REMOVAL OF HEAVY METALS FROM INDUSTRIAL WASTEWATER USING FRUITS PEEL AS A LOW-COST BIO-ADSORBENT

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ABSTRAK

Untuk menghilangkan logam berat dari air kumbahan industri, proses rawatan konvensional yang biasanya digunakan mempunyai beberapa kelemahan. Kaedah penyerapan adalah salah satu proses alternatif untuk menghilangkan logam berat. Walau bagaimanapun, harga bagi penggunaaan "activated carbon" sebagai penyerap adalah mahal. Salah satu penyelesaian yang disyorkan adalah dengan menggunakan kulit buah sebagai bio-penyerapan. Kajian ini bertujuan untuk menentukan kapasiti optimum kulit pisang, mangga dan oren sebagai bio-penjerapan dalam merawat air kumbahan industri. Selain itu, ia juga bertujuan untuk membandingkan kesan dari segi masa,pH awal dan suhu dalam penyingkiran logam berat. Selain itu, kajian ini akan menganalisis kajian penjerapan dari segi "dosage", tahap pH, suhu dan masa. "Langmuir adsorption model" disahkan dengan cara plot linear Ce / qe terhadap Ce. Hasilnya menunjukkan bahawa kapasiti optimum penyerapan untuk penyerap oren, pisang dan mangga mengurai sekitar 1.2 gram, 0.8 gram dan 1.6 gram dengan tahap pH terbaik 4 untuk oren dan mangga manakala pH 2 untuk pisang. Suhu tidak mempengaruhi kecekapan penjerapan dalam lingkungan 29°c hingga 49°c dan untuk kesan masa,penyerap menyerap dengan cepat pada 20 minit pertama dan secara beransur-ansur meningkat dan kekal stabil selepas beberapa minit. Kajian ini mendedahkan bahawa kulit buah-buahan terbaik yang boleh digunakan sebagai penyerap adalah kulit oren kerana ia dapat menyerap banyak ion plumbum berbanding dengan dua buah yang lain.

ABSTRACT

In order to remove heavy metal from industrial wastewater, the conventional treatment processes that usually been use have several disadvantages. Adsorption method is the alternative process to remove heavy metal. However, the cost of using activated carbon as an adsorbent is expensive. One of the recommended solutions is to use fruits peel as a bio-adsorbent. This study aims to determine the optimum capacity of banana, mango and orange peel as bio-adsorption in treating industrial wastewater. Besides that, it also aims to compare the effect of contact time, initial pH and temperature in the removal of heavy metals. Other than that, this study will analyze the batch adsorption study base on dosage, pH level, temperature and contact time. Langmuir adsorption model was used which is confirmed by a linear plot of Ce/qe against Ce. The results showed that optimum adsorption capacity for orange, banana and mango peel adsorbent is around 1.2gram, 0.8gram and 1.6gram respectively with the best pH level of 4 for orange and mango meanwhile pH 2 for banana. The temperature does not influence the efficiency of adsorption in the range of 29ºc until 49ºc and for the effect of contact time, the adsorbent absorbs rapidly at the first 20 min and gradually increase and remained stable after a few minutes. This study revealed that the best fruits peel that can be used as an adsorbent is orange peel as it can absorb many lead ions compare with the other two fruits peel.

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LIST OF SYMBOLS

mg/l	Milligram per litre
^{o}c	Degree Celsius
ppm	Parts per million
mol/l	Molar concentration per litre
mm	Millimetre
L/mg	Litre per milligram
mg/g	Milligram per gram
g	Gram
q_e	Amount of adsorption at equilibrium
C_o	Initial concentration
C_e	Equilibrium concentration
V	Volume of solution
X	Weight of adsorbent
b	Constant related to the energy
Q_o	Mass of adsorbed solute required to saturate a unit mass of adsorbent
R_L	Equilibrium parameter

LIST OF ABBREVIATIONS

Cu	Copper
Pb	Lead
Cd	Cadmium
Hg	Mercury
As	Arsenic
Cr	Chromium
Se	Selenium
Ni	Nickel
Ag	Silver
Zn	Zinc
Fe	Iron
AAS	Atomic adsorption spectrophotometry
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
WHO	World Health Organization
DOE	Department of Environment
-OH	Hydroxide
HNO_3	Nitric acid
NaOH	Sodium hydroxide

CHAPTER 1

INTRODUCTION

1.1 Introduction

Water is valuable natural resources to human, all living things and a healthy environment. Human needs water to complete their routine in daily life. Water also has been used in industrial in order to make sure their plants are running well instead as the main resource for drinking. Water is a transparent fluid which produces the streams, lakes, oceans, and rain, and is the principal constituent of the fluids of organisms. As a chemical compound, a water molecule contains one oxygen and hydrogen atoms that are related through covalent bonds. All living things will not survive without water for a long term and same goes to the industry which is it cannot be functional without existing of water. Besides, water plays an important role in the population growth and rapid development as the clean water resources needed as the pre-requisite in the existing of remain population.

Nowadays, because of the rapid growth of the industrial sector, the productions of heavy metal wastes into the water have been increasing day by day. Heavy metal pollution in the environment is one of the serious pollutions that occur globally. In recent years, ecological and global public health concern associated with environmental by these heavy metals has increased. The discharge of heavy metals from various sources especially from industry and agricultural into the aquatic ecosystem can accumulate in living tissues causing various disease and disorders. The industrial effluents which contain different derivatives of heavy metal such as copper, lead, cadmium, mercury, arsenic, chromium, selenium, nickel, silver, and zinc are continuously discharging to the ecosystem and producing a significant toxic on the aquatic environment. These heavy metals will persist in the environment since they cannot be degraded and finally reach to the human food chain and result in the health problems.

Among these heavy metals, lead and copper is the most common pollutants found in the industrial effluents (Kahraman & Erdemoglu, 2008). The excess for lead in the water poses severe health risks to humans such as cancer, reproductive system disorders, high blood pressure, heart disease and skin disease (Abbaszadeh et al., 2018). Besides that, although copper is an essential present element the high level of it can cause harmful effects to human health (Kahraman & Erdemoglu, 2008). In most of the wastewaters, the concentration of heavy metals present is much larger than the safe permission limit. Therefore, the removal of heavy metal is one of the most important environmental issues that need to be solved.

In order to remove the heavy metal, there are several treatment processes that can be done such as chemical precipitation, membrane filtration, ion exchange, adsorption, co-precipitation and extraction (Bhatnagar et al., 2010). Among these treatment processes, the adsorption method is the most effective method to remove the heavy metals as it offers some benefit such as easy to operate, do not require any high skilled labour, environmentally safe and the process is non-destructive so that contaminants can be separated and recycled (Ahmad & Danish, 2018). The main parameter for doing adsorption is the adsorbent for removal and extraction purpose. The adsorbent that has been used is usually activated carbon as it has known for the effectiveness in removing heavy metal especially copper and lead from wastewater. Recently the researches have been made to use the nature adsorbent to replace the activated carbon.

1.2 Problem Statement

In order to remove the heavy metal, several treatment processes can be done such as chemical precipitation, membrane filtration, ion exchange, co-precipitation, and extraction. However, these methods proved either inefficient or expensive in case of low concentration (1-100mg/l) of heavy metals prevailing in the environment and generate a huge amount of sludge which is difficult to be disposed of (Ahmad & Danish, 2018). Other than that, most of these methods are not suitable for a small-scale industry which affects the operational cost and excess amount of chemical usage

Because of that, adsorption method is been select as an alternative to removing the heavy metal due to their low cost, easy to operate, do not require any high skilled labour, environmentally safe and the process is non-destructive so that contaminants can be separated and recycled. However, the use of commercial activated carbon as an adsorbent makes the adsorption process expensive. The high demand for activated carbons in other advanced application make in increasing their cost.

Therefore, in order to decrease the cost of the adsorbent, many kinds of research have been conducted to find the low cost of adsorbent with the high metal binding which is by using agricultural waste. The agricultural waste has been developed as it shows some advantages as it was cheap, readily available, low-cost, simple to use and environment friendliness. The agricultural waste such as chitosan, chitin, sugarcane bagasse, apple and orange juice residue, banana, wheat straw, rice husk, tea waste has been investigated as bio-sorbent for removal of heavy metals (Ahmad & Danish, 2018). Fruits peel is one of the agricultural wastes that can be used as bio-adsorbent. While these materials are considered wastes with a low or no economic value, and usually present removal and disposal, this transformation toward bio-adsorbent material add economic value and also help on reducing the disposal costs (Romero-Cano, 2016).

In this study, banana, mango, and orange peel have been select in order to produce bio-adsorbent though environment-friendly process. The residues of this fruit can be processed and convert it to be adsorbents because it's had a large surface area, high swelling capacities, and excellent mechanical strength and is convenient to use and have great potential to adsorb harmful contaminants such as heavy metals. At the end of this study, it was indicated which of this fruit's peel has an optimum adsorption capacity with good effect of the contact time adsorbent dose, pH level, and temperature variation for each fruit's peel.

1.3 The objective of the Study

The main objectives of this study are as followed below;

i. To determine the optimum adsorption capacity of banana, mango and orange peel as bio-adsorption in treating industrial wastewater.
ii. To compare the effect of contact time, initial pH and temperature in the removal of heavy metals

1.4 Scope of the Study

In this study, it was focusing on the heavy metal study which was cooper and lead which is highly present on the industrial wastewater that has been produced by industry. The industrial wastewater sample was collected at the industrial company at Gebeng area and was tested and analyzed in Environmental Laboratory, Faculty of Civil Engineering, University Malaysia Pahang. Based on both environmental and economic point of view, special attention has been focusing on the use of the natural adsorbents from agricultural waste as an alternative to replace the commercial activated carbon. Banana, mango and orange peels are been choices as bio-adsorbent to remove the heavy metal ions in industrial wastewater. These fruits were collected at the fruit juice stalls at Café of Kolej Kediaman 3, University Malaysia Pahang. The preparations of bio-adsorbent were conducted at Laboratory and the time frame for preparing the wastewater, bio-adsorbent and test the wastewater was around 10 weeks. This study was focusing on determining the optimum adsorption capacity of banana, mango and orange peel as bio-adsorbent on removing the heavy metal and the effect of pH level, temperature and contact time of the bio-adsorbent.

1.5 Significance of the Study

The study on the wastewater treatment by using bio-adsorption method was important in order to overcome the heavy metal pollution that can not only harm the environment but also human health. Other than that, it also helps in reducing the cost of the heavy metal treatment process. As we know the adsorption treatment is the cheaper treatment that can remove heavy metal but by replacing activated carbon with bio-adsorbent which is fruits peel not only reducing the cost but also can reducing the fruits peel waste and disposal costs of the fruits peel waste. This study determined which of this fruit's peel has optimum adsorption capacity as bio-adsorbent and produces the lower cost as bio-adsorbent. At the end of this study, the fruit's peel that has a lower effective cost treatment as bio-adsorbent in order to remove the heavy metal ion was proposed. This adsorbent can be used and practice widely by government authorities and industrial management in order to control and reduce the pollution by industrial wastewater at Malaysia.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Water is very important in life. Human use water every day in order to drink, washing their hands, preparing food, water plants, and many other things. Without water, the plant and aquatic life might die and same goes to the human which may be dehydrated and will affect the health. Because of that, clean water is one of the most important resources to life, and when the clean water was polluted it is not only destroying the environment but also to human health.

In addition, much of that water that supply to human was comes from rivers which we do not know where it comes from. There has water that been discharge from an industry which involves chemical usage or the agricultural industry which produce heavy metal ion to the water. Therefore, it is very important to remove the heavy metal and other polluted before can discharge it into the river. In Malaysia, there has allowable content of heavy metal that needs to be followed by the factory before they can discharge the wastewater. Because that is very important to find an alternative in order to remove the heavy metal which easies to conduct and have a very low-cost method.

One of the alternative methods that can be used is by using adsorption method. This type of method is a low-cost method but the use of activated carbon as an adsorbent make the method expensive. Nowadays, one of the methods to reduce the cost of the adsorption method is by replacing activated carbon with an agricultural adsorbent such as coconut coir, fruits peel and others (Kahraman & Erdemoglu, 2008).

2.2 Wastewater

Wastewater can be defined as dirty water which has been affected by municipal use, the water of agriculture and industrial. This type of water has been thrown away from gutters, on the land, follow into the kitchen drains and bathroom drain after have been used. The wastewater can be referring into two different types which are affluent that refers to sewage or liquid waste that is discharged into water bodies either from direct sources or from the treatment plant such as discharge from industries household, urban runoff, agriculture and so on. Meanwhile influent is referring to wastewater that flows into a reservoir, basin and treatment plant.

According to Odlare (2014), wastewater is been define as a complex mixture of inorganic and organic materials. Carbohydrates, lignin, soaps, fats, decomposition product as well as various natural and synthetic organic chemicals from the process industries are among the organic substance that present in sewage. Meanwhile, inorganic materials consist of pH, alkalinity, nitrogen, phosphorus, chlorides, heavy metal and toxic inorganic compounds.

Odlare (2014) has also stated that wastewater can be divided into three types which are domestic wastewater which known as sewage, industrial wastewater, and municipal wastewater. For the municipal wastewater, it is the combination between the domestic and industrial wastewater.

2.2.1 Industry Wastewater

Industrial wastewater is one of the pollution sources in the water environment. Among the different types of pollution, industrial wastes constitute the major sources of metal pollution. Akpor (2014) has stated that the toxic metal that usually can be found in the industrial wastewater is copper, lead, selenium, nickel, silver, and zinc. All of this heavy metal usually comes from mining activities, metal plating industries, battery manufacturing, pigments and stabilizers of alloys industries. Table 2.1 show different type of sector with a different type of pollutant (Shi, 2017).

Table 2.1 Water pollutants by the industrial sector (Shi, 2017)

Sector	Pollutant
Iron and Steel	BOD, COD, Oil, Metals, Acids, Phenols and Cyanide
Textiles and Leather	BOD, Solids, Sulphates, and Chromium
Pulp and Paper	BOD, COD, Solids, Chlorinated Organic Compounds
Petrochemicals and Refineries	BOD, COD, Mineral Oils, Phenols, and Chromium
Chemical	COD, Organic Chemicals, Heavy Metals, Suspended Solid and Cyanide
Non-Ferrous Metals	Fluorine and Suspended Solid
Microelectronics	COD and Organic Chemicals
Mining	Suspended Solid, Metals, Acids and Salts

2.3 Water Quality Parameter

Water quality testing is an important part of environmental monitoring. Because of that, it important to know the water quality parameter that had in the water. Water quality parameter is divided into three different types of the parameter which are physical, chemical and biological. This water quality parameter was used to illustrate the qualitative and quantitatively of tester water. Water quality parameter provides the base guide information on water safety. Since water quality in any source of water and at the point of use, can change with time and other factors, continuous monitoring of water is very important. A substance that suspended and dissolves in water body needs to be analyzed in order to identify the water quality level. The raw water source should be free from any toxic elements and dangerous organisms that may hazardous to health.

2.4 Heavy Metal

Heavy metal is one of the chemical parameters of water quality. Heavy metals exist along with phosphorus, aluminum, chromium, and lead inside the water. Those metals distributed into the groundwater by surrounding human activities. Phosphorus presence affects the groundwater excellent by algae growth and also in eutrophication.

Metal ions can be incorporated into food chains and concentrated in aquatic organisms to a level that affects their physiological state. Of the effective pollutants are the heavy metals which have a drastic environmental impact on all organisms. Trace metals such as copper, lead, zinc and iron play a biochemical role in the life processes of all aquatic plants and animals. Therefore, they are essential in the aquatic environment in trace amounts. In the Egyptian irrigation system, the main source of copper and lead are industrial wastes.

According to Tun et al. (2017), heavy metals are applied to a group of metals and metalloids with atomic density five times more than water. Usually, the wastewater generated from industries may contain a number of heavy metals which give a significant toxic effect. The amount and number of metals present in the wastewater are related directly to the operations carried out in an industry (Taylor et al., 2012). The heavy metals that enter the water are non-biodegradable and it will result on the food chain as its accumulation through the food chain and bio-magnifications which will increase the toxicity and threat to the ecosystem and human health. This heavy metal will cause a bad effect to human health such as to cause damage to the nervous system, reproductive system, kidney, brain, impaired blood synthesis, hypertension and even cause miscarriage in a pregnant woman (Jena & Sahoo, 2017).

2.4.1 Cooper

Copper is a reddish metal that occurs naturally in rock, soil, water, sediment, and air. It has many practical uses in our society and is commonly found in coins, electrical wiring, and pipes. It is an important element for living organisms, including humans, and in small amounts-necessary in our diet to ensure good health. However, excessive intake of copper ion can cause adverse health effects, including vomiting, stomach cramps, nausea, hepatic and renal damage. It has also been related to liver damage and kidney disease. Water is one of the ways that copper may enter our bodies. Because of that, the World Health Organization (WHO) to provide a guideline value limited to 2 mg/l for copper content of drinking water.

According to Arbabi and Golshani (2016), copper is usually discharged from different type industries such as metal cleaning, paints and pigment, mining, smelting, fertilizer, wood pulp, and printed circuit board production. The excessive amount of copper discharge from industries into the fresh resources and aquatic ecosystem damage the osmoregulatory mechanism of the freshwater animal. Malaysia Department of Environment (DOE) has set the acceptable conditions for industries discharge for cooper for Standard A is 0.2 mg/l meanwhile for Standard B is 1 mg/l. Figure 2.1 shows the illustration of copper metal in the form of solid state.

Figure 2.1 Cooper metal

2.4.2 Lead

Lead is a bluish grey metal that has been found in natural deposits, it is commonly used in household plumbing materials and water service lines. It is industrial pollutants that enter the ecosystem through the soil, air, and water. The greater exposure to lead is swallowing or breathing in lead paint chips and dust. However, lead in drinking water can also cause a variety of adverse health effects. In adults, it can cause increases in blood pressure. Adults who drink this water over many years could develop kidney failure or high blood pressure. Lead is rarely found in source water but enters tap water through corrosion of plumbing materials (Environment Protection Agency, 2008).

According to Arbabi et al. (2015), lead usually come from industrial effluents such as acid battery manufacturing, metal plating, ammunition and tetraethyl lead manufacturing, and others. High levels of lead in the environment can cause a variety of adverse health effects when people are exposed to it at levels above the action level for relatively short periods of time. These effects may include interference with red blood cell chemistry, delays in normal physical and mental development in babies and young children, slight deficits in the attention span, hearing and learning abilities of children and slightly increases in the blood pressure of some adults (Madden et al., 2002).

World Health Organization (WHO) has stated that the permissible limit of lead in water cannot exceed 0.05 mg/l. Meanwhile, Malaysia Department of Environment (DOE) has stated that the acceptable conditions for industrial effluent for Standard A are 0.1 mg/l and for Standard, B is 0.5 mg/l. Figure 2.2 shows the illustration of lead metal in the form of solid state.

Figure 2.2 Lead metal

2.5 Treatment Methods

Wastewater treatment is very important in removing the unwanted particle in the wastewater. There are several conventional methods on removal the heavy metal in the wastewater. According to Science and Juang (2014), the method to remove the heavy metal includes chemical precipitation (Figure 2.3), ion exchange (Figure 2.4), electrochemical reduction, reverse osmosis, and lime coagulation. However, these types of method have been found to be limited since they often resulting problem. Most of them involve high capacity costs with recurring expenses which are not suitable for small-scale industries. It also generates a huge amount of sludge which is difficult to be disposed of. Besides that, the conventional removal treatment involving a high maintenance cost, expensive equipment, high sensitivity to operational condition and significant energy consumption.

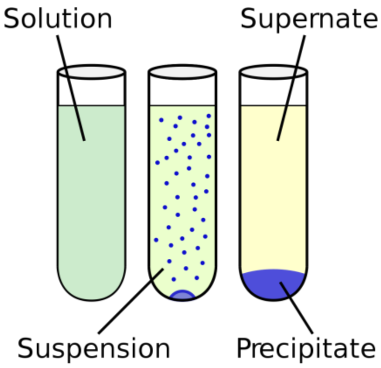

Figure 2.3 Chemical precipitation

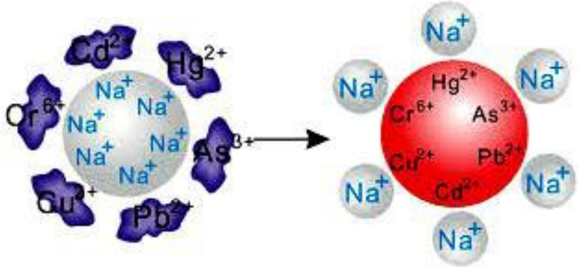

Figure 2.4 Ion exchange

2.5.1 Adsorption Process

Adsorption is referring to the process that occurs when gas and liquid solute accumulates on the surface of a solid and forming a molecular or atomic film or in other words, is the ability of a substance to physically hold another substance in its surface. This adsorption process happens when an unbalance force of attraction which is present at the solid surface has the property to attract and retain the molecules of a gas or a dissolved substance on to their surface which they come in contact. Figure 2.5 illustrates the adsorbate and adsorbent substance that occurs in an absorption process which adsorbate is referring to the substance which gets adsorbed on any surface. Meanwhile, the adsorbent is referring to the substance on the surface of which adsorption takes place.

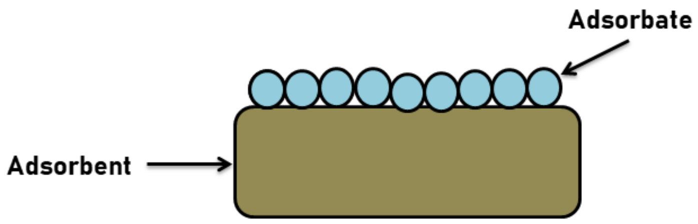

Figure 2.5 Adsorption process

Adsorption is one of the methods on removal heavy metal with lower cost. This method is classified as an easy method to be conducted and does not require highly skilled labour. The cost of this method also is cheaper than the other conventional method. Romero-Cano (2016) has stated that adsorption techniques have been applied because of their high removal efficiency of stable wastewater pollutants compared to other conventional methods. The adsorbent that has been used in this method is usually by using activated carbon. Because of the high demand of the activated carbon in other advanced application make in increasing the cost of the adsorbent and effect on the cost of the adsorption method.

2.6 Bio-adsorbent

In recent years the use of low-cost materials as alternatives to activated carbon has been encouraged by all parties. Tun et al. (2017) stated that bio-adsorption is an environmentally friendly method to remove heavy metal. A lot of agricultural wastes that can be chosen as a bio-adsorbent. This method offers the advantage of low cost, good efficiency and production of sludge with high metal content are possible to avoid by the existence of metal recovery method from the loaded bio-adsorbent. According to Jena and Sahoo (2017) based on both environmental and economic points of view, the special attention has been focused on the use of natural adsorbents obtained from the natural materials and waste agricultural products as an alternative to replace the activated carbon on reducing the cost of the adsorption method. According to Tun et al. (2017), the bio-adsorption is the process of using bio-adsorbent involves a solid phase and a liquid phase (solvent) containing dissolved species to sorbet which is shown in Figure 2.6.

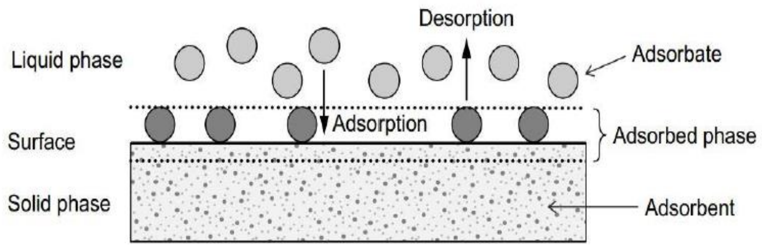

Figure 2.6 Adsorption phase

Recently, the use of fruits and its by-product have been widely investigated for their potential to remove heavy metals from wastewater. These include coconut shell, durian rind, banana peel, mango peel, mangosteen shell, pomegranate peel, mandarin peel, papaya wood, yellow passion fruit shell, grape waste, orange peel, coconut coir, and citrus peels. Fruits peel has been chosen because fruits wastes are cheap, unlimited, easily disposed by incineration and even can be reusable after being rejuvenated, can reduce the disposal cost and at the same time can reduce the fruits peel waste.

2.6.1 Orange Peel

Orange is the citrus-Sinensis species in the Rutaceae family also known as sweet orange. This fruits is originally from China and were found to be the most cultivated fruit tree. This type of fruits is widely grown in tropical and subtropical climates. According to Romero-Cano (2016), this material is considered waste in the food industry, for instance considering that in the preparation of an orange drink only the pulp is used and the rest of the fruit is discarded is evident that these residues have disposal due to the large volume they represent.

Orange peel consists of cellulose, pectin, hemicellulose, lignin, chlorophyll pigments and other low molecular weight hydrocarbons (A.G.El Said, 2012). However, these residues contain functional surface groups that are capable to bind contaminants. It has been observed that the properties of this material can be modified by a physical, chemical or physical-chemical previous treatment. Thereby, it is possible to accomplish higher adsorption capacities compared with untreated materials. Figure 2.7 illustrates the orange peel.

Figure 2.7 Orange peel

2.6.2 Banana Peel

Banana has come from two wild species which is known as Musa sapientum and Musa balbisiana. This type of fruits is variable in size and firmness with soft flesh rich in starch covered with a rind. It was also very rich in potassium and fibers. According to Wachirasiri et al. (2009), this material is classified as one of the most common crops grown in almost all tropical countries including, Malaysia.

This material is the cheaper agricultural product and banana chip and banana juice are the main products from the flesh produced. The banana peels waste is normally disposed of in municipal landfill which contributes to the existing environmental problem. It has been observed that the properties of this material can be modified by a physical, chemical or physical-chemical previous treatment. Thereby, it is possible to accomplish higher adsorption capacities compared with untreated materials. Figure 2.8 shows the banana peel.

Figure 2.8 Banana peel

2.6.3 Mango peel

Mango is one of the species from Mangifera indica L. which grows in 85 different counties and considered the most important tropical fruits in the world as it consumes 50% from the entire tropical fruits consumption. Mango fruit is highly perishable and has a limited shelf life due to postharvest desiccation and senescence, which limits their global distribution. Mango peel is the major by-product of mango processing and compromises 7-24% of the total mango weight. Mango is a highly perishable seasonal fruit and large quantities are wasted during the peak season as a result of poor postharvest handling procedures. Jawad et al. (2016) stated that mango peel contains different phytochemicals such as polyphenols, carotenoids, vitamin E, lactic acid, dietary fibers and exhibited good antioxidant properties which good in order to modify it becomes adsorbent. The illustration of mango peel is shown in Figure 2.9.

Figure 2.9 Mango peel

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter presents the methodology used in order to complete this study. The descriptions of each material and equipment are provided in section 3.2. Meanwhile, the analytical methods are explained in section 3.3. Section 3.4, illustrated the full experiment procedure from collecting wastewater until completing the test. Figure 3.1 below illustrates the study framework of the whole experimental work of the study.

3.2 Materials and Equipment

3.2.1 Wastewater Composition

The wastewater that has been used as the industrial wastewater which contents high heavy metal ions. The industrial wastewater has been taken from UMP Holding as the third party. UMP Holding was collected the industrial wastewater from some company located around Gebeng Industrial area and has informed that the company detail is confidential. The physical appearance of the wastewater that was provided was quite clear even through the heavy metal content in the water was high. Figure 3.2 shows the wastewater that had been collected from UMP Holding and ready for testing.

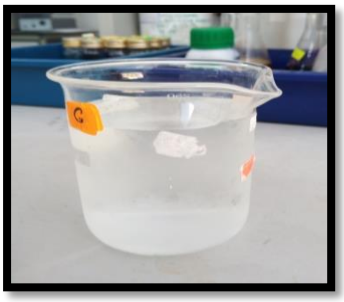

Figure 3.1 Sample of wastewater

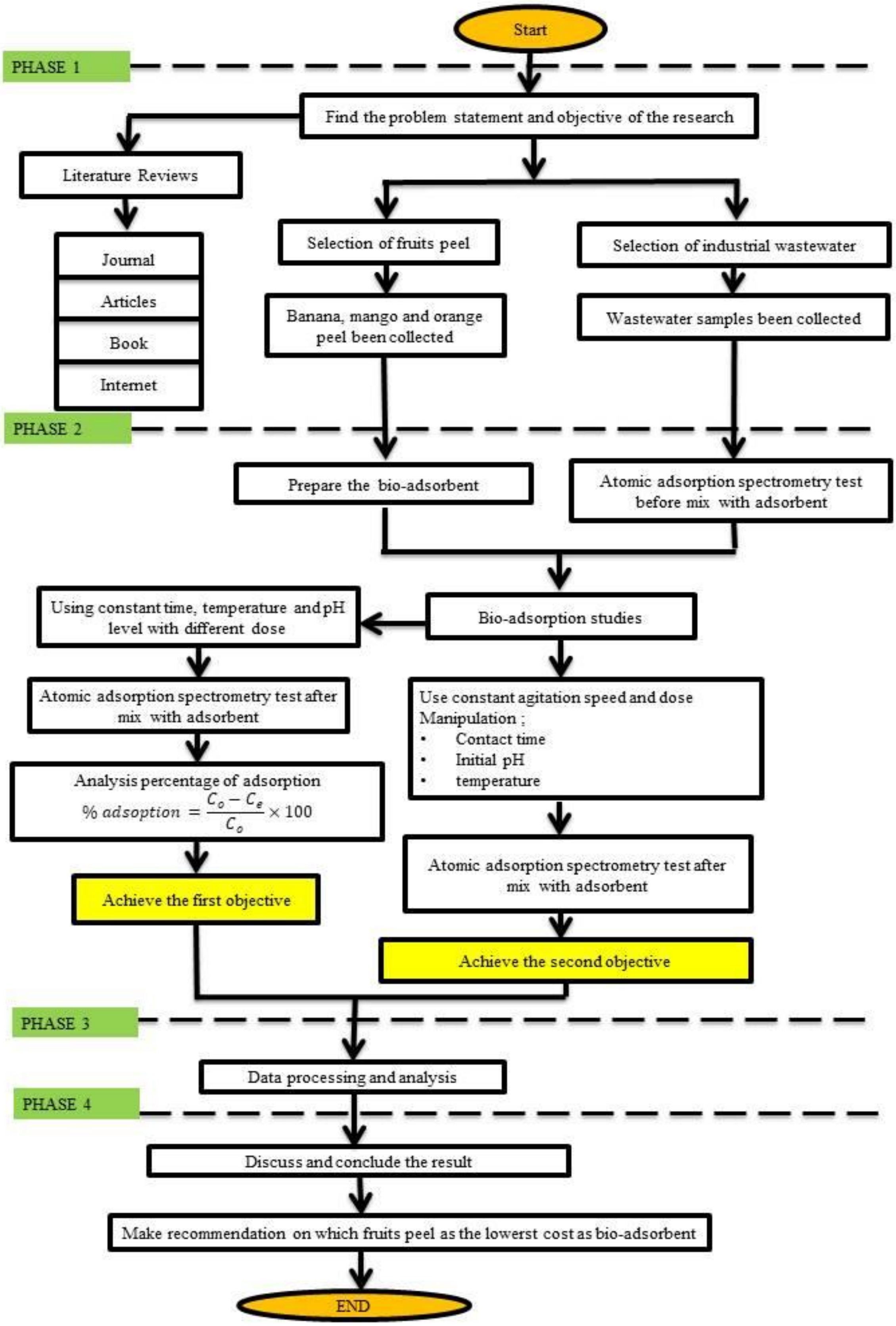

Figure 3.2 Study flowchart

3.2.2 Bio-adsorbent

In this study, the bio-adsorbent that had been produced was taken from the agriculture wastes which were orange, mango and banana peels. This type of fruits is among the popular fruits that can be easily found at any stall around Malaysia as it is producing widely at the factory because of the high demand for it. Orange, mango, and banana were usually had been used in order to get juice from it. Other than that, banana also is widely used to produce a healthy snack which is banana chips and usually, its peel will be treated as a waste. Nowadays, mango pickle has been very popular and become a high demand product. The production of mango pickle has made mango peel waste every day and because of that when the mango peel can be used as an adsorbent, it can reduce the waste. Besides that, this type of fruits peel is mostly composed of cellulose, hemicellulose, chlorophyll pigments which contain many hydroxyls functional group (-OH) which makes it as a potential matrix which can adsorb heavy metals. Figure 3.3, 3.4 and 3.5 show the adsorbent that used in this study in order to remove the heavy metal which is orange, banana and mango adsorbent.

Figure 3.3 Orange Adsorbent

Figure 3.4 Banana Adsorbent

Figure 3.5 Mango Adsorbent

3.2.3 Chemical and Reagents

3.2.3.1 Sample Preservation

Each of the wastewater samples should a representative of the environment condition. When the wastewater was collected, the physical and chemical properties of the wastewater may involve in changing of the composition. Because of that in order to keep the composition of the wastewater, the wastewaters need to be preserved. In this study, the water sample for heavy metals test should be preserved with nitric acid (HNO_3) with a concentration of 1:1. Besides, the water sample should be kept in the refrigerator with a temperature below than 4^0C. In addition, before the water samples are conducted for a laboratory test, it should be put out from the refrigerator for a few minutes until the wastewater sample temperature is in room temperature. This is because to ensure the chemical reaction between the water sample and reagent that used in the test can perfectly react. Nitric Acid (HNO_3) had been shown in Figure 3.6.

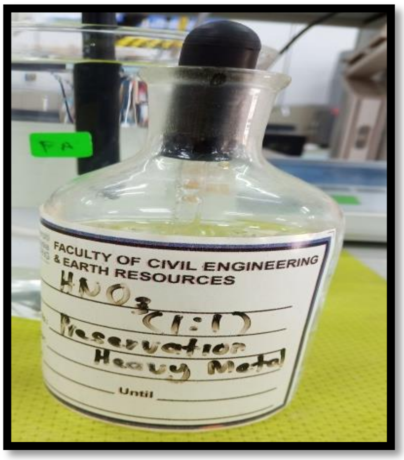

Figure 3.6 Nitric Acid (HNO_3)

3.2.3.2 pH Control

In order to check the effect of pH in this study, controlling the pH level is very important. The determination of standard pH in water and wastewater was conducted by the traceable procedure to APHA 4500H^{+} B (21^{st} Edition), Standard method for the Examination of Water and Wastewater. The principle of measuring pH is the determination of the activity of the hydrogen ions is by potentiometric measurement using a standard hydrogen electrode and a reference electrode. In order to adjust the pH level to the desired values, the chemical that had used was sodium hydroxide (NaOH) for increasing the pH level meanwhile to decrease the pH level, nitric acid (HNO_3) had been used. Figure 3.7 shows the equipment of the pH meter in order to control the pH value.

Figure 3.7 pH Meter

3.2.3.3 The standard for Atomic Absorption Spectrophotometry (AAS)

Atomic Absorption Spectrophotometry is one of the methods of checking heavy metal in a solution. In order to use AAS, it very important to prepare a standard solution for each heavy metal that needs to be checking. The standard solutions had been prepared with 5 different concentrations which are 0.25, 0.5, 0.75, 1.0 and 2.0 ppm. For copper standard, it used copper standard solution traceable to SRM from NIST Cu $(NO_3)_2$ 0.5mol/l and for lead standard, it used lead standard solution traceable to SRM from NIST Pb $(NO_3)_2$ 0.5mol/l. The calibration curve range for the standard must not less than 0.997 otherwise the standard cannot be used. Figure 3.8 and 3.9 show the cooper and lead standard that had used in this study.

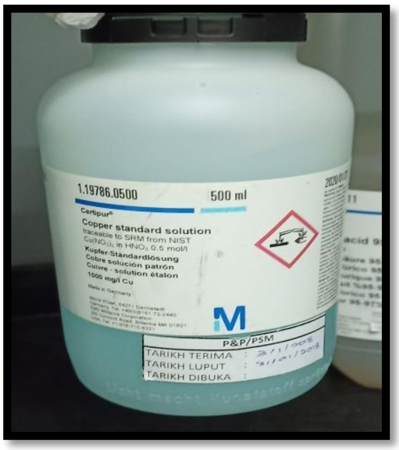

Figure 3.8 Cooper Standard

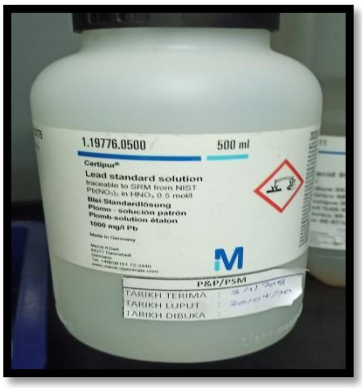

Figure 3.9 Lead Standard

3.2.4 Equipment

In this study, the equipment that had been used was list as Table 3.1.

Table 3.1 List of equipment

Equipment	Application
Drying oven	Use to dry out the moisture in the fruits peel about 24 hours at a temperature of 100°c.
Mortar and pestles	Use to prepare the adsorbent by crushing the fruit's peel.
Laboratory sieve	To sieve the fruit's peel that had been crush to the desired size which is 1.15 mm.
Precision balance	A device that uses to weight the adsorbent that will be used in the experiment. This is to control the dosage of the adsorbent.
Thermometer	Use to check the temperature of the wastewater, so when doing the experiment it can control the temperature.
pH meter	To detect the pH value of the sample of wastewater either it acidic, neutral or alkaline condition.
Shaker (IKA)	Used to mix, blend and agitate substances in the conical flask with the constant shaker speed which is 150 rpm.
Water bath	To control the temperature of wastewater in order to check the effect of temperature.
AAS	Use to determine the chemical element in the wastewater by using the adsorption of optical radiation by free atoms in the gaseous state.

Figure 3.10 shows the AAS that had been used in order for checking the presence of heavy metal in solution.

Figure 3.10 AAS equipment

3.3 Analytical Method

3.3.1 Batch Adsorption Studies

For this study, the parameter analysis that has been conducted was for determining the concentration of heavy metal before and after treatment for copper and lead. In order to achieve the objective of this study on determining the concentration of heavy metal, the water sample was analyzed by using Atomic Absorption Spectrometry (AAS). Eq.1 and Eq.2 show the equation for the removal efficiency of heavy metal.

$$Amount\ of\ adsorption\ at\ equilibrium(q_e) = \frac{(C_o - C_e)V}{X} \quad \text{(Eq. 1)}$$

$$Percentage\ of\ adsorption(\%) = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \quad \text{(Eq. 2)}$$

$C_o = initial\ \ concentration\ (mg/l)$

$C_e = \ equilibrium\ concentration\ (mg/l)$

$V = \ volume\ of\ solution\ (l)$

$X = weight\ of\ adsorbent\ (g)$

3.3.2 Adsorption Isotherms

Adsorption isotherm expresses the relation between the amount of adsorbed metal ions per unit mass of bio-sorbent (q_e) and the metal concentration in solution (C_e) at equilibrium. The data of sorption equilibrium in this work was tested with Langmuir adsorption isotherm using Eq.3.

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad \text{(Eq. 3)}$$

$C_e = \ equilibrium\ concentration\ (mg/l)$
$q_e = amount\ of\ adsorption\ at\ equilibrium (mg/g)$
$b = constant\ related\ to\ the\ energy\ (L/mg)$
$Q_o = \ mass\ of\ adsorbed\ solute\ required\ to\ saturate\ a\ unit\ mass\ of\ adsorbent\ (mg/g)$

By plotting C_e/q_e vs C_e, Q_o and b can be determined from the slope and intercepts respectively. The important features of the Langmuir Isotherm can be expressed in term of equilibrium parameter R_L which is a dimensionless constant which as Eq.4.

$$R_L = \frac{1}{1+bC_o} \quad \text{(Eq.4)}$$

3.4 Experimental Procedures

3.4.1 Preparation of Adsorbent

In this study, the fruits peel waste that has been used is banana, mango, and orange peel. The fruits were collected from fruit juice stalls at Café of Kolej Kediaman 3, University Malaysia Pahang. The fruits peel was washed with the tap water and 3 times in distilled water to remove the unwanted materials such as dirt and sand from the peels. Then the fruit's peel was dried under the hot sun until the water on it dried. After that, the fruit's peel was cut into a small piece. Next, the fruit's peel was dried in an oven at 100^oc for about 24 hours. After the drying, the adsorbent was crush using mortar and pestles and was sieved using sieve size 3.35 mm, 1.18 mm and pan. The adsorbent that retains at size 1.18 mm is the only one that has been used. Figure 3.11 shows the step in preparing the adsorbent.

(a)

(b)

(c)

(d)

Figure 3.11 Step of adsorbent preparation (a) washed the fruit's peel, (b) dried the fruits peel in the oven, (c) crush the fruits peel and (d) sieve the adsorbent

3.4.2 Preparation of Wastewater

The industrial wastewater was collected at UMP Holding, Jalan Sungai Karang Darat, 26100 Kuantan Pahang. After collecting the wastewater, the samples were preserved by reducing the pH level under 2 (Figure 3.12) before store it inside the refrigerator with a temperature below 4ºc. Before the wastewater was conducted for a laboratory test, it should be put out from the refrigerator for a few minutes until the wastewater sample temperature is in room temperature.

Figure 3.12 Preservation of wastewater

3.4.3 Bio-adsorption Studies

A batch of bio-adsorption studies was conducted to determine the adsorption capacity of a metal. The tests were performed for the bio-adsorption of heavy metal as a function of adsorbent dose, initial pH, and temperature and contact time. The entire test was using a constant volume of sample which is 50 ml. Adsorption test was carried out in 100ml conical flask at a constant shaking speed of 150 rpm. For investigate the optimum dosage, the dose that was used in this experiment is 0.4, 0.8, 1.2, 1.6 and 2 g. In order to investigate the effect of pH level, the pH range on conducting this test is 2-8. All the experiments were carried out at room temperature 28^{o}c ± 2^{o}c but to look at the effect of temperature, the temperature was controlled by using a water bath at range 29-49^{o}c. For the effect of time, the contact time that was used is 60, 80, 100, and 120 minutes and for the other test, the contact time is constant by using 120 minutes. The controls without the bio-adsorbent were also were run parallel. The concentration of the heavy metal ions in solution before and after bio-adsorption was determined using atomic adsorption spectrophotometer by monitoring the absorbance for metal ion used but before the testing, the sample needs to be filler first before can check in AAS.

Figure 3.13 Adsorption test

Figure 3.14 Checking heavy metal using AAS

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

The objective for this study was to determine the optimum adsorption capacity of three types of fruits peel which was orange, banana, and mango as a bio-adsorption in treating industrial wastewater and comparing the effect in term of initial pH, temperature and contact time in removal heavy metal. This chapter describes the results of the experimental study. The result and explanation of the adsorption studies contained in section 4.2 in term of dosage, pH level, temperature and contact time. Meanwhile, in section 4.3 contain about adsorption isotherms study.

4.2 Batch Adsorption Studies

4.2.1 Adsorption in term of dosage

In order to find the optimum adsorption capacity for different fruit peel, the different dosage of adsorbent has been used with constant size of adsorbent, contact time, the volume of sample, temperature, pH level and agitation speed which were 1.18mm, 120min, 50ml, 28°c, pH 4 and 150 rpm respectively. Table 4.1, 4.2 and 4.3 shows the result of orange, banana and mango adsorbent in term of dosage.

Table 4.1 Result of Orange adsorbent

Dose (g)	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal, C_e (mg/l)	Amount of adsorption at equilibrium (mg/g)	Percentage of adsorption (%)
0.4	0.886	0.675	0.182	24
0.8	0.888	0.648	0.200	27
1.2	0.885	0.583	0.244	34
1.6	0.920	0.620	0.273	33
2	0.923	0.664	0.259	28

Table 4.2 Result of Banana adsorbent

Dose (g)	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal, C_e (mg/l)	Amount of adsorption at equilibrium (mg/g)	Percentage of adsorption (%)
0.4	0.961	0.784	0.184	18
0.8	0.951	0.710	0.268	25
1.2	0.991	0.750	0.251	24
1.6	1.017	0.794	0.196	22
2	1.035	0.854	0.174	17

Table 4.3 Result of Mango adsorbent

Dose (g)	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal, C_e (mg/l)	Amount of adsorption at equilibrium (mg/g)	Percentage of adsorption (%)
0.4	0.981	0.873	0.108	11
0.8	0.984	0.864	0.109	12
1.2	0.988	0.845	0.159	14
1.6	0.999	0.828	0.134	17
2	0.991	0.850	0.124	14

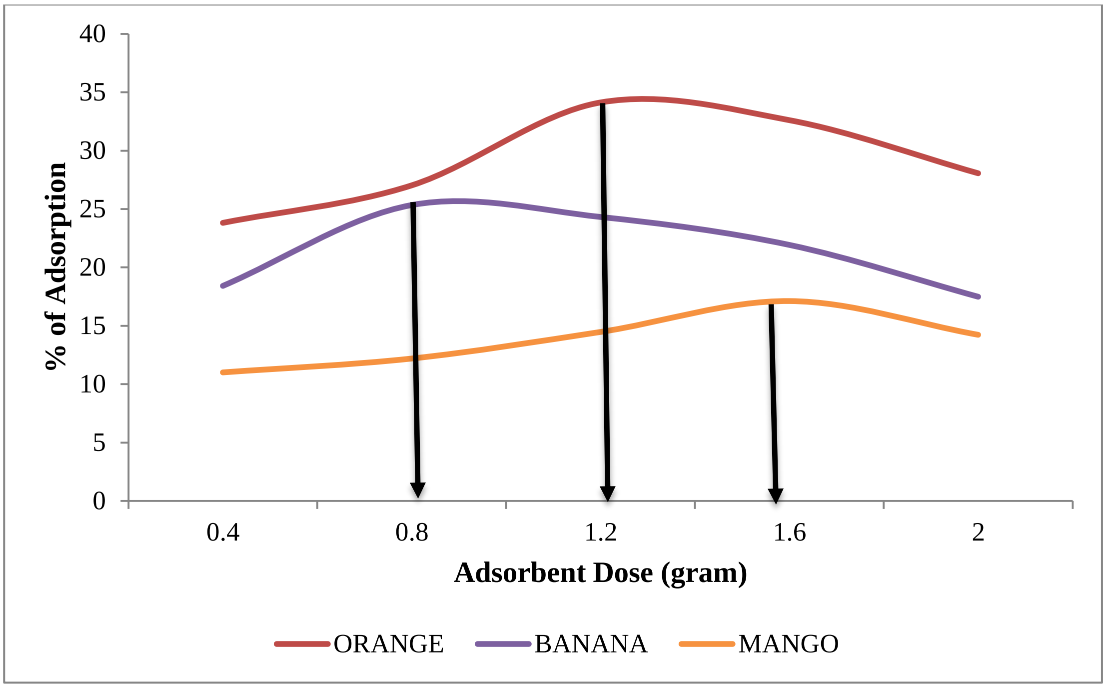

Figure 4.1 The percentages of adsorption against adsorbent dose

Based on Figure 4.1, the percentage of adsorption increases for an increase in adsorbent dose but it drops down when it achieves the optimum capacity of that adsorbent. Based on that, the optimum capacity that can be absorbed by orange adsorbent is 1.2 gram meanwhile for the mango adsorbent it reaches to 1.6 gram while banana adsorbent only needs 0.8 gram to reach the optimum dosage. The maximum adsorption capacities for orange, banana and mango are 0.273mg/g, 0.268mg/g and 0.159mg/g. By comparing the percentage of adsorption, mango adsorbent can absorb much lower than the other adsorbent. It only absorbs around 15% compared to orange and banana adsorbent which can absorb 35% and 25% respectively. It indicates that the orange adsorbent has much surface area compared to the other two as its availability of binding more heavy metal.

4.2.2 Adsorption in term of pH

Different pH level was used with constant size of adsorbent, contact time, the volume of sample, temperature and agitation speed which is 1.18mm, 120 min, 50 ml, 28°c ± 2°c (room temperature) and 150 rpm. The dose that was used was using the optimum dose that has been got from the previous experiment. Meanwhile, the dosage that has been used for orange, banana, and mango was 1.2, 0.8 and 1.6 gram respectively. Table 4.4 indicated the result of adsorption for 1.2-gram dosage. Meanwhile, Table 4.5 and 4.6 shows the result of adsorption for 0.8 gram and 1.6 gram respectively.

Table 4.4 Result of Orange adsorbent

pH Level	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal, C_e (mg/l)	Amount of adsorption at equilibrium (mg/g)	Percentage of adsorption (%)
2	0.478	0.395	0.048	17
4	0.458	0.394	0.039	14
6	0.448	0.375	0.045	16
8	0.567	0.485	0.051	14

Table 4.5 Result of Banana adsorbent

pH Level	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal, C_e (mg/l)	Amount of adsorption at equilibrium (mg/g)	Percentage of adsorption (%)
2	0.789	0.476	0.191	40
4	0.846	0.446	0.256	47
6	0.789	0.492	0.186	38
8	0.815	0.513	0.174	37

Table 4.6 Result of Mango adsorbent

pH Level	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal, C_e (mg/l)	Amount of adsorption at equilibrium (mg/g)	Percentage of adsorption (%)
2	0.812	0.555	0.153	32
4	0.811	0.559	0.166	31
6	0.791	0.604	0.115	24
8	0.811	0.608	0.145	25

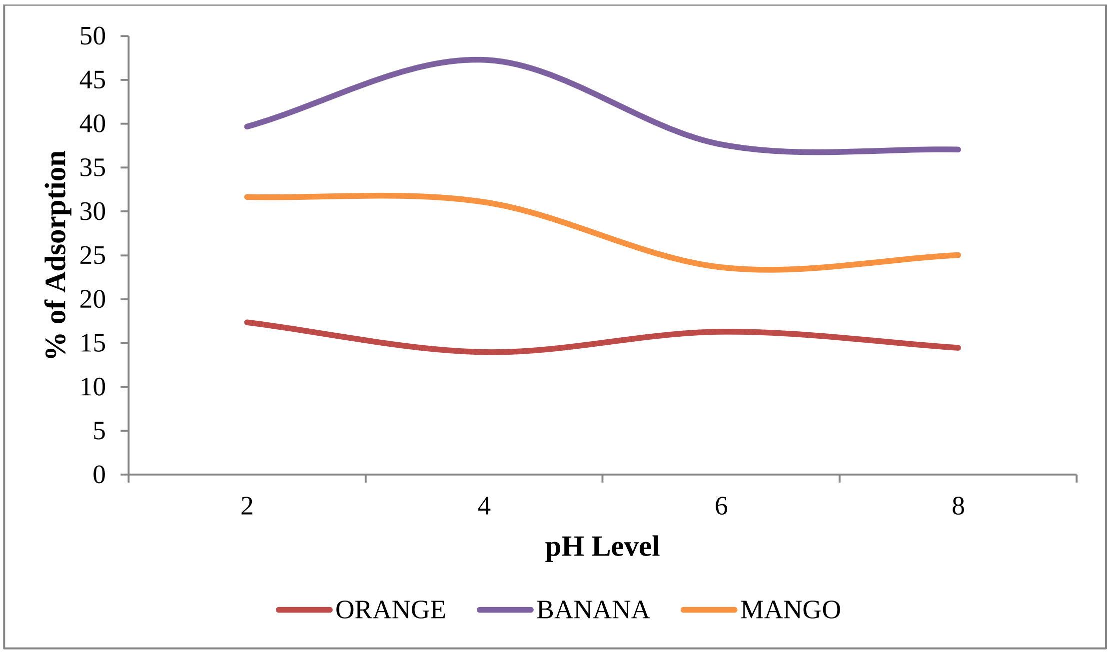

Figure 4.2 Result between the percentages of adsorption against pH level

The effect of pH level is the important factor that affects the percentage of adsorption due to its ability to affect the solution chemistry of metal as well as the surface properties of adsorbent. The maximum percentage of adsorption for orange, banana, and mango was 17%, 47%, and 32% respectively. Meanwhile, the maximum uptake of the orange, banana, and mango is 0.051mg/g, 0.256mg/g and 0.166mg/g respectively. It indicates that banana adsorbent can absorb more heavy metal compared to the other adsorbent. Based on Figure 4.2, the best pH level for orange and mango was in pH level 2 meanwhile for the banana the best pH level was in level 4.

4.2.3 Adsorption in term of temperature

In order to determine the effect of the temperature for different fruit's peel, the different temperature was used with constant size of adsorbent, contact time, the volume of sample, pH level and agitation speed which is 1.18mm, 120 min, 50ml, pH 4 with 150rpm. Meanwhile, the dose that was used was using the optimum dose that has been got from the previous experiment. The dosage that has been used for orange, banana, and mango is 1.2, 0.8 and 1.6 gram respectively. Result of adsorption for orange, banana and mango adsorbent with different dosage is shown in Table 4.7, 4.8 and 4.9 respectively

Table 4.7 Result of Orange adsorbent

Temperature (°c)	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal, C_e (mg/l)	Amount of adsorption at equilibrium (mg/g)	Percentage of adsorption (%)
29	0.864	0.255	0.435	70
39	0.879	0.253	0.489	71
49	0.845	0.239	0.439	72

Table 4.8 Result of Banana adsorbent

Temperature (°c)	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal, C_e (mg/l)	Amount of adsorption at equilibrium (mg/g)	Percentage of adsorption (%)
29	0.862	0.292	0.460	66
39	0.870	0.284	0.431	67
49	0.875	0.273	0.478	69

Table 4.9 Result of Mango adsorbent

Temperature (°c)	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal, C_e (mg/l)	Amount of adsorption at equilibrium (mg/g)	Percentage of adsorption (%)
29	0.890	0.356	0.405	60
39	0.877	0.314	0.327	64
49	0.875	0.285	0.351	67

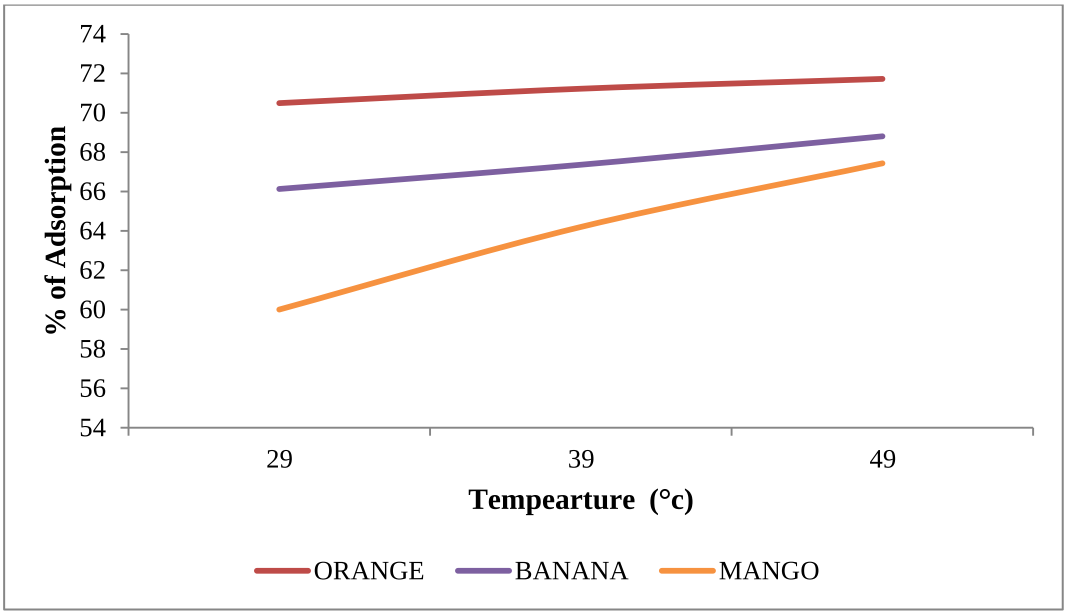

Figure 4.3 Graph between the percentages of adsorption against temperature

Based on Figure 4.3, it shows that the graph is increased gradually which indicates that the adsorption process was endothermic in nature. Other than that, it shows that the percentage of adsorption for orange adsorbent is much higher compared with banana and mango adsorbent. The percentage of adsorption was insignificantly changed at the temperature of 29ºc until 49ºc. In average, it only absorbs about 71%, 67% and 64% for orange, banana and mango adsorbent. Meanwhile, the uptake of metal adsorption for orange, banana and mango adsorbent is about 0.489mg/g, 0.478mg/g and 0.405mg/g respectively. It can indicate that the temperature at an average of 29ºc until 49ºc does not influence the efficiency of adsorption.

4.2.4 Adsorption in term of contact time

Different contact time was used with a constant size of adsorbent, temperature, the volume of sample, pH level and agitation speed which is 1.18mm, 28°c ± 2°c (room temperature), 50 ml, pH 4 and 150 rpm in order to identify the effect of the contact time. The dose was using the optimum dose that has been got from the previous experiment. The dosage of the absorbent that was used for orange, banana, and mango is 1.2, 0.8 and 1.6 gram respectively. The adsorption results in term of contact time for orange, banana and mango adsorbent has shown in Figure 4.10, 4.11 and 4.12.

Table 4.10 Result of Orange adsorbent

Contact time (min)	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal, C_e (mg/l)	Amount of adsorption at equilibrium (mg/g)	Percentage of adsorption (%)
60	0.356	0.314	0.060	12
80	0.352	0.254	0.126	28
100	0.340	0.231	0.160	32
120	0.333	0.216	0.154	35

Table 4.11 Result of Banana adsorbent

Contact time (min)	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal, C_e (mg/l)	Amount of adsorption at equilibrium (mg/g)	Percentage of adsorption (%)
60	0.340	0.249	0.126	27
80	0.375	0.257	0.159	31
100	0.381	0.251	0.186	34
120	0.402	0.264	0.197	34

Table 4.12 Result of Mango adsorbent

Contact time (min)	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal, C_e (mg/l)	Amount of adsorption at equilibrium (mg/g)	Percentage of adsorption (%)
60	0.420	0.310	0.172	26
80	0.403	0.289	0.173	28
100	0.455	0.310	0.213	32
120	0.524	0.342	0.276	35

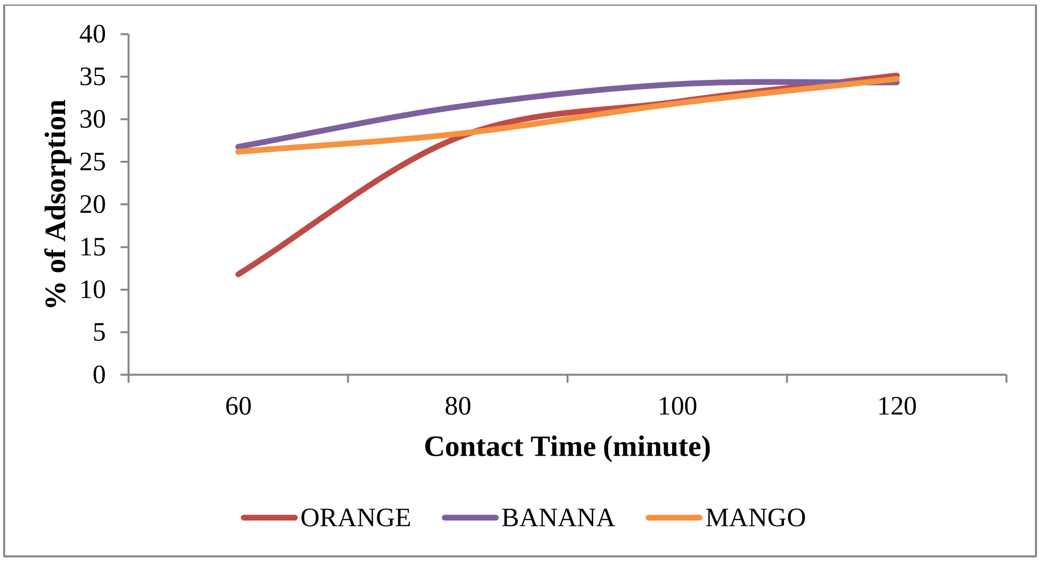

Figure 4.4 Profile of adsorption efficiency at different contact time

Figure 4.4 shows the increments of the percentage of adsorption against contact time. For the orange adsorbent, it increases rapidly at the first 20min and increases slowly at the remaining contact time. A possible reason for these results may be because there was a large number of vacant active binding sites available in the first phase which can absorb more metal ion. For banana and mango adsorbent, it gradually increases with the increase of contact time and the percentage of adsorption for these three adsorbents were insignificantly from one another. The maximum adsorption capacities for orange, banana and mango adsorbent found to be 35%, 34%, and 35% respectively. Meanwhile, the highest uptake is about 0.16mg/g, 0.197mg/g and 0.276mg/g for the orange, banana and mango adsorbent.

4.3 Adsorption Isotherms

4.3.1 Adsorption in term of dosage

Table 4.13, 4.14 and 4.15 shows a table of Langmuir results for orange, banana and mango adsorbent respectively. Meanwhile, Figure 4.5, 4.6 and 4.7 illustrate the graph C_e/q_e against C_e for each fruit's peel.

Table 4.13 Result of Orange adsorbent

Dose (g)	C_o (mg/l)	C_e (mg/l)	q_e (mg/g)	C_e/q_e	Q_o (mg/g)	b (L/mg)	R_L
0.4	0.886	0.675	0.182	3.711	11.609	4.5705	0.19
0.8	0.888	0.648	0.200	3.240			
1.2	0.885	0.583	0.244	2.394			
1.6	0.920	0.620	0.273	2.273			
2	0.923	0.664	0.259	2.564			

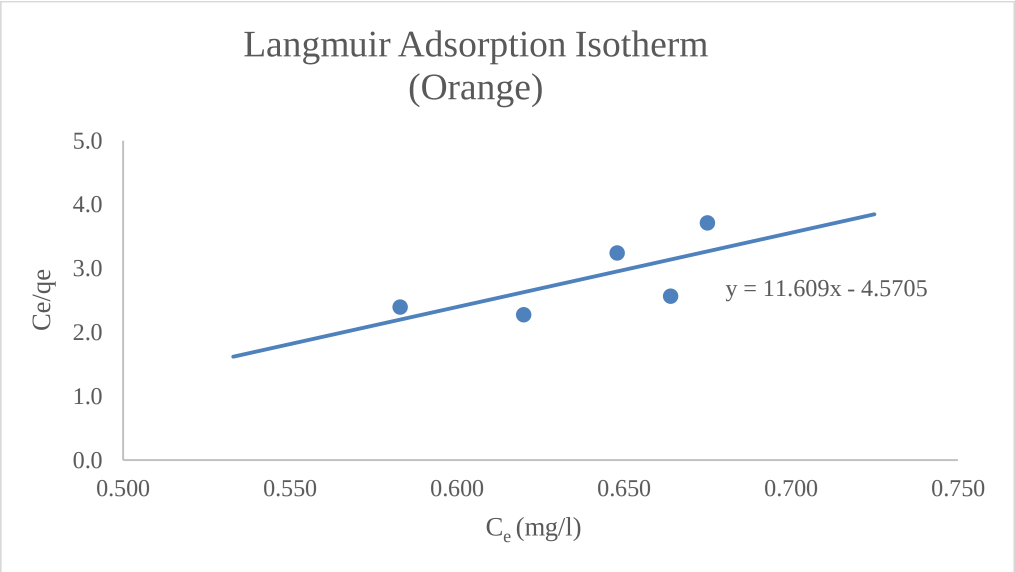

Figure 4.5 Langmuir adsorption isotherm for orange

Table 4.14 Result of Banana adsorbent

Dose (g)	C_o (mg/l)	C_e (mg/l)	q_e (mg/g)	C_e/q_e	Q_o (mg/g)	b (L/mg)	R_L
0.4	0.961	0.784	0.184	4.252	16.722	9.2453	0.09
0.8	0.951	0.710	0.268	2.651			
1.2	0.991	0.750	0.251	2.988			
1.6	1.017	0.794	0.196	4.059			
2	1.035	0.854	0.174	4.907			

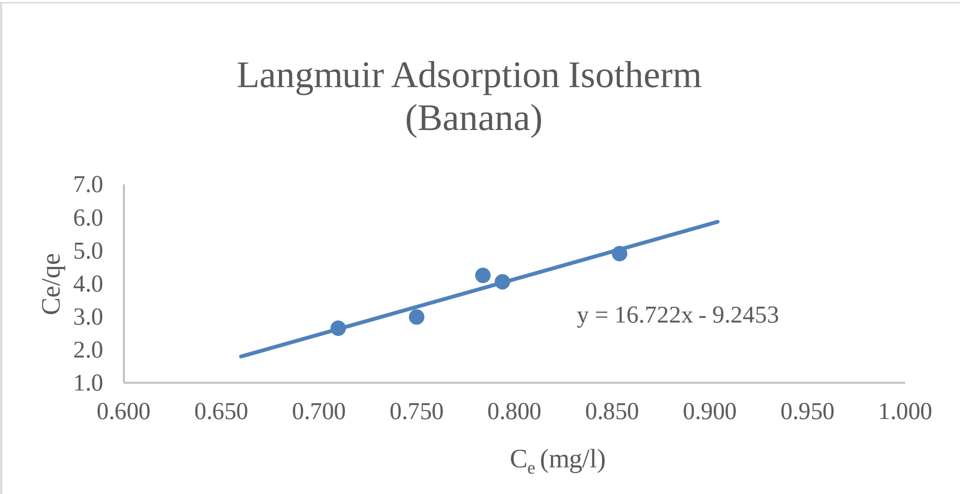

Figure 4.6 Langmuir adsorption isotherm for banana

Table 4.15 Result of Mango adsorbent

Dose (g)	C_o (mg/l)	C_e (mg/l)	q_e (mg/g)	C_e/q_e	Q_o (mg/g)	b (L/mg)	R_L
0.4	0.981	0.873	0.108	8.083	53.598	38.788	0.03
0.8	0.984	0.864	0.109	7.920			
1.2	0.988	0.845	0.159	5.318			
1.6	0.999	0.828	0.134	6.198			
2	0.991	0.850	0.124	6.872			

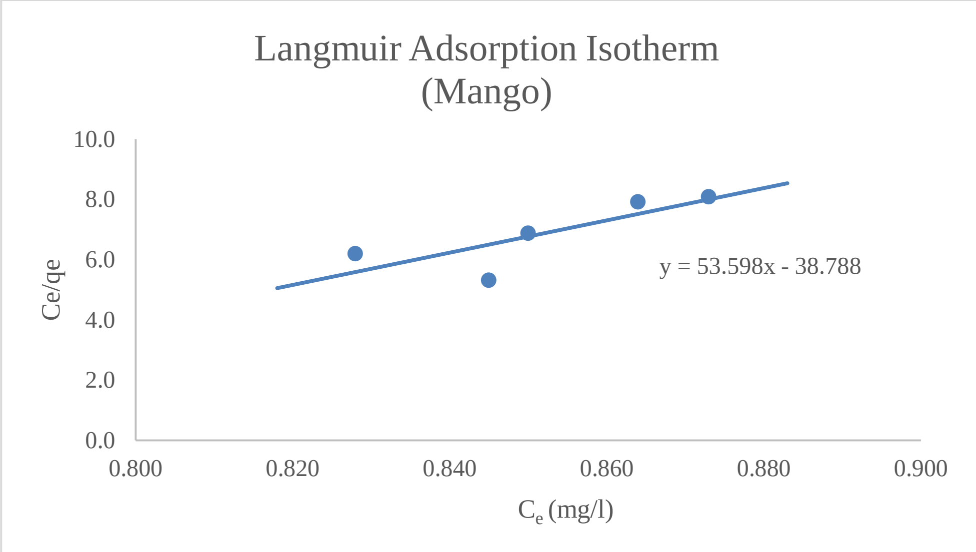

Figure 4.7 Langmuir adsorption isotherm for mango

For the orange absorbent, based on Figure 4.5 by plotting graph C_e/q_e against C_e it indicates that Q_o is 11.609 mg/g meanwhile b equal to 4.5705 L/mg. For banana and mango adsorbent, it indicates that Q_o is 16.722 mg/g and 53.598 mg/g. The value of b is equal to 9.2453 L/mg and 38.788 L/mg. Based on further analysis of the Langmuir equation, it may be expressed in term of equilibrium parameter R_L which referred to as separation factor or equilibrium parameter. Based on Table 4.13, 4.15 and 4.16 the value of R_L is about 0.19, 0.09 and 0.03 respectively which indicate favorable adsorption which proving that the adsorption data fitted well to Langmuir Isotherm Model.

4.3.2 Adsorption in term of pH level

The Langmuir result for orange, banana and mango adsorbent is shown in Table 4.16, 4.17 and 4.18 and the graph of Langmuir is shown in Figure 4.8, 4.9 and 4.10

Table 4.16 Result of Orange adsorbent

pH Level	C_o (mg/l)	C_e (mg/l)	q_e (mg/g)	C_e/q_e	Q_o (mg/g)	b (L/mg)	R_L
2	0.478	0.395	0.048	8.281	8.2042	5.688	0.24
4	0.458	0.394	0.039	10.096			
6	0.448	0.375	0.045	8.322			
8	0.567	0.485	0.051	9.582			

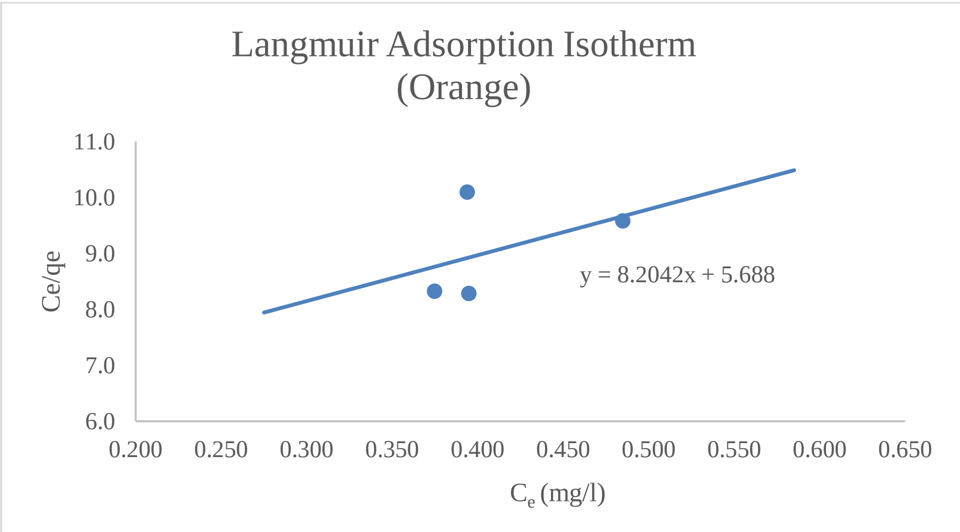

Figure 4.8 Langmuir adsorption isotherm for orange

Table 4.17 Result of Banana adsorbent

pH Level	C_o (mg/l)	C_e (mg/l)	q_e (mg/g)	C_e/q_e	Q_o (mg/g)	b (L/mg)	R_L
2	0.789	0.476	0.191	2.494	17.975	6.1994	0.17
4	0.846	0.446	0.256	1.739			
6	0.789	0.492	0.186	2.651			
8	0.815	0.513	0.174	2.956			

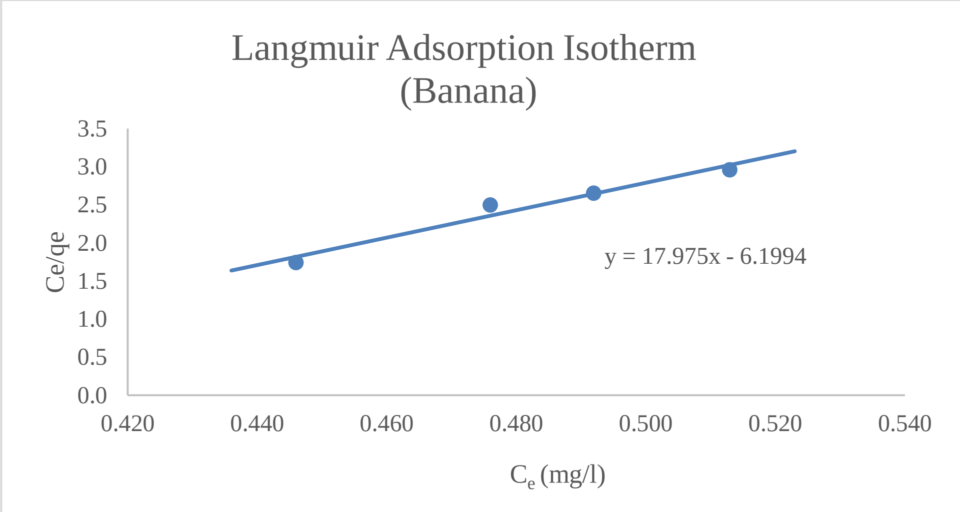

Figure 4.9 Langmuir adsorption isotherm for banana

Table 4.18 Result of Mango adsorbent

pH Level	C_o (mg/l)	C_e (mg/l)	q_e (mg/g)	C_e/q_e	Q_o (mg/g)	b (L/mg)	R_L
2	0.812	0.555	0.156	3.628	23.518	9.5692	0.11
4	0.811	0.559	0.166	3.372			
6	0.791	0.604	0.115	5.233			
8	0.811	0.608	0.145	4.193			

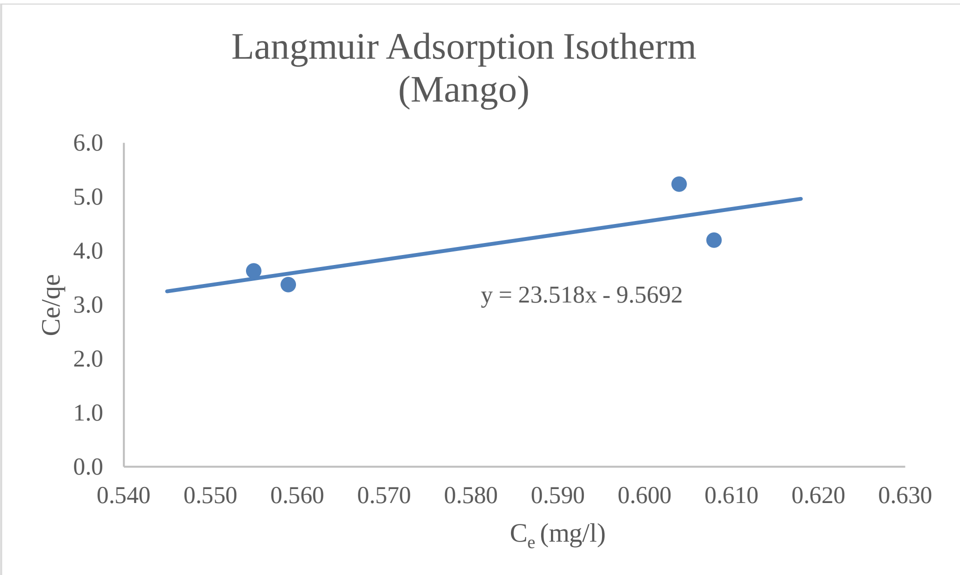

Figure 4.10 Langmuir adsorption isotherm for mango

Based on Figure 4.8, 4.9 and 4.10, by plotting graph Ce/qe against Ce, it indicates that the value of Q_o is 8.2042 mg/g, 17.975 mg/g and 23.518 mg/g respectively. Meanwhile, the value of b is equal to 5.688 L/mg, 6.1994 L/mg and 9.5692 L/mg. Based on further analysis of the Langmuir equation, it may be expressed in term of equilibrium parameter R_L which referred to as separation factor or equilibrium parameter. Based on Table 4.16, 4.17 and 4.18, the value of R_L is about 0.24, 0.17 and 0.11 respectively which indicate favorable adsorption which proving that the adsorption data fitted well to Langmuir Isotherm Model.

4.3.3 Adsorption in term of temperature

Figure 4.11, 4.12, 4.13 shows the graph of Langmuir and Table 4.19, 4.20, and 4.21 shows the result of Langmuir for each fruit's peel.

Table 4.19 Result of Orange adsorbent

Temperature (ºc)	C_o (mg/l)	C_e (mg/l)	q_e (mg/g)	C_e/q_e	Q_o (mg/g)	b (L/mg)	R_L
29	0.864	0.255	0.435	0.586	0.9469	0.3135	0.78
39	0.879	0.253	0.489	0.517			
49	0.845	0.239	0.439	0.544			

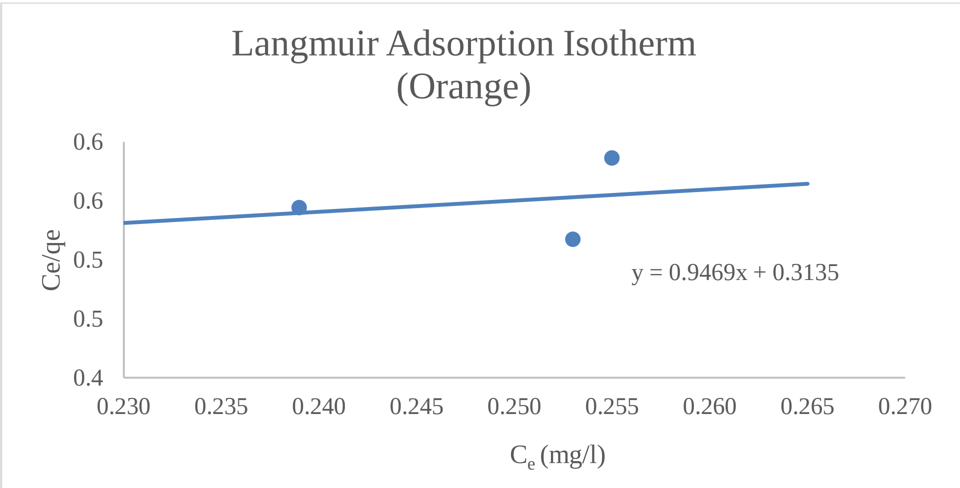

Figure 4.11 Langmuir adsorption isotherm for orange

Table 4.20 Result of Banana adsorbent

Temperature (ºc)	C_o (mg/l)	C_e (mg/l)	q_e (mg/g)	C_e/q_e	Q_o (mg/g)	b (L/mg)	R_L
29	0.862	0.292	0.460	0.635	3.6385	0.4078	0.74
39	0.870	0.284	0.431	0.659			
49	0.875	0.273	0.478	0.571			

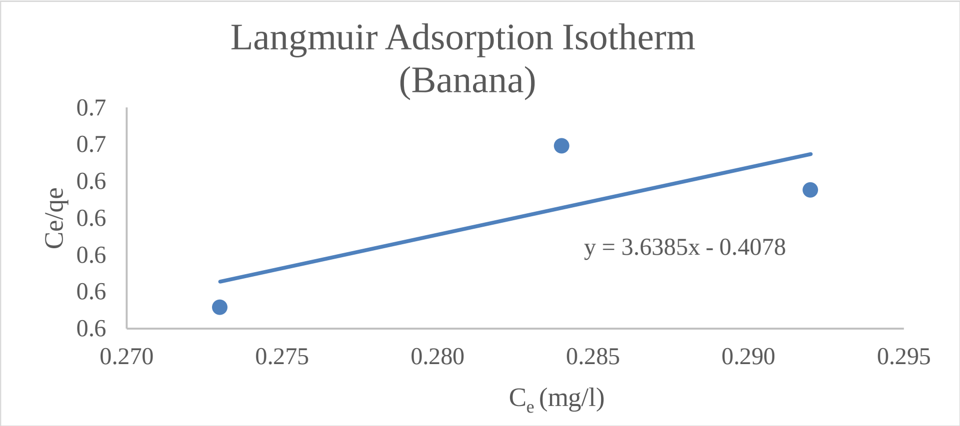

Figure 4.12 Langmuir adsorption isotherm for banana

Table 4.21 Result of Mango adsorbent

Temperature (ºc)	C_o (mg/l)	C_e (mg/l)	q_e (mg/g)	C_e/q_e	Q_o (mg/g)	b (L/mg)	R_L
29	0.890	0.356	0.405	0.880	0.7607	0.6414	0.64
39	0.877	0.314	0.327	0.959			
49	0.875	0.285	0.351	0.812			

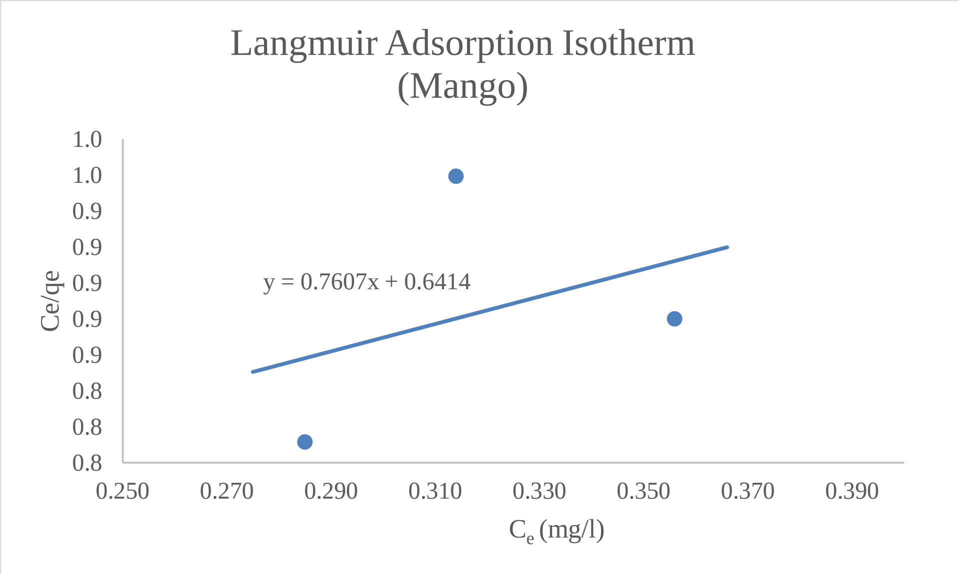

Figure 4.13 Langmuir adsorption isotherm for mango

For the orange absorbent, based on Figure 4.11 by plotting graph C_e/q_e against C_e it indicates that Q_o is 0.9469 mg/g meanwhile b equal to 0.3135 L/mg. For banana and mango adsorbent, it indicates that Q_o is 3.6385 mg/g and 0.7607 mg/g. The value of b is equal to 0.4078 L/mg and 0.6414 L/mg respectively. Based on further analysis of the Langmuir equation, it may be expressed in term of equilibrium parameter R_L which referred to as separation factor or equilibrium parameter. Based on Table 4.19, 4.20 and 4.21 the value of R_L is about 0.78, 0.74 and 0.64 respectively. All this adsorbent can be concluded as favorable adsorption which proving that the adsorption data fitted well to Langmuir Isotherm Model.

4.3.4 Adsorption in term of contact time

Table 4.22, 4.23 and 4.24 shows the table of Langmuir results for orange, banana and mango adsorbent respectively. Meanwhile, Figure 4.14, 4.15 and 4.16 illustrate the graph C_e/q_e against C_e for each fruit's peel.

Table 4.22 Result of Orange adsorbent

Contact Time (min)	C_o (mg/l)	C_e (mg/l)	q_e (mg/g)	C_e/q_e	Q_o (mg/g)	b (L/mg)	R_L
60	0.356	0.314	0.060	5.233	47.269	9.6906	0.23
80	0.352	0.254	0.126	2.022			
100	0.340	0.231	0.160	1.441			
120	0.333	0.216	0.154	1.403			

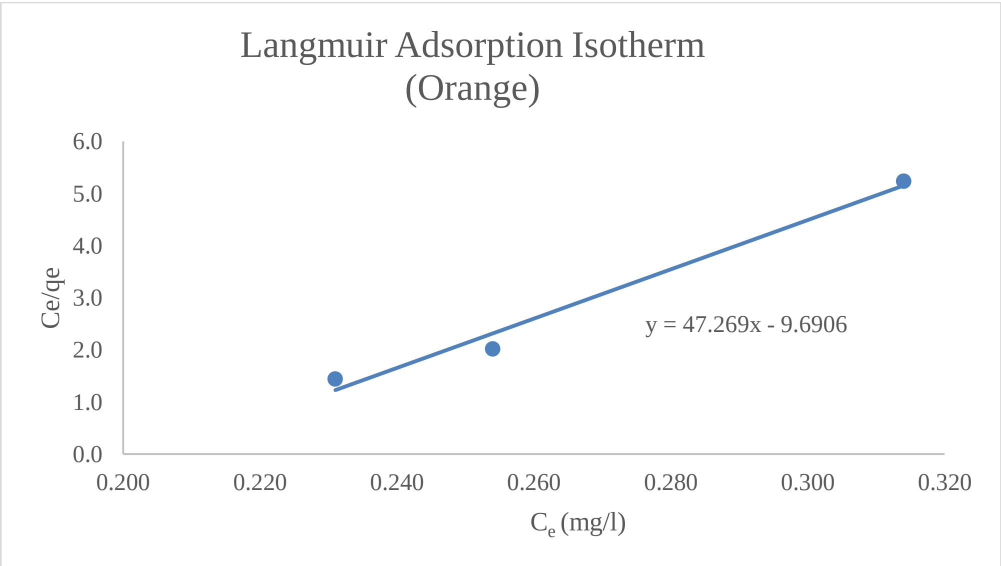

Figure 4.14 Langmuir adsorption isotherm for orange

Table 4.23 Result of Banana adsorbent

Contact Time (min)	C_o (mg/l)	C_e (mg/l)	q_e (mg/g)	C_e/q_e	Q_o (mg/g)	b (L/mg)	R_L
60	0.340	0.249	0.126	1.970	-24.457	7.8158	0.25
80	0.375	0.257	0.159	1.612			
100	0.381	0.251	0.186	1.352			
120	0.402	0.264	0.197	1.339			

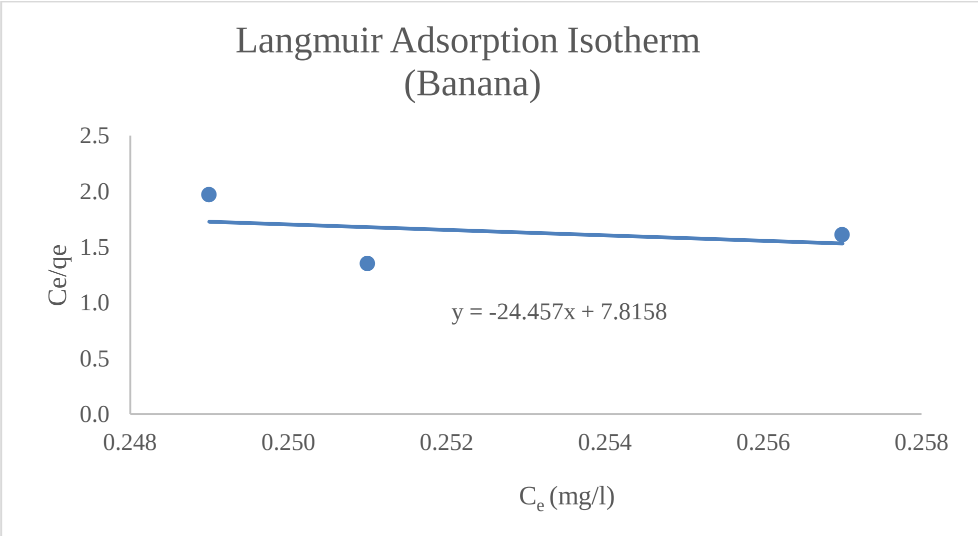

Figure 4.15 Langmuir adsorption isotherm for banana

. Table 4.24 Result of Mango adsorbent

Contact Time (min)	C_o (mg/l)	C_e (mg/l)	q_e (mg/g)	C_e/q_e	Q_o (mg/g)	b (L/mg)	R_L
60	0.420	0.310	0.172	1.804	-2.1163	2.2848	0.52
80	0.403	0.289	0.173	1.673			
100	0.455	0.310	0.213	1.454			
120	0.524	0.342	0.276	1.240			

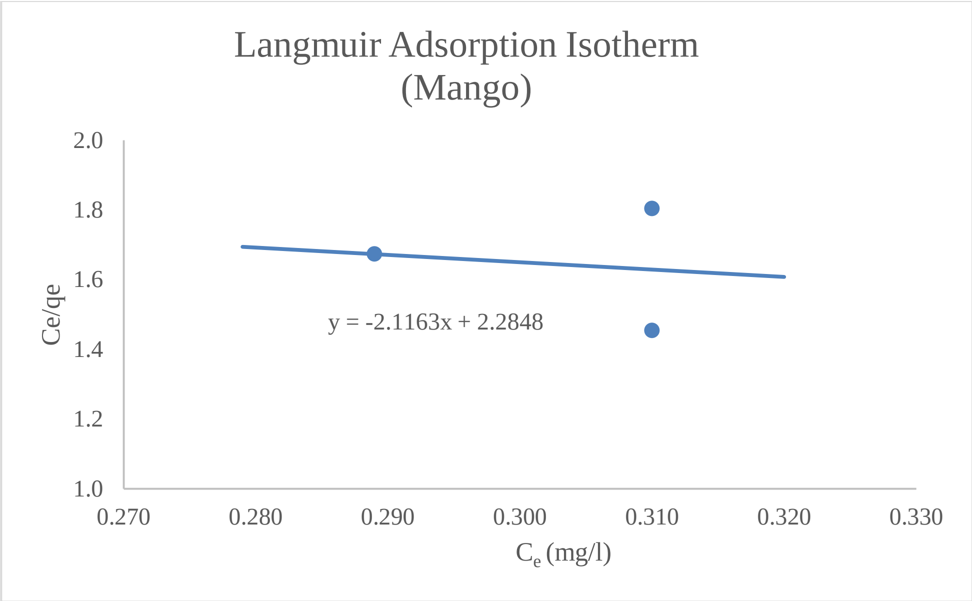

Figure 4.16 Langmuir adsorption isotherm for mango

For the orange absorbent, based on Figure 4.14 by plotting graph C_e/q_e against C_e it indicates that Q_o is 47.269 mg/g meanwhile b equal to 9.6906 L/mg. The graph shows linearly proportional foe orange adsorbent but for banana and mango adsorbent shows inversely proportional. For banana and mango adsorbent, it indicates that Q_o is -24.457 mg/g and -2.1163 mg/g. The value of b is equal to 7.8158 L/mg and 2.2848 L/mg. Based on further analysis of the Langmuir equation, it may be expressed in term of equilibrium parameter R_L which referred to as separation factor or equilibrium parameter. Based on Table 4.22, 4.23 and 4.24 the value of R_L is about 0.23, 0.25 and 0.52 respectively which indicate favorable adsorption which proving that the adsorption data fitted well to Langmuir Isotherm Model.

CHAPTER 5

CONCLUSION

5.1 Conclusion

In the present study, the performance of orange, banana and mango adsorbent in removing heavy metals from industrial wastewater was explored. In order to achieve the objective of this study, to determine the optimum adsorption capacity of orange, banana and mango peels adsorbent and to compare the effect of initial pH, temperature and contact time in removal heavy metal from industrial wastewater several tests have been conducted in the laboratory and analyzing the data based on four batch study that has been discussed in Chapter 4.

The following conclusions are drawn from the results obtained from this study:

1) The optimum adsorption capacity for an orange, banana, and mango peel adsorbent is around 1.2gram, 0.8gram, and 1.6gram respectively.

2) By comparing the effect of pH level by using optimum dosage for each fruit's peel, it shows that the best pH level for orange and mango is pH 4 meanwhile for banana pH 2 is the best pH level for that fruit's peel. This pH level is very important in order to control the adsorption capacities. By adjustment of the pH level, the activity of binding sites can also be altered. For the effect of temperature, we can conclude that the temperature at range 29^{o}c until 49^{o}c do not influence the efficiency of adsorption capacity. In term of contact time, the adsorbent will absorb rapidly at the first 20 min and gradually increase and remained stable after that as at the first phase of the experiment the lead ions were bound rapidly on the adsorbent and shortly become limited after that as the surface is full with those metal ions.

3) Langmuir adsorption model, the entire sample proving that the adsorption data fitted well to Langmuir Isotherm Model as the equilibrium parameter R_L is between 0 to 1 which indicate favorable adsorption.

4) The study revealed that the best fruits peel that can be used as an adsorbent is orange peel as it can absorb many lead ions compare with the other two fruits peel. Besides that, it can uptake about 0.489 mg/g which consider high compared to others and optimum dosage of orange peel in 1.2gram for 500ml of industrial wastewater.

5.2 Recommendation

There are several suggestion and recommendation for better research analysis and outcomes in the future. Recommendations for further students are as follows:

1) Conduct the study on the effect of concentration, agitation speed, and size of adsorbent to remove the heavy metal and need to verify and justification.

2) It highly recommended conducting the study on the effect of temperature at the high temperature as at the room temperature the adsorption is not much change.

3) Use different isotherm model for isotherm studies so that it can compare between one another can determine which of the model is the most suitable one.

4) Use different agriculture waste as adsorbents such as sugarcane bagasse, wheat straw, rice husk, tea waste, and others.

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APPENDIX A
TEMPLATE OF DATA COLLECTION

OBJECTIVE 1

Type of fruits peel: Orange

The volume of industrial wastewater: 50ml

Temperature: 28°c ± 2°c (room temperature)

Contact time: 120min @ 2jam

Size of adsorbent: 1.18mm

Agitation speed: 150rpm

pH level: 4

Label of wastewater	Dose (g)	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal after adsorption, C_e (mg/l)	Percentage of adsorption (%)
1	0.4			
2	0.8			
3	1.2			
4	1.6			
5	2.0			

Type of fruits peel: Banana

The volume of industrial wastewater: 50ml

Temperature: 28°c ± 2°c (room temperature)

Contact time: 120min @ 2jam

Size of adsorbent: 1.18mm

Agitation speed: 150rpm

pH level: 4

Label of wastewater	Dose (g)	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal after adsorption, C_e (mg/l)	Percentage of adsorption (%)
6	0.4			
7	0.8			
8	1.2			
9	1.6			
10	2.0			

Type of fruits peel: Mango

Size of adsorbent: 1.18mm

The volume of industrial wastewater: 50ml

Agitation speed: 150rpm

Temperature: 28°c ± 2°c (room temperature)

pH level: 4

Contact time: 120min @ 2jam

Label of wastewater	Dose (g)	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal after adsorption, C_e (mg/l)	Percentage of adsorption (%)
11	0.4			
12	0.8			
13	1.2			
14	1.6			
15	2.0			

OBJECTIVE 2

a. Effect of pH level

Type of fruits peel: Orange

Dose: optimum dose

Size of adsorbent: 1.18mm

Volume of industrial wastewater: 50ml

Agitation speed: 150rpm

Temperature: 28°c ± 2°c (room temperature)

Contact time: 120min @ 2jam

Label of wastewater	pH level	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal after adsorption, C_e (mg/l)	Percentage of adsorption (%)
16	2			
17	4			
18	6			
19	8			

Type of fruits peel: Banana | Dose: optimum dose

Size of adsorbent: 1.18mm | Volume of industrial wastewater: 50ml

Agitation speed: 150rpm | Temperature: 28°c ± 2°c (room temperature)

Contact time: 120min @ 2jam

Label of wastewater	pH level	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal after adsorption, C_e (mg/l)	Percentage of adsorption (%)
20	2			
21	4			
22	6			
23	8			

Type of fruits peel: Mango | Dose: optimum dose

Size of adsorbent: 1.18mm | Volume of industrial wastewater: 50ml

Agitation speed: 150rpm | Temperature: 28°c ± 2°c (room temperature)

Contact time: 120min @ 2jam

Label of wastewater	pH level	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal after adsorption, C_e (mg/l)	Percentage of adsorption (%)
24	2			
25	4			
26	6			
27	8			

b. Effect of temperature

Type of fruits peel: Orange | Dose: optimum dose

Size of adsorbent: 1.18mm | Volume of industrial wastewater: 50ml

Agitation speed: 150rpm | pH level: 4

Contact time: 120min @ 2jam

Label of wastewater	Temperature (°c)	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal after adsorption, C_e (mg/l)	Percentage of adsorption (%)
28	29			
29	39			
30	49			

Type of fruits peel: Banana | Dose: optimum dose

Size of adsorbent: 1.18mm | Volume of industrial wastewater: 50ml

Agitation speed: 150rpm | pH level: 4

Contact time: 120min @ 2jam

Label of wastewater	Temperature (°c)	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal after adsorption, C_e (mg/l)	Percentage of adsorption (%)
31	29			
32	39			
33	49			

Type of fruits peel: Mango

Dose: optimum dose

Size of adsorbent: 1.18mm

Volume of industrial wastewater: 50ml

Agitation speed: 150rpm

pH level: 4

Contact time: 120min @ 2jam

Label of wastewater	Temperature (°c)	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal after adsorption, C_e (mg/l)	Percentage of adsorption (%)
34	29			
35	39			
36	49			

c. Effect of time

Type of fruits peel: Orange

Dose: optimum dose

Size of adsorbent: 1.18mm

Volume of industrial wastewater: 50ml

Agitation speed: 150rpm

pH level: 4

Temperature: 28°c ± 2°c (room temperature)

Label of wastewater	Contact time (min)	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal after adsorption, C_e (mg/l)	Percentage of adsorption (%)
37	60			
38	80			
39	100			
40	120			

Type of fruits peel: Banana
Dose: optimum dose
Size of adsorbent: 1.18mm
Volume of industrial wastewater: 50ml
Agitation speed: 150rpm
pH level: 4
Temperature: 28°c ± 2°c (room temperature)

Label of wastewater	Contact time (min)	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal after adsorption, C_e (mg/l)	Percentage of adsorption (%)
41	60			
42	80			
43	100			
44	120			

Type of fruits peel: Mango
Dose: optimum dose
Size of adsorbent: 1.18mm
Volume of industrial wastewater: 50ml
Agitation speed: 150rpm
pH level: 4
Temperature: 28°c ± 2°c (room temperature)

Label of wastewater	Contact time (min)	The concentration of heavy metal before adsorption, C_o (mg/l)	The concentration of heavy metal after adsorption, C_e (mg/l)	Percentage of adsorption (%)
45	60			
46	80			
47	100			
48	120			