Potential of Agricultural Waste Materials: (*Ananas comosus*) peels as Biosorbent for Heavy Metals Removal

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DECLARATION

I hereby declare that this thesis entitled "Potential of Agricultural Waste Materials: (*Ananas comosus*) peels as Biosorbent for Heavy Metals Removal" is the result of my own research except as cited in the references. The thesis has been accepted for any degree and is concurrently submitted in candidature of any degree.

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LIST OF ABBREVIATION AND SYMBOLS

L	Liter
g	Gram
mL	Milliliter
mg	Milligrams
mm	Millimeters
µm	Micrometre
cm	Centimetre
ppm	Parts-per million
%	Percentage
rpm	Revolutions per minute
min	Minute
ºC	Degree Celsius
Cd	Cadmium
Cr	Chromium
Pb	Lead
Fe	Ferum
Cu	Copper
Ni	Nickel
Zn	Zinc
Hg	Mercury
AAS	Atomic Absorption Spectrometric
FT-IR	Fourier Transform Infrared Spectrometer
PLP	Pineapple Leaf Powder
TPP	Treated Pineapple Peels

HM	Heavy Metals
NaoH	Sodium Hydroxide
$CdCl_2$	Cadmium Chloride
$Pb(NO_3)_2$	Lead Nitrate
$K_2Cr_2O_7$	Potassium Dichromate
H_2SO_4	Sulphuric Acid
$KMnO_4$	Potassium Permanganate
HCl	Hydrochloric Acid
HNO_3	Nitric Acid
-OH	Hydroxyl Group
COOH	Carboxyl Group
H^+	Hydrogen Ions
V	Volume of Solution
M	Mass of Adsorbent
q_{max} (mg/g)	Adsorption Capacity
R^2	Correlation Coefficient
C_o (mg/L)	Initial Metals Ions Concentration
C_e (mg/L)	Equilibrium Metals Ions Concentration
K_L (L/mg)	Langmuir Equilibrium Constant of Adsorption
K_f (mg/g)	Freundlich Multilayer Adsorption Capacity
n	Intensity of Adsorption Constant for Freundlich
q_e	The Amount of Metals Ions Adsorbed at Equilibrium Time

Potential of Agricultural Waste Materials: (*Ananas comosus*) peels as Biosorbent for Heavy Metals Removal

ABSTRACT

Since the industrial world is growing, the issue of environmental pollution has become more severe due to the disposal of heavy metals discharged by industrial factories into the river. Conventional method to remove heavy metals are expensive and not environmentally friendly. This study tries to find out the potential of biomaterial (*Ananas comosus*) as biosorbent for heavy metals removal. Pineapple peels seem to be useless and turned out to be agricultural waste. Therefore, the aim of this research is to reveal the use of pineapple peels as adsorbent for the removal of heavy metals (Cd, Cr and Pb) in standard metals solution. In this study, Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the functional group contain in pineapple peels. The effect of various parameters such as adsorbent dosage, contact time and pH were studied. The result show the best value adsorbent dosage, contact time and pH for Cd, Cr and Pb are similar which is at 12 g (54.11%, 62.98% and 78.51% respectively), 90 minutes (32.67% for Cd and 89.99% Pb) and pH 9 (98.44%, 88.35% and 93.65%) respectively. In addition, Langmuir adsorption isotherm model gave a better result for all effect of adsorbent dosage, contact time and pH for Cd, Cr and Pb with the maximum adsorption capacity 0.002, 0.017 and 0.038 mg/g respectively.

Keywords: Chemical modification, Pineapple peels, Heavy metals, Standard metal solution, Langmuir and Freundlich.

Potensi Bahan Sisa Pertanian: Kulit (*Ananas comosus*) sebagai Biosorben untuk Penyingkiran Logam Berat

ABSTRAK

Semenjak dunia perindustrian semakin berkembang, masalah pencemaran alam sekitar telah menjadi lebih teruk disebabkan pelupusan logam berat yang dikeluarkan oleh kilang-kilang industri ke dalam sungai. Kaedah konvensional untuk menyingkirkan logam berat adalah mahal dan tidak mesra alam. Kajian ini dibuat untuk mengetahui potensi bahan sisa pertanian (*Ananas comosus*) sebagai biosorben untuk menyingkirkan logam berat. Kulit nanas kelihatan tidak berguna dan ternyata menjadi sisa pertanian. Oleh itu, tujuan penyelidikan ini adalah untuk mendedahkan penggunaan kulit nanas sebagai penyerap untuk penyingkiran logam berat (Cd, Cr dan Pb) dalam larutan logam. Transformasi Fourier Spektroskopi Inframerah (FTIR) digunakan untuk mengenalpasti kumpulan berfungsi yang terdapat dalam kulit nanas. Kesan pelbagai parameter seperti dos penjerap, tempoh masa yang digunakan dan pH telah dikaji. Data eksperimen menunjukkan nilai terbaik bagi dos penjerap, tempoh masa dan pH untuk Cd, Cr dan Pb adalah sama iaitu 12 g, (54.11%, 62.98% dan 78.51% masing-masing), 90 minit (32.67% bagi Cd dan 89.99% Pb) dan pH 9 (98.44%, 88.35% dan 93.65% masing-masing). Di samping itu, model isoterma penjerapan Langmuir memberikan data yang lebih baik bagi semua kesan dos penjerap, tempoh masa dan pH untuk Cd, Cr dan Pb dengan kapasiti penjerapan maksimum 0.002, 0.017 dan 0.038 mg/g masing-masing.

Kata kunci: Pengubahsuaian Kimia, Kulit Nanas, Logam berat, Larutan logam, Langmuir dan Freundlich.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The water contamination normally happens due to heavy metals discharged by industrial and domestic activities. In long-term effect, the contamination of water from heavy metals may cause damage to ecology and affect human health due to higher concentration heavy metals in polluted water. Example of health problem that can be affected towards peoples nearby includes skin manifestation by arsenic, kidney damage by cadmium, headache by chromium, dermatitis by nickel, depression by zinc and damage of fatal brain by lead (Tripathi and Ranjan, 2015). The water contamination can be treated with removal of heavy metal in the water by using adsorbent.

Heavy metals are a major category of contamination reported to be present in large measure in wastewater. There are few methods for treatment of municipal and industrial wastewater includes physical, chemical and biological methods. All of this method can be applied to the wastewater depend on the target heavy metal that wants to remove. The conventional techniques such as membrane filtration, chemical adsorption, and ion exchange had been used to remove heavy metals from wastewater (Ahluwalia and Goyal, 2007). However, the conventional techniques are costly and non-environmentally friendly. Another alternative process of removal heavy metal is by adsorption using adsorbent. The type of adsorbent that used in this research is adsorbent from an agricultural waste of pineapple (*Ananas comosus*) peels. Agricultural waste is a low-cost adsorbent that can get from any skin peel of fruit and vegetables.

In Malaysia, the famous agricultural waste as adsorbent was banana peels. It is because banana peels contain the high number of cellulose that can be trapped or removed a high number of heavy metal. Beside banana peels, pineapples and dragon fruit peels also contain a high number of cellulose (Hossain, Ngo, Guo & Nguyen, 2012). In 2011, the state of Johor was known as the largest pineapple producer with its estimated production quantity at 80,389.22 metric tons (Jaji, Man & Nawi, 2018). Not only that, others state such as Kelantan, Terengganu, Perak and Negeri Sembilan also contain abundances of pineapples. These states are intentionally planted pineapple trees for domestic consumption and others small-scale industry (Rajendran, 2013). The bioactivity of this agricultural product is because of the existence of compounds likes polyphenols and ascorbic acid which contribute to the antioxidant activity of the fruit extract (Yuris, 2014).

However, lacks of studies have been conducted relating to pineapple peels as biosorbent. Therefore, pineapple peels have been used as biosorbent to remove Cadmium (Cd), Chromium (Cr) and Lead (Pb) in standard solutions.

1.2 Problem Statement

As mentioned above, there are abundances of pineapple at Kelantan, Terengganu and other state due to their benefit in small scale food industry (Jaji et al., 2018). Thus this also resulting to the abundances of the pineapple peels because peoples just throw away their peels after the production happened and it known as agricultural waste.

Nowadays, agricultural waste is a recognized materials that is effective and low cost in order to remove heavy metals in polluted water. In previous study, there are many agricultural waste that use as an adsorbents likes banana, papaya, honeydew melon, watermelon and also pomegranate peel (Othman and Asharuddin, 2013). However, there are lack of study regarding removal of heavy metals from polluted water by using pineapple (*Ananas comosus*) peels. Other than that, it also limited studies about how important the function of functional group in removing the heavy metals. This research has been carried out to investigate the usage of pineapple (*Ananas comosus*) peels as adsorbent to remove heavy metals in standard aqueous solution. In addition, FTIR spectra also has been used to determine presence of functional groups in adsorbents (Jena and Sahoo, 2017).

1.3 Justification

There are many studies have been carried out about the ability of agricultural waste in order to remove heavy metals in aqueous solution (Jaishankar, Mathew & Shah, 2014). For instance, based on the research by Pandey et al. (2013) the sample of Cucumber (*Cucumis sativus*) peels have been used for cadmium sorption from aqueous solution under different experimental conditions. However, there are lack of study regarding removal of heavy metal from aqueous solution by using pineapple peels. Besides, there are also lack of knowledge about the role of functional group in removing heavy metals from effluent.

Therefore, this research has been carried out to investigate the ability of pineapple (*Ananas comosus*) peels as adsorbent to remove heavy metals in standard solution. This study also meant to identify affinity of functional groups present in adsorbent materials for removal of heavy metal in standard solution.

1.4 Objectives

- To identify the functional groups of pineapple (*Ananas comosus*) peels by using FTIR spectra.
- To investigate the adsorbent dosage, contact time and pH needed for adsorbent to remove heavy metals in standard solution.
- To determine adsorption capacity using Langmuir Adsorption Isotherm Model and Freundlich Adsorption Isotherm Model.

1.5 Scope of Study

This research has been focused on agricultural waste (pineapple peels) as biosorbent. In this study, the effectiveness of agricultural waste that contribute higher adsorption in order to remove heavy metals in standard solution has been investigated. The functional group of this agricultural waste has been characterized by using FTIR spectra.

Next, a few parameters were carried out from this studied such as the effect of adsorbent dosage, contact time and pH. In addition, Langmuir and Freundlich adsorption model has been used to determine the adsorption isotherm which reveals the degree of adsorption favorability. Furthermore, there are lack of study regarding removal of heavy metals from polluted water by using pineapple peel. Thus, introducing the pineapple peel as a biosorbent will be a new thrust area.

1.6 Significant of Study

The research has been conducted to treat the standard solution that contain high toxicity caused by heavy metals that has been introduced in that water. The heavy metals that has been conducted in this research are cadmium Cd (II), chromium Cr (VI) and Lead Pb (II). Pineapple known as natural adsorbent, beneficial, economically feasible because it can be easily found as agricultural waste in food based industry. For instance, there are many small scale food industry that used pineapple as their product. Therefore, the aim of this study is to identify the functional groups of pineapple (*Ananas comosus*) peels as adsorbent by using FTIR spectra. The optimum parameters involved in the removal of Cd, Cr and Pb are studied and determined.

CHAPTER 2

LITERATURE REVIEW

2.1 Pineapple (*Ananas comosus*) peels as Biosorbent for Heavy Metals Removal

Heavy metals are dangerous to human due to their toxicities. According to Nazir et al. (2015) heavy metals are bio-accumulated and bio-transferred both by natural and anthropogenic sources. One of the major issues to be faced throughout the world cause by contamination of heavy metals happened in plants, soil and water. This issues was important because heavy metals above their normal ranges are extremely endangered to all human, plant and animal life. Table 2.1 shows the World Health Organization (WHO) permissible limits for heavy metals in plant and water and Dutch limit in soil meanwhile Table 2.2 shows the international guideline values for drinking water samples.

Table 2.1: World Health Organization (WHO) permissible limits for heavy metals in plant and water and Dutch limit in soil.

Element	World Health Organization (WHO)		Dutch limit	References
	Plant (mg/kg)	**Water (mg/L)**	**Soil (mg/kg)**	
Cd	0.02	0.01	0.8	Nazir et al. (2015); Ogundele, Adlio & Oludele (2015)
Cr	1.30	0.1	100	Nazir et al. (2015); Ogundele et al. (2015)
Pb	2.00	0.05	85	Nazir et al. (2015); Ogundele et al. (2015)

Table 2.2: International guideline values for drinking water samples.

Element	WHO guideline value (mg/L)	US-EPA guideline value (mg/L)	EU guideline value (mg/L)	References
Cd	0.003	0.005	0.005	Ayenew and Ahmad (2016); Oyem, Oyem & Usese (2015)
Cr	0.05	0.1	0.05	World Health Organisation (2008); Oyem et al. (2015)
Pb	0.05	0.02	0.01	World Health Organisation (2008); Oyem et al. (2015); Colin Hayes and Eddo (2010)

Research conducted by Hegazi (2013) described the removal of heavy metal from wastewater by using agricultural and industrial waste. According to the study, the less expensive absorbent has been used to remove the heavy metal from wastewater. Agricultural and industrial waste such as rice husk and fly ash has been used to remove heavy metal. A lot of agricultural waste has been recycle to be a low cost agricultural waste by-product for removal of heavy metals from wastewater such as sugarcane bagasse, rice husk, sawdust, coconut husk, and oil palm shell. Their research stated that wastewater produces by El-Ahlia from electroplating department was about 250 m^3/day become the major source of contamination of wastewater in this company with a high concentrations of Fe, Pb, Cd, Cu and Ni.

Previous research carried out by Hegazi (2013) stated that rice husk was successful in the synchronous expulsion of Fe, Pb and Ni. The optimum pH range for heavy metal adsorption was pH 6 to pH 7 and the maximum contact time for absorption was at least to be two hours (Hegazi, 2013).

Tripathi and Ranjan (2015) conducted research on heavy metal removal from wastewater by using low cost adsorbents. Three type of adsorbent had been used for removal of heavy metal in wastewater that is natural origin adsorbent, agricultural wastes, and industrial by-product. Natural origin like clay, zeolite and peat moss was becomes effective adsorbent for removal poisonous heavy metal such as Pb, Zn, Cd, Cu, Hg, and Cr. Examples of agricultural waste was rice husk, black gram, waste tea, walnut shell and Turkish coffee while example for industrial by-product was fly ash, blast furnace sludge, slurry waste, lignin, and iron (III) hydroxide.

The adsorbent for removal of heavy metal may be of mineral, organic based or biological origin. One of the conventional adsorbent that has been used widely was activated carbon but the cost of the treatment highly costing. Three main step for adsorption of heavy metal by solid adsorbent was transport of the contamination from wastewater to outside surface of the adsorbent. Second, inside mass transfer by pore dissemination from external surface of adsorbent to the inward surface of permeable structure. Lastly, adsorption of adsorbate on the dynamic locales of the pores of adsorbent. As conclusion, this research shown modification of agricultural waste reveal tremendous heavy metal removal capability from water (Tripathi and Ranjan, 2015).

Research conducted by Taylor (2010) described about the alteration of pineapple peel fibre with succinic anhydride for Cu^{2+}, Cd^{2+} and Pb^{2+} removal from effluent. According from the study, the introduction of carboxylic functional group had been through the modification of pineapple fibre peel via reaction with succinic anhydride after the pre-treatment with iso-propyl alcohol and NaOH.

Fourier transform infrared spectroscopy (FTIR) had been used to characterize the adsorptive ability of modified pineapple peel fibre for Cu^{2+}, Cd^{2+} and Pb^{2+} from synthetic metal solutions (Taylor, 2010). Then, the result through this study showed the modified pineapple peel fibre has higher adsorptive capacity for Cu^{2+}, Cd^{2+} and Pb^{2+} compared with pre-treated pineapple peel fibre and raw pineapple peel.

The modification of pineapple peel fibre with succinic anhydride shows effective removal of Cu^{2+}, Cd^{2+} and Pb^{2+} from the synthetic aqueous solutions through adsorption. The modified pineapple peel follows well the pseudo-second-order energy show and depends on the initial metal concentration, the contact time for adsorption and the arrangement of pH (Taylor, 2010).

Next, Neupane et al. (2015) was conducted research about removal of crystal violet from aqueous solution by using pineapple (*Ananas comosus*) leaf powder as a biosorbent. This researched was investigated using pineapple leaf powder (PLP) to decolorized crystal violet (CV). In this research, the parameter that was studied included contact time, adsorbent dose, initial dye concentration, agitation speed, pH, temperature and particle size of adsorbent.

Neupane et al. (2015) evaluate a few parameter that is pH (2–12), temperature (30, 40, and 50 ℃), contact time (1–210 min), particle size (<150, 150–300 and >300 μm), biosorbent dose (1–70 mg), and agitation speed (100, 150, and 200 rpm). The findings of this research was shown the pineapple leaf powder can remove the crystal violet dye from aqueous solution with equilibrium time taken to be 120 min and the optimum dose used was 1 g/l. Pineapple leaf powder adsorbent ability to remove crystal violet dye shown by decreasing initial concentration of aqueous solution, increasing pH up to pH 8, increasing agitation speed, decreasing temperature (T), and decreasing particle size in this researched. The biosorption capacity of the PLP was 158.73 mg/g. Table 2.3 shows various types of agricultural waste that has been used as natural biosorbent for removal of heavy metals in wastewater.

Table 2.3: Types of agricultural waste used for heavy metals removal.

Agricultural waste used	Heavy metals removed	References
Corn Cob	Ni (II)	Arunkumar, Perumal, Lakshmi Narayanan & Arunkumar (2014)
Rice Husk	Cd (II) Pb (II)	Hoyos-sánchez, Córdoba-pacheco, Rodríguez-herrera & Uribe-kaffure (2017); Rajkumar (2015)
Banana Peels	Cd (II) Pb (II)	Anwar, Shafique, Salman Dar & Anwar (2010)
Spent Tea Leaves	Cu (II)	Bajpai and Jain (2010)
Cucumis Melo Rind	Fe (II) Mn (II)	Othman and Asharuddin (2013)
Orange Peels	Cd (II) Cu (II) Pb (II) Ni (II) Zn (II)	Guo Xueyi and Liang Sha (2011)
Coconut Shell Carbons	Pb (II)	Song et al. (2014)
Rice Straw	Cr (VI)	Thallapalli and Prasad (2015)
Pineapple Peels	Cd (II) Cr (VI) Pb (II)	This study

2.2 Potential Functional Group of Agricultural Waste

Deshmukh (2017) reported the efficiency of banana peels as an adsorbent to remove cadmium from effluent. Deshmukh (2017) stated the functional group that constitute in banana peels by using FTIR spectra includes hydroxyl, carboxylic and amine group. Then, because of those functional group, the researcher stated this study shows that banana peels has great ability for removal of heavy metals likes cadmium ions due to a great efficiency for the removal of cadmium ions from effluent.

Other study conducted by Ahmad et al. (2016) chemically oxidized pineapple (*Ananas comosus*) peels as an adsorbent to remove heavy metal from aqueous solutions. They stated the biosorption efficiency of pineapple peel for cadmium and lead greatly enhanced after chemical oxidation due to the presence of carboxylic and hydroxyl group onto biosorbent surface (Ahmad et al., 2016).

The study about biosorption of cadmium ion as a biosorbent by using dragon fruit peel has been done by Tanasal et al. (2015). Hydroxyl group is a functional group that involve in metal ion biosorption of cadmium by the dragon fruit peel. To determine the binding functional group cadmium ion, biosorbent dragon fruit peel was analysed by using FTIR. The process of FTIR analysis in this study has been done by looking at the change of the IR spectra before and after biosorption of Cd (II) ion by dragon fruit peel.

As a conclusion from the previous study, a composition that constitute in agricultural waste likes cellulose, hemicellulose, lignin, pectin and others is important due to its biomass containing functional group likes carboxyl, hydroxyl and amine that play an important role in adsorption process due to its ability to bind of metal ions.

2.3 Factors Affecting Adsorption of Heavy Metals

There are various factor that can affect the adsorption of heavy metals removal using pineapple peels as biosorbent such as adsorbent dosage, contact time and pH. All of these factors are very important to investigate the optimum adsorption capacity that can be achieved using agricultural wastes as biosorbent.

Adsorbent dosage is an amount of substances that used in the study that act as an adsorbent to adsorb the heavy metals. The percentage of heavy metals removal increase by the increasing of adsorbent dose because of the accessibility of more number of exchangeable sites or the surface of the adsorbent (Rajput, Sharma, Sharma & Verma, 2015). Research conducted by Garg, Kaur, Jawa, Sud & Garg (2008) described the capacity uptake of Cd (II) from aqueous solution by using agricultural waste biomass such as sugarcane bagasse, maize corncob and Jathropha oil cake at varying adsorbent doses which is 2.5 g to 2 g. According to the study, the maximum removal of Cd (II) was obtained at 2 g/100 mL for all of the adsorbent with highest value contributed by Jathropha oil cake (99.5%). Based on the observation, the increasing of adsorbent doses lead to the increasing of percentage removal of Cd (II) due to the more accessibility of adsorption sites. However, the adsorption capacity was decreases by the increasing of adsorbent dosages due to the overlapping or accumulation of adsorption sites thus resulting in reduction in total adsorbent surface obtainable to metal ions (Garg et al., 2008).

Next, contact time also plays an important role in the success of the study. The longer the contact time or retention, more entire adsorption will be accomplished. However, the percent removal of metals ion will not increase after the achievement of equilibrium phase due to the limiting surface area of sorption sites on adsorbent surface (Shah, Kumar, Sharma, Sharma & Sharma, 2016). According to Rafidah, Alwi, Muhamad & Webb (2014) the study of Pb (II) removal in aqueous solution using papaya peel was investigated under varying contact time of 5 to 120 minutes with 0.005 g of activated carbon of papaya peels and 50 mg/L of Pb (II) was added in aqueous solution. Based on the study, the maximum percentage removal of Pb (II) was obtained after 90 minutes with 79.26%. Next, research conducted by Arunkumar et al. (2014) described the removal of nickel (II) from aqueous solution by using corn cob as an adsorbent. The study was investigated under different contact time from 15 to 90 minutes. The optimum percentage removal of nickel (II) was obtained at 90 minutes with 70.9%. The rapid uptake of nickel (II) was happened at the initial phase due to the approachability of active site in the adsorbent. However, it was reach equilibrium phase after 90 minutes due to the minor availability of active site (Arunkumar et al., 2014).

Gowda, Nataraj & Rao (2012) stated pH is one of the most standout among the most imperative parameters controlling the adsorption procedure. The study about removal of nickel (II) from electroplating effluents was conducted by Gowda et al. (2012) using coconut leaves as an adsorbent was run over pH range of 2 to 12 by adding 0.1 M HCl or 0.1 M NaOH in order to control the pH of the solution. Based on the result, the maximum uptake of nickel ions was achieved at pH 8 with 93.18%. Nevertheless at pH 10-12 it was slightly decreases due to the decreases electrostatic repulsion because of reduction of positive charges density on the sorption edges, thus resulting in an increase in adsorption of nickel (II) ions on the surface. Other than coconut leaves, nickel (II) ions also had been removed from aqueous solution by using *Moringa Oleifera* seeds that conducted by Thiago, Marques, Vanessa & Alves (2012) at different pH which is from pH 2 to pH 12. The efficiencies of metal removal was obtained at pH 4 with the value greater than 90%. At low pH ranges, it enable hydrogen and hydronium ions to contend with metal binding sites on the biosorbent, causing poor uptake meanwhile the solution with higher pH values leading to a precipitation occurs, thus resulted decreases of sorption capacity (Thiago et al., 2012).

2.4 Adsorption capacity using Langmuir Adsorption Isotherm Model and Freundlich Adsorption Isotherm Model

Patiha, Heraldy, Hidayat & Firdaus (2016) stated there are five types of interaction in adsorption process according to monolayer theory for Langmuir adsorption isotherm. The interaction should be between adsorbate-adsorbent, adsorbate-adsorbate, adsorbate-solvent, adsorbent-solvent and solvent-solvent. Physical or chemical bonding should be appear between adsorbate-adsorbent with the chemical bonding give the stronger bonding compare to physical bonding. They also mentioned, the strongest interaction between adsorbent-adsorbate lead to the adsorption process occur. Then, the strongest bond between adsorbate-adsorbent molecules resulting the formation of monolayer which it is only absorb a single layer of molecules on the adsorbent surface. Adsorbent surface is homogenous and it considered contain a fixed adsorption site on the surface where there are no further adsorption could take place once a pollutant occupies a site (Dalgleish et al., 2007; Saadi et al., 2015). Hence, the higher equilibrium concentration of the adsorbate reached at a saturation in adsorption. This kind of adsorption happened because of short range chemical forces which do not permit penetration through the primary adsorbed molecules (Dalgleish et al., 2007). Figure 2.1 shows a monolayer model of Langmuir adsorption.

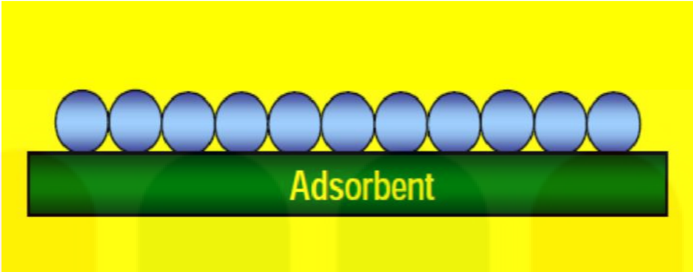


Figure 2.1: Monolayer model of Langmuir adsorption.
Source: (Baxter et al., 2008)

Next, according to Saadi et al. (2015) the multilayer adsorption could be applied to Freundlich isotherm model where adsorbent surface for this model assumed as heterogeneous and their active sites and energies distribute exponentially. Based on the theory, the formation of multilayer had been identified when molecules absorbed through weak forces usually under physical adsorption because of the cohesive forces applied by the molecules of the adsorbate (Dalgleish et al., 2007). Figure 2.2 shows the monolayer and multilayer model adsorption while Table 2.4 shows the adsorption capacity of agricultural waste materials as an adsorbent.

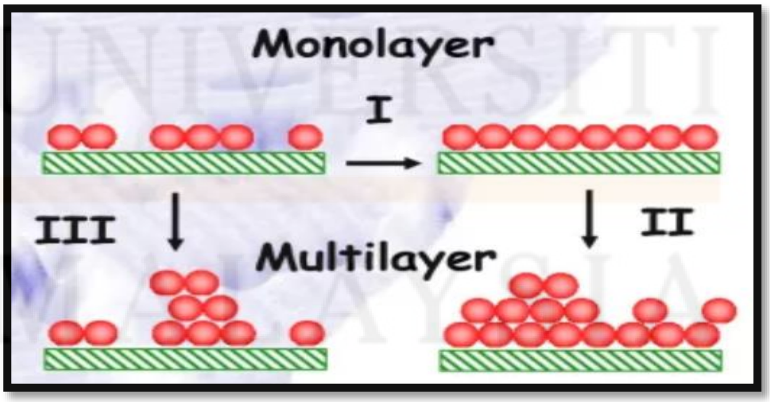


Figure 2.2: Monolayer and multilayer formation for Langmuir and Freundlich model respectively.
Source: Shah (2016). The Chemical Engineering eResources Portal.

Table 2.4: Adsorption capacity (q_{max}) of agricultural waste materials as an adsorbent.

Adsorbent	Heavy Metal	q_{max} (mg/g)	References
Mango stone	Pb (II)	1.90	Olu-owolabi (2012)
Rice husk	Cu (II)	43.5	Ye, Zhu & Du (2010)
Bagasse	Cr (VI)	0.001	Rao, Parwate & Bhole (2002)
	Ni (II)	0.001	
Orange peel	Cd (II)	4.90	Mahmoud and El-Halwany (2014)
Dragon fruit peel	Mn (II)	15.47	Priyantha, Lim & Dahri (2013)
Custard apple peel	Cr (VI)	7.874	Krishna and Sree (2013)
Guava seed	Ni (II)	7.46	Parate, Gulve, Labhane & Talib (2016)

CHAPTER 3

MATERIALS AND METHODOLOGY

This section shown the overall material and method for this study. The flowchart of overall study was shown in Appendix A.1.

3.1 Apparatus

The apparatus that was used in this study are beakers, measuring cylinder, volumetric flask, conical flask, glass rod, glove, face mask, spatula, zipper bags, aluminium foil, reagent bottle, filter funnel, filter paper, syringe, syringe filter, falcon tube, micropipette, grinder, sieve 1.0 mm, weighing balance, hot plate and magnetic stirrer, vacuum pump, drying oven, orbital shaker, pH meter, Fourier-Transform Infrared Spectroscopy (FT-IR) and Atomic Absorption Spectroscopy (AAS).

3.2 Chemicals and Reagents

Cadmium Chloride ($CdCl_2$), Lead Nitrate ($Pb(No_3)_2$), Potassium Dichromate ($K_2Cr_2O_7$), Sulphuric Acid (H_2SO_4), Potassium Permanganate ($KMnO_4$), Hydrochloric Acid (HCl), Sodium Hydroxide (NaOH) and Nitric Acid (HNO_3) were used in this study.

3.3 Materials

Pineapple peels was collected from Pineapple Cannery of Malaysia Sdn. Bhd. located at Pontian, Johor. It was used as adsorbent while standard solution was used as adsorbate. Distilled water was used to prepare all the solution needed for this study. The concentration of Cd, Pb and Cr was analyzed by using atomic absorption spectroscopy (AAS) (Radulescu et al., 2014).

3.4 Preparation of Heavy Metals Solutions

The preparation of standard solution for Cd (II) was prepared by dissolving 1.631 g analytical reagent of Cadmium Chloride in 1000 mL of distilled water. The source of hexavalent chromium, Cr (VI) is potassium dichromate ($K_2Cr_2O_7$). The preparation of standard solution for Cr (VI) was prepared by dissolving 2.829 g of potassium dichromate in 1000 mL distilled water. Then, the preparation of standard solution for Pb (II) was prepared by dissolving 1.598 g of Lead Nitrate in distilled water and made up to 1000 mL in volumetric flask. The concentration of cadmium (Cd), chromium (Cr) and lead (Pb) in this stock solution are 0.9 ppm, 4.8 ppm and 7.5 ppm respectively. This stock solution was used as adsorbate.

3.5 Preparation of Biosorbent (*Ananas comosus*) peels

Pineapple fruit peels that used as adsorbent in this study was collected from estate of Pineapple Cannery of Malaysia Sdn. Bhd. located at Pontian, Johor. This pineapple peels was thoroughly washed with distilled water to remove dirt and unwanted materials.

Then the washed materials was dried under sunlight for a week. After that, dried pineapple peels was grinded and sieve. Next, the powder materials was treated with an oxidizing agent which is 100 mL of 0.1 M H_2SO_4 and 100 mL of 0.1 M $KMnO_4$ solution. All of those functional group was bind with metal ions through sharing of electron pair. The solution was stirred by using rotary shaker at 60ºC for 24 hours. Chemically activated pineapple peels was filtered by using vacuum pump. Then it was washed again with distilled water and filtered again by using vacuum pump. Lastly, it was dried in a drying oven at 85ºC for further use.

3.6 Fourier Transform Infrared Spectrometer (FTIR) Analysis

FTIR is a preferred method in infrared spectroscopy which IR radiation is pass through a sample which some of infrared radiation is absorbed by the sample (Ganzoury, Allam, Nicolet & All, 2015). In order to characterize the functional groups of samples, the powder of raw and treated pineapple peels has been put under iZ10 FTIR machine. Then the functional group of the samples was analyzed at the computer screen through OMNIC software.

3.7 Adsorption Study

3.7.1 Effect of Adsorbent Dosage, Contact Time and pH

In order to study the effect of adsorbent dosage, different weight of biosorbent was put into each 4 beakers contain 100 mL of aqueous solution for 90 minutes with the different weight of adsorbent. All of those weight of adsorbent can be referred in Table 3.1.

Table 3.1: Effect of Adsorbent Dosage.

Weight of adsorbent (g)	Contact time (min)
3	90
6	90
9	90
12	90

Other important factors affecting the adsorption of cadmium (Cd), chromium (Cr) and lead (Pb) is contact time. To study the effect of contact time, the most effective weight of pineapple peels powder was put into each 4 beakers contain 100 mL of aqueous solution with different time interval by keeping adsorbent dosage constant (Deshmukh, 2017). All of those time interval can be referred in Table 3.2.

Table 3.2: Effect of Contact Time.

Weight of adsorbent (g)	**Contact time (min)**
12	30
12	60
12	90
12	120

To study the effect of pH, the best adsorbent dosage and contact time was used constantly with a different pH in 4 different beakers. The pH was measured by using pH meter for each beakers. All of those pH can be referred in Table 3.3.

Table 3.3: Effect of pH.

Weight of Adsorbent (g)	Contact time (min)	pH
12	90	2
12	90	4
12	90	7
12	90	9

All the mixture between adsorbent and water sample was stirred by using hot plate and magnetic stirrer. Then the adsorbent was filtered out from beaker by using filter paper. 50 mL filtrate solution from filtration was filter again by using syringe filter. The pH of solution for the study effect of pH was adjusted by using 0.1 M HCl or 0.1 M NaOH (Elias, 2013). Then the dilution 10^{-1} and 10^{-2} was prepared for heavy metals analysis. The amount of total heavy metals was analyzed by using atomic absorption spectrometric (AAS).

3.8 Removal Percentage of Adsorbent

The removal of metal ion by the biosorbent was calculated by using Equation (3.1).

$$\text{Removal (\%)} = \frac{C_o - C_e}{C_o} \times 100\ \% \qquad (3.1)$$

where C_o represent the initial concentration of metals ion (mg/L) and C_e represent the concentration of metals ion (mg/L) at equilibrium.

3.9 Adsorption Capacity

The adsorption capacity of amount metal ion absorbed by the biosorbent was calculated by using the following Equation (3.2) (Elias, 2013).

$$q_e = \frac{C_o - C_e}{M} \times V \tag{3.2}$$

where q_e (mg/g) represent the amount of metal ion absorbed per unit mass of biosorbent, C_o and C_e are represent the initial and final equilibrium of metal ion concentration (mg/L) at liquid phase respectively. V represent the solution volume while M represent the mass of biosorbent.

3.10 Type of Adsorption Isotherm Model

3.10.1 Langmuir Adsorption Isotherm

For a Langmuir adsorption isotherm, Elias (2013) stated there are further adsorption takes place when adsorbate on the outer surface of the adsorbent form a monolayer. Thus, monolayer adsorption onto the surface containing a finite number of identical sites only valid for a Langmuir isotherm (Dada et al., 2012). Four assumptions that characterized by this model includes all site are corresponded, adsorption result in monomolecular layer of coverage, molecule is adsorbed on a site independent and constant temperature (Elias, 2013). The equation of Langmuir isotherm can be expressed as Equation (3.3).

$$\frac{C_e}{q_e} = \frac{1}{(q_{max})K_L} + \frac{1}{q_{max}} C_e$$

(3.3)

where C_e indicates equilibrium metals ion concentration in solution (mg/L), q_e is concentration of adsorbate on adsorbent at equilibrium (mg/g), q_{max} represents monolayer adsorption capacity of sorbent (mg/g) and K_L is Langmuir constants (L/mg) (Rao, 2018).

3.10.2 Freundlich Adsorption Isotherm

The Freundlich adsorption isotherm is used for single solute system with heterogeneous energetic distribution of active site. This model commonly used with the interaction among adsorbed molecule (Elias, 2013). The equation of Freundlich isotherm model can be expressed as Equation (3.4).

$$q_e = K_F C_e^n$$

(3.4)

However, the equation above can be rearrange into a linear form as Equation (3.5).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

(3.5)

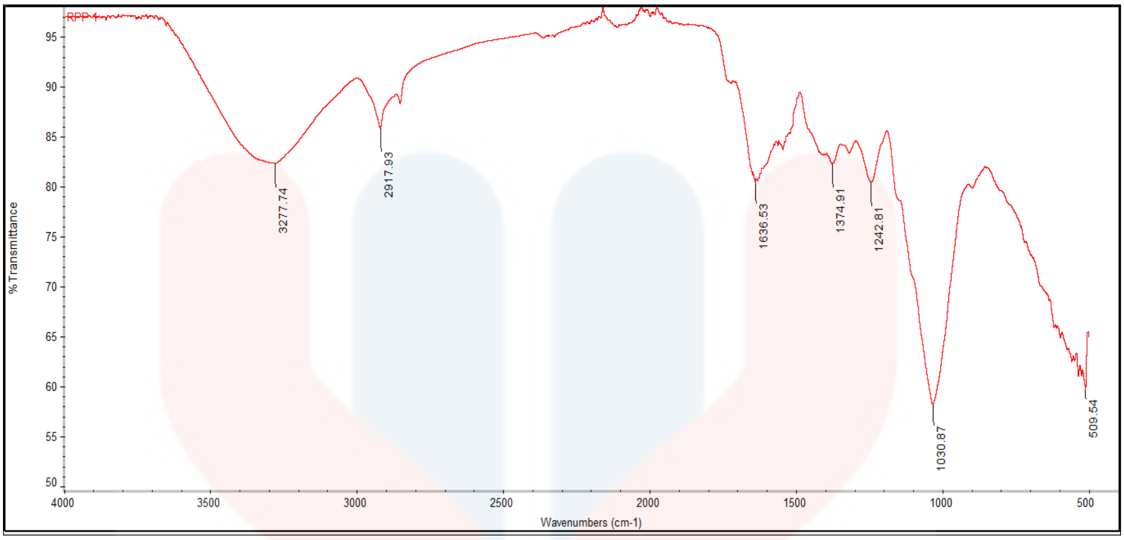
where $\frac{1}{n}$ indicates empirical parameter related to the adsorption intensity which depends on heterogeneity while K_F represents constant value which related to adsorption capacity (mg/g) (Rao, 2018). The coefficient of (n) in this model has a value in the range of 1 to 10 for classification as favourable adsorption. Elias (2013) mentioned if the partition between the two phases are independent of the concentration then the value of n = 1. Besides, they also mention a normal adsorption happen when value $\frac{1}{n}$ is below one and cooperative adsorption will be indicated when the value $\frac{1}{n}$ being above one.

CHAPTER 4

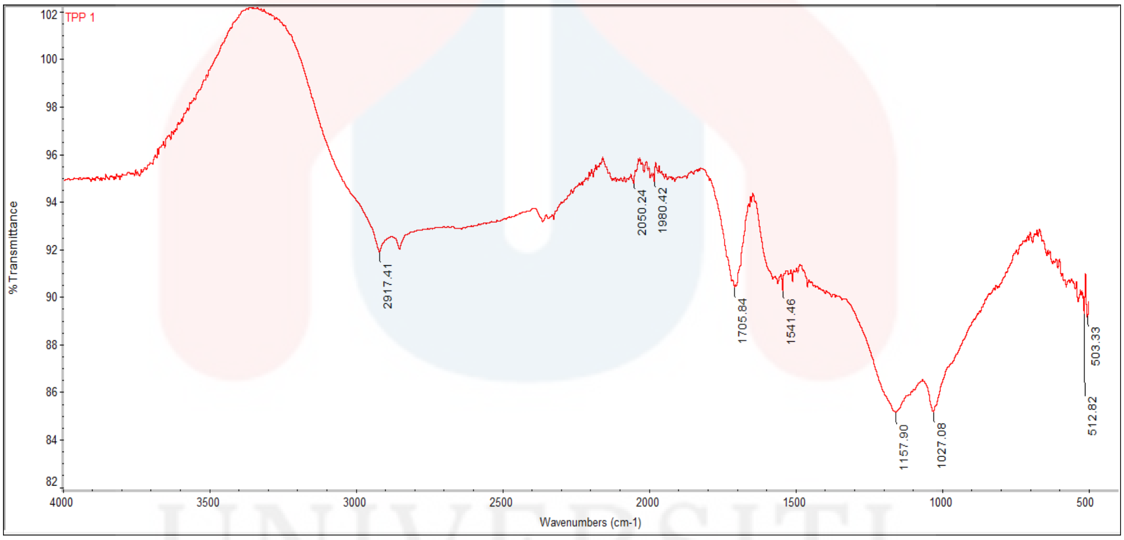
RESULT AND DISCUSSION

4.1 Characterization of Pineapple Peels Using Fourier Transform Infrared Spectrometer (FTIR)

FTIR analysis was used to characterise the functional group of the biosorbent based on raw pineapple peels and treated pineapple peels. Both of the pineapple peels might contain different of functional group. This is because, the treated pineapple peels might have addition of functional group after the chemical oxidation process happened. The FTIR spectra for both biosorbent were shown in Figure 4.1. The FTIR spectrums was recorded in the region from 500 – 4000 cm^{-1} for both type of pineapple peels. Ahmad et al. (2016) stated the efficiency of biosorption on pineapple peels was greatly enhanced after the oxidation process happened in the treated pineapple peels. It is because, the functional group likes carboxylic was introduced onto the biosorbent surface during that process. The functional group that contain on the surface of pineapple peels really help in the process of removing heavy metals. The result of some functional groups containing in both types of biosorbent that have been identified by iZ10 FTIR spectrometer was highlighted in Figure 4.1.



(a)



(b)

Figure 4.1: Interpreted peaks in raw pineapple peels for (a) and treated pineapple peels for (b).

All IR spectra contain many peaks. Basically only large peaks on the spectrum will be determined. It is because, the large peaks was provided the data that necessary to read the spectrum. The IR spectrum can be divided into four regions. The ranges for the first, second, third and fourth regions from 4000 to 2500, 2500 to 2000, 2000 to 1500 and 1500 to 400 respectively (D, 2017).

From Figure 4.1 it was discovered that the FTIR spectrum for the raw pineapple peels showed strong broad band at peaks 3277.74 cm^{-1} which was due to the O-H stretching for alcohol while the peak at 2917.93 cm^{-1} correspond to the alkane (C-H) group. At 1636.53 cm^{-1} it was discovered in the alkene (C=H) group. Next, phenol was discovered at 1374.91 cm^{-1} while amine (C-N) at 1242.81 cm^{-1}. Another two peaks of raw pineapple peels which is 1030.87 cm^{-1} and 509.54 cm^{-1} was corresponds to S=O and C-l functional groups respectively. Then there are new functional group occurred after the treated pineapple peels. Based on the Figure 4.1 (b) above showed the strong band at peaks 1705.84 cm^{-1} which was due to (C=O) stretching for carboxylic acid at wavenumbers range 1720-1706 cm^{-1} and it was be proven by the previous study conducted by Ahluwalia and Goyal (2005) stated the carboxyl group was exist at the peak 1651 cm^{-1}. Table 4.1 shows the range of wavenumber cm^{-1} and the correspond functional group.

Table 4.1: FTIR wavenumber (cm^{-1}) and functional group for raw pineapple peels for (a) and treated pineapple peels for (b).

(a) FTIR wavenumber (cm^{-1})					
3200-3550	strong	broad	O-H	stretching	alcohol
3000-2840	medium	-	C-H	stretching	alkane
1662-1626	medium	-	C=C	stretching	alkene
1390-1310	medium	-	O-H	bending	phenol
1250-1020	medium	-	C-N	stretching	amine
1070-1030	strong	-	S=O	stretching	sulfoxide
600-500	strong	-	C-l	stretching	halo compound

Source: Infrared Spectroscopy Absorption Table

(b) FTIR wavenumber (cm^{-1})					
3000-2840	strong	broad	N-H	stretching	amine salt
2140-1990	strong	-	N=C=S	stretching	isothiocyanate
2000-1900	medium	-	C=C=C	stretching	allene
1720-1706	strong	-	C=O	stretching	carboxylic acid
1550-1500	strong	-	N-O	stretching	nitro compound
1160-1120	-	-	-	-	-
1250-1020	medium	-	C-N	stretching	amine
600-500	strong	-	C-l	stretching	halo compound

Source: Infrared Spectroscopy Absorption Table

4.2 Effect of Adsorbent Dosage, Contact Time and pH

4.2.1 Effect of Adsorbent Dosage

Figure 4.2 shows the effect of adsorbent dosage on removal of heavy metals (HM) by treated pineapple peels (TPP). The adsorption studies conducted through this experiment have used various number of different adsorbent dosages (3 g, 6 g, 9 g, and 12 g) with fixed volume of heavy metals (100 mL) and contact time (90 min). Data for effect of adsorbent dosage was shown in Appendix A.2.

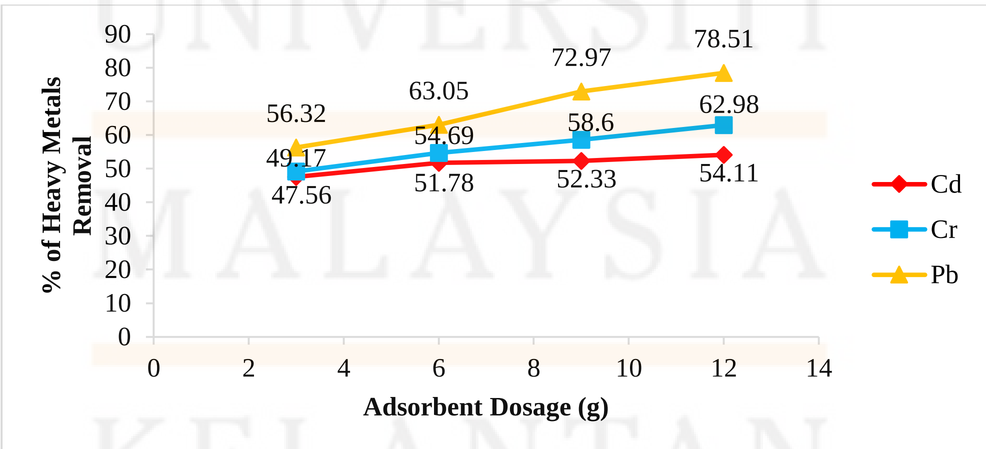


Figure 4.2: Effect of adsorbent dosage on the removal of heavy metals (Cd, Cr and Pb) using treated pineapple peels (TPP).

The highest percentage of heavy metals (HM) removal for Cd, Cr and Pb was obtained at 12 g with their percentage are 54.11%, 62.98% and 78.51% respectively. As can see from Figure 4.2, Pb shows the highest (78.51%) removal of heavy metal compared to Cd and Cr. Lakshmipathy (2016) stated the percentage of heavy metals removal increase by increasing dose of adsorbent and it was extremely depends on concentration of the adsorbent. Thus, the result of present study was highest for Pb because the initial concentration (ppm) for Pb is highest (7.5 ppm) compared to both Cd and Cr with 0.9 and 4.8 ppm respectively. This initial concentration has been used depends on how much adsorption atomic spectrometer (AAS) machine can read the result. The lowest percentage of HM removal for Cd, Cr and Pb was obtained at 3 g which is 47.56%, 49.17% and 56.32% respectively.

Based on Figure 4.2, the adsorption efficiency of treated pineapple peels towards Cd, Cr and Pb was increase with the increasing value of adsorbent dosage. From the graph, both of percent removal of HM for Cd and Cr was slowly increase from 3 g until 12 g. The percentage obtained for Cd removal was 47.56%, 51.78%, 52.33% and 54.11% respectively. According to Brahmaiah, Spurthi, Chandrika, Ramanaiah & Prasad (2015) the percent removal of Cr (VI) and Ni (II) from wastewater by using untreated and treated rice straw was rapidly increase with the increasing of adsorbent dosages due to the more accessibility of the interchangeable sites or surface area of the adsorbent. Based on the study, the maximum of adsorbent doses by using untreated rice straw for Cr (VI) and Ni (II) were 8 g/100 mL and 12 g/100 mL respectively with the percent removal for Cr (VI) up to 60% while Ni (II) nearly to 50%. Meanwhile, the optimum for both heavy metals using treated rice straw obtained at dosages 8 g/100 mL with the percent removal up to 50% percent for Cr (VI) and 70% for Ni (II). For the present study of removal heavy metals using treated pineapple peels shown the percentage of Cd removal was nearly constant at 6 g and 9 g of adsorbent dosage. However, the percentage slowly increase until the optimum phase has been achieved at 12 g of adsorbent. Then, the efficiency for Cr removal were 49.17%, 54.69%, 58.60% and 62.98% respectively. Meanwhile, the percentage of Pb was slightly increase from 6 g to 9 g with 63.05% and 72.97% respectively. Then it slowly increase for 12 g that showed 78.51% of heavy metal removal after 90 minutes and the lowest percentage of heavy metal removal of Pb for adsorbent dosage was obtained at 3 g is 56.32%.

The results showed for all heavy metals ions adsorption was increased till the surface of adsorbents reach optimal concentration (Rao, Eranna & Berekute, 2018). Hence, the amount of ions bound to the adsorbents and the amount of free ions remains constant even with further addition of adsorbent dosages (Jena and Sahoo, 2017). Lastly, the optimum dosage of adsorbent that has been chosen for continue this experiment was 12 g due to its higher maximum capacity uptake.

4.2.2 Effect of Contact Time

The adsorption study was carried out at several contact time (30, 60, 90 and 120 min). Meanwhile adsorbent dosage, volume and initial HM concentration for cadmium (Cd), chromium (Cr) and lead (Pb) were fixed at 12 g, 100 mL and 0.9, 4.8 and 7.5 ppm respectively. Data for effect of contact time was shown in Appendix A.3.

Based on Figure 4.3, the highest percentage of heavy metals removal for Cd was obtained at 90 minutes. From Figure 4.3, it clearly can be seen that the percentage removal was reached up to 35.11%. The result was increase by increasing the contact time. However, the graph slowly decrease to 32.67% heavy metals removal at contact time 120 minutes. The lowest heavy metals removal for Cd in this experiment obtain at 30 minutes. It only showed 27.22% of heavy metals removal. Next, the highest percentage for Pb removal also was indicated at 90 minutes with the percentage up to 90.24%. The percent of heavy metals removal for Pb is highest than Cd due to different in initial concentration for both heavy metals where the initial concentration for Pb is higher (7.5 ppm) than Cd (0.9 ppm).

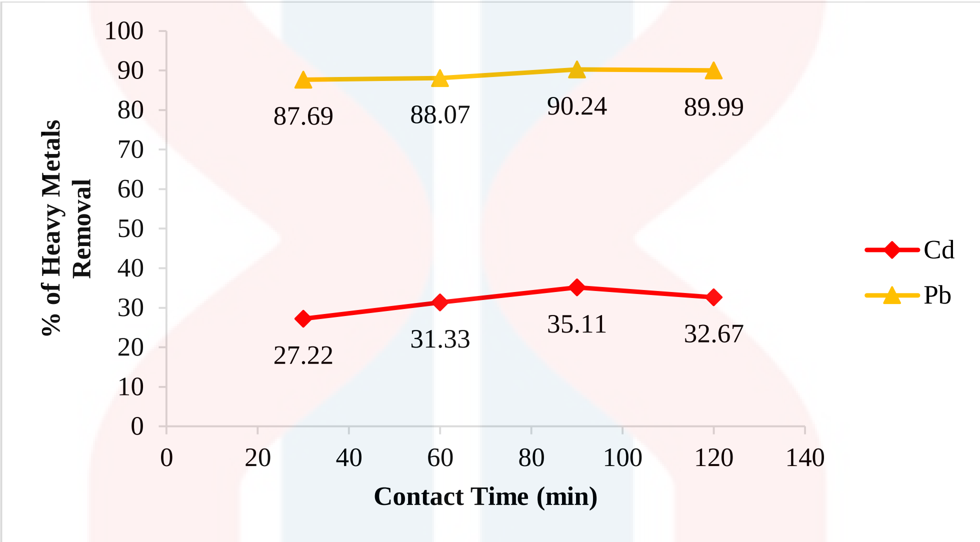


Figure 4.3: Effect of different contact time on the removal of heavy metals (Cd, Cr and Pb) using treated pineapple peels (TPP).

Based on the graph Pb above, it can be seen that the removal of heavy metal is slowly increase from 30 minutes until 90 minutes with their percentage removal were 87.69%, 88.07% and 90.24% respectively. From previous study conducted by Rafidah et al. (2014), the maximum percentage removal of Pb (II) by using papaya peels as an adsorbent was achieved after 90 minutes with 72.26% while the study of removal Cr (VI) by using boiled sunflower stem was generated at 120 minutes with 81.7% (Jain, Garg & Kadirvelu, 2016). However, the adsorption of HM removal for Cr in this study was contaminated due to several factors. One of the factor that contributed to the sample contamination includes the change of pH in the sample during analysis or due to complicated reduction or oxidation process that involve during the study that might cause the contamination towards sample of Cr thus contributed to errors in the analysis (Moreira, Ricardo & Tarley, 2015). Other than that, the laboratory apparatus can be another factor that cause the contamination. Therefore, it should be rinse properly or kept overnight in a nitric acid solution (HNO_3) to avoid the Cr contamination (Moreira et al., 2015).

After 90 minutes, the adsorption process showed the adsorption of HM was reached the equilibrium state due to theirs metal removal that attained after about 90 minutes of contact time (Hefny, 2007). Hence, this 90 minutes of contact time was chosen for continue this experiment.

4.2.3 Effect of pH

A series of adsorption study was carried out at different pH (2, 4, 7 and 9) with fixed amount of adsorbent dosage, contact time, HM solutions and initial concentration of cadmium (Cd), chromium (Cr) and lead (Pb) which is 12 g, 90 minutes, 100 mL, 0.9, 4.8 and 7.5 ppm respectively. Data for effect of pH was shown in Appendix A.4.

The effect of pH is shown in Figure 4.4. pH is a standout amongst the most imperative components influencing adsorption process for binding of Cd, Cr and Pb. This binding process only occur at acidic phase. Based on the graph for Cd, the pH is slightly increase during acidic pH range 2 to 7 which is 31.33%, 51.44% and 86.56% respectively. As can see, the pH range between 2 to 4 is highly increase due to competition of metal cation of cadmium and hydrogen ions H^+ for the adsorption site (Deshmukh, 2017). Later, the metal ion uptake is slowly increase at pH 7 to pH 9 (86.56% and 98.44% respectively) due to nearly reach of equilibrium state.

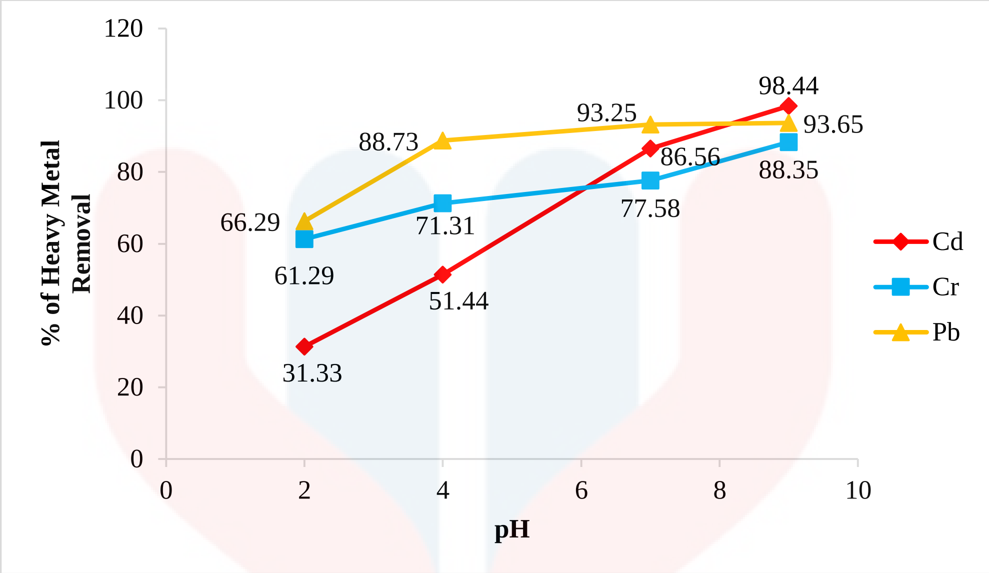


Figure 4.4: Effect of different pH on the removal of heavy metal (Cd, Cr and Pb) using treated pineapple peels (TPP).

Next, same goes with Cr, large number of H^+ was presence at low pH range. Negative charge was neutralizes adsorbent surface thereby lowering the obstacle to diffusion of dichromate ion (Anah and Astrini, 2017). The graph for Cr dramatically increase with the highest percent of Cr removal is achieved at pH 9 (88.35%) while the lowest removal indicated at pH 2 with 61.29%.

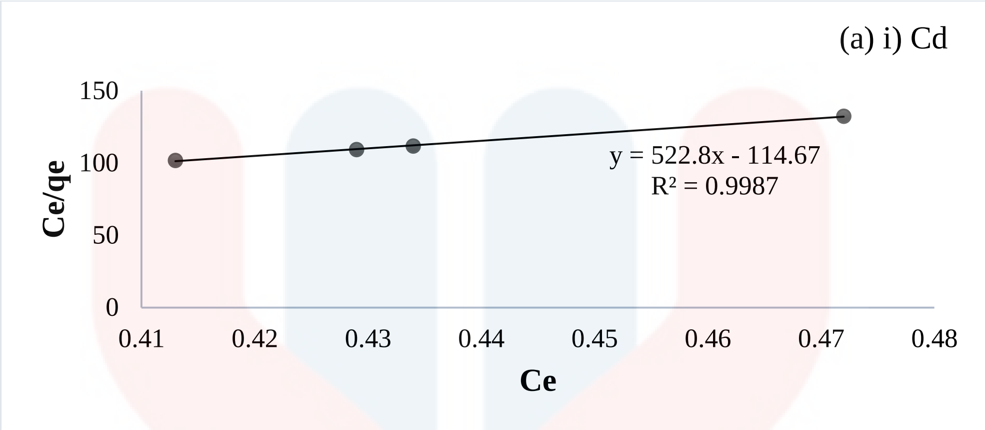
Lastly, the lowest percentage (61.29%) removal of Pb by using TPP was obtained at pH 2 due to low pH levels do not effective for removal of Pb ion from standard solution. According to Rajput et al. (2015) the optimum removal of Pb from aqueous solution by using orange peels was achieved at pH 7 with the value nearly 78%. Based on previous study, it was clearly indicate that the optimum condition for removal of Pb ions from wastewater solution was obtained in pH 9 to pH 11 (Barreira et al., 2009). Then, based on this study, it was been proven that the highest percent removal of Pb ions was resulted in pH 9 with 93.65% of removal.

4.3 Adsorption Capacity

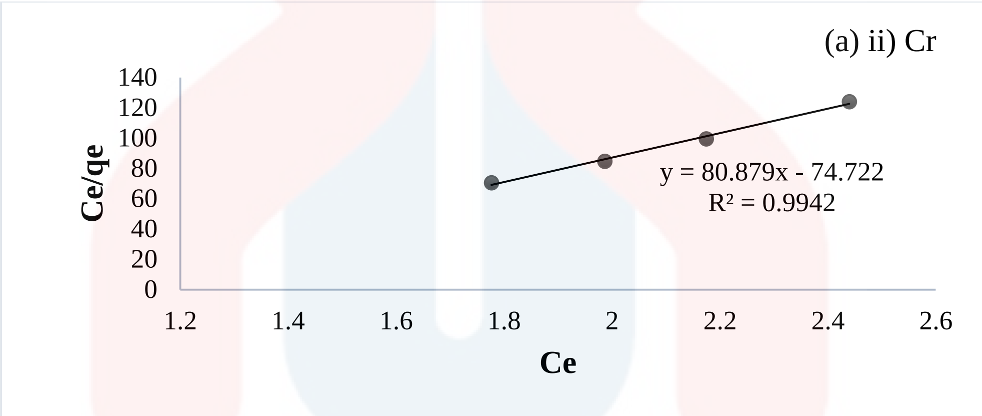
The adsorption isotherm used in this study was Langmuir adsorption isotherm model and Freundlich adsorption isotherm model. Langmuir isotherm model identified with the high congruity and consistency of the surface topography which implies the surface active sited have a comparable adsorption vitality prompting a monolayer coverage (Dada et al., 2012). However, the Freundlich isotherm model refers to the heterogeneity which means the surface holds high roughness and different functional groups with different adsorption energy (Dada et al., 2012).

This isotherm was described by constant value that express the properties of surface and adsorbent affinity in comparing the adsorptive limit of the adsorbent. Adsorbent dosage, contact time and pH was chosen to study for both of the isotherm towards all of those three heavy metals (Cd, Cr and Pb). The most suitable isotherm for the adsorption studied were estimated dependent on correlation coefficient (R^2). Figure 4.5 until 4.10 are the plotted graph for those three heavy metals (Cd, Cr and Pb) based on the Langmuir adsorption isotherm model and Freundlich adsorption isotherm model for adsorbent dosage, contact time and pH studies respectively. The equilibrium adsorption capacity data for heavy metals adsorption onto pineapple peels at different adsorbent dosage, contact time and pH was shown in Appendix A.5, A.6 and A.7 respectively.

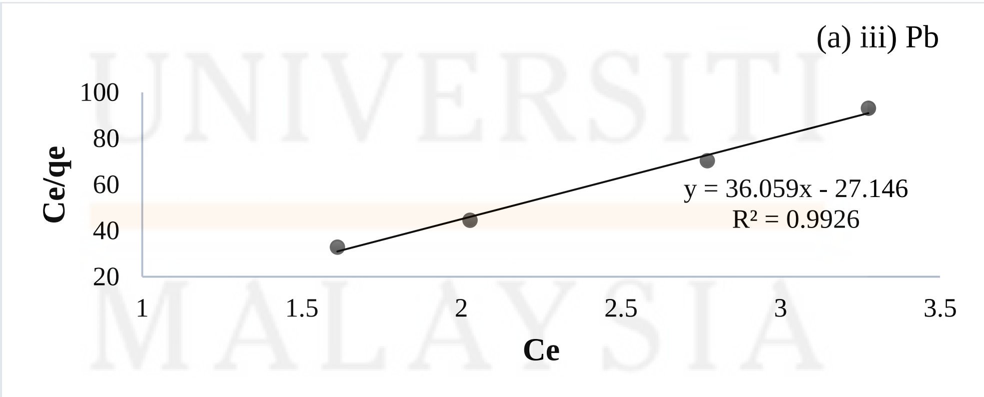
i) Langmuir Adsorption Isotherm Model.



(a) i) Cd

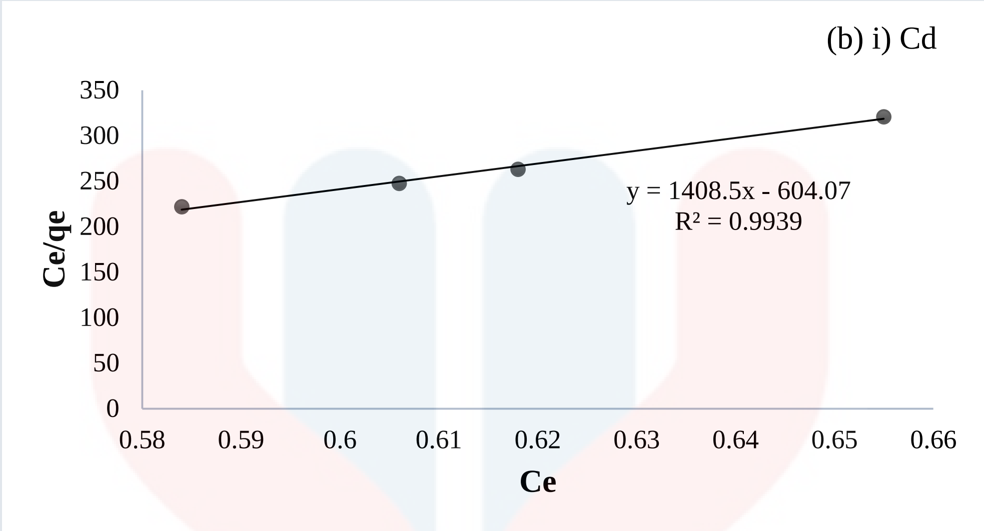


(a) ii) Cr

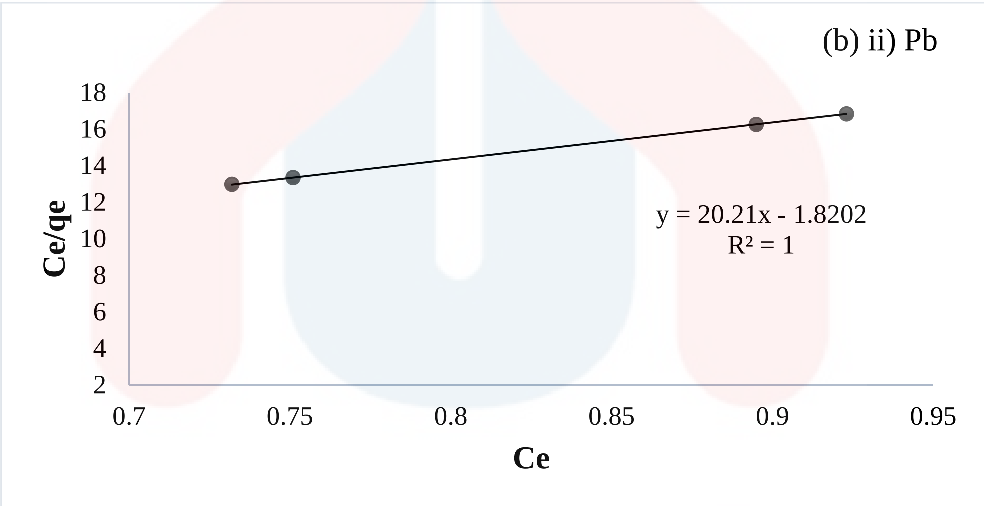


(a) iii) Pb

Figure 4.5: Equilibrium adsorption data for (a) i (a) ii and (a) iii adsorbent dosage fitted to the Langmuir Adsorption Model.

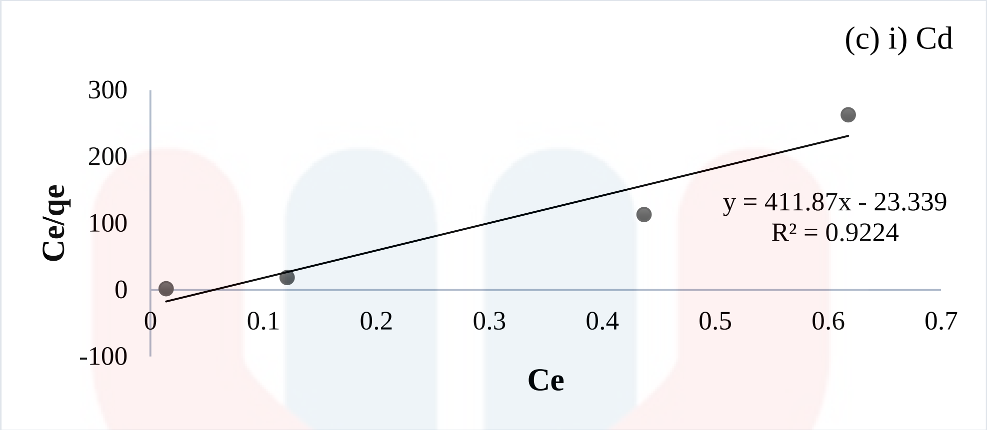


(b) i) Cd

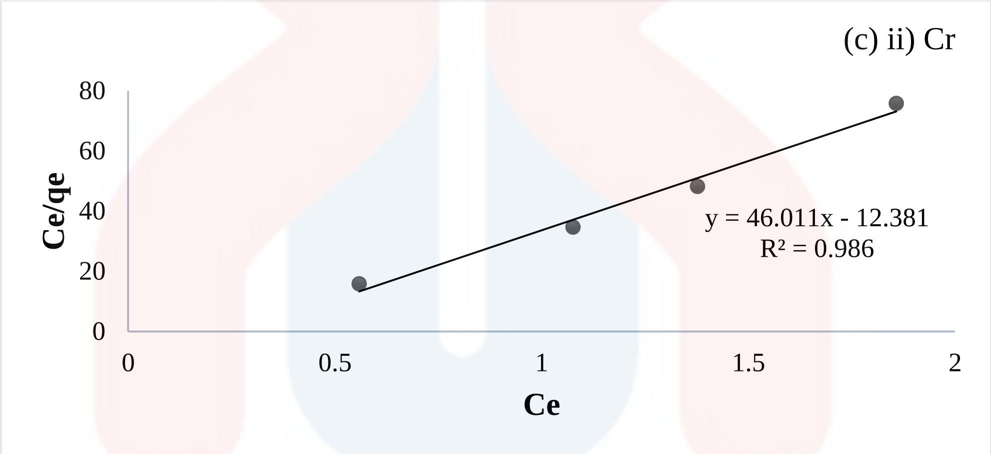


(b) ii) Pb

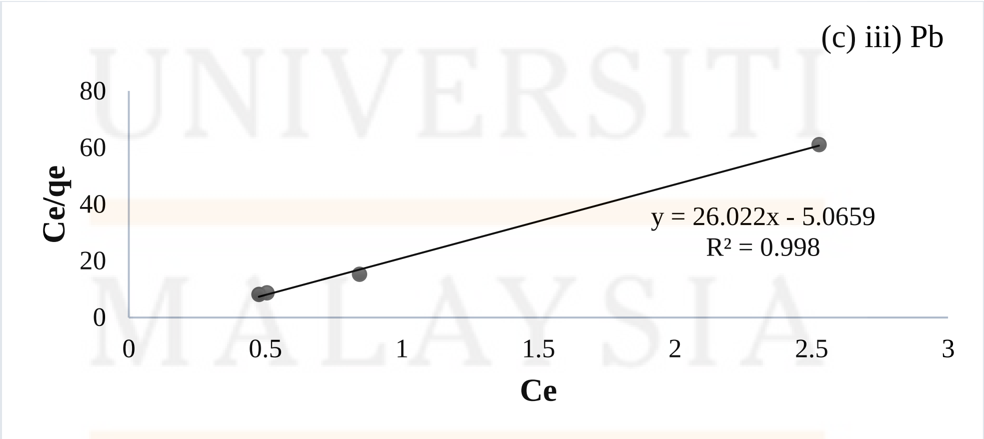
Figure 4.6: Equilibrium adsorption data for (b) i and (b) ii contact time fitted to the Langmuir Adsorption Model.



(c) i) Cd



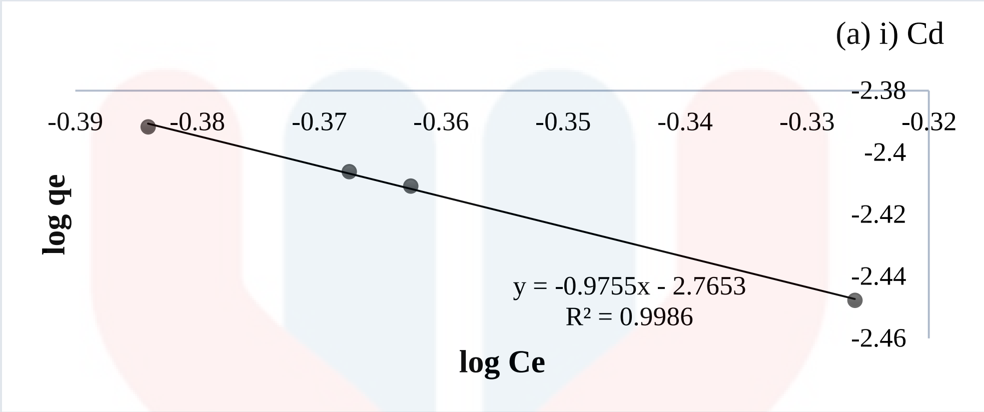
(c) ii) Cr



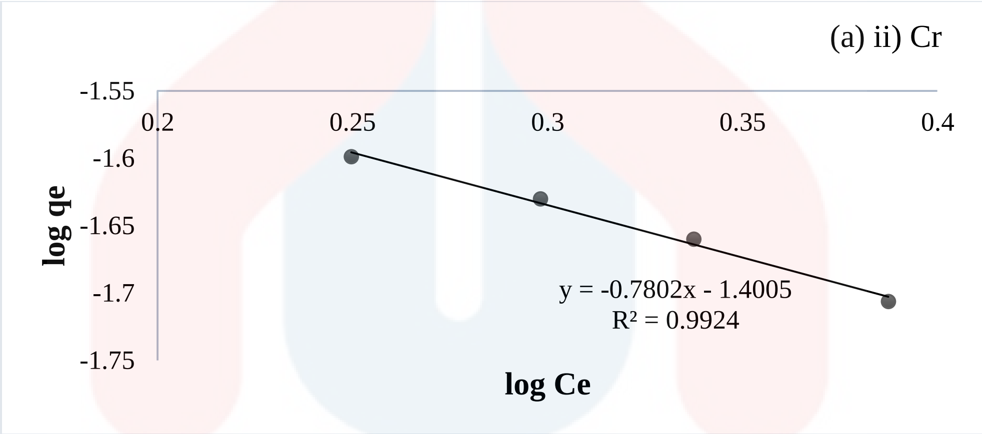
(c) iii) Pb

Figure 4.7: Equilibrium adsorption data for (c) i (c) ii and (c) iii pH fitted to the Langmuir Adsorption Model.

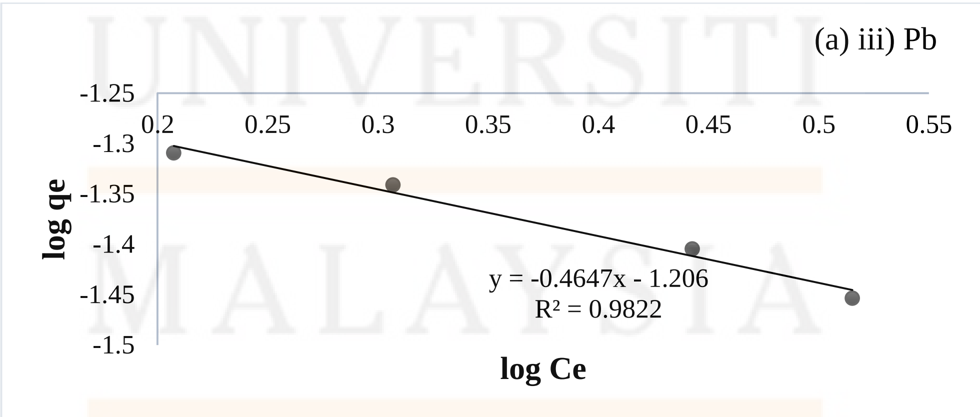
(ii) Freundlich Adsorption Isotherm Model



(a) i) Cd

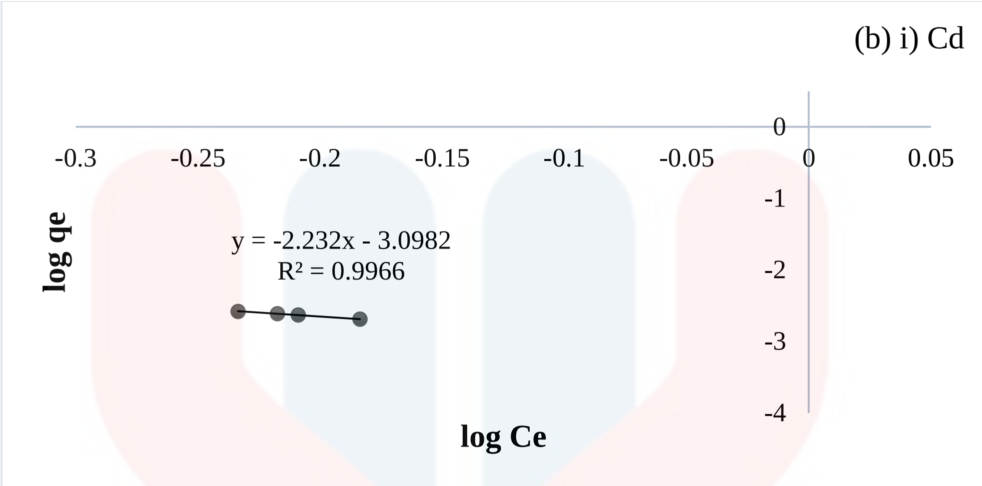


(a) ii) Cr

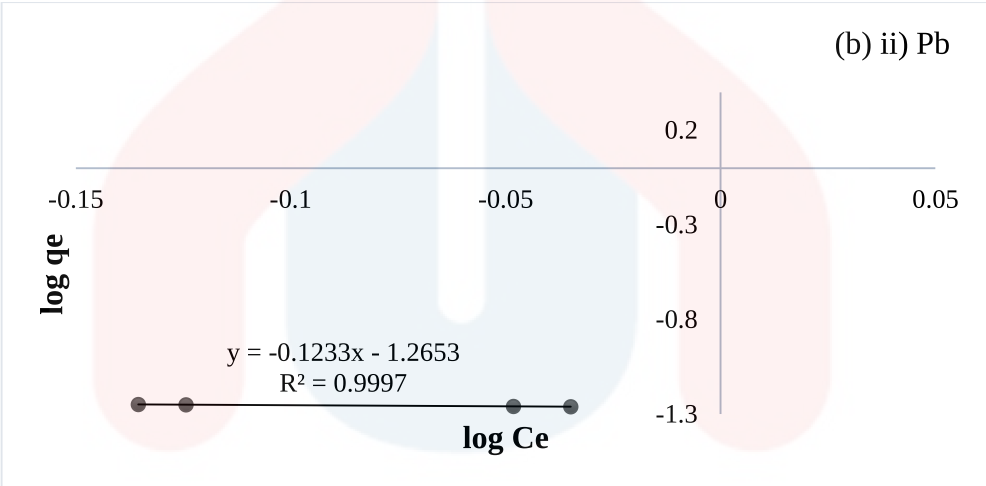


(a) iii) Pb

Figure 4.8: Equilibrium adsorption data for (a) i (a) ii and (a) iii adsorbent dosage fitted to the Freundlich Adsorption Model.

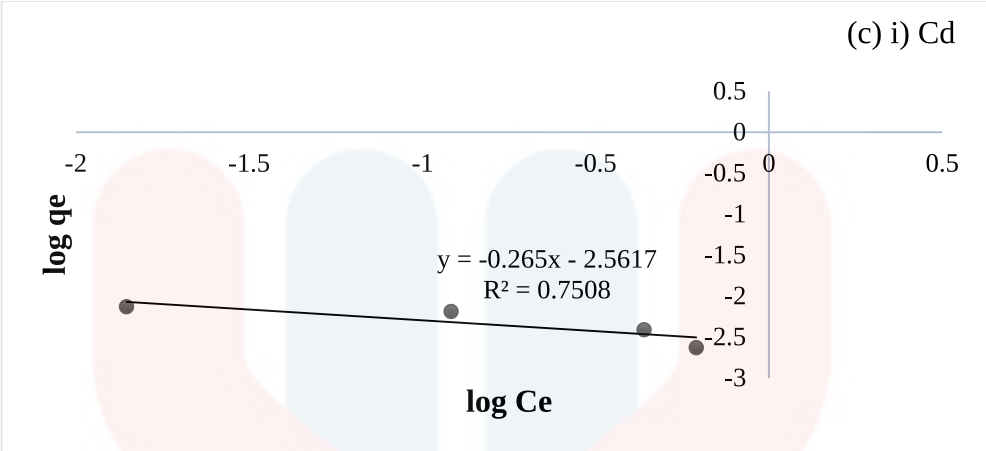


(b) i) Cd

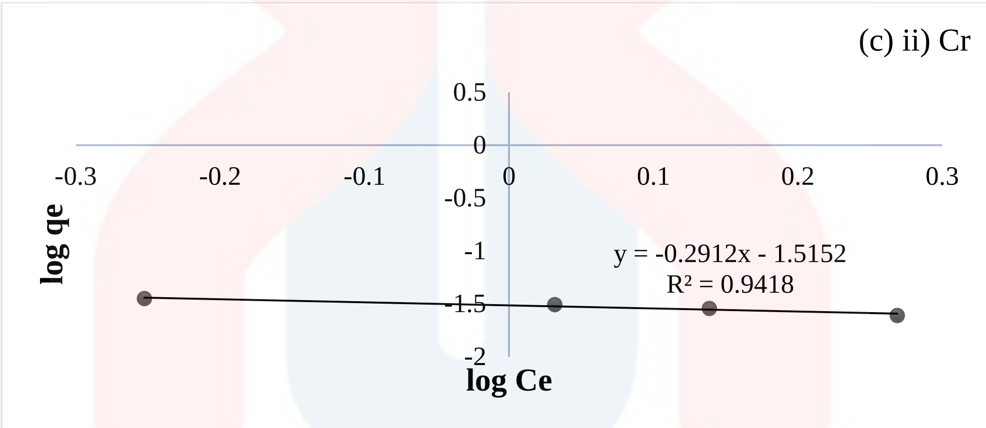


(b) ii) Pb

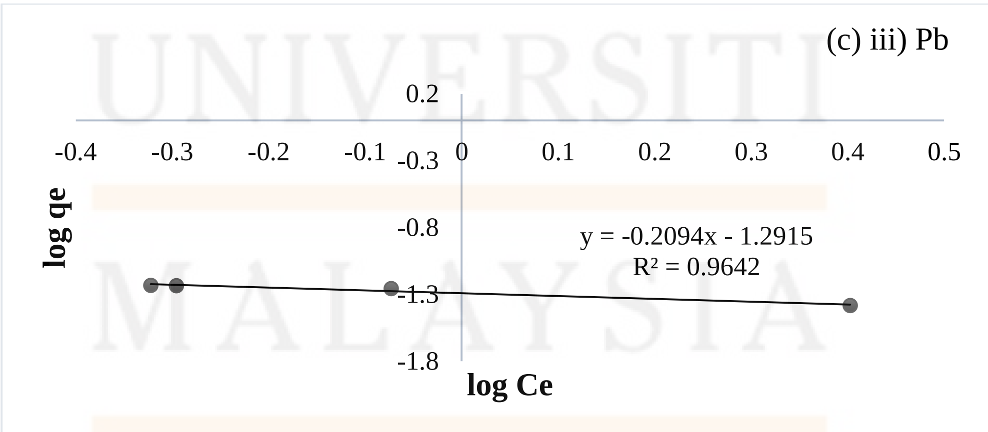
Figure 4.9: Equilibrium adsorption data for (b) i and (b) ii contact time fitted to the Freundlich Adsorption Model.



(c) i) Cd



(c) ii) Cr



(c) iii) Pb

Figure 4.10: Equilibrium adsorption data for (c) i (c) ii and (c) iii pH fitted to the Freundlich Adsorption Model.

Table 4.2: Adsorption parameters for HM adsorption on TPP using Langmuir Isotherm (a) and Freundlich Isotherm (b).

(a) Langmuir Isotherm Model

Heavy Metal (HM)	Parameter	R^2	K_L (L/mg)	q_{max} (mg/g)
Cd	Adsorbent dosage (g)	0.999	-0.229	0.002
	Contact time (min)	0.994	-0.604	0.001
	pH	0.922	-0.047	0.002
Cr	Adsorbent dosage (g)	0.994	-0.897	0.012
	Contact time (min)	-	-	-
	pH	0.986	-0.272	0.022
Pb	Adsorbent dosage (g)	0.993	-0.760	0.028
	Contact time (min)	1.000	-0.089	0.049
	pH	0.998	-0.193	0.038

(b) Freundlich Isotherm Model

Heavy Metal (HM)	Parameter	R^2	n	K_F (mg/g)
Cd	Adsorbent dosage (g)	0.999	-1.025	0.063
	Contact time (min)	0.997	-0.448	0.045
	pH	0.751	-3.774	0.077
Cr	Adsorbent dosage (g)	0.992	-1.282	0.246
	Contact time (min)	-	-	-
	pH	0.942	-3.434	0.220
Pb	Adsorbent dosage (g)	0.982	-2.152	0.299
	Contact time (min)	1.000	-8.110	0.282
	pH	0.964	-4.776	0.275

Based on the Table 4.2, it can be concluded this study relatively best fitted to the Langmuir adsorption isotherm due to the highest correlation coefficient (R^2) value of Cd, Cr and Pb for all effect of the adsorbent dosage, contact time and pH which is near to 1 and the n value showed negative value which is not favorable for adsorption study in Freundlich adsorption isotherm (Dada et al., 2012; Saadi et al., 2015). Thus, the adsorption of Cd, Cr and Pb onto treated pineapple peels is a monolayer adsorption.

Next, data shown the correlation coefficient (R^2) values of Cd, Cr and Pb in the effect of adsorbent dosage were 0.999, 0.994 and 0.993 respectively with the maximum adsorption capacity (q_{max}) for all of these heavy metals were 0.002, 0.012 and 0.028 mg/g respectively. Then, the effect of contact time for Cd shown the value of R^2 was 0.994 with maximum adsorption capacity 0.001 mg/g while the R^2 value for Pb was 1.000 with 0.049 mg/g of maximum adsorption capacity. There are lack of Cr value due to the sample contamination. Lastly the effect of pH give the R^2 value for Cd, Cr and Pb were 0.922, 0.986 and 0.998 respectively with the maximum adsorption capacity for all of these heavy metals were 0.002, 0.022 and 0.038 mg/g respectively. Table 4.3 shows the comparison of adsorption capacity for various types of agricultural waste used as biosorbent for removal of heavy metals in wastewater.

Table 4.3: Comparison of adsorption capacity for various types of agricultural waste.

Adsorbent	Heavy metals	q_{max} (mg/g)	References
Banana peels	Cd (II)	5.71	Anwar et al. (2010)
	Pb (II)	2.18	
Cucumis melo rind	Fe (II)	4.98	Othman and
	Mn (II)	1.37	Asharuddin (2013)
Pineapple peels	Cd (II)	0.002	This study
Pineapple peels	Cr (VI)	0.017	This study
Pineapple peels	Pb (II)	0.038	This study

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This study shown that the agricultural wastes such as pineapple peels were able to remove heavy metals in the polluted water and it also able to become one of the low cost adsorbent due to the introduction of functional group such as carboxyl in treated pineapple peels after the oxidation process happened. There are three parameters included adsorbent dosage, contact time and pH that has been investigated to obtain the optimum condition for the removal of heavy metals. There are three types of heavy metals that has been conducted in this experiment by using all of these parameters. The heavy metals included cadmium (Cd), chromium (Cr) and lead (Pb). The outcome obtained from this study showed that the optimum parameters in adsorption of those three heavy metals for adsorbent dosage, contact time and pH are similar which is at 12 g of pineapple peels, 90 minutes and pH 9 respectively.

Next, the amount of heavy metals uptake was demonstrated that when the adsorbent dosage increase, the percent of heavy metals removal also increase due to the increase of the adsorption capacity of the adsorbent. For the contact time, there are no result obtained for chromium due to the contamination of that sample. However, the adsorption rate for Cd and Pb was slowly increase and reached the optimum of adsorption of heavy metals at 90 minutes. Lastly, the result obtained with Langmuir isotherm model for all of the parameters for Cd, Cr and Pb includes 0.002, 0.017 and 0.038 mg/g respectively.

5.2 Recommendation

There are many parameters such as adsorbent size, initial heavy metal concentration, agitation, temperature and others have not been studied. If those parameters will be contemplated later on, it will uncover the capability of pineapple peels as adsorbent more profoundly and obviously. Additionally, investigations of characterization of pineapple peels by using scanning electron microscopy (SEM) also will help to better understanding about surface morphology of an adsorbent. Other than that, studies on the adsorption dependent on the kinetic and thermodynamics model can be esteem added to understand absolutely about the mechanism of pineapple peels adsorption. At last, adsorption isotherm also can be controlled by using Temkin isotherm and D-R isotherm (Dubinin-Radushkevich isotherm) to assess the best fittings to adsorption isotherms.

In addition, all of the preparation sample should be done properly to avoid from contamination happen. The laboratory apparatus can be a factor that cause the contamination. Therefore, it should be rinse properly or kept overnight in a nitric acid solution (HNO_3) to avoid from the contamination. Overall, this study gave the information that the pineapple peels have a potential as adsorbent to evacuate heavy metals (Cd, Cr and Pb) effectively.

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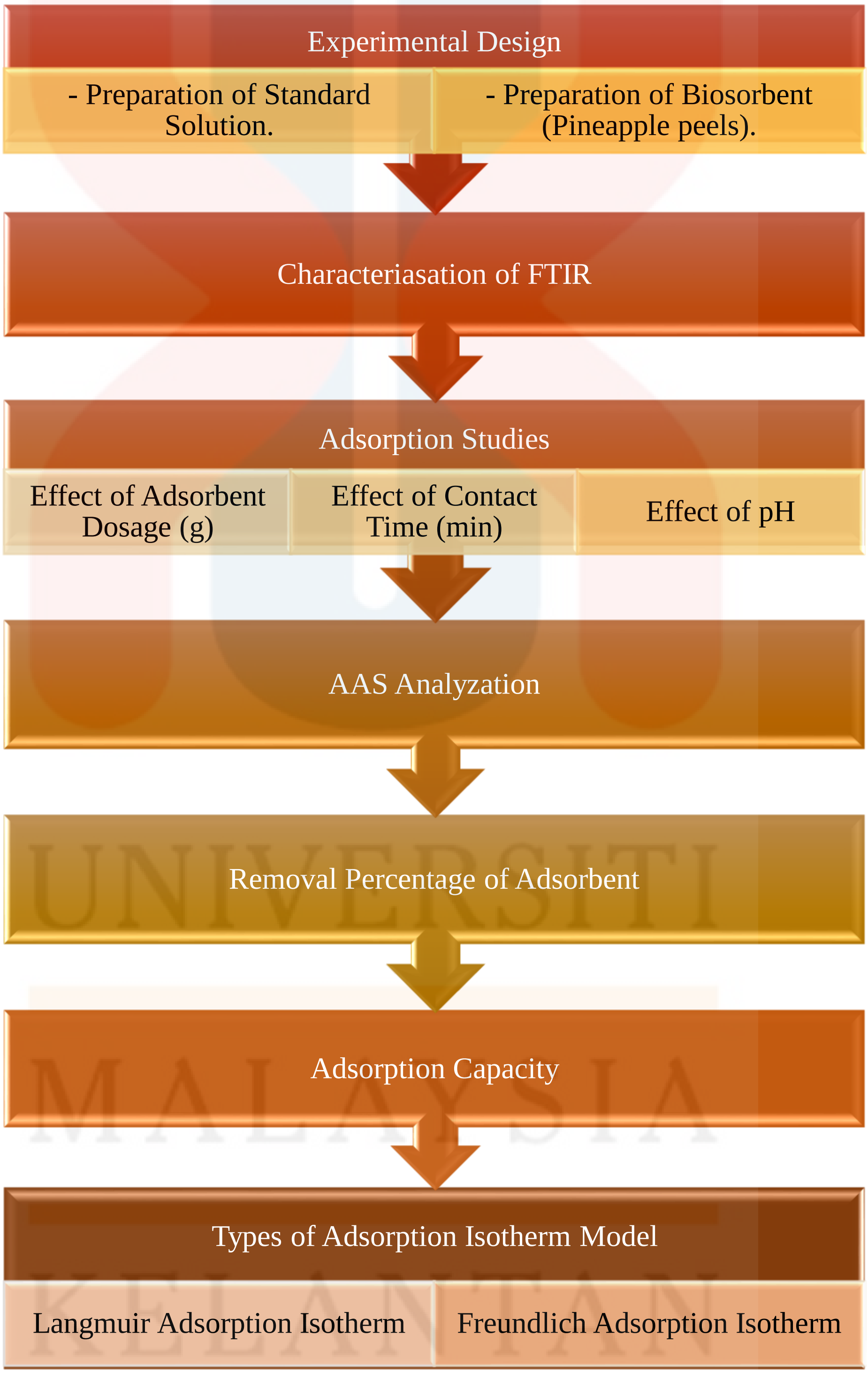
APPENDIX A

(RESULT AND DATA ANALYSIS)

A.1: Flowchart of Overall Study.



A.2: Adsorption of heavy metals on different weight (g) of adsorbent (Treated Pineapple peels).

Metal ion	Adsorbent dosage (g)	Initial concentration (ppm)	Final concentration (ppm)	Percentage of removal (%)
Cd	3	0.9	0.472	47.56
	6	0.9	0.434	51.78
	9	0.9	0.429	52.33
	12	0.9	0.413	54.11
Cr	3	4.8	2.440	49.17
	6	4.8	2.175	54.69
	9	4.8	1.987	58.60
	12	4.8	1.777	62.98
Pb	3	7.5	3.276	56.32
	6	7.5	2.771	63.05
	9	7.5	2.027	72.97
	12	7.5	1.612	78.51

A.3: Effect of different contact time (min) on the removal of heavy metals using adsorbent (Treated Pineapple peels).

Metal ion	Adsorbent dosage (g)	Contact time (min)	Initial concentration (ppm)	Final concentration (ppm)	Percentage of removal (%)
Cd	12	30	0.9	0.655	27.22
	12	60	0.9	0.618	31.33
	12	90	0.9	0.584	35.11
	12	120	0.9	0.606	32.67
Cr	12	30	4.8	-	-
	12	60	4.8	-	-
	12	90	4.8	-	-
	12	120	4.8	-	-
Pb	12	30	7.5	0.923	87.69
	12	60	7.5	0.895	88.07
	12	90	7.5	0.732	90.24
	12	120	7.5	0.751	89.99

A.4: Effect of different pH on the removal of heavy metals using adsorbent (Treated Pineapple peels).

Metal ion	Adsorbent dosage (g)	Contact time (min)	pH	Initial concentration (ppm)	Final concentration (ppm)	Percentage of removal (%)
Cd	12	90	2	0.9	0.618	31.33
	12	90	4	0.9	0.437	51.44
	12	90	7	0.9	0.121	86.56
	12	90	9	0.9	0.014	98.44
Cr	12	90	2	4.8	1.858	61.29
	12	90	4	4.8	1.377	71.31
	12	90	7	4.8	1.076	77.58
	12	90	9	4.8	0.559	88.35
Pb	12	90	2	7.5	2.528	66.29
	12	90	4	7.5	0.845	88.73
	12	90	7	7.5	0.506	93.25
	12	90	9	7.5	0.476	93.65

A.5 Equilibrium adsorption capacity for heavy metals adsorption onto treated pineapple peels at different adsorbent dosage.

Metal ion	Adsorbent dosage (g)	C_e	q_e	C_e/q_e	log C_e	log q_e
Cd	3	0.472	3.567	0.132	-0.326	-2.448
	6	0.434	3.883	0.112	-0.362	-2.411
	9	0.429	3.923	0.109	-0.368	-2.406
	12	0.413	4.058	0.102	-0.384	-2.392
Cr	3	2.440	0.020	124.068	0.387	-1.706
	6	2.175	0.022	99.429	0.337	-1.660
	9	1.987	0.023	84.764	0.298	-1.630
	12	1.777	0.025	70.539	0.250	-1.599
Pb	3	3.276	0.035	93.068	0.515	-1.453
	6	2.771	0.039	70.315	0.443	-1.404
	9	2.027	0.046	44.444	0.307	-1.341
	12	1.612	0.049	32.853	0.207	-1.309

A.6 Equilibrium adsorption capacity for heavy metals adsorption onto treated pineapple peels at different contact time.

Metal ion	**Contact time (min)**	**C_e**	**q_e**	**C_e/q_e**	**log C_e**	**log q_e**
Cd	30	0.655	0.002	320.816	-0.184	-2.690
	60	0.618	0.002	262.979	-0.209	-2.629
	90	0.584	0.003	221.772	-0.234	-2.579
	120	0.606	0.002	247.347	-0.218	-2.611
Cr	30	-	-	-	-	-
	60	-	-	-	-	-
	90	-	-	-	-	-
	120	-	-	-	-	-
Pb	30	0.923	0.055	16.841	-0.035	-1.261
	60	0.895	0.055	16.260	-0.048	-1.259
	90	0.732	0.056	12.979	-0.135	-1.249
	120	0.751	0.056	13.353	-0.124	-1.250

A.7 Equilibrium adsorption capacity for heavy metals adsorption onto treated pineapple peels at different pH.

Metal ion	**pH**	**C_e**	**q_e**	**C_e/q_e**	**log C_e**	**log q_e**
Cd	2	0.618	0.002	262.979	-0.209	-2.629
	4	0.437	0.004	113.261	-0.340	-2.414
	7	0.121	0.006	18.639	-0.917	-2.188
	9	0.014	0.007	1.896	-1.854	-2.131
Cr	2	1.858	0.025	75.785	0.269	-1.611
	4	1.377	0.029	48.273	0.139	-1.545
	7	1.076	0.031	34.672	0.032	-1.508
	9	0.559	0.035	15.817	-0.253	-1.452
Pb	2	2.528	0.041	61.014	0.403	-1.383
	4	0.845	0.055	15.237	-0.073	-1.256
	7	0.506	0.058	8.682	-0.296	-1.234
	9	0.476	0.058	8.132	-0.322	-1.233

APPENDIX B

(PHOTO GALLERY)

B.1: Pineapple peels.

B.2: Dried pineapple peels.

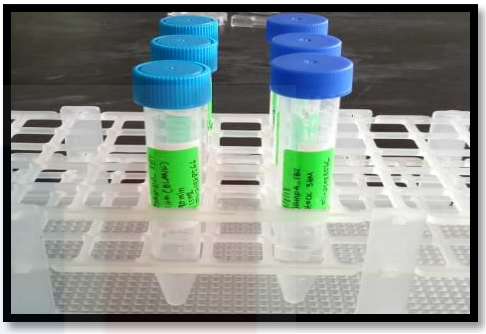
B.3: Grinded pineapple peels.

B.4: Treated pineapple peels.

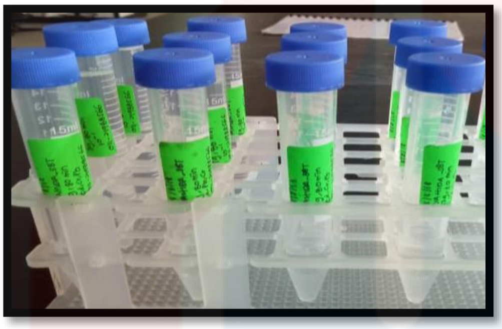
B.5: Treated pineapple peels after stir using rotary shaker.

B.6: The solution has been filtered using vacuum pump.

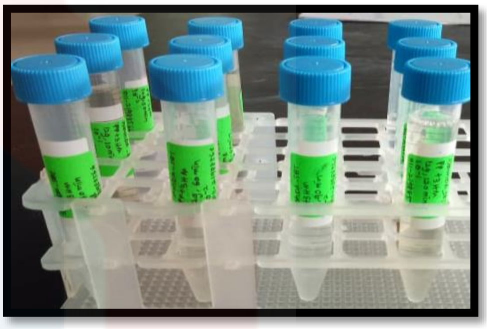
B.7: Standard metals solution (Cd, Cr and Pb).



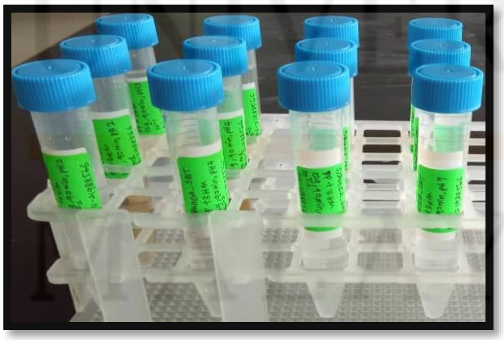
B.8: Dilution of stock metals solution.



B.9: Dilution of different adsorbent dosage (3, 6, 9 and 12 g).



B.10: Dilution of different contact time (30, 60, 90 and 120 min).



B.11: Dilution of different pH (2, 4, 7 and 9).

B.12: Samples has been analyzed using AAS machine.