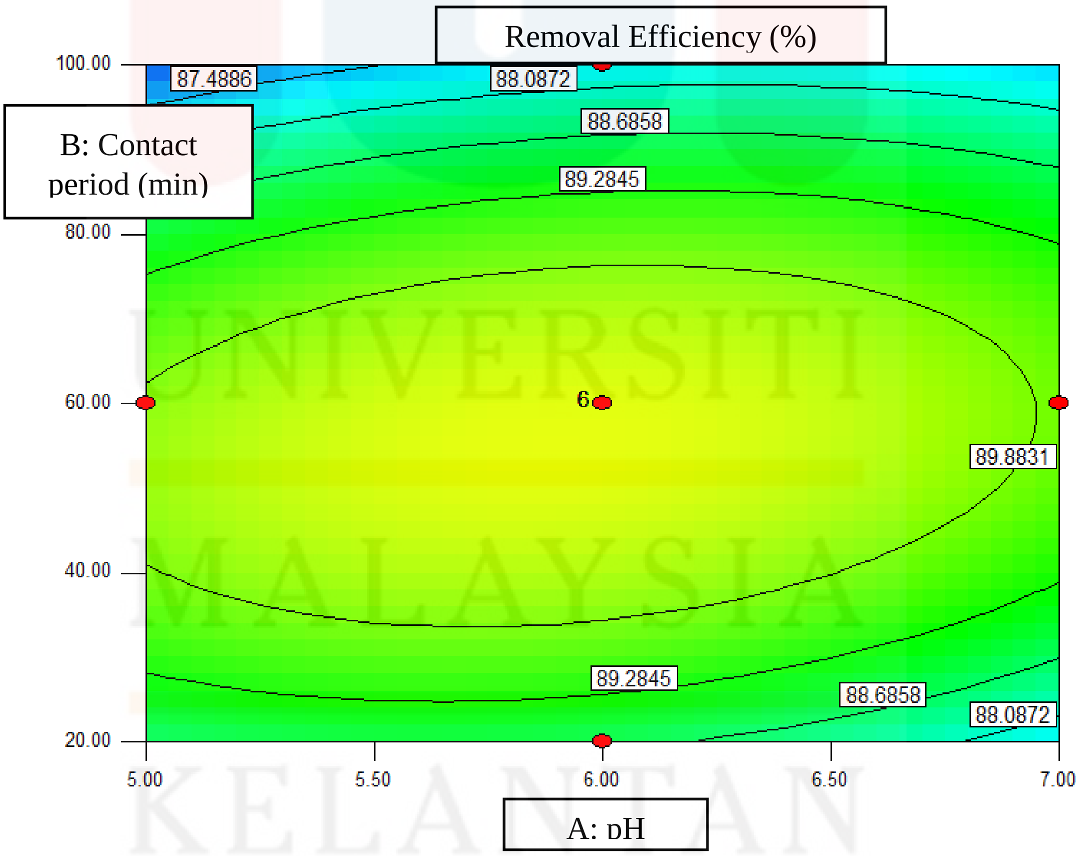


Figure 4.7: Contact period vs pH that been untreated with acid (2D-contour)

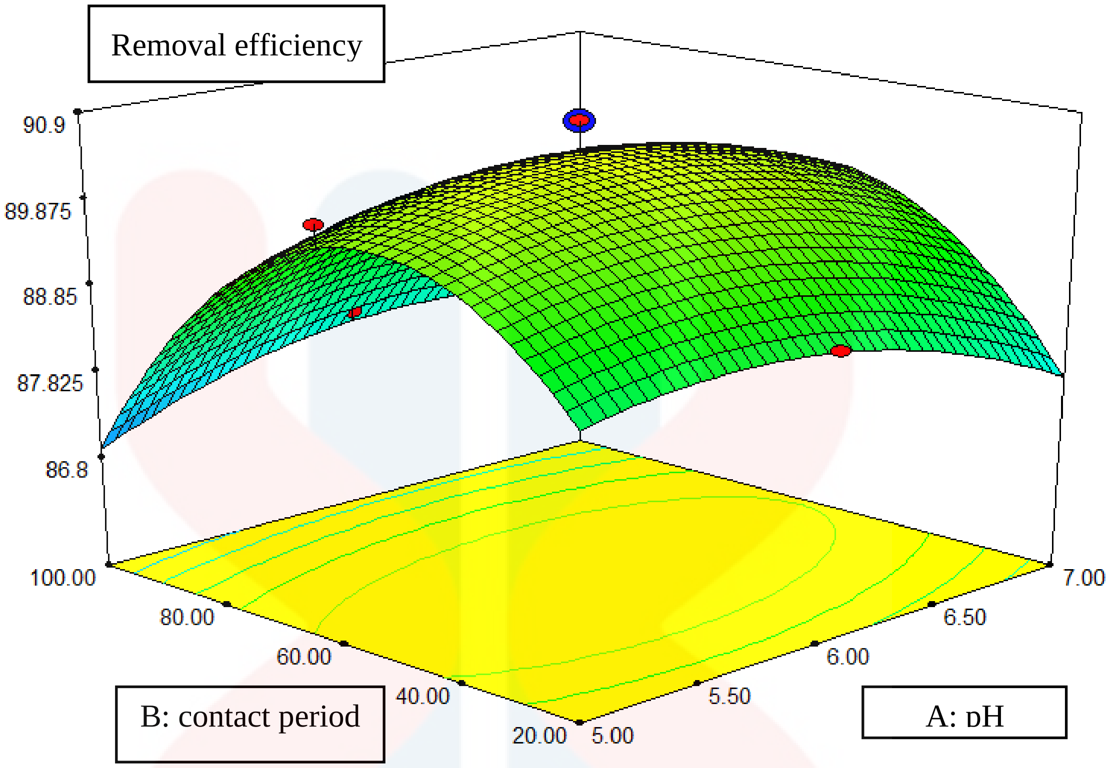


Figure 4.8: Contact period vs pH that been untreated with acid (3D-contour)

In addition, interaction between pH and agitation rate between treated and untreated adsorbent are been pointed out in Figure 4.9 to Figure 4.11 respectively. Based on the Figure 4.9, the pH and agitation rate was the suitable factor due to the darker regions is between pH 6-6.50 and agitation rate is at 187.50 rpm until 225 rpm that indicated 99.20% removal efficiency. While, the untreated adsorbent the pH is between 6.00 until 6.50, and agitation rate is between 150 rpm until 187.50 rpm that can give 90.83% of removal efficiency. This is because, during that time boundary layer resistance were reduced and mobility of the system were rise.

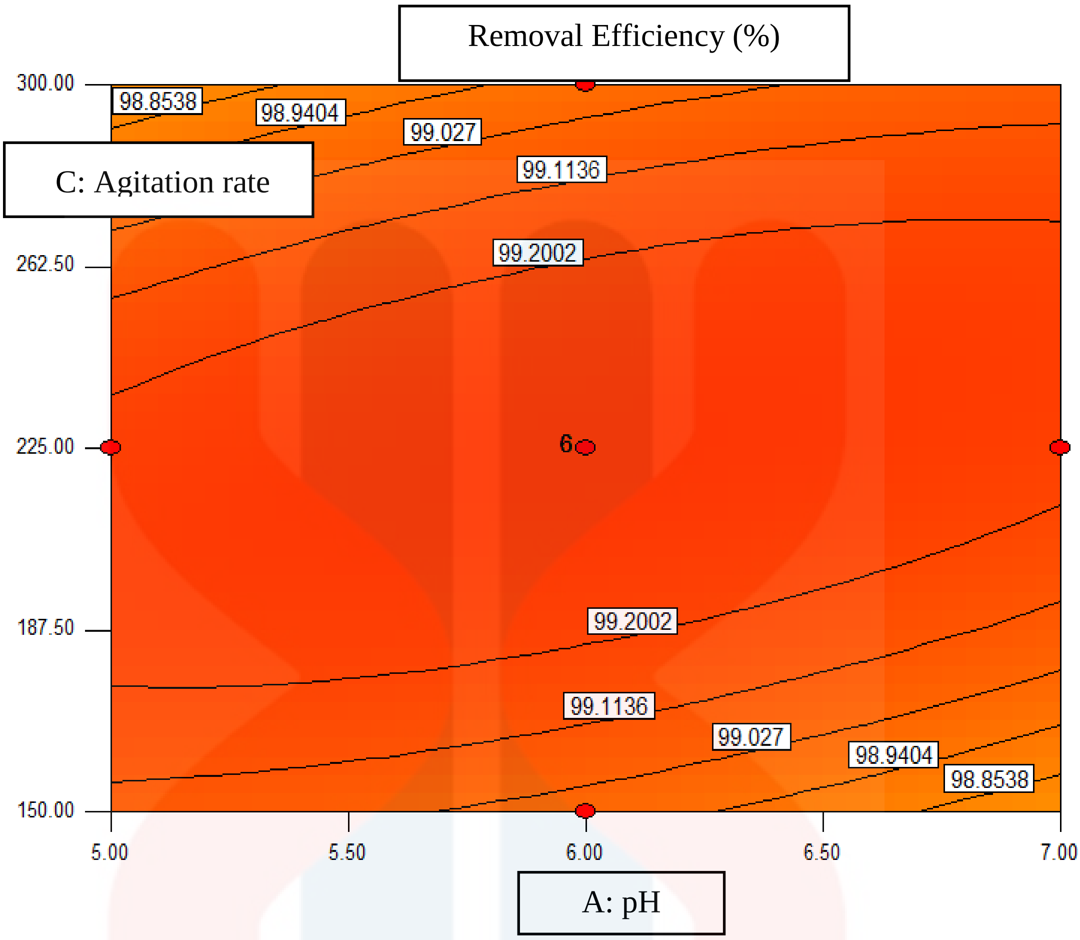


Figure 4.9: agitation rate vs pH that been treated with acid (2D-contour)

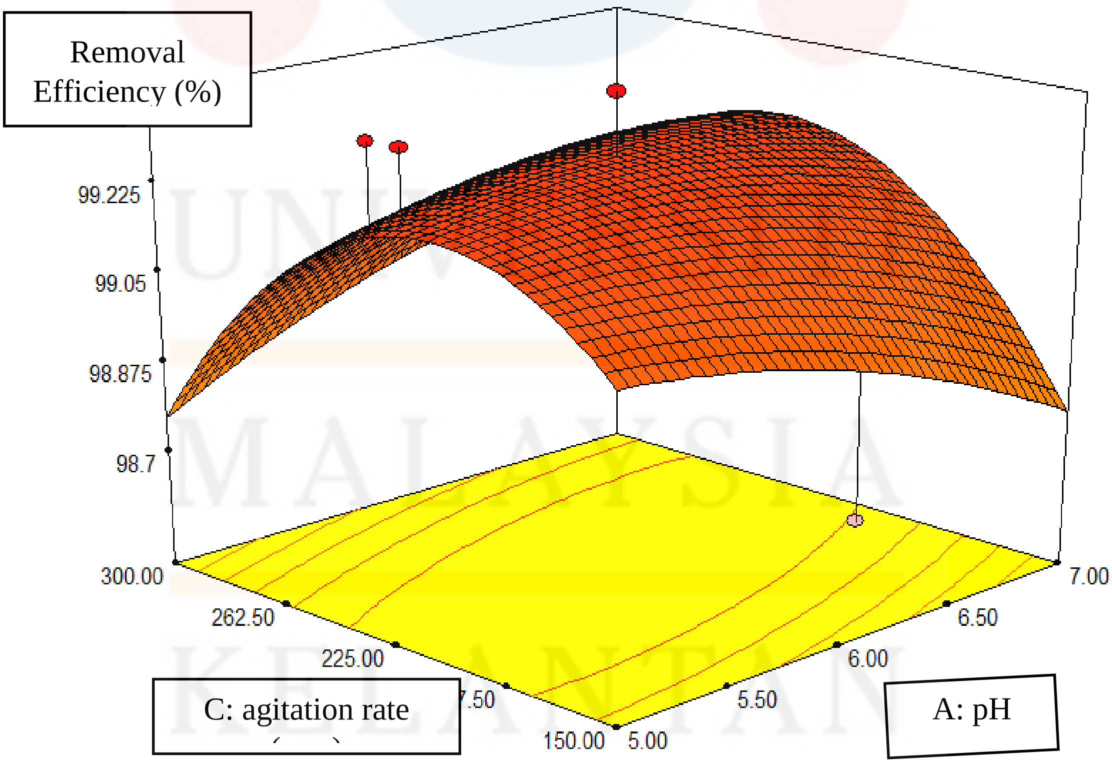


Figure 4.10: Agitation rate vs pH that been treated with acid (3D-contour)

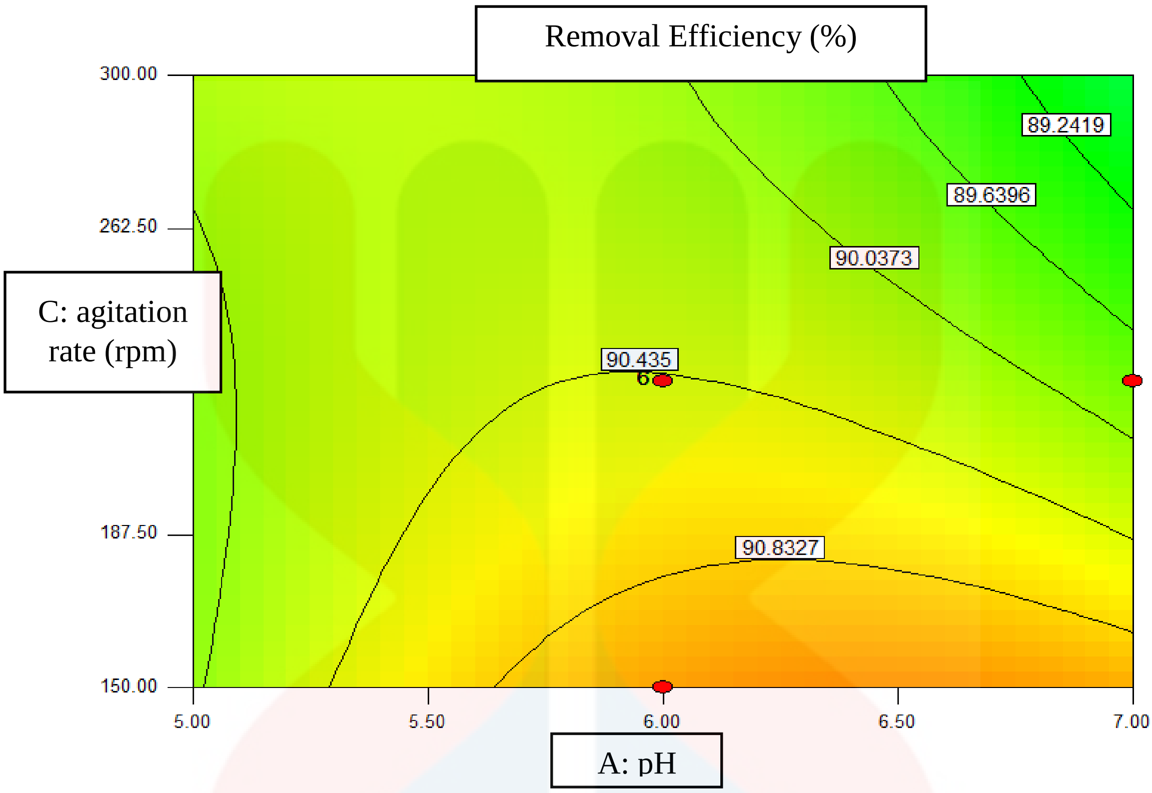


Figure 4.11: Agitation rate vs pH that been untreated with acid (2D-contour)

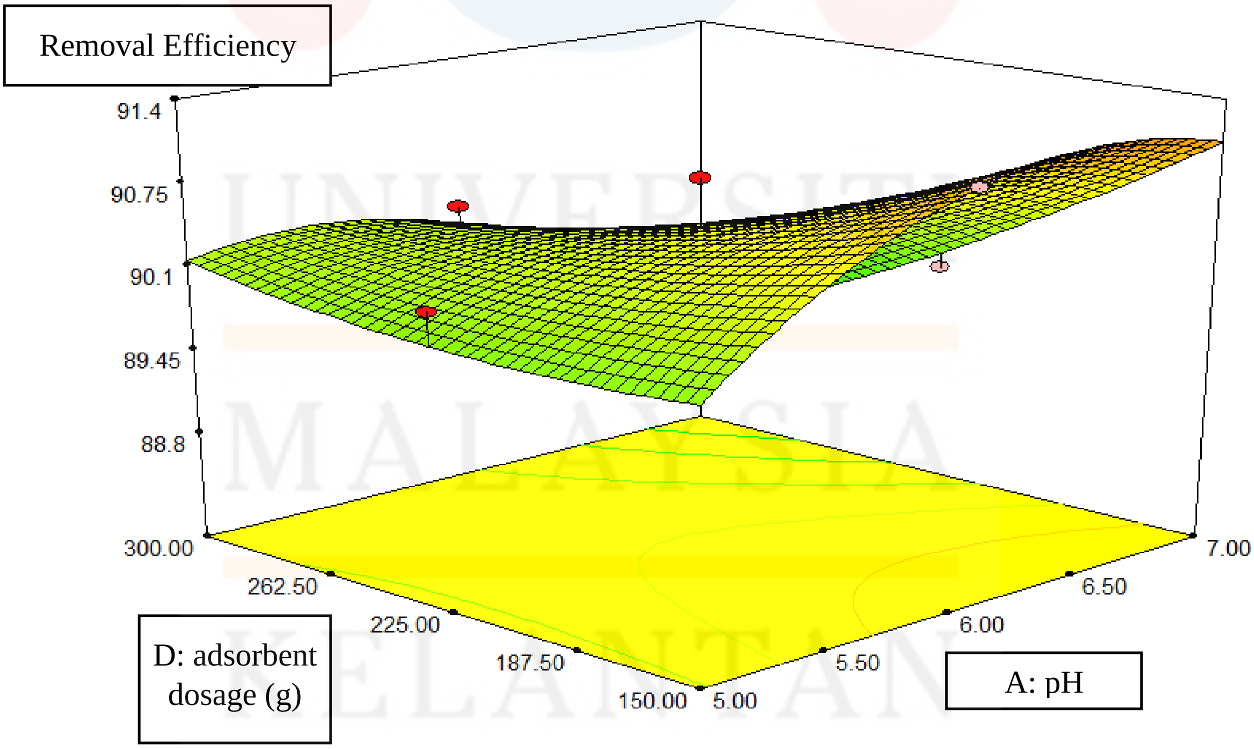


Figure 4.12: agitation rate vs pH that been untreated with acid (3D-contour)

Compared it with interaction between pH and adsorbent dosage Figure 4.12 and Figure 4.15 indicated that during the pH between 5.00 until 5.50, and adsorbent dosage is between 3 g until 4 g can give higher percentage of removal efficiency. In addition, untreated adsorbent can give 91.66% of removal efficiency heavy metals at the pH between 5.50 until 6.50, while for the adsorbent dosage it is between 3 g until 4 g. This may be because of higher pH enhance the increasing of negative charge on the surface of adsorbent, and will lower the attraction heavy metal adsorbent.

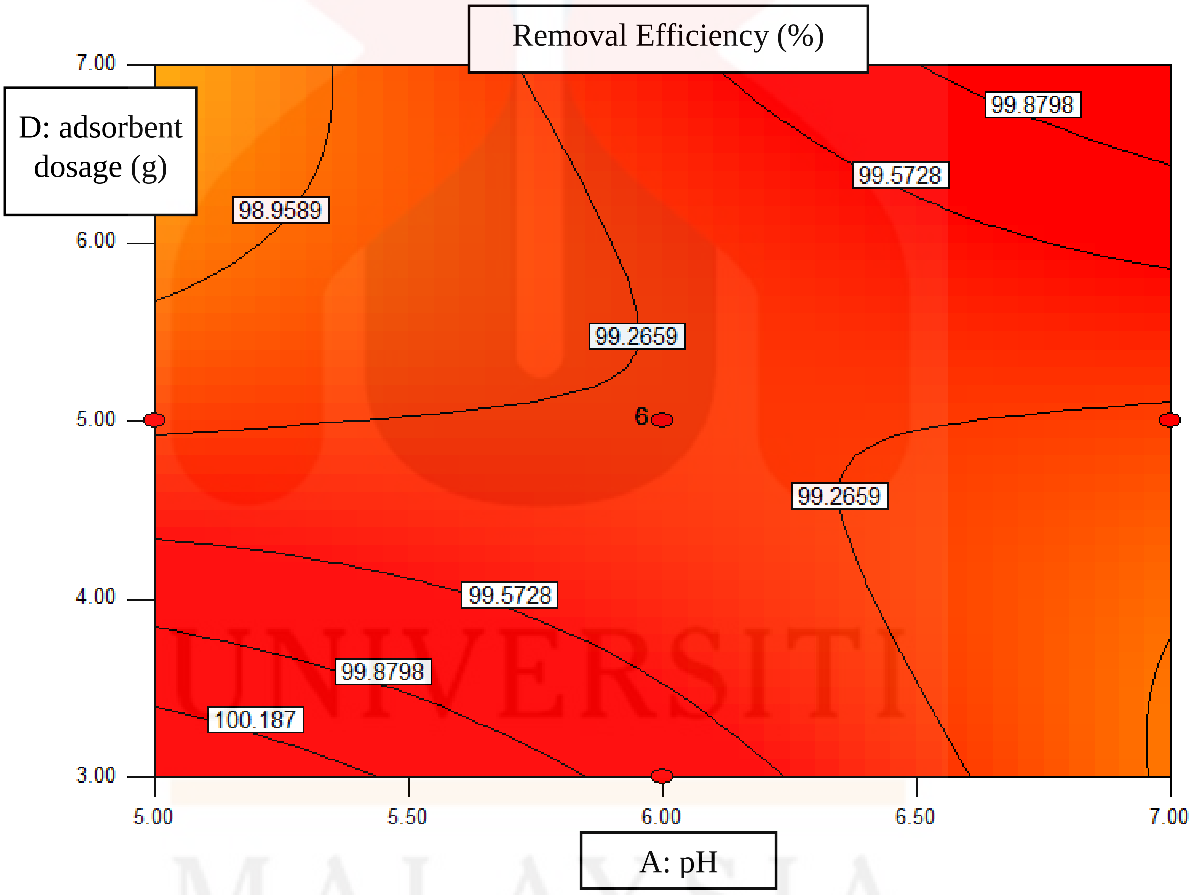


Figure 4.13: Adsorbent dosage vs pH treated with acid (2D-contour)

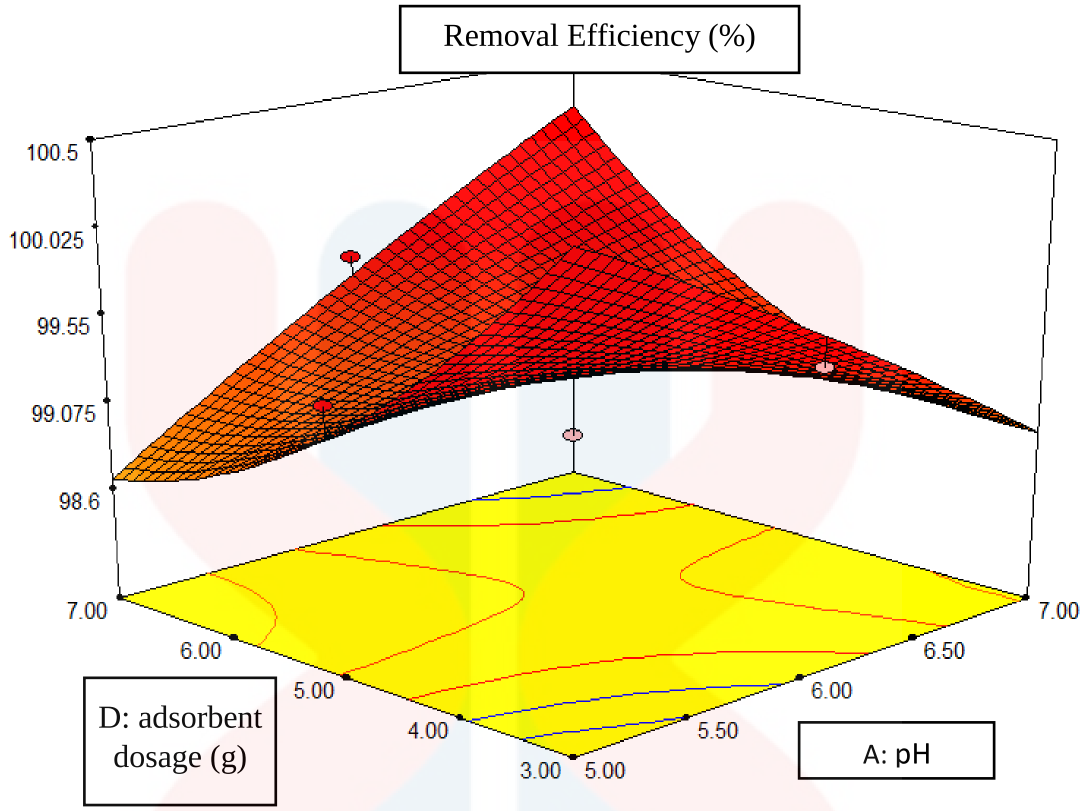


Figure 4.14: Adsorbent dosage vs pH treated with acid (2D-contour)

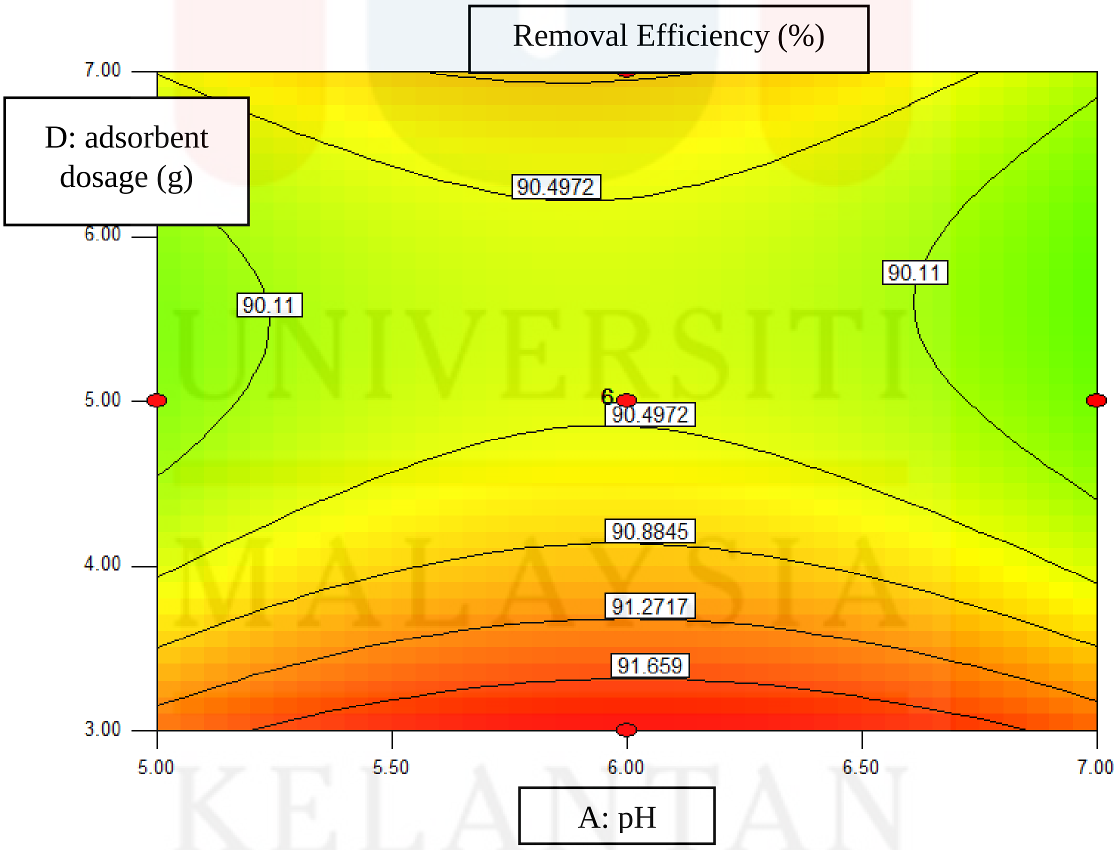


Figure 4.15: Adsorbent dosage vs pH untreated with acid (2D-contour)

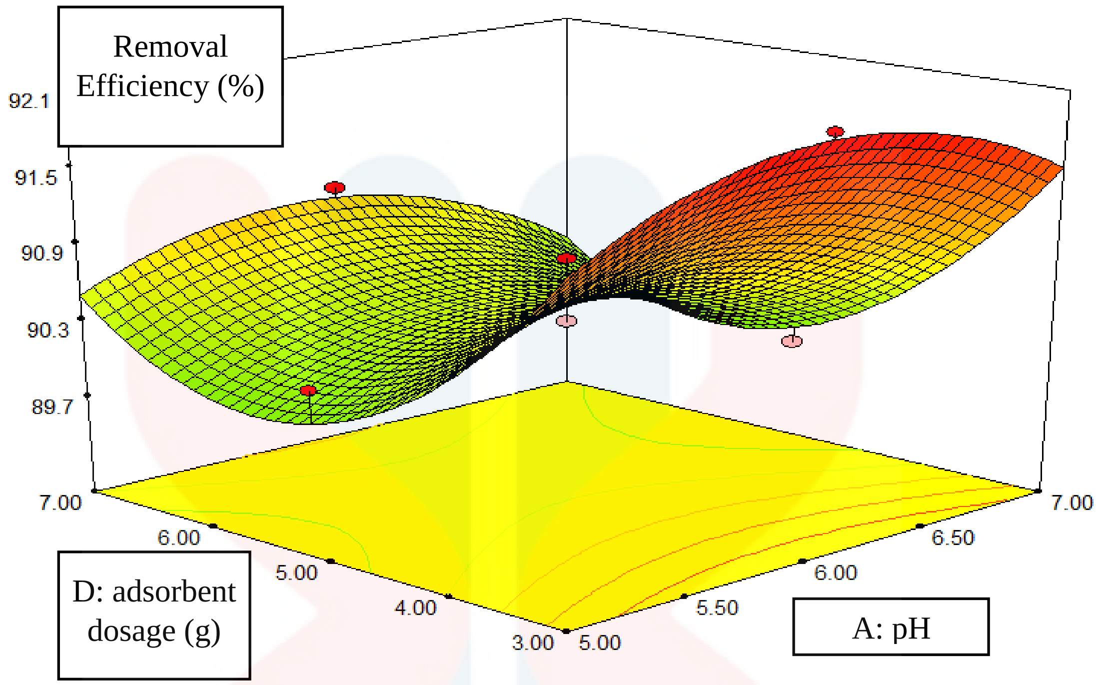


Figure 4.16: Adsorbent dosage vs pH untreated with acid (3D-contour)

4.3.5 Optimization Process

Table 4.10 can conclude the predicted optimum conditions for treated and untreated. Optimum conditions for pH of treated adsorbent are in 6.67, agitation rate in 279.71 rpm, contact period is 52.25 min and adsorbent dosage in 6.93 g that referred to 99.62% removal efficiency.

Contrarily, optimum condition for pH of untreated is 5.50, agitation rate are 162.40 rpm, adsorbent dosage in 3.08 g and contact period are 52.14 min indicate 92.32% of removal efficiency for untreated adsorbent.

Table 4.10: Optimum result obtained using RSM software

Parameters	Ph	Agitation rate	Adsorbent dosage	Contact period	Removal efficiency (%)
Treated adsorbent	6.67	279.71 rpm	6.93 g	52.25 min	99.6236
Untreated adsorbent	5.50	162.40 rpm	3.08 g	52.14 min	92.322

Based on previous research by Sahu *et al*. (2016), optimum pH of 4.07 and adsorbent dosage are 1.44 g, in 99.28% removal Lead (II) by using activated tamarind wood. Lastly, according to the Aravind *et al.* (2015), 96.23% removal Nickel (II) ions comes from optimum pH at 9.0, and contact period 75 min.

Last but not least, comparison between this study and from the previous studies, showed that different types pf adsorbent were gave different optimum conditions.

4.4 Adsorption Isotherm

Adsorption isotherm used to develop the most appropriate correlation for the balance curve in order to optimize the design of the adsorption processes. It is referred to the relationship between the quantities of a substances adsorbed at constant temperature by unit mass of adsorbent and its concentration in balance solutions. Adsorption isotherms were carried out using Langmuir and Freundlich isotherm.

4.4.1 Langmuir isotherm equation

Based on the Langmuir adsorption theory, molecules are adsorbed at a fixed number of well-defined active sites homogenously distributed across the adsorbent surface. At the mono molecular layer of the adsorption indicated the affinity of the active sites. Besides that, there are no interactions between the adsorbed molecules.

So, based on Table 4.11 showed for Langmuir model, the agitation rate of adsorption capacity (Q_{max}) for higher 0.0292, equilibrium constant of Langmuir model (K_L) is 21.646 and correlation coefficient R^2 values are 0.9972 that indicated approximately with 1.00. Contrarily, untreated adsorbent for higher value of Q_{max} is adsorbent dosage, 0.0220. K_L value are 12.598 and correlation coefficient is 0.9947.

4.4.2 Freundlich isotherm equation

Freundlich isotherm model interprets the adsorption on heterogeneous surfaces with interaction occurring between the adsorbed molecules and is not restricted to the formation of a mono-layer. Naturally, this isotherm are used to explain the adsorption of organic and inorganic compound on a wide variety of adsorbent.

For Table 4.12, Freundlich model shows constant value of Freundlich K_f values are 0.2671, adsorption intensity (n) are -6.25 and correlation coefficient R^2 are 0.9981. Beside, for untreated adsorbent, K_f value are 0.336, n values are -39.68 and R^2 are 0.9904.

Table 4.11 : Langmuir and Freundlich isotherm for the adsorbent that treated with acid.

Parameter	Langmuir model			Freundlich model		
	Q_{max}	K_L	R^2	K_F	n	R^2
pH	0.0148	10.481	0.9849	0.2734	- 34.48	0.9872
Adsorbent dosage	0.0143	10.070	0.9710	0.2743	- 33.33	0.9751
Contact period	0.0112	7.595	0.9906	0.2799	- 27.10	0.9898
Agitation rate	0.0292	21.646	0.9972	0.2671	- 6.25	0.9981

Table 4.12 : Langmuir and Freundlich isotherm for the adsorbent that untreated with acid.

Parameter	Langmuir model			Freundlich model		
	Q_{max}	K_L	R^2	K_F	n	R^2
pH	0.0098	6.036	0.9969	0.303	-22.88	0.9845
Adsorbent dosage	0.0220	12.598	0.9947	0.336	-39.68	0.9904
Contact period	0.0102	5.380	0.9918	0.344	-21.60	0.9919
Agitation rate	0.0098	6.074	0.9958	0.280	-27.40	0.9873

From the Table 4.11 and Table 4.12, determination of behavioural adsorption, R^2 values are required. In this case, if R^2 values approximately to the 1, it can be concluded either it is Langmuir or Freundlich model. The value of 0.9981 that represented at agitation rate. Hence, it explained that, adsorption capacity were been effected by agitation rate. Furthermore, the adsorbent treated leads to the Freundlich model. It can interpret that, adsorption process of treated adsorbent in agitation rate were occurred and were interact on the heterogeneous surface.

Meanwhile, for untreated adsorbent, the value of the pH are 0.9969. pH were caused the adsorption capacity of the untreated adsorbent to become 0.0098. Thus, the model for untreated adsorbent been follow the Langmuir's model. So, it can be concluded that untreated adsorbent are occurred on the monolayer surface during the adsorption process.

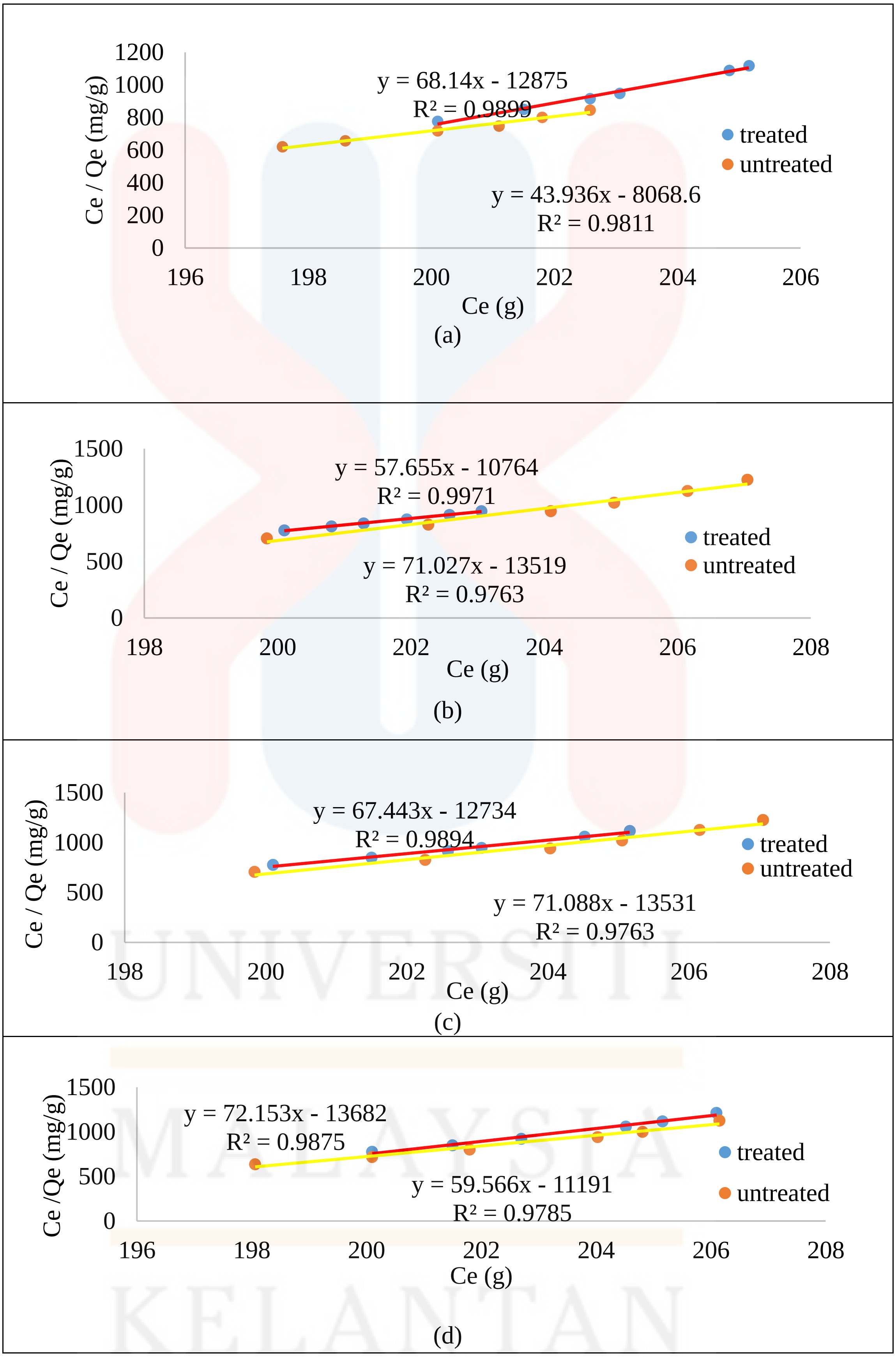


Figure 4.17: Adsorbent dosage (a), agitation rate (b), pH (c), and contact period (d)

for Langmuir model

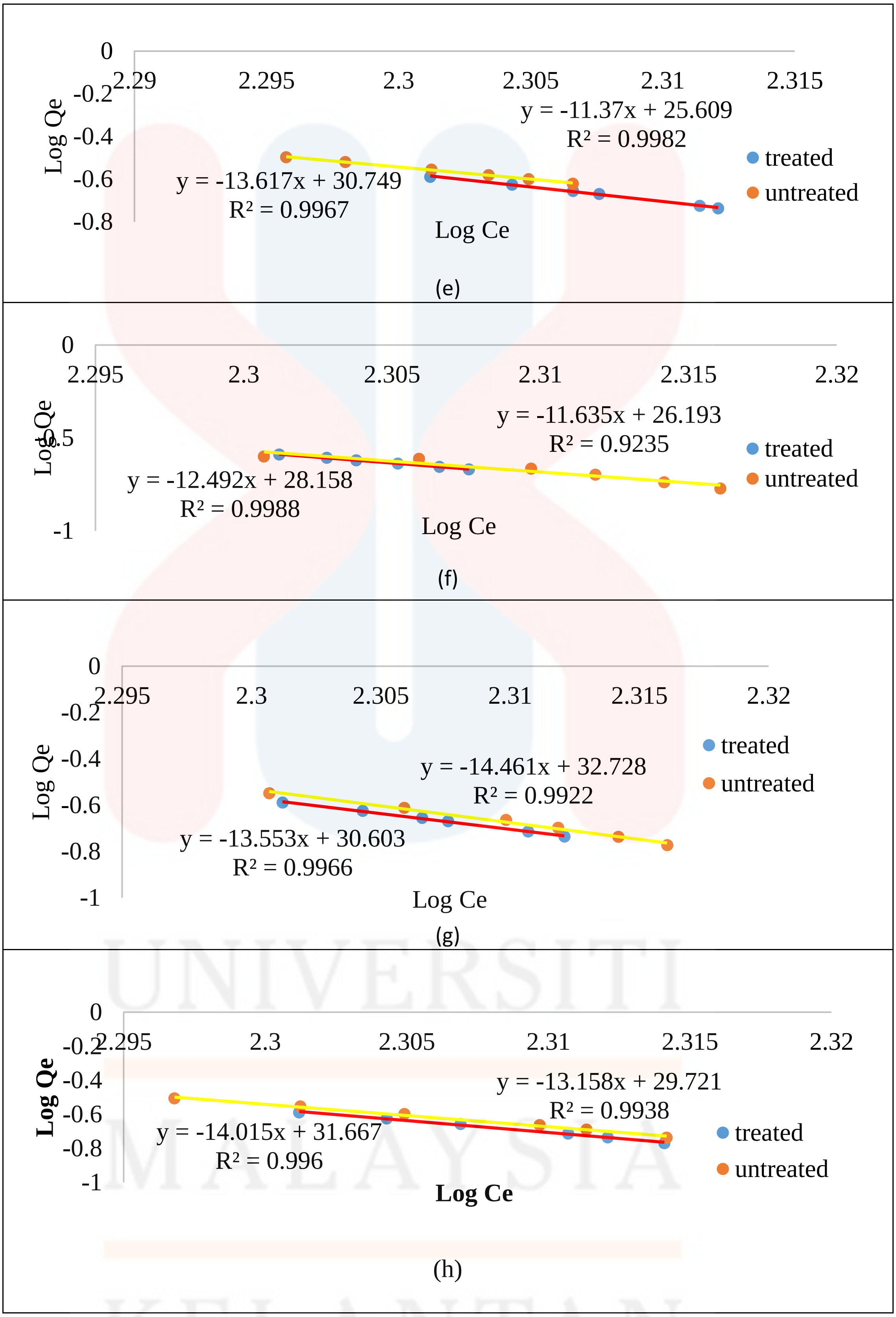


Figure 4.18: Adsorbent dosage (e), agitation rate (f), pH (g), and contact period (h) for Freundlich model

4.5 Characterisation of adsorbent

Fourier-transform infrared spectroscope (FT-IR) were used to observe the functional groups of treated adsorbent before and after the removal of heavy metals. Figure 4.19 shows the FT-IR spectra of the treated before and after remove heavy metals. Interpretation of Figure 4.19, indicate the functional groups are exist which are inorganic phosphate, aliphatic phosphites, and aliphatic hydrocarbons.

Result can be interpreted by observed the wavelength to obtain the functional groups. Based on the before graph of treated adsorbent, 3274.19 cm^{-1} are located in the range 3200-2700 cm^{-1}, indicate the treated adsorbent are in the weak alcohol that were bind with intramolecular bond of O-H. After the treatment, the peak was increase to 3331.31. This is because, adsorbent had been adsorb the bond of O-H in the heavy metals of cadmium and chromium in leachate.

Furthermore, 1030.83 cm^{-1} represented carbonyl groups because it the range between 1275-1200 cm^{-1}. After the removal heavy metal, the reducing of spectra were showed. This is because of donation of electron pair from adsorbent to form metal complexes with cadmium and chromium.

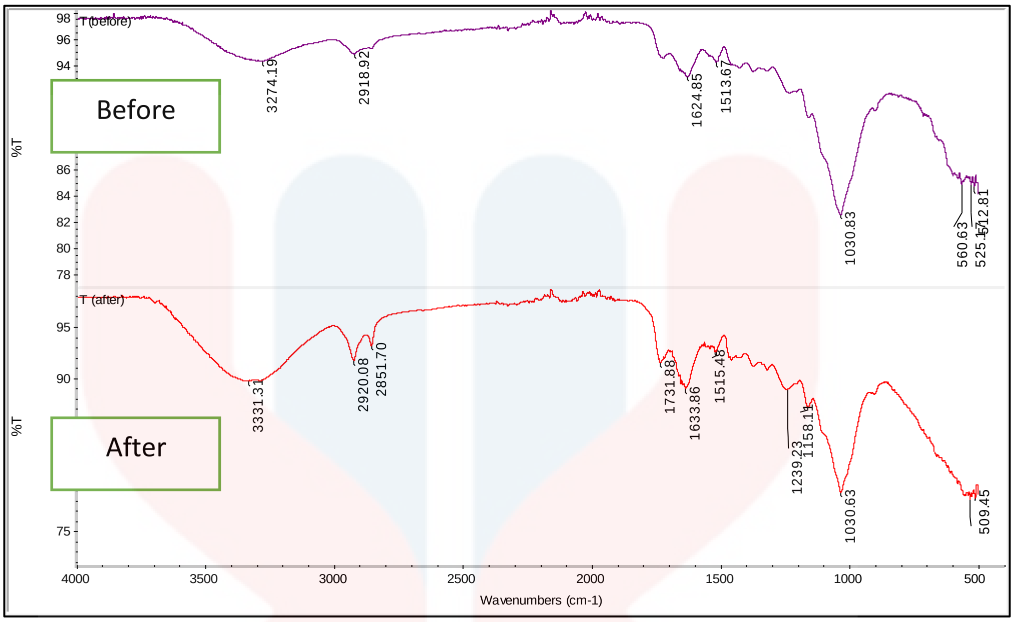


Figure 4.19: FT-IR spectra of the treated before and after remove heavy metal

Figure 4.20 shows the crystallinity of the treated and untreated adsorbent in removal heavy metal of leachate by analysed using XRD. The signals corresponding to the crystalline phase of the sludge samples can also be seen in these diffractgrams and quartz is identified as the main crystalline phase.

Figure 4.20 shows treated adsorbent, black peaks represent before and red peaks are after the removal heavy metal of leachate. Crystallinity phase for before and after are in the range of 2ϴ = 20 - 23° region which described the percentage of the crystallinity in the adsorbent. But, there are differences in term of the intensity value of crystallinity, which is before (468) and after (474) respectively.

Based on that figures, it also can see there is no crystallinity were occurred, but amorphous were showed. This is because, from the percentage crystallinity showed that, crystallinity are 45.2%, while amorphous are 54.8%.

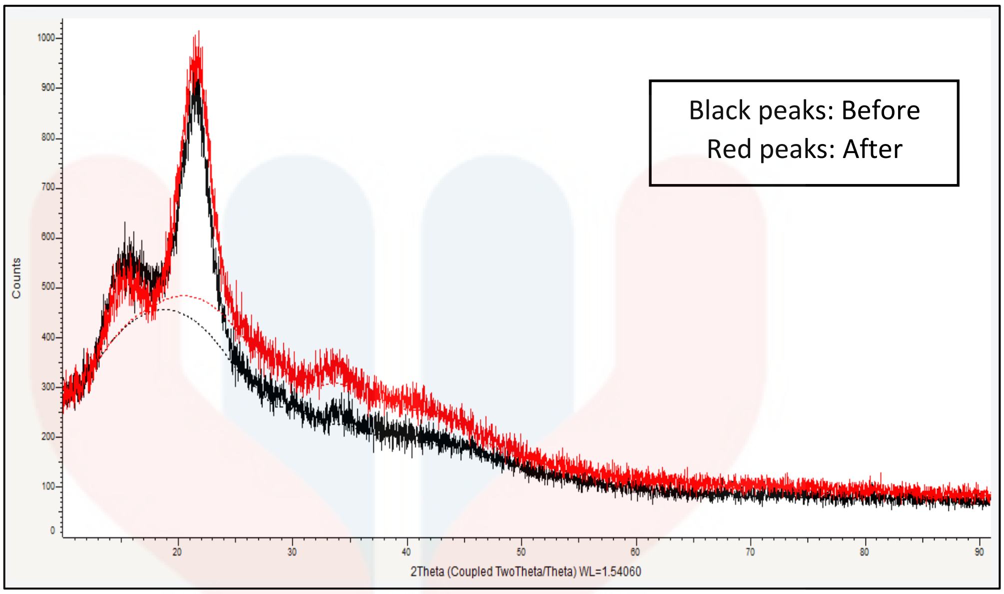


Figure 4.20: Crystallinity of treated adsorbent

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Optimization of heavy metals of leachate using the ratio 1:1 of maize leaves and papaya barks as adsorbent were successfully investigated. Adsorbent has been distinguished into treated and untreated to determine the most effective removal efficiency. From this study, it can be concluded that, treated adsorbent give higher removal efficiency of cadmium and chromium compare to the untreated adsorbent which are 99.6% and 92.1% respectively. This is because treated modification can reduce the lignin, hemicellulose, and enhance the surface area to be wider in order to adsorb heavy metal.

Besides that, for the adsorption studies, 4 parameters had been chosen: pH, agitation rate, agitation rate, and contact period. From the RSM software, optimum removal efficiency for treated and untreated had been evaluated. Optimum result, treated pH are 6.67, agitation rate is 279.71 rpm, contact period is 52.25 min and adsorbent dosage in 6.93 g. Contrarily, untreated adsorbent pH are 5.50, agitation rate are 162.40 rpm, adsorbent dosage in 3.08 g and contact period are 52.14 min.

Adsorption isotherm were assessed to identify the behavioural adsorption of the treated and untreated adsorbent. Concluded from the data, for the treated 0.9981 that represented agitation rate. Therefore, the adsorbent treated follow to the Freundlich model. It can interpret that, adsorption process occurred of treated adsorbent are interact on the heterogeneous surface.

Meanwhile, untreated adsorbent value R^2 is 0.9969. Thus, the model for untreated adsorbent been follow the Langmuir's model. So, untreated adsorbent are occurred on the monolayer surface during the adsorption process.

Characteristics of adsorbent were been observed by FTIR, and XRD. FTIR analysis have confirmed that adsorbent have the carboxylate groups to adsorb the ions of heavy metals. XRD were analysed to obtain the crystallinity of the adsorbent. Based on the result that were obtained, the treated adsorbent showed effective removal adsorbent due to can reduce the hydroxyl groups and carbonyl groups as well.

5.2 Recommendation

As the recommendation, the adsorbent need to undergo process of pyrolysis in order to enhance the increment surface tension of the adsorbent. Furthermore, if this method were observed to be highly efficient for heavy metals removal, the potential toxicity due to heavy metal will also benefits not only for industry, but also living organisms and the surrounding environment. Therefore, by using the low cost of adsorbent can contribute to the sustainability of environment surrounding. Low-cost adsorbent undoubtedly offer many promising advantages for commercial purposes in future.

Physical characteristic need to further analysed by SEM and BET analysis. In order to obtain the morphology and surface characteristic of the adsorbent. Other than maize leaves and papaya barks, other type of low cost agriculture waste can be research for adsorption studies. Lastly, adsorption studies on removing the heavy metals need to further study but focused on certain heavy metals. This is because, can make the comparing to the previous studies.

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APPENDIXS

Table A.1: Heavy metals located in leachate by using AAS

Heavy metals	Concentration of heavy metals (mg / L)
Cadmium	0.005
Chromium	0.056

PHOTO GALLERY

Figure A.1: Maize leaves

Figure A.2: Papaya barks

Figure A.3: Collection of leachate

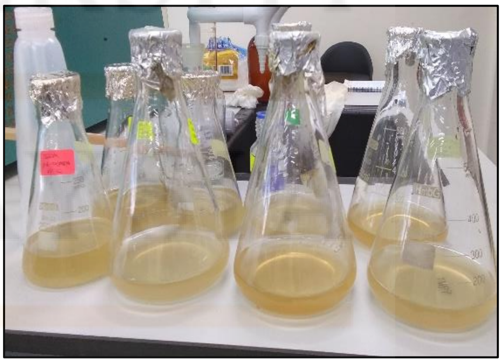

Figure A.4: 100mL of leachate

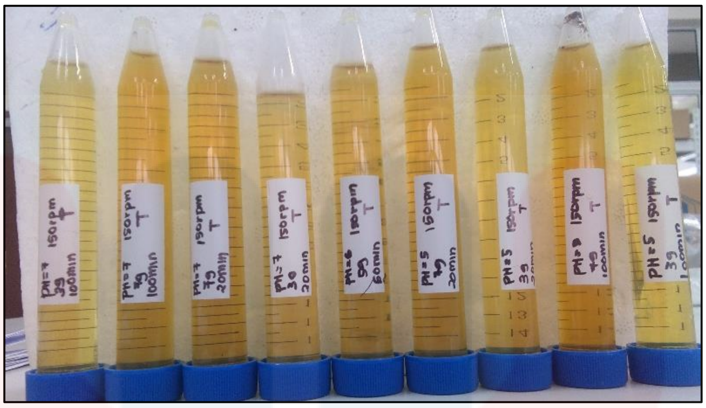

Figure A.5: Treated adsorbent under 150 rpm

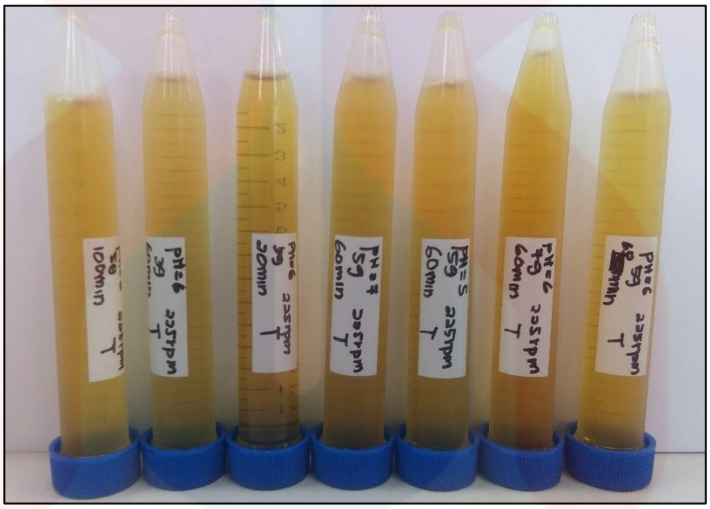

Figure A.6: Treated adsorbent under 225 rpm

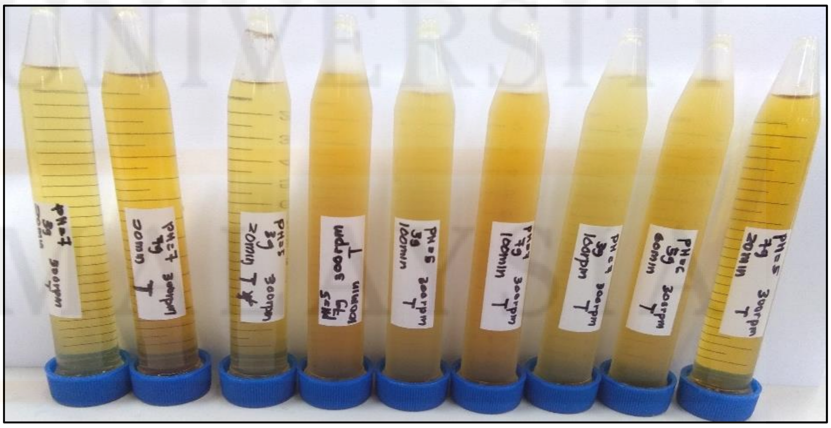

Figure A.7: Treated adsorbent under 300 rpm

Figure A.8: Untreated adsorbent under 150 rpm

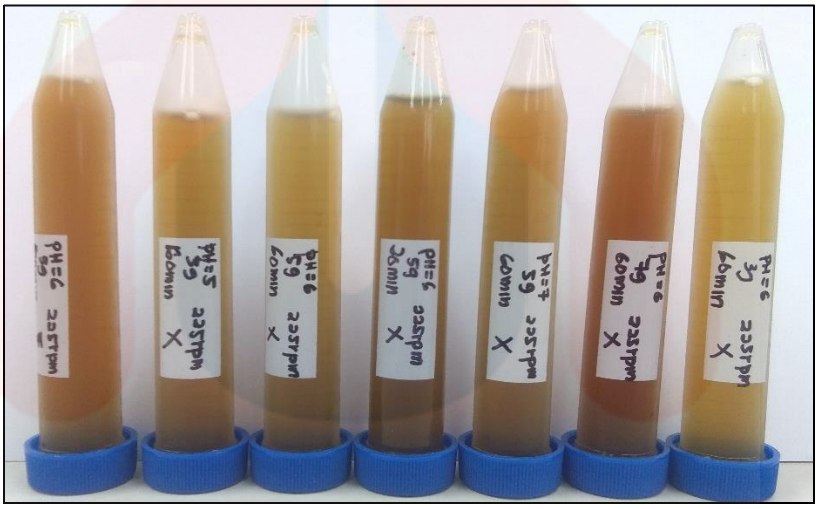

Figure A.9: Untreated adsorbent under 225 rpm

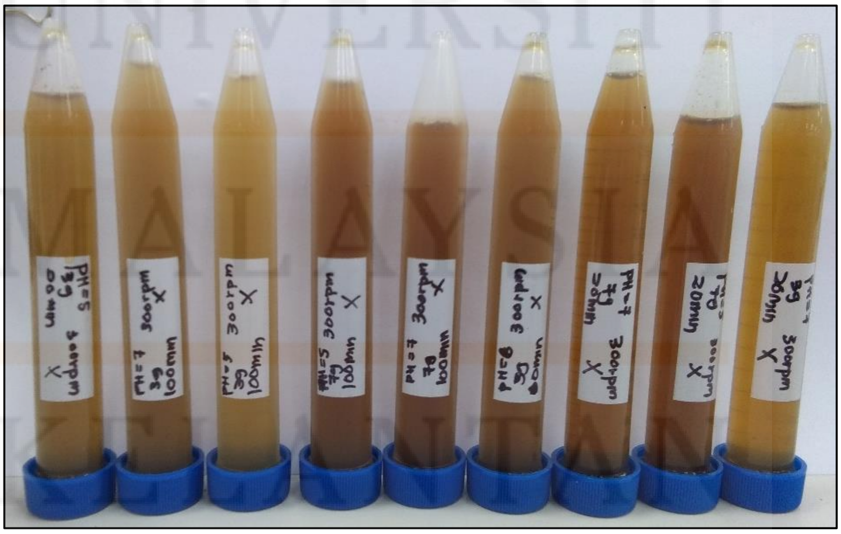

Figure A.10: Untreated adsorbent under 300 rpm