

REMOVAL OF HEAVY METALS FROM
INDUSTRIAL WASTEWATER USING
ACTIVATED CARBON MADE FROM LEMON
PEELS

NUR AMNANI BINTI ROSMAN

B. ENG(HONS.) CIVIL ENGINEERING

UNIVERSITI MALAYSIA PAHANG

UNIVERSITI MALAYSIA PAHANG

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Position : SENIOR LECTURE

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ID Number : AA13235

Date : 16 June 2017

REMOVAL OF HEAVY METALS FROM INDUSTRIAL WASTEWATER USING
ACTIVATED CARBON MADE FROM LEMON PEELS

NUR AMNANI BINTI ROSMAN

Thesis submitted in fulfillment of the requirements
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UNIVERSITI MALAYSIA PAHANG

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ABSTRACT

The heavy metal which is known as the toxic metal and normally caused by chemical waste, manufacturing, sewage, electroplating, mining and pharmaceuticals have been a main reason for various industrial wastewater nowadays. There are many common conventional wastewater treatment for removing of heavy metal like chemical precipitation and reverse osmosis that have been done in Malaysia. But mostly these methods are very expensive even they are commonly used. The solution to save the cost for treatment of heavy metal, there is one method which is adsorption. Adsorption method by using agriculture waste like lemon peel have been used as biosorbents to remove heavy metal from industrial wastewater. Lemon is commonly known used for culinary and non-culinary purpose but also can be used as agriculture waste which can be used as the activated carbon to remove heavy metal from industrial wastewater. In this study lemon peel have been used as the activated carbon to achieve the objective. The aim of this research is to determine the effect of size activated carbon and the effect of contact in reducing the percentage of heavy metal for cadmium and zinc. The analysis of heavy metal was determined by using the Atomic Adsorption Spectrophotometer (AAS). The lemon peels were obtained, washed and dried in the oven. Then, the peels were grounded into powder, separated into according size and burnt in furnace. Later, the activated carbon of lemon peels were tested by size of particle and effect of the contact time. The size of activated carbon used are 1.18mm, 600 micron, and powder. The contact time tested was four weeks. As the treatment conducted, the content of cadmium was reducing from week one to week four where 1.18mm removed 73% of cadmium, 600 micron removed 81% of cadmium and powder removed 92% of cadmium while the content of zinc from week one to week four reducing drastically where 1.18mm removed 83% of zinc, 600 micron removed 91% of zinc and powder removed 100% of zinc. The heavy metal of cadmium and zinc with COD reduce by week during the treatment conducted proving that longer period of contact are able to remove all organic matter in industrial wastewater.

ABSTRAK

Logam berat yang dikenali sebagai logam toksik dan biasanya disebabkan oleh sisa kimia, pembuatan, kumbahan, penyaduran, perlombongan dan farmaseutikal telah menjadi sebab utama untuk pelbagai air sisa industri pada masa kini. Terdapat banyak rawatan air sisa konvensional yang biasanya untuk mengeluarkan logam berat seperti pemendakan kimia dan osmosis berbalik yang telah dilakukan di Malaysia. Tetapi kebanyakan kaedah ini sangat mahal walaupun kaedah ini biasa digunakan. Penyelesaian untuk menjimatkan kos untuk rawatan logam berat, terdapat satu kaedah yang adalah penyerapan. Kaedah penyerapan dengan menggunakan sisa pertanian seperti kulit lemon telah digunakan sebagai biosorben untuk menghilangkan logam berat dari air sisa industri. Lemon lazimnya digunakan untuk tujuan kulinari dan bukan kulinari tetapi juga boleh digunakan sebagai sisa pertanian yang boleh digunakan sebagai karbon aktif untuk menghilangkan logam berat dari air sisa industri. Dalam kajian ini, kulit lemon telah digunakan sebagai karbon aktif untuk mencapai matlamatnya. Tujuan penyelidikan ini adalah untuk menentukan kesan saiz karbon aktif dan kesan masa dalam mengurangkan peratusan logam berat untuk kadmium dan zink. Analisis logam berat ditentukan dengan menggunakan Spektrofotometer Atomic Adsorption (AAS). Kulit lemon diperolehi, dibasuh dan dikeringkan di dalam ketuhar. Kemudian, kulitnya dihancurkan menjadi serbuk, diasingkan mengikut saiz yang sesuai dan dibakar dalam relau. Kemudian, karbon aktif kulit lemon diuji dengan saiz zarah dan kesan masa. Saiz karbon aktif yang digunakan ialah 1.18mm, 600 mikron, dan serbuk. Waktu eksperimen yang diuji adalah empat minggu. Semasa rawatan yang dijalankan, kandungan kadmium berkurangan dari minggu pertama hingga minggu keempat di mana 1.18mm dikeluarkan 85% kadmium, 600 mikron dikeluarkan 90% kadmium dan serbuk dikeluarkan 95% kadmium manakala kandungan zink dari minggu pertama hingga ke minggu empat dapat mengurangkan secara drastik di mana 1.18mm dikeluarkan 90% zink, 600 mikron dikeluarkan 95% zink dan serbuk dikeluarkan 100% zink. Logam berat kadmium dan zink serta COD dikurangkan oleh minggu semasa rawatan dijalankan membuktikan bahawa tempoh hubungan yang lebih panjang dapat menghapuskan semua bahan organik dalam air sisa industri.

TABLE OF CONTENT

DECLARATION	
TITLE PAGE	
ACKNOWLEDGEMENTS	ii
ABSTRAK	iii
ABSTRACT	iv
TABLE OF CONTENT	v
LIST OF TABLES	ix
LIST OF FIGURES	x
LIST OF SYMBOLS	xi
LIST OF ABBREVIATIONS	xii
CHAPTER 1 INTRODUCTION	1
1.1 Introduction	1
1.2 Problem Statement	3
1.3 Objective	4
1.4 Scope of Study	4
1.5 Significant of Study	5
CHAPTER 2 LITERATURE REVIEW	6
2.1 Wastewater	6
2.1.1 Industrial Wastewater	7
2.2 Type of Water Pollution	7

2.2.1	Surface Water Pollution	8
2.2.2	Groundwater Pollution	8
2.2.3	Microbiological Pollution	8
2.2.4	Oxygen Depletion Pollution	8
2.2.5	Nutrients Pollution	9
2.2.6	Suspended Matters Pollution	9
2.2.7	Chemical Pollution	9
2.3	Characteristic of Industrial Wastewater	10
2.3.1	Physical Characteristics	10
2.3.1.1	Total Solids	10
2.3.1.2	Colour	10
2.3.1.3	Odour	11
2.3.1.4	Temperature	11
2.3.1.5	Turbidity	12
2.3.2	Chemical Characteristics	12
2.3.2.1	pH	12
2.3.2.2	Biochemical Oxygen Demand (BOD)	12
2.3.2.3	Chemical Oxygen Demand (COD)	13
2.3.2.4	Dissolved Oxygen (DO)	13
2.3.2.5	Total Suspended Solid (TSS)	13
2.3.2.6	Organic Matter	14
2.3.2.7	Inorganic Matter	14
2.4	Wastewater Treatment	14
2.5	Carbon Adsorption	15
2.5.1	Factors Affecting Adsorption Equilibria	16
2.5.2	Activated Carbon	16

2.5.3	Formulation of Adsorption	16
2.5.4	Agricultural Adsorbent	17
2.6	Lemon Peels	18
CHAPTER 3 METHODOLOGY		20
3.1	Introduction	20
3.2	Materials and Method	20
3.2.1	Introduction	20
3.2.2	Study Area	21
3.2.3	Material	21
3.2.4	Equipment	22
3.2.5	Sample Collection	22
3.3	Flow Chart of Research Design	23
3.4	Experiment Set Up	24
3.5	Analysis of Sample	24
3.5.1	Biochemical Oxygen Demand (BOD)	24
3.5.2	Chemical Oxygen Demand (COD)	25
3.5.3	Total Suspended Solid (TSS)	25
3.5.4	Heavy Metal	25
3.6	Data Analysis	25
3.7	Research Outcomes	27
CHAPTER 4 RESULTS AND DISCUSSION		28
4.1	Introduction	28
4.2	Characteristics of Industrial Wastewater	28

4.3	Effect of Size on the Performance of Lemon Peels	29
4.3.1	Heavy Metal	29
4.3.2	Chemical Oxygen Demand (COD)	32
4.3.3	Biochemical Oxygen Demand (BOD)	34
4.3.4	Total Suspended Solid (TSS)	35
4.3.5	Turbidity	37
4.3.6	Colour	38
4.3.7	Ammoniacal Nitrogen	40
4.3.8	pH	42
CHAPTER 5 CONCLUSION		44
5.1	Conclusion	44
5.2	Recommendation	45
REFERENCES		46
APPENDIX A		47
APPENDIX B		48
APPENDIX C		52

LIST OF TABLES

Table 2.1	Unpleasant odours in some industries	11
Table 4.1	Characteristics of industrial wastewater	29
Table 4.2	Cadmium concentration in wastewater	30
Table 4.3	Zinc concentration in wastewater	31
Table 4.4	COD concentration in wastewater	32
Table 4.5	BOD concentration in wastewater	34
Table 4.6	TSS concentration in wastewater	36
Table 4.7	Turbidity concentration in wastewater	37
Table 4.8	Colour concentration in wastewater	39
Table 4.9	Ammoniacal Nitrogen concentration in wastewater	40
Table 4.10	pH concentration in wastewater	42

LIST OF FIGURES

Figure 1.1	Proportion of population equivalent (PE) served by the various sewerage system	2
Figure 2.1	Lemon	19
Figure 2.2	Lemon peels	19
Figure 3.1	The view of the Sungai Baluk, Gebeng, Kuantan	21
Figure 4.1	The percentage of Cadmium removal against time	30
Figure 4.2	The percentage of Zinc removal against time	31
Figure 4.3	The percentage of COD removal against time	32
Figure 4.4	The percentage of BOD removal against time	34
Figure 4.5	The percentage of TSS removal against time	36
Figure 4.6	The percentage of turbidity removal against time	37
Figure 4.7	The percentage of colour removal against time	39
Figure 4.8	The percentage of ammoniacal nitrogen removal against time	40
Figure 4.9	The percentage of pH against time	42

LIST OF SYMBOLS

%	Percentage
°	Degree

LIST OF ABBREVIATIONS

BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
TSS	Total Suspended Solid

CHAPTER 1

INTRODUCTION

1.1 Introduction

Wastewater is liquid waste discharged by domestic residences, commercial properties, industry, agriculture, which often contains some contaminants that result from the mixing of wastewater from different sources. Wastewater mostly consists of pure water more than 95% and there are numerous processes that can be used to clean up waste waters depending on the type and extent of contamination. Treated wastewater can then be reused as the drinking water after it has been cleared of contaminants. Nowadays, environmental pollution have become the huge issues to the society in this century. This is because the development of the industries and commercial building that mostly affected the sources of pollution. Without the proper wastewater treatment many ecosystems would be severely damaged once the treated water gets recharged back into the environment.

In Malaysia, there are about 28.3 million population based on the Report of Census 2010 by the Department of Statistics. The estimated volume of wastewater generated by municipal and industrial sectors is 2.97 billion cubic meters per year. The proportions of population equivalent (PE) served by the various sewerage systems are shown in Figure 1.1.

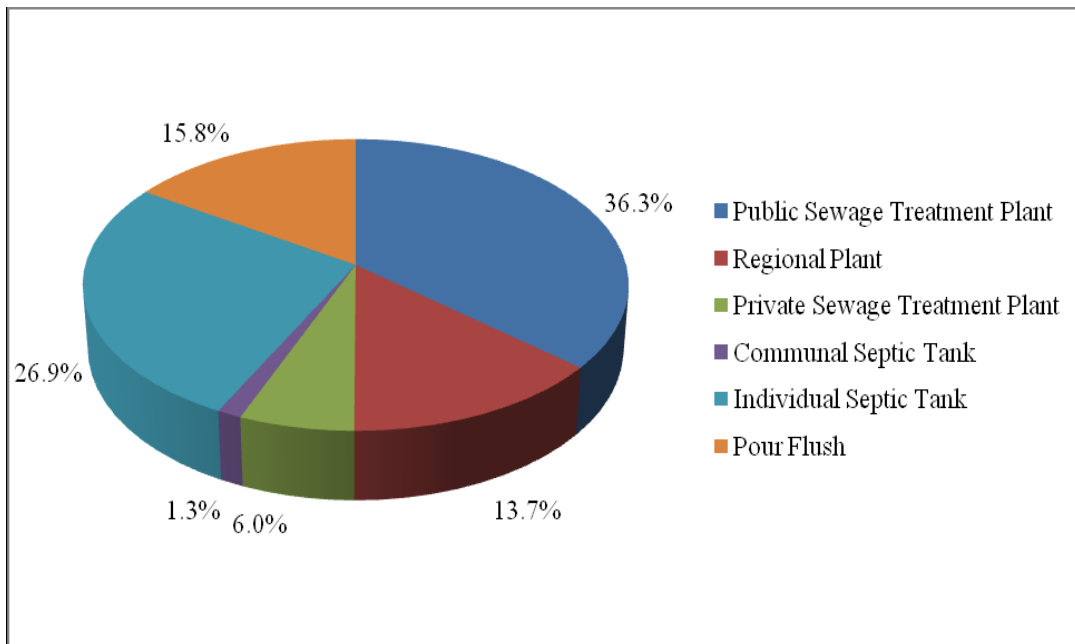


Figure 1.1: proportions of population equivalent (PE) served by the various sewerage systems

According to Indah Water Konsortium which is the country's main sewerage operator, mostly the dominant wastewater treatment types are preliminary which is removal of rags, rubbish, grit, oil and grease while the example primary are removal of settle able and floatable materials and the last one which is secondary treatment similar to biological treatment which is to remove organic and suspended solids. For this moment time in Malaysia, there is no plan to build the tertiary treatment systems in Malaysia. The focus has been providing a basic standard of preliminary, primary and secondary treatment.

The major constraint to wastewater treatment faced by Malaysia are low sewerage tariff is unable to support the high operation and maintenance costs. Besides, there is non-compliance or mediocre compliance that are mainly caused by the high influent of oil and grease discharged into STP serving industrial and commercial area that do not have grease traps or do not maintain grease traps adequately. Other contributory factors are excessive discharge of soaps, detergents and other cleaning agents into sewerage system. Furthermore, sewerage services collection by operators is not conducive as it is unfortunate that many Malaysians fail to realize the importance of sewage management with regards to a safer environment. In addition, the dynamics of the sewerage industry where sewerage infrastructures are constructed by private developers and handed over to

the public operator opens up the risk factor of quality being compromised which would subsequently have the impact of treatment processes and operations.

The common method methods applied to remove heavy metal from wastewater are in physical or chemical treatment where the process includes chemical precipitation, chemical on oxidation, air stripping and adsorption (Renou et al. 2008). This treatment can remove 99% percent of the pollutant from the raw sewage. But, the cost of the treatment is very high including operation, maintenance and construction (Mackenzie et al. 2004). The alternative method to solve this problem are by using lemon peel activated carbon adsorption. These biosorbent materials are characterized being less expensive, metal selective, non-sludge generation, high bio-removal efficiency, possible ion recovery and environmentally sound methodology (Deans, 1992).

1.2 Problem Statement

Industrial processes generate wastewater that are containing heavy metal contaminants. Since most of heavy metal are non-degradable into nontoxic end products, their concentrations must be reduced to level that will be acceptable before it will discharge into environment. (Madhukar J. Phadtare, 2015). At least 20 metal are being classified as toxic, and half of this are emitted into environment in large quantities that pose high risks to the aquatic life. (Kortenkamp *et al.*, 1996). Chromium is one of the major heavy metals that present in the wastewater which has high toxic effect and as the strong oxidizing agent that are capable of being absorbed through human skin. The heavy metals are having the most hazardous effect on the human health can be treated from wastewater by using various physicochemical methods. There are many negative impacts of heavy metals on the plants which are decrease of the seed germination and lipid content by cadmium, decreased enzyme activity and plant growth by chromium, reduction of the chlorophyll production by nickel and plant growth by lead. (Gardea-Torresdey *et al.*, 2005). Besides, the effect of heavy metal on animals include reduced growth, cancer, organ damage and sometimes in extreme cases, death. (Canada Gazette,2010).

To prevent the negative impact of heavy metals toxicity in wastewater, there are many solution that have been discovered to reduce the amount of heavy metal in

wastewater such as precipitation method, electrochemical reduction, ion exchange method, reverse osmosis and reduction method. But, most of this treatment are very expensive. Hence, to reduce the expensive cost of treatment, the cheaper treatment have been found which is adsorption. The most common adsorbent that have been used for removal of heavy metal in wastewater are very expensive. So that, this research aim to find out the cheapest absorbent from the agriculture waste as an effective way to remove heavy metal from wastewater.

1.3 Objective

There are two objectives for this study based on the problem statement. The objective are as below:

1. To determine the characteristic of wastewater from industrial wastewater.
2. To determine the effectiveness of the size of lemon peel activated carbon adsorption.

1.4 Scope of Study

This study mostly focuses on characteristic on the industrial wastewater and the efficiency of the lemon peel activated carbon on removal of heavy metal in industrial wastewater. The industrial wastewater samples are obtained from the Sungai Tunggak in Gebeng area industry. Characteristic of the wastewater are identified based on physical and chemical characteristics. A couple of experiments are conducted to determine the chemical characteristic which is the parameter of pH, biological oxygen demand (BOD), chemical oxygen demand (COD), and metal ions. Besides, the observation for the physical characteristic are leachate color, odor, temperature and suspended solids (SS) must be done. The main focus of this study is to determine the effectiveness of using lemon peel activated carbon as heavy metal ions removal in industrial wastewater. The purpose of conducting this experiments are to measure the optimum pH, time contact, agitation speed and the optimum dosage for this treatment. Hence, the lower cost of wastewater treatment by using lemon peel activated carbon adsorption are proposed as the cheaper effective cost treatment compared to the other conventional treatment.

1.5 Significant of Study

The study on the wastewater treatment by using lemon peel activated carbon with adsorption method is important in order to improve the efficiency, eco environmental, lower cost and provide variation methods of the wastewater treatment. By using carbon adsorption method for the industrial wastewater treatment, it will become another alternative which could reduce the high cost of conventional treatment. This study will determine the effectiveness of using lemon peel activated carbon as an agent for removal of heavy metal ions in industrial wastewater. End of this study, the method of lower cost and effective wastewater treatment will be proposed. This treatment can be used and practice widely by government authorities and industrial management in order to control and reduce pollution that produce by industrial wastewater from the industries all over Malaysia.

CHAPTER 2

LITERATURE REVIEW

2.1 Wastewater

Wastewater is the any water that have been adversely affected in quality parameter by anthropogenic influence. Wastewater also can originate from the combination of the domestic, industrial, commercial or agriculture activities, surface runoff or storm water and also from the sewer inflow or infiltration. There are also municipal wastewater which called as the sewage is usually conveyed in a combined sewer or the sanitary sewer and treated at a wastewater treatment plant. Wastewaters usually generated in the areas without access to centralized sewer systems rely on the onsite wastewater systems. Domestic households, industrial and agricultural practices produce wastewater that can cause pollution of many lakes and rivers. Untreated wastewater also produce a lot of heavy metals that have many effect on the human and also environment.

Wastewater is liquid waste discharged by domestic residences, commercial properties, industry, agriculture, which often contains some contaminants that result from the mixing of wastewater from different sources. Based on its origin wastewater can be classed as sanitary, commercial, industrial, agricultural or surface runoff. Term wastewater need to be separated from the term sewage, sewage is subset of wastewater that is contaminated with faeces or urine though many people use term sewage referring to any waste water.

Wastewater mostly consists of pure water (more than 95%), and there are numerous processes that can be used to clean up waste waters depending on the type and extent of contamination. Treated wastewater can then be reused as the drinking water after it has been cleared of contaminants. The treatment of wastewater is not only

important for our own health but also to keep our environment clean and healthy. Without the proper wastewater treatment many ecosystems would be severely damaged once the treated water gets recharged back into the environment.

2.1.1 Industrial Wastewater

Industrial wastewater is the wastewater that are discharge from the industrial and commercial sources that may contain pollutants at the hazardous levels that could affect the quality of receiving waters or interfere with the publicly owned treatment works that will received those discharges of the effluents. In general, industrial wastewater may contain suspended solid, colloidal solid, and dissolved solids. Furthermore, industrial wastewater may contain excessively high acidity or high alkalinity and may contain high or low concentrations of coloured matters. In addition, these industrial wastewater may contain inerts, organic or inorganic materials, toxic materials and pathogenic bacteria. Industrial wastewater such as food processing, electrical appliance processing, chemical substances processing may generates wastewater that are containing heavy metal contaminants. (Madhukar J. Phadtare, 2015). Removal of heavy metals from industrial wastewater is the primary importance because they are not only causing contamination of water bodies and are also toxic to many life forms. (Madhukar J. Phadtare, 2015). Heavy metal water pollution represents an important environmental problems due to the possible toxic effects of the metal to both human and environment. (Z.A. Husoon, 2013).

2.2 Type of Water Pollution

Water pollution is the contamination of water bodies for example the lakes, rivers, oceans, aquifers and groundwater. Water pollution occurs when the pollutants are directly or indirectly discharged into water bodies without the proper treatment for removal of the harmful compound. Water pollution can come from many of the different sources. If the pollution comes from a single sources such as a spilt of the oil, it is called as the point sources pollution. But, if the pollution comes from many sources, it will called as the non- point sources pollution. Most the types of pollution will affect the immediate area surrounding the sources. There are many type of the water pollution such as surface water pollution, groundwater, microbiological, oxygen depletion, nutrients, suspended matter and chemical.

2.2.1 Surface Water Pollution

Surface waters are the natural water resources of the Earth. They are found on the exterior of the Earth's crust and it is also included the oceans, rivers and lakes. Hazardous substances coming into contact with this surface water, dissolving or mixing physically with the water can be called as the surface water pollution. Surface water pollution can be from the oil and grease that submerged in the surface of the water.

2.2.2 Groundwater Pollution

A lot of the Earth's water is to be found in the underground of the soil or the under rock structures that are called aquifers. Human often use the aquifers water to obtain the drinking water and build wells to access it. When this water become polluted, it is called groundwater pollution. When humans apply the pesticides and chemicals to the soils, it will washed deep into the ground by rainwater. When this chemical gets to the underground water, it will cause the underground pollution. This means when the human digs well and bore holes to get the water from the underground, it needs to be checked for groundwater pollution.

2.2.3 Microbiological Pollution

Microbiological water pollution is usually a natural form of the water pollution caused by the microorganisms. There are many types of the microorganisms that live in the water and causes fish, land animals and humans to become unhealthy. There are many types of the microorganisms such as bacteria, viruses and protozoa. Besides, there are some of the example of the serious disease that come from the microbiological pollution such as cholera which is come from the microorganisms that live in the water. These diseases usually affect the health of people in the poorer countries as they do not have the facilities to treat polluted water.

2.2.4 Oxygen Depletion Pollution

Oxygen depletion pollution is the microorganisms that live in the water feed on the biodegradable substances. When there are too much degradable material is added to the water, the number of microorganisms increase and use up as the available oxygen.

This is called oxygen depletion. Besides, when the oxygen levels in the water are depleted, it will relatively harmless aerobic microorganisms to die and directly the anaerobic microorganisms begin to survive. Some of the anaerobic microorganisms are harmful to people, animals, and environment because they are produce harmful toxins such as ammonia and sulphides.

2.2.5 Nutrients Pollution

Nutrients are essential for plant growth and development. Many nutrients are found in the wastewater and fertilisers and these can cause excess weed and the algae growth if large concentration end up in water. These fertilisers and sewage were contain high levels of the nutrients. It will make the water cannot be drink and clog filters. Too much algae will also use up all the oxygen in the water, and other water organisms in the water will die out of oxygen starvation.

2.2.6 Suspended Matters Pollution

Some of the pollution do not dissolve in the water as their molecules are too big to mix with the water molecules. Some of the example of the pollution which cannot be mix with water molecules such as rubbish, fruit seed and the other else. This material is called as the particulate matter and can often be a cause of water pollution. The danger of the suspended particles is eventually settle and cause a thick silt at the bottom. This is harmful to the marine life that lives on the floor of rivers or lakes. Besides, the biodegradable substances that are often suspended in water and can cause problems by increasing the amount of anaerobic microorganisms present. Then, toxic chemical suspended in water can be harmful to the development and survival of the aquatic life.

2.2.7 Chemical Pollution

Chemical pollution are comes from the industrial and agricultural development which these two development of the country work are involves the use of many different chemicals that can run off into water and pollute it. There are some metals and solvents from industrials work can pollute rivers and lakes. These are very poisonous to many forms of aquatic life and may slow their development so that it will make them infertile

or even result in death. Besides, pesticides are also used in farming to control weeds, insects and fungi. Run off of these pesticides can cause water pollution and poison aquatic life. Subsequently, animals or humans may be poisoned if they eat infected fish. Then, another form of chemical pollutant which is petroleum that usually contaminates water through oil spills when a ship ruptures. Oil spills usually have only a localised affected on the wildlife but can spread for miles. The oil also can cause death of many fish and stick to the feathers of seabirds causing them to lose the ability to fly.

2.3 Characteristic of Industrial Wastewater

There are many types of the characteristic of the wastewater. The physical and chemical characteristic of industrial wastewater presented is for most wastewater.

2.3.1 Physical Characteristics

The physical characteristics of the industrial wastewater include the solid content, colour, odour, turbidity and temperature.

2.3.1.1 Total Solids

The total solid in a wastewater consists of the insoluble or suspended material and the soluble compound dissolved in water. (Alturkmani). The suspended solid that were found in the sample of wastewater were drying and weighing the residue that were removed by filtering of the sample. When, the residue is burned in oven, the residue are burned off. Some of the organic matter will not burn and some inorganic salts break down at the high temperature. But, some of the organic matter may consists the mainly sources of proteins, carbohydrates and fats. Then, between 40% and 65% of the solids in the average of wastewater are suspended.

2.3.1.2 Colour

Colour is one of the type of qualitative characteristic that can be used to know the general condition of the industrial wastewater. Wastewater that is light brown in colour are still in standard water quality condition while if the wastewater are light to medium grey colour which is the characteristic of wastewaters that have undergone some degree

of decomposition. But, if the colour of industrial wastewater are in dark grey or black colour, the wastewater are in typically septic or having undergone extensive bacterial decomposition under anaerobic conditions. The blackening of industrial wastewater is often due to the formation of the several of sulphide.

2.3.1.3 Odour

Another characteristic of industrial wastewater is odour. The determination of odour has become very important in environmental issues because the general public has become more concerned with the proper operation of wastewater treatment facilities. The odour of the fresh wastewater is usually not offensive, but a variety of odorous compounds are released when biologically under anaerobic conditions. The different unpleasant odours produced by certain industrial wastewater are presented in Table 2.1.

Industries	Origin of Odours
Cement works, lime kilns	Acrolein, amines, mercaptans, dibutyl sulphide, H ₂ S, SO ₂ , etc.
Pharmaceutical industries	Fermentation produces
Food industries	Fermentation produces
Food industries (fish)	Amines, sulphides, mercaptans
Rubber industries	Sulphides, mercaptans
Textile industries	Phenolic compounds
Paper pulp industries	H ₂ S, SO ₂
Organics compost	Ammonia, sulphur compounds

Table 2.1 Unpleasant odours in some industries

2.3.1.4 Temperature

The industrial wastewater industries temperature is commonly higher than that of the water supply because warm municipal water has been added. The measurement of temperature is very important because the most wastewater treatment procedure include the biological processes that are temperature dependent. Sometimes, the temperature also effect the microorganisms that live in the industrial wastewater move actively and create more oxygen or make the wastewater dirtier. Besides, the temperature of wastewater will be different follow the daily weather that are sometimes hot and cool. Furthermore, the geographic location also give the effect to the different temperature of wastewater.

2.3.1.5 Turbidity

Turbidity is the measurement of the cloudiness of the water. It caused by the presence of the solid and the suspended solid such as silt, clay, organic matter and by the microorganism that interfere with the passage of light trough the water. When the water turn cloudiness its mean that the water have high turbidity. Turbidity also has the parameter that give the normal parameter which is higher or normal. Turbidity is not major health concern, but if the turbidity is higher than usual parameters, it can interfere with disinfection and provide a medium for microbial growth (Moshiri, 1993). Turbidity of the wastewater industrial can be checked by using Turbidity measurement or by the water quality equipment.

2.3.2 Chemical Characteristics

The characteristic of the industrial wastewater can be determined by the analysis that we determined from the laboratory.

2.3.2.1 pH

pH parameter will determine the acidity, neutral or the alkalinity. The alkalinity or acidity of the industrial wastewater will determine the activities of the microorganism. The higher the alkalinity of the industrial wastewater, the higher the activities of the microorganism. But when the alkalinity is too higher, the microorganism also cannot live. The pH wastewater needs to remain between 6 and 9 to protect living organisms. The acidity of the pH is below than 6 and the alkalinity is higher than 7. The most suitable range of pH for water is 6.5 to 8.5. Acidity can inactive the treatment process when they are available in the industrial wastewater from the industries and commercial industry.

2.3.2.2 Biochemical Oxygen Demand (BOD)

The BOD test is to measure the amount of dissolved oxygen that is likely use by the organisms to degrade the waste in the wastewater. It is important to evaluate the how much the treatment is required and the potential impact on the living things that receive the water. The parameters of the biochemical oxygen demand are expressed in terms of mg/l of BOD. As the measurement of BOD takes too long time (20 days at 20°C), the

determination of BOD after 5 days incubations is preferred as the values BOD5 being nearly 65% of the total BOD.

2.3.2.3 Chemical Oxygen Demand (COD)

One of another test that measured the oxygen demand is chemical oxygen demand (COD). It only takes 2 hours to measure the oxygen required for oxidation of all substances of the water includes one that cannot biologically decomposable. This type of test has its own correlation with biological oxygen demand. The COD test is conducted by heating a portion of sample in an acidic chromate solution, which oxidizes organic matter chemically.

2.3.2.4 Dissolved Oxygen

Dissolved oxygen is necessary to many forms of life including fish, invertebrates, bacteria and plants. These organisms use oxygen in respiration, similar to organisms on the land. Fish and crustaceans obtain oxygen for respiration through their gills, while plant life and phytoplankton require dissolved oxygen for respiration when there is no light for photosynthesis. The amount of dissolved oxygen needed varies from creature to creature. Bottom feeders, the crabs, oysters and worms need minimal amounts of oxygen (1-6 mg/L), while shallow water fish need higher levels (4-15 mg/L). Microbes such as bacteria and fungi also require dissolved oxygen. These organisms use DO to decompose organic material at the bottom of a body of water. Microbial decomposition is an important contributor to nutrient recycling. However, if there is an excess of decaying organic material in a body of water with infrequent or no turnover that is also known as stratification, the oxygen at lower water levels will get used up quicker.

2.3.2.5 Total Suspended Solid (TSS)

TSS includes all particles suspended in water which will not pass through a filter. Suspended solids are present in sanitary wastewater and many types of industrial wastewater. TSS can include a wide variety of material, such as silt, decaying plant and animal matter, construction sites, agriculture, industrial wastes, and sewage.

High concentrations of suspended solids can cause many problems for stream health and aquatic life. As level of TSS increase, a water body begins to lose its ability to support a diversity of aquatic life. Such as Suspended solids can harm fish directly by clogging gills, reducing growth rates, and lowering resistance to disease, changes to the aquatic environment may result in a diminished food sources. Natural movements and migration of aquatic populations may be disrupted.

2.3.2.6 Organic Matter

Organic matter refers to the large pool of carbon-based compounds that are found within the natural, engineered, terrestrial and aquatic environments. It is the matter that composed of the organic compounds that has come from the remains of organisms such as plants and animals and their waste products in the environment. The organic molecules can also be made by chemical reactions that do not involve life which is basic molecules like cellulose, tannin, cutin and lignin. Over the years, there are many different tests that have been developed to determine the organic content in the wastewaters. In general, the tests may be divided into those used to measure the trace concentrations in the range of 10^{-12} to 10^{-3} mg/l. Laboratory methods commonly used now to measure the gross amounts of the organic matter in wastewater treatment include BOD and COD.

2.3.2.7 Inorganic Matter

The principal chemical tests include the free ammonia, organic nitrogen, nitrites, nitrates, organic phosphorus and inorganic phosphorus. Nitrogen and phosphorus are important because these two nutrients are responsible for the growth of the aquatic plants. Other tests such as chloride, sulphate, pH and alkalinity are performed to assess the suitability of reusing the treated wastewater and in controlling the various treatment processes (Rein, 2005). Heavy metals in inorganic matters also can produce toxic effects. Therefore, the determination of the amount of heavy metals especially important where the further use of treated effluent or sludge is to be evaluated. Many of the metals are also classified as priority pollutants such as arsenic, cadmium, chromium, mercury and etc.

2.4 Wastewater Treatment

Wastewater treatment are needed to environment because it contain high percentage of the heavy metals such as zinc, iron, lead, cadmium, chromium and etc. So the wastewater treatment for the removal of the heavy metal are needed. The heavy metal in the industrial wastewater may give a lot of problem and health defect to human, plants and environment. There are many types of wastewater treatment such as precipitation method, electrochemical reduction, ion exchange method, reverses osmosis, reduction method and constructed wetland. But the above methods are very expensive to use for the treatment of wastewater. So this research are about to find new method which is activated carbon adsorption.

2.5 Carbon Adsorption

The meaning of adsorption is the accumulation of a substance at the interface between two phases such as liquid onto solid while the adsorbate means molecules that are accumulate at the interface and the adsorbent are means that solid on which the adsorption occurs for example activated carbon, ion exchange and metal hydroxides. The objective of the carbon adsorption are to remove the dissolved odorous compound or trace of organics in water treatment, to remove dissolved organics that are refractory which cannot be removed using the conventional biological treatment and to remove the heavy metals from the industrial wastewater.

There is mechanism of the carbon adsorption which is adsorbents are held on the surface of adsorbent by chemical forces such as hydrogen bonds, dipole-dipole interaction and van der Waals. Molecules are continue to accumulate at the surface until it reach the rate of adsorption equals with the rate of desorption which means equilibrium has been reached and no further accumulation will occur. Adsorbents are held by using the transport mechanisms where there are four transport mechanisms which are bulk solution transport, film diffusion transport, pore transport and adsorption.

The first one which is bulk solution transport is the bulk solution initially to the boundary layer of water surrounding to the adsorbent particle. Then, the second one is film diffusion transport which is molecular diffusion through the boundary layer of water

surrounding the adsorbent particle. After that, pore transport is the adsorbent's pores are through the available adsorption sites. The last one which is adsorption which is the adsorption bond is formed between the adsorbate and adsorbent.

2.5.1 Factors Affecting Adsorption Equilibrium

There are many factors of the adsorption equilibrium. The factors of adsorption equilibrium are divide into two which are adsorbent characteristics and adsorbate characteristics. The first one is adsorbent characteristics which are surface area, pore size distribution and surface chemistry. The second one is adsorbate characteristics which are solubility, molecular structure and degree of ionisation.

2.5.2 Activated Carbon

Activated can be made from the any carbonaceous material for example wood, coal and coconut shell. The procedure to make activated carbon is heating in the absence of air to liberate carbon from its associated atoms that is called carbonisation. It must passing the mildly oxidative hot gasses which is CO₂ or steam must be at 315°C to 925°C for the formation of pores or tiny fissures. The activated carbon surface area are divided into two surface area which are granular surface area (GAC) and powdered activated carbon (PAC). The surface area for GAC are 600- 1600 m²/g or 0.425mm to 2.36mm and for the PAC the surface area are less than 0.025mm. There is no difference in surface area and adsorption capacity but smaller diameter means the faster equilibrium.

2.5.3 Formulation of Adsorption

There are two formulation of the adsorption which are Freundlich isotherm that is empirical relationship and Langmuir equation that is theoretical relationship. Both equation are to determine the adsorption capacity. The Freundlich isotherm are as below:

$$X/(M) = KC^{(1/n)} \quad 2.1$$

Where:

X = weight of substance adsorbed

M = weight of adsorbent

C = concentration of substance remaining in solution

K, n = constant, depending on temperature, adsorbent and substance to be adsorbed

The value of K and 1/n need to be determined based on the laboratory evaluation which are fixed carbon dosage with variable time and vary carbon dosage with fixed time. Then, the Langmuir equation are as follow:

$$X/M = abC/(1 + aC) \quad 2.2$$

Where:

A = constant, increases with increasing molecular size

B = amount adsorbed to form a complete monolayer on the surface

2.5.4 Agricultural Adsorbent

Different types of adsorbents are classified into natural adsorbents and synthetic adsorbents. Natural adsorbents are include the charcoal, clay minerals, zeolites and ores. These natural minerals, for many instances are relatively cheap, abundant in supply and have significant potential for modification and ultimately enhancement of their adsorption capabilities. Synthetic adsorbents are adsorbents that are prepared from the agricultural products and wastes, household wastes, industrial wastes, sewage sludge and polymeric adsorbents. Each adsorbent has its own characteristics such as porosity, pore structure and nature of its adsorbing surfaces. Many waste materials used include fruit wastes, coconut shell, scrap tyres, bark and other tannin rich materials, sawdust, rice husk, petroleum wastes, fertilizer wastes, fly ash, sugar industry wastes blast furnace slag, chitosan and seafood processing wastes, seafood processing wastes, seaweed and algae, peat moss, clays, red mud, zeolites, sediment and soil and ore minerals.

Adsorbent materials derived from low cost agricultural wastes can be used for the effective removal and recovery of heavy metal ions from wastewater streams. Agricultural by products usually are composed of lignin and cellulose as the major constituents and may also include the other polar functional groups of lignin which include the aldehydes, alcohol, ketones, carboxylic, phenolic and ether group. (Demirbas, 2008). Those groups have the high function to extent to bind some heavy metals by donation of an electron pair from these groups to form complexes with the metal ions in solution. Agriculture waste material that have being highly efficient, low cost and renewable source of biomass can be exploited for heavy metal remediation. (Dhiraj Sud, 2008). The utilization of the agro wastes as the adsorbents is currently receiving the wide attention because of their abundant availability and low cost owing to relatively high fixed carbon content and presence of the porous structure. (Amit Bhatnagar, A.K Minocha, Mika Sillanpaa, 2010)

2.6 Lemon Peels

The lemon which is the scientific name is *Citrus limon*. Citrus lemon is a species of small evergreen tree in the flowering plant family Rutaceae where is native to Asia. The origin of the lemons are thought to have first grown in Assam which is the region in northeast India. The tree's ellipsoidal yellow fruit is used for the culinary and non-culinary purposes throughout the world, primarily for its juice which has both culinary and cleaning uses. The juice of the lemon is about 5% to 6% citric acid which gives a sour taste. The distinctive sour taste of lemon juice makes it a key ingredients in drinks and foods such as lemonade and lemon meringue pie.

Lemon peels is one of the type of agricultural wastes that is used for the carbon adsorption. Bhatnagar *et al* (2010) proved that the present system of cobalt adsorption on lemon peel adsorbent could be described more favourably by the pseudo second order kinetic model. Bhatnagar *et al* (2010) suggested that lemon peel waste can be also used beneficially in treating industrial effluents containing heavy metal ions. Schiewer *et al* (2008) proved that lemon peels and lemon- based protonated pectin peels (PPP) had the Langmuir sorption capacities of 0.7 -1.2 mequv/g or 39 mg/g of Cadmium per biosorbent dry weight. The lemon peel have high pectin rich sorbent and contain carboxylate groups. The commercial pectin are found in the acetyl group which is acetylation of pectin

decreases the affinity for the heavy metals, with the different binding mechanisms involved for strongly bound Pc and weakly bound Ca. (C.M.G.C Renard, 1999). Citrus peel typically have the lower degree of acetylation.

Peel of the citrus plant that have contain up to 80% water and the remaining 20% are solid fractions consisting pectin, soluble sugars, cellulose, proteins and phenols, (Z.A. Husoon, 2013). The most abundant represented class of biomolecules in citrus peels are polysaccharides that offer with the presence of pectin that is a greatest potential for enzymatic or chemical conversion to create desired properties such as ion exchange capacity, galacturonic acid which is the major sugar that found in the citrus pectin. Z.A. Husoon (2013) indicates that the ability of lemon peels for the removal of heavy metal ions from industrial wastewater would successfully be applied for various heavy metals from industrial wastewater since it seems environmentally good.



Figure 2.1 : Lemon

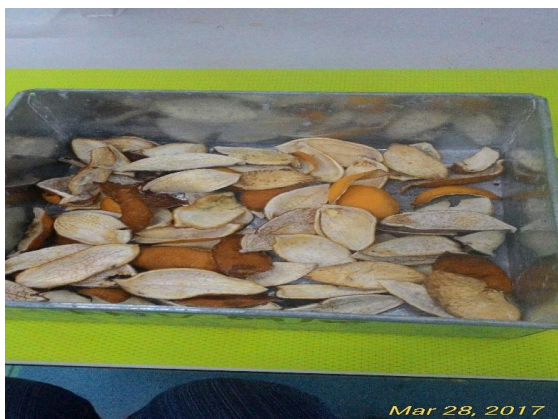


Figure 2.2 : Lemon peels

CHAPTER 3

METHODOLOGY

3.1 Introduction

Methodology in this study can be translate as systematic, analysis of the methods or procedures to a field of study. The methods section that are identifies the explanation for the specific techniques or the method of procedures that are used to recognize, select and analyze the information that are applied to understanding the comprehensive research problem. Hence, by doing that way, it will allow the reader to examine a study's overall validity and reliabilty.

Methodology also can be described as the planning for the comprehensive research work from the beginning until the end. Hence, the methodology in this study explained about the procedures which are related to the selected agricultural activated carbon which is lemon peel and the industrial wastewater sample that were collected from the Industrial Gebeng Area at Gebeng, Kuantan, Pahang. The equipment involved and approach to experiment that were found in this study.

3.2 Materials and Method

3.2.1 Introduction

Before start conducting the experiment, the study area and the agricultural fruit waste need to be identify first. There are some factors that need to be considered such as the location of the actual sampling, the quantities of sampling, agricultural fruit waste that need to be used, the size of the activated carbon and the capability of conducting the experiment.

3.2.2 Study Area

The location of the research is at the Sungai Baluk, Industrial Gebeng Area which is located in Gebeng District at Pahang state. The town is located near Kuantan port. The Gebeng Industrial Estate, Pahang's main petrochemical cluster is well connected via the East Coast Expressway to the West Coast of Peninsular Malaysia. The Gebeng Industrial Estate, five kilometres from Kuantan has a vast expanse of land for investment. It's strategic location has made it home to many multinational corporations of the industries company. The by pass is directly linked with the East West Expressway which is its connects Kuala Lumpur and Kuantan. This direct link provides a cost effective means of transportation and greater accessibility in the transfer of freight raw materials to and from Gebeng Industrial Estate to domestic and international markets. It has also great increase the viability of Kuantan Port in the domestic and international freight movements on a land – bridge concept.

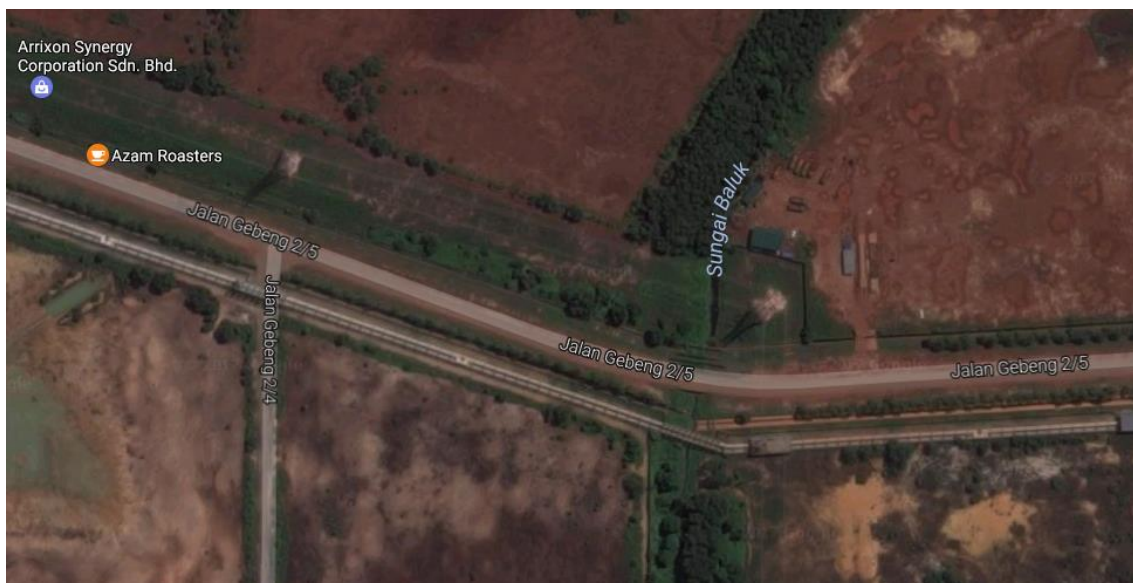


Figure 3.1 : The view of the Sungai Baluk, Gebeng, Kuantan
Sources : Google Maps (2017)

3.2.3 Material

Material that will be used during this study to achieve the overall objectives that were proposed which are three storage box for storage of the industrial wastewater sample. Every sample for each storage box will be provide three litre of sample. Each

sample will be collected in March. Then, the lemon peel that will be collected from the supermarket and the fresh lemon will be peel out.

3.2.4 Equipment

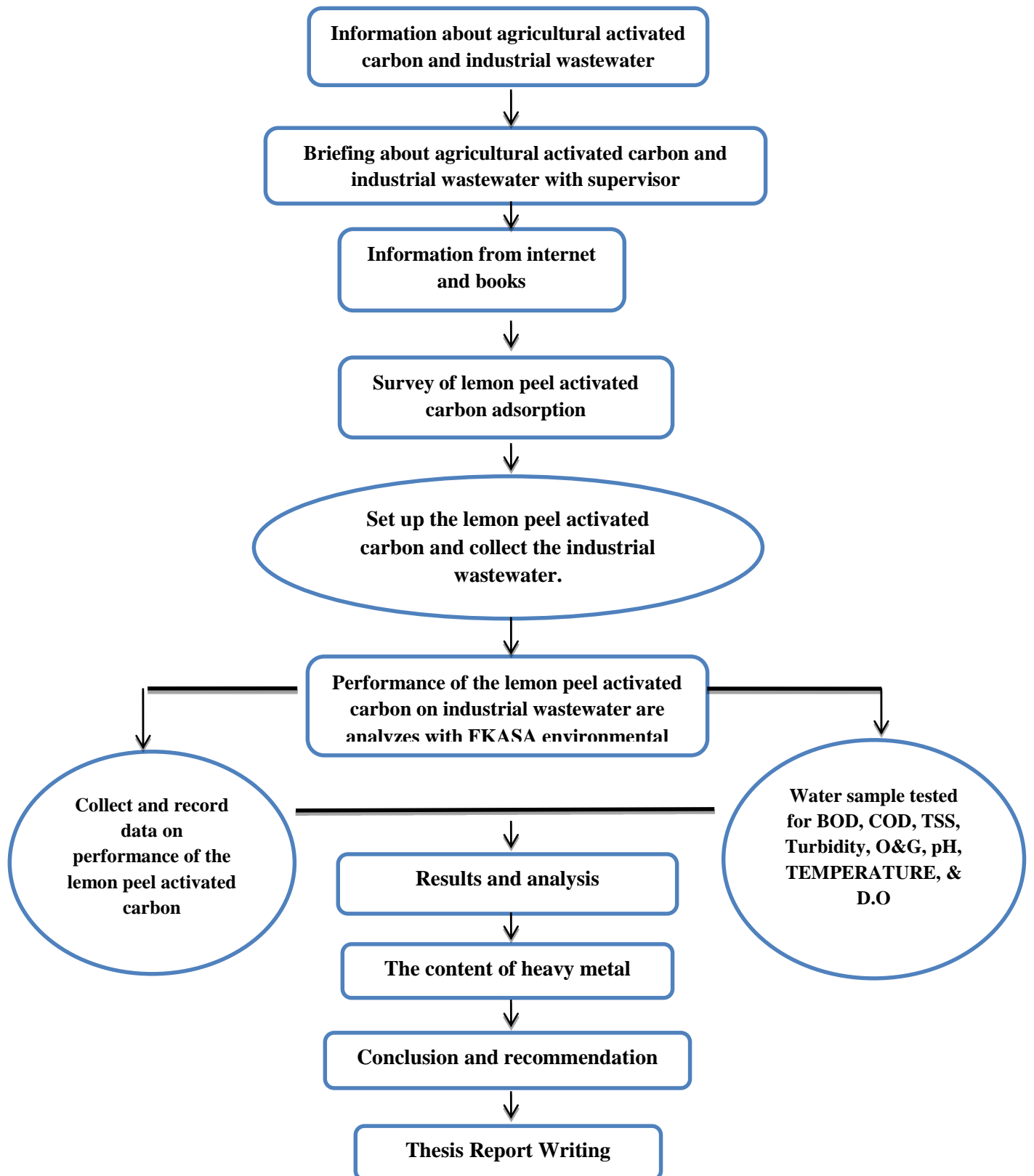
The equipment that will be used in this study are the first one is Atomic Adsorption Spectrophotometer (AAS) for the analysis of the heavy metals, aluminium weighing dishes, glass fiber filter disks, suction flask, membrane filter funnel, crucible, filter paper (45 μm), measuring cylinder (100ml), analytical balance (accuracy 0.01g), desiccator, beaker (100ml), pH meter (Wagtech N374,M128) which are used for the measurement of the pH of the raw and the treated leachate as well. Incubator that will be used for the BOD analysis at the temperature 20 °C.

3.2.5 Sample Collection

Before any experiment can be run, the lemon peel need to be dry out and convert into granular activated carbon or powder activated carbon. Then, for this research, the industrial wastewater sample need to be taken from the Sungai Baluk at the Industrial Gebeng Area using 3 container where the each container must collect three litre of the sample in a trip. Then, the raw industrial wastewater sample were taken to the laboratory for selected heavy metals analysis and some analysis which is pH, temperature, turbidity, COD and BOD. Leachate sample was taken before and after the experiment for analysis of selected heavy metals which Cd, Ammonia Nitrogen and Zn.

Cd, Ammonia Nitrogen and Zn were selected based on the environment risk and standards for analysis in the sediment. This sample was conducted by taking a sample before the raw industrial wastewater sample and after the industrial wastewater sample being treated from the lemon peel activated carbon which means at the termination of the study to identify the initial and final heavy metals composition of the industrial wastewater.

3.3 Flow Chart of Research Design



3.4 Experiment Set Up

Lemon Citrus fruit is obtained from the market and supermarket. The lemon is peel out. The lemon peels are washed with distilled water and dried under the hot sun until the water on it dried. Then, the lemon peels are oven dried at 103°C for 24 hours. After 24 hours, the lemon peels are weight and grinned per sizing. The size chosen are 1.18mm, 600 micron and powder. The size of the lemon peel activated carbon to treat the wastewater are 1.18mm, 600 micron and powder form. The granular activated carbon range is (0.425mm – 2.36mm) while the powder activated carbon is in the range below than 0.025mm. after grinned and seived according the sizes, the lemon peels are placed in the furnace for an hour under 500°C. When, the activated carboon is cool down, it is placed in an tighten container. 20g of each size activated carbon from the lemon peel is mixed with the activated carbon in the container. The wastewater then rapidly stirred about 10 minutes. The industrial wastewater was let for 4 week and each week the chemical characteristic, physical characteristic and microbiological characteristic is tested to know the progress of the treatment.

3.5 Analysis of Sample

Analysis of heavy metals will be done on leachate liquid. All the laboratory analysis will be done in environment laboratory, Faculty of Civil Engineering and Earth Resources. There are seven parameters selected analysis of the leachate liquid which are pH, temperature, Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Dissolved Oxygen (DO), Total Suspended Solid (TSS) and heavy metal.

3.5.1 Biological Oxygen Demand (BOD)

The biochemical oxygen demand or BOD is the amount of oxygen consumed by the microorganism which is bacteria in the decomposition of the organic materials. BOD is oxygen required in the oxidation process of various chemicals in the wastewater such as sulphides, ferrous, iron and ammonia. The BOD test will record the amount of the oxygen needed. The differences between the two oxygen in the sample will be recorded BOD in mg/L (Sharon, 1997). The formula for BOD as shown below:

$$\text{BOD}_t = (\text{DO}_i - \text{DO}_t)/P \quad 3.1$$

Where:

BOD_t = biochemical oxygen demand, mg/L

DO_i = initial DO of the diluted waste water sample about 15 minutes after preparation, mg/L

DO_t = final DO of the diluted wastewater sample after incubation for t days, mg/L

P = dilution factor

3.5.2 Chemical Oxygen Demand (COD)

The COD test is used to determine the organic strength of wastewaters. The basic of the test is that all organic compounds, with some exception, can be oxidizing agents under highly acidic conditions. The chemical oxygen demands test is much quicker than biochemical oxygen demand test about 3 hours compared to BOD determination.

3.5.3 Total Suspended Solid (TSS)

A well-mixed sample is filtered through standard glass-fibre filter and the retained residue on the filter is dried to a constant weight at 103 to 105°C. The increase in weight of the filter indicates the total suspended solids. If the total suspended solids material and substances clogs the filter and prolong filtration process, it may be necessary to increase the diameter of the filter or reduce the volume of the sample. To obtain the amount of the total suspended solid (TSS), the difference between total dissolved solid and total solid is calculated.

$$\text{Total Suspended Solid, mg/L} = (A - B \times 100) / C \quad 3.2$$

Where:

A = weight of filter and dish + residue in mg

B = weight of filter in mg

C = volume of sample filtered in mL

3.5.4 Heavy Metal

pH is determine by using pH meter and total heavy metal concentration were analyse by using AAS (Atomic Absorption Spectrometry) (Abrha, 2013). The equation for removal efficiency of heavy metal by using AAS as the formula below:

$$\text{Removal efficiency} = (c_i - c_e) / c_i \times 100 \quad 3.3$$

Where:

C_i = concentration of the heavy metal in the influent

C_e = concentration of the heavy metal in the effluent

3.6 Data Analysis

All the data that obtained through the in situ test and ex situ were analysed by using Microsoft Excel in order to achieve objectives throughout this study. The objective that to be achieved were to determine the characteristic of the solid waste leachate in the study area. All the result from the data analysis will be discussed and showed more detail in Chapter 4 which is Result and Discussion.

There are many methods to evaluate and classify the raw data which is a statistical method. There are many statistical methods that can be used in order to organize the raw data to become informative data. The various statistical methods that can be used to analyse the data in this study are mean, variance, standard deviation and deviation. Mean is described as the most widely used for the measurement of central tendency. Next, the variance is described as the mean of the squares of the deviations. This statistical method is the most efficient, unbiased estimate of the population variance, s^2 is the sample variance s^2 . Besides, the standard deviation is described as the positive square root of the variance. Then, deviation is also a statistical method that describes the quantity by which each individual data point differs from the arithmetic mean of the sample. The removal efficiency of the Horizontal Sub-surface Constructed Wetland for each heavy metal was calculated by using the removal efficiency equation.

3.7 Research Outcomes

The research outcomes for this study area is the heavy metal removal efficiency. Heavy metals which are commonly occurred in the industrial wastewater are iron, copper, lead, zinc and manganese that are the contaminants of concern in this study. The effluent that come from the food industries, petrochemical industries and electroplating industries give the higher contamination of the heavy metal. The outcomes for removal of the heavy metal in industrial wastewater by using lemon peel activated carbon will be higher and the characteristic of the industrial wastewater will be determined. Besides, the effectiveness size of the lemon peel activated carbon will be proposed as the new solution for treatment of the industrial wastewater.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter will cover out about the result and discussion of the heavy metal removal from industrial wastewater by using the lemon peels. This chapter discussed about the effect of size on the performance of lemon peels and the effect of contact time on the performance of lemon peels.

4.2 Characteristic of Industrial Wastewater

The wastewater sample was collected from the Sungai Baluk. Location of the Sungai Baluk is nearby industrial place in Gebeng, Pahang. The river have been much polluted since the effluent of the industrial area discharged to the river. Before treating the water, the characteristic of the wastewater have been studied to achieve the first objective and to know if the water meet the standard in Environmental Quality (Sewage and Industrial Effluents Regulations 1979, Environment Quality Act 1974). Jabatan Alam Sekitar have been strict with this to avoid the river pollution and water pollution. The Environment Quality is a guideline where a company of industries should take to avoid the water pollution and river pollution. Table 4.1 show that the water characteristic study that have been conducted after collecting the wastewater sample.

Table 4.1 : Characteristic of the Industrial Wastewater

Parameters	Reading
Ph	6.23
Biochemical Oxygen Demand (BOD) (mg/L)	29.95
Chemical Oxygen Demand (COD) (mg/L)	188
Total Suspended Solid (mg/L)	100
Turbidity (NTU)	120
Colour (PtCo)	806
Ammoniacal Nitrogen (mg/L NH ₃ -N)	0.36
Heavy Metals	
Cadmium (mg/L)	0.361
Zinc (mg/L)	0.063

From the table 4.1 above, these are the characteristics of the industrial wastewater. From the table, the result that have been collected from COD reading of the industrial wastewater was high which 188 mg/L. The allowable range that should be the effluent discharged to the river is supposed 100 or below than that. The wastewater sample is not matching the standard in Environment Quality (Sewage and Industrial Effluents Regulations 1979, Environmental Quality Act 1974). The reasons of the badly water quality of Sungai Baluk in Gebeng are because of improper discharges of sewage and domestic wastewater to the river without the proper treatment, manufacturing activities, mining activities, agricultural and earthworks. Furthermore, the domestic wastewater and surface runoff from industrial areas are the reason why the wastewater did not meet the standard of quality. Because of the high reading of COD, so that there are a lot of chemical content present in the wastewater. This wastewater are need to be treated to remove the content of chemical so that the effluent can be discharged to the river with proper treatment. Hence, the method that have been applied to treat the water are by the activated carbon using adsorption process to achieve the objective of the study which is to remove heavy metal in the wastewater.

4.3 Effect of Size on the Performance of Lemon Peels

4.3.1 Heavy Metal

The heavy metal that were choose to be tested are cadmium and zinc. The size of the activated carbon of lemon peels that have been used are 1.18mm, 600 micron and

powder form. The maximum rate of removal occurred constantly on week one, week two and week three. After week three, the result is almost reaching zero for all the sizes but the powder form of the activated carbon seems to be very effective. The water sample from every size that have been treated were obtained for every week. The table 4.2 shows the cadmium concentration in wastewater before and the after treated with lemon peels activate carbon. Figure 4.1 show the graph that represent the data analysis of the concentration of cadmium in wastewater.

Table 4.2 : Cadmium concentration in wastewater

Week	1.18 mm (mg/L)	600 mic (mg/L)	Powder (mg/L)
0	0.361	0.361	0.361
1	0.280	0.280	0.280
2	0.154	0.147	0.119
3	0.128	0.107	0.093
4	0.096	0.070	0.030

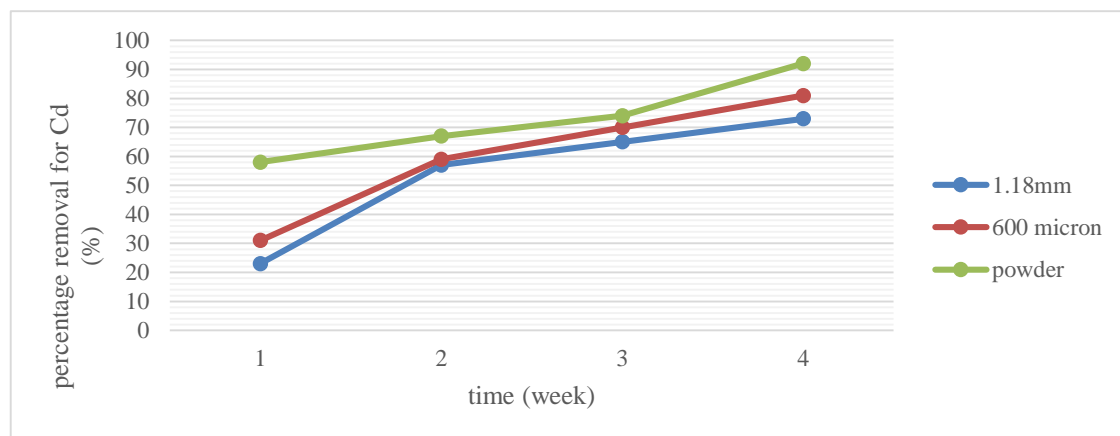


Figure 4.1 : The percentage of Cadmium removal against time

From the figure 4.1, cadmium was removed effectively from the wastewater. The concentration of cadmium before the treatment in the wastewater is 0.361 mg/L. The removal efficiency of lemon peels activated carbon on week 1 for 1.18mm is 23%, for 600 micron is 31% and for the powder is 58%. At the treatment continued, the content of cadmium was decreasing constant on week two where for the 1.18mm removed about the 57% while for the 600 micron removed 59% of cadmium and for the powder about 67% of cadmium removed. On the third week, the cadmium content was removed 65% for the 1.18mm, 70% cadmium content was removed for 600 micron and 74% cadmium content

was removed for powder. The last week which is week four, the content of cadmium was reducing constantly which is for 1.18mm was 73%, for 600 micron was 81% and for powder was 92%. If the treatment were continue for week five and week six, all the sizes may removed 100% of the cadmium present in the water. This happened because cadmium were adsorbed to the porous surface on the activated carbon. All the sizes adsorb the cadmium but the equilibrium that reach faster by the powder because the diameter sizes is small compared to the other sizes. The smaller diameter size of activated carbon, the faster activated carbon will reach equilibrium compared to the bigger size of diameter.

Table 4.3 show that the zinc concentration in wastewater before and the after treated with lemon peels activated carbon. Figure 4.2 show the graph that represent the data analysis of the concentration of zinc in wastewater.

Table 4.3 : Zinc concentration in wastewater

week	1.18 mm (mg/L)	600 mic (mg/L)	Powder (mg/L)
0	0.063	0.063	0.063
1	0.041	0.038	0.022
2	0.032	0.024	0.014
3	0.021	0.016	0.008
4	0.011	0.006	0.000

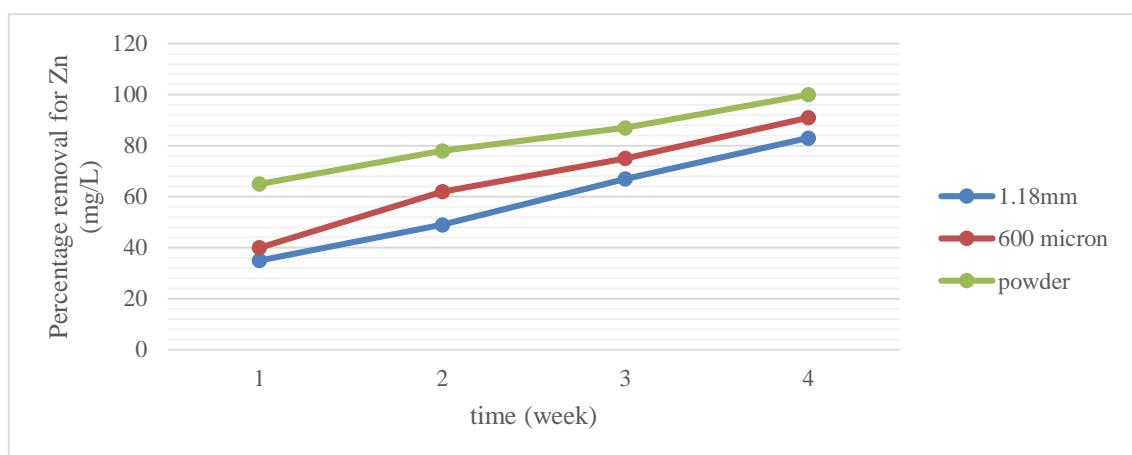


Figure 4.2 : The percentage of Zinc removal against time

From figure 4.2, the graph for the concentration of zinc shows that the treatment is effective. The zinc was effectively removed by the lemon peel activated carbon on the

powder form for the week four. The initial concentration of zinc content in the wastewater is 0.063 mg/L. Then, the removal efficiency of the lemon peels activated carbon on the week one for the 1.18mm is 23%, for the 600 micron is 31% and for the powder is 58%. As the treatment continued, the content of zinc was reducing constantly on week two where 1.18mm removed 49% of zinc, for 600 micron about 62% of zinc and powder about 78% of zinc. For the third week, the zinc content was removed 67% for the 1.18mm, 75% zinc content was removed for 600 micron and 87% zinc content was removed for powder. The last week which is week four, the content of zinc was reducing constantly which is for 1.18mm was 73% of zinc removed, for 600 micron of zinc removed was 81% and for powder was 92% of zinc removed. The powder activated carbon is very effective compared to the size 1.18mm and 600 microns activated carbon as the percentage of removal of zinc on week four achieved 100 percent. This is because the smaller diameter size of activated carbon, the faster activated carbon will reach equilibrium compared to the bigger size of diameter.

4.3.2 Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is a test the capacity of water to consume oxygen during the decomposition of organic matter and the oxidation of inorganic matter and the oxidation of inorganic chemicals. COD is tested every week for each size of activated carbon of lemon peels to know the latest COD reading of the water sample. Table 4.4 shows the data analysis of COD reading for every week.

Table 4.4 : COD concentration in wastewater

week	1.18 mm (mg/L)	600 mic (mg/L)	Powder (mg/L)
0	188	188	188
1	154	143	130
2	112	104	96
3	96	84	65
4	75	52	29

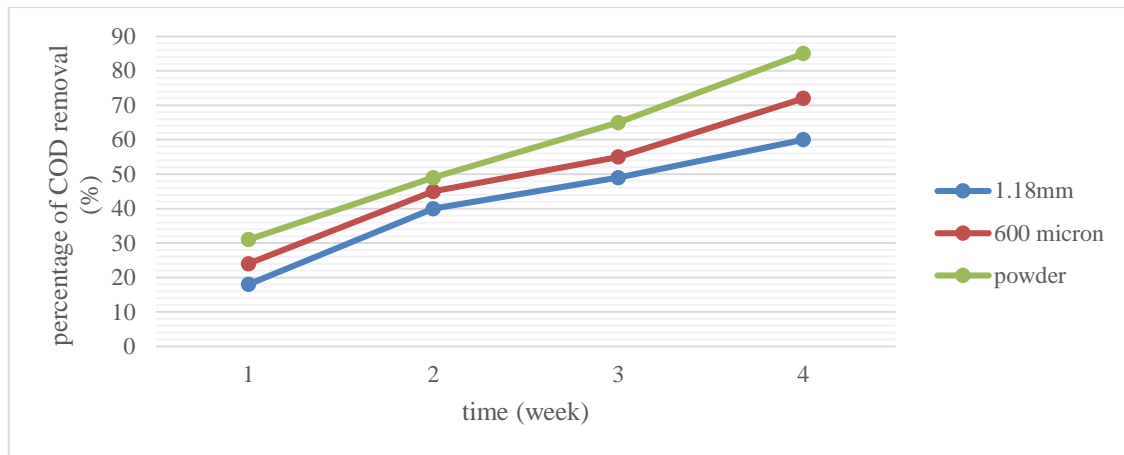


Figure 4.3 : The percentage of COD against time

The initial COD reading of the wastewater is 188 mg/L. This is because the inorganic content in the wastewater was very high due to the activity surrounding the river. The industrial effluent is directly discharge to the river and causes the COD of the wastewater is high. The COD does not meet the standard B in Environmental Quality (Sewage and Industrial Effluents Regulations 1979, Environmental Quality Act 1974). The COD drop slowly on the first week of treatment where for the 1.18mm is 18%, for the 600 micron is 24% and for the powder is 31%. For the second week, the COD reading drop rapidly which is for 1.18mm 63% COD removed, for the 600 micron 65% COD removed and for the powder 68% COD were removed. As the treatment continued on the third week, the size of 1.18mm removed 75% of COD, the size of 600 micron removed 83% of COD and the powder size removed 93% of COD. Then, for the fourth week, the percentage of COD constantly removed 82% by the 1.18mm, 88% by the 600 micron and 94% by the powder size.

This percentage of the COD drop constantly every week and if the treatment continue on another week, the COD removed might be 100% by the all sizes. This COD reading drop every week because of the activated carbon by the lemon peels adsorb the chemical substances in the wastewater hence the wastewater will be cleared from COD. From the graph, the powder size show the most effective in removing COD in the water rather than the 1.18mm size and 600 micron size. The reason of the performing powder size is the smallest diameter of the powder which is if the size of activated carbon is smaller, then faster the activated carbon could reach the equilibrium.

4.3.3 Biochemical Oxygen Demand (BOD)

The Biochemical Oxygen Demand (BOD) is a measure the amount of dissolved oxygen that is likely use by the organisms to degrade the waste in the wastewater under aerobic condition. It is important to evaluate the how much the treatment is required and the potential impact on the living things that receive the water. As the treatment of the adsorption process were take place in the wastewater, the amount of the dissolved oxygen in the water will decrease. This is happens because if the amount of BOD higher in the wastewater, the more bacteria will appear in the wastewater because less amount of oxygen will retarded the consuming of bacteria while decomposing organic matter. Figure 4.5 shows the data analysis of BOD reading for every week.

Figure 4.5: BOD concentration in wastewater

week	1.18 mm (mg/L)	600 mic (mg/L)	Powder (mg/L)
0	29.95	29.95	29.95
1	18.05	13.83	17.85
2	11.03	10.4	9.65
3	7.9	4.98	2.15
4	5.4	3.67	1.87

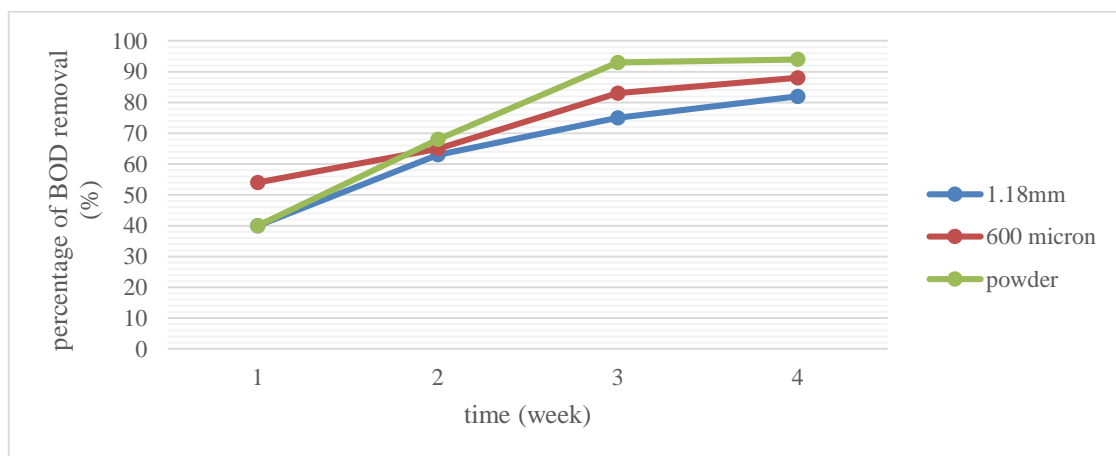


Figure 4.4 : The percentage of BOD removal

The initial reading of the BOD is 29.95 mg/L. The higher reading of the BOD because of the amount of organic matter present in the wastewater is higher for the oxygen consuming bacteria. The effluent that were discharged into the river contain the greater amount of organic matter because the wastewater treatment plants in the industrial

area did not remove organic matter properly before discharged into the natural waters. The initial reading of the BOD did not reach the standard Environmental Quality which is 20 mg/L. For the treatment of week one, the size of 1.18mm removed 40% of BOD content, for the size 600 micron removed 54% of BOD content and for the size of powder removed 40% of BOD content. For the second week, the BOD reading decrease constantly with 63% for 1.18mm, 65% for 600 micron and 68% for powder. As the treatment continued on the third week, the size of 1.18mm removed 75% of BOD content, 600 micron size removed 83% of BOD content and powder removed 93% of BOD content. The last week of treatment which is week fourth show that the BOD reading decrease slowly for the 1.18mm removed 82%, 600 micron removed 88% and the powder removed 94% of BOD content.

This percentage of the BOD drop constantly every week and if the treatment continue on another week, the BOD removed might be 100% by the all sizes. This BOD reading drop every week because of the activated carbon by the lemon peels adsorb the organics substances in the wastewater hence the wastewater will be cleared from bacteria. From the graph, the powder size show the most effective in removing BOD in the water rather than the 1.18mm size and 600 micron size. The reason of the performing powder size is the smallest diameter of the powder which is if the size of activated carbon is smaller, then faster the activated carbon could reach the equilibrium.

4.3.4 Total Suspended Solid (TSS)

Total suspended solid are the solids in water that can be trapped by a filter. TSS can include a larger variety of substances such as silt, decaying plant or animal matter, industrial wastes and sewage. The high concentrations of suspended solids can cause many problems for stream health and aquatic life. As level of TSS increase, a water body begins to lose its ability to support a diversity of aquatic life. Natural movements and migration of aquatic populations may be disrupted. Table 4.5 shows the data analysis for TSS for every weeks.

Table 4.6: TSS concentration in wastewater

week	1.18 mm (mg/L)	600 mic (mg/L)	Powder (mg/L)
0	100	100	100
1	95	84	80
2	87	68	60
3	73	53	40
4	41	28	10

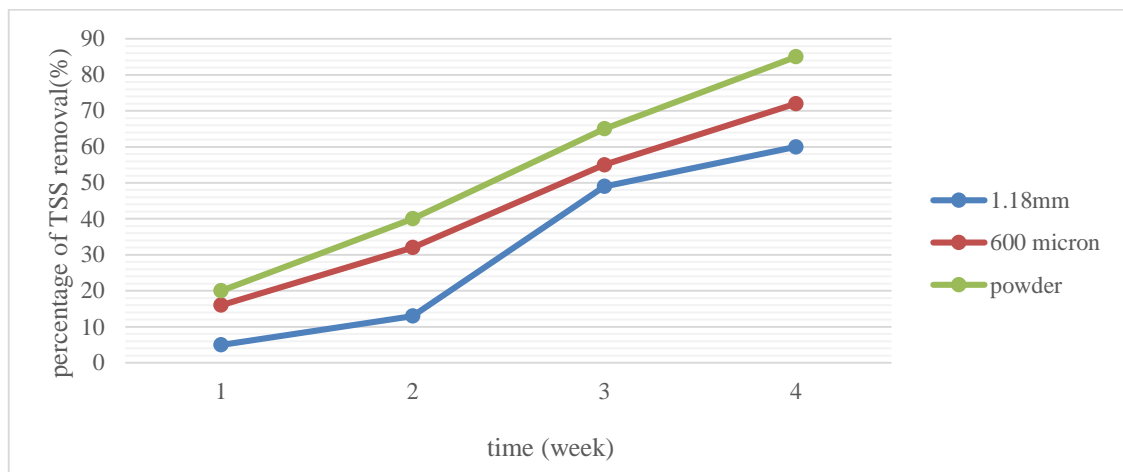


Figure 4.5 :The percentage of TSS removal

The initial concentration of the TSS is 100 mg/L. The higher reading of TSS because of the higher suspended solid that come from the industrial waste and sewage, the decaying of plant and the soil from the bauxite that come from the lorries of bauxite. From the treatment that have been done, on the week one, for the 1.18mm removed 5% of the suspended solids, for the 600 micron removed 16% of the suspended solids and for the powder removed 20% of the suspended solids. The treatment continued on the week two where the suspended solids decrease slowly for 1.18mm which removed 13%, for the 600 micron removed 32% and for the powder removed 40%. For the third week, the percentage removal of TSS decrease constantly for the 1.18mm is 27%, for the 600 micron 47% of TSS removed and for the powder 60% of TSS removed. Then, for the last week of treatment which is fourth week, suspended solid content in the water reduce rapidly where for the size 1.18mm is 59%, the size of 600 micron is 72% and for the powder size is 90%.

This percentage of the TSS drop constantly every week and if the treatment continue on another week, the TSS removed might be 100% by the all sizes. This TSS reading drop every week because of the activated carbon by the lemon peels adsorb the organics substances in the wastewater hence the wastewater will be cleared from suspended solid. From the graph, the powder size show the most effective in removing TSS in the water rather than the 1.18mm size and 600 micron size. The reason of the performing powder size is the smallest diameter of the powder which is if the size of activated carbon is smaller, then faster the activated carbon could reach the equilibrium.

4.3.5 Turbidity

Turbidity is the cloudiness or hazed of a fluid that caused by the large numbers of individual particles that are generally invisible to the naked eye which is same to the smoke in air. It is an optical characteristic of water and is an expression of the amount of light that is scattered by material in the water when a light is shined through the water sample. The measurement of turbidity is a key test of water quality. The higher the intensity of scattered light, the higher the turbidity. Table 4.6 shows the data analysis for turbidity for every week.

Table 4.7 : Turbidity concentration in wastewater

week	1.18 mm (NTU)	600 mic (NTU)	Powder (NTU)
0	120	120	120
1	101	77.1	65.6
2	94.5	62.5	41.9
3	53.6	42.2	32.1
4	36.2	29.7	13.9

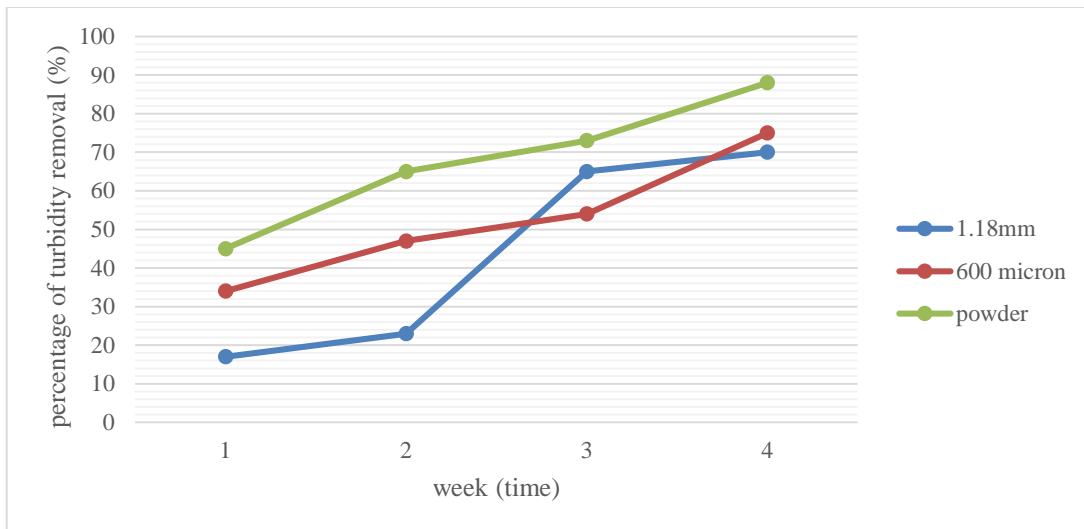


Figure 4.5 : The percentage of turbidity removal

The initial reading of turbidity is 120 NTU. The higher reading of turbidity because of the wastewater contain too much algae or sediment, suspended or dissolved solid in water that scatter light making the water appear cloudy and milky. The higher turbidity in water may cause by the growth of phytoplankton. So the wastewater have been treated by the lemon peels activated carbon which is for the week one the size of 1.18mm the turbidity drop 17%, for the size of 600 micron the turbidity drop 34% and for the powder size turbidity drop 45%. For the second week, the turbidity reading decline slowly which for the 1.18mm 23% removed, for the 600 micron 47% removed and for the powder 65% removed. As the treatment continued on the third week, the turbidity constantly decrease where 65% removed for 1.18mm size, 54% removed for 600 micron size and 73% for the powder size. Then, for the fourth week turbidity was removed 70% for 1.18mm size, 75% for the size 600 micron and the powder size 88% removed. The powder size of lemon peels activated carbon effectively rather the 1.18mm size and 600 micron because the turbidity reading dropped effectively.

4.3.6 Colour

Colour is one of the type of qualitative characteristic that can be used to know the general condition of the industrial wastewater. Colour analysis is important for monitoring process liquids and as a measurement of water quality for distribution or discharge. Wastewater that is light brown in colour are still in standard water quality condition while if the wastewater are light to medium grey colour which is the

characteristic of wastewaters that have undergone some degree of decomposition. Table 4.7 shows the data analysis of colour every weeks.

Table 4.8 : Colour concentration in wastewater

week	1.18 mm (PtCo)	600 mic (PtCo)	Powder (PtCo)
0	806	806	806
1	353	336	285
2	348	316	256
3	319	267	214
4	289	215	162

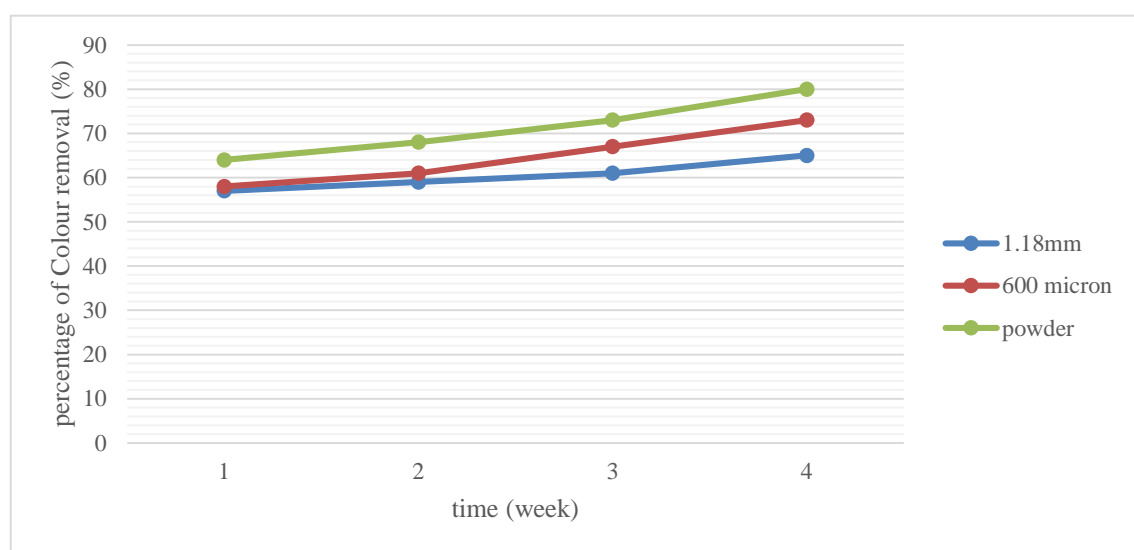


Figure 4.6 : Percentage of colour removal against time

The initial data analysis before treatment for colour is 806 PtCo. The initial reading for colour is higher because of the presence of natural metallic ions which is iron and manganese, humans and peats, plankton, weeds and industrial wastes. Some of the highly coloured industrial wastewaters colour is contributed principally by colloidal or suspended material. So the treatment by activated carbon lemon peels to reduce reading of the colour have been done. First week of treatment shows that the colour reading decrease rapidly for 1.18mm size where 57% reduced, for the 600 micron size 58% reduced and for the powder size 64% reduced. Then, for the second week, the reading of colour reduce slowly for the size 1.18mm where 59% removed, for the size 600 micron 61% removed and for the powder size 68% removed. As the treatment goes for third week, the size of 1.18mm reduce 62%, 600 micron size reduce 67% and powder remove 73%. The last week of treatment which is fourth week, the percentage of colour for

1.18mm reduce 65%, for 600 micron reduce 73% and the powder size reduce 80%. As the figure above, the powder size shows the most effective in reducing colour reading rather than the 1.18mm and 600 micron size.

4.3.7 Ammoniacal Nitrogen

Ammoniacal nitrogen ($\text{NH}_3\text{-N}$) is a measure for the amount of ammonia, a toxic pollutant often found in landfill leachate and in waste products such as sewage, liquid manure and other liquid organic waste products. The wastewater that are obtained from Sungai Baluk contain ammonia since the industrial effluent is discharged to the river. The reason why ammonia nitrate should be removed from wastewater are it will lead to eutrophication and oxygen depletion in water. Ammonia is excreted by animals and produced during decomposition of plants and animals thus returning nitrogen to the aquatic system. Nitrogen can be important factor in controlling algal growth when other nutrients such as phosphate are abundant. Table 4.8 shows the ammoniacal nitrogen data analysis for every week during treatment period.

Table 4.8 : Ammoniacal Nitrogen concentration in wastewater

week	1.18 mm (mg/L)	600 mic (mg/L)	Powder (mg/L)
0	0.36	0.36	0.36
1	0.23	0.21	0.16
2	0.20	0.15	0.13
3	0.16	0.13	0.09
4	0.13	0.09	0.04

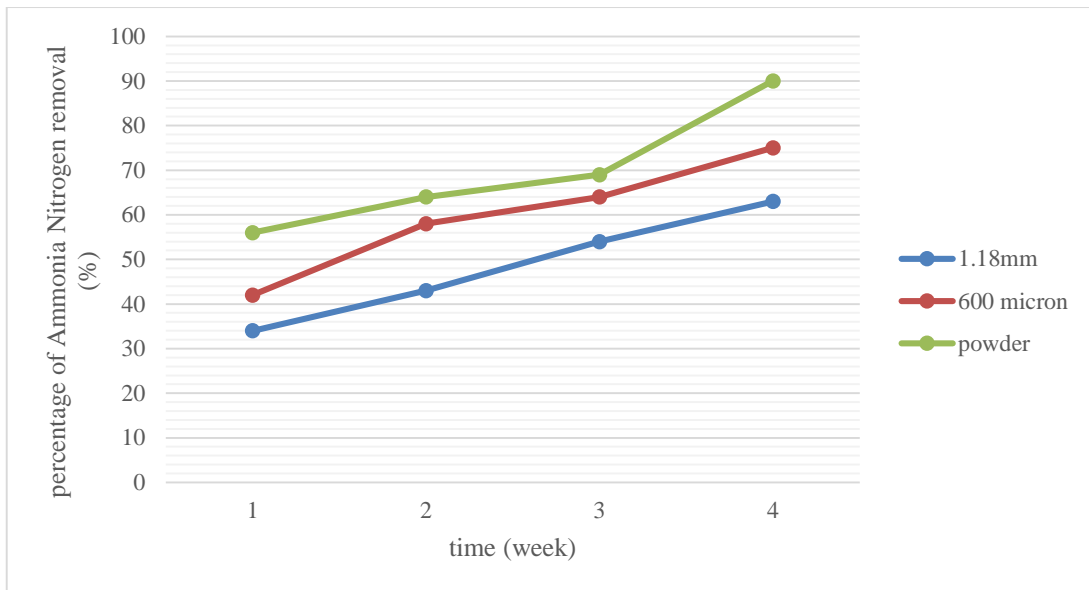


Figure 4.7 : The percentage removal of Ammoniacal Nitrogen removal

The initial reading of ammoniacal nitrogen before treatment is 0.36 mg/L $\text{NH}_3\text{-N}$. The higher ammoniacal nitrogen before treatment because the effluent from industrial area contain high content of ammonia where it is discharged to Sungai Baluk. The high content of ammonia because of organic waste product, sewage, agricultural pollution, chemical waste product and primarily from fertilizers or faecal matter from industrial companies. From the figure 4.7 above, the percentage removal of ammonia by the lemon peels activated carbon on week one by the 1.18mm size is 34%, 600 micron is 42% and the powder size is 42%. For the second week of treatment, the removal of ammonia increase slowly for the size of 1.18mm is 43%, for the 600 micron is 58% and the powder is 64%. The treatment continued on the third week where for the size of 1.18mm remove 54% of ammonia, 600 micron remove 64% of ammonia and the powder size remove 75% of ammonia. The percentage removal efficiency seem more effective to the size of powder rather than 600 micron and 1.18mm. Hence, the size of activated carbon give the most effect to the faster removal of ammonia nitrogen where the smaller size of activated carbon the faster removal of ammonia nitrogen which activated carbon faster reach the equilibrium.

4.3.8 pH

pH is a measure of the amount of free hydrogen ions in water. Specifically, pH is the negative logarithm of the molar concentration of hydrogen ions. pH is a numeric scale

used to specify the acidity or alkalinity of a solution. The pH of water affects the solubility of many toxic and nutritive chemical so that the availability of these substances to aquatic organisms is affected. As acidity increases, most metals become more water soluble and more toxic. Alkalinity is the capacity to neutralize acids and the alkalinity of natural water is derived principally from the salts of weak acids. The industrial wastewater from Sungai Baluk might influences the pH value of wastewater. Table 4.9 shows the pH reading of wastewater for every week.

Table 4.9: pH result in wastewater

week	1.18 mm	600 mic	Powder
0	6.23	6.23	6.23
1	7.85	7.95	7.13
2	6.98	8.07	6.83
3	6.55	7.32	6.53
4	6.26	6.81	6.83

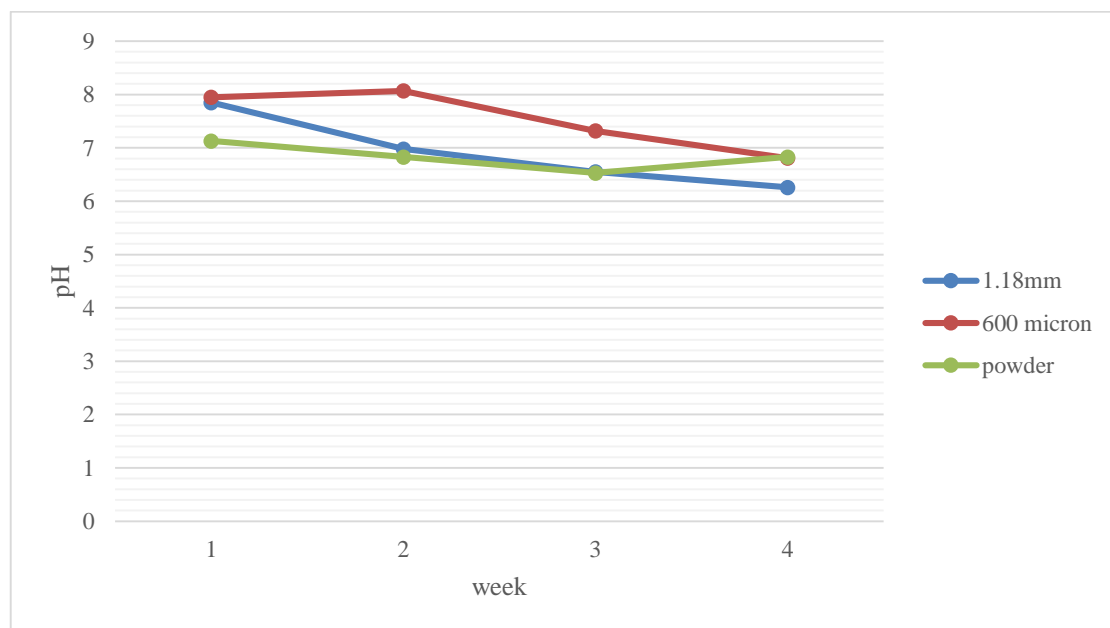


Figure 4.8 : the pH meter in wastewater

The initial pH reading the water sample is 6.23 @ 24.5 °C. The reading of the pH value increases during the treatment which makes the water to be more alkaline. But the pH value never go beyond 10. The highest reading of pH is on the week two where for the size of 600 micron goes to the pH value of 8.07. However, on the third and fourth

week, the pH value dropped because of the formation of algae in the water. This is because the wastewater that is kept and treated did not flow. From figure 4.8, the size of 600 micron activated carbon has a moderate rise in pH value. The value of pH did not shoot up too much.

CHAPTER 5

CONCLUSION

5.1 Conclusion

From the objective of this study which are to determine the characteristic of wastewater from industrial wastewater and to determine the effectiveness of the size of lemon peel activated carbon adsorption which is effective. As the treatment continued, the content of cadmium reducing constantly from week one to the fourth week. For the treatment on week two, the removal efficiency for the size of 1.18mm is 57%, for the 600 micron is 59% and for the powder form is 67%. On the third week, the removal efficiency of cadmium slowly increase. As treatment goes on the fourth week, percentage removal of cadmium for treatment for 1.18mm is 73%, for the size 600 micron is 81% and for the powder size is 92%. On the other hand, the content of zinc was reduce constantly from the week one to week four. The content of zinc reduce drastically on week two where for the size of 1.18mm is 49%, for the size of 600 micron is 62% and for the powder size is 78%. The powder size on the fourth week was perform 100% removal of zinc rather than the 1.18mm which is 83% and 600 micron is 91%. Thus, it show that the powder form of lemon peels activated carbon is very effective in removing heavy metals in water.

All the sizes of lemon peels activated carbon can remove 100% heavy metal for cadmium and zinc also COD if the treatment continue until to five or six week. The cadmium, zinc and COD drop constantly during the treatment period. Thus, it proving that longer period of treatment will able to remove all the inorganic matter in water. Lemon peels as the adsorbent that has bond between the inorganic or organic particles solution to its surface side. So that the longer the time contact time of adsorption, the bigger collision between particle of adsorbate and adsorbent. The lemon peels activated carbon was successfully removed the organic and inorganic matter that high in the

wastewater with adsorbed the suspended solids and heavy metal that contain in the wastewater. The equilibrium between the wastewater and activated carbon was successfully achieved for all the sizes.

As a conclusion, the lemon peels can be used in treating wastewater for the adsorption process. There are many other ways to treat wastewater and to remove heavy metal in water which is used a lot of money and energy that make it difficult to treat the wastewater. From the result and discussion above, adsorption process for the lemon peels activated carbon can be used to treat wastewater which give more advantages such as the cheapest method. Lemon peels has the tendency to be a good adsorbent and the adsorption process can be carried on.

5.2 Recommendation

As shown in the result and discussion above, lemon peels can be used to treat wastewater from industrial. But, to get the lemon for this treatment it is expensive enough and not commercial to be used. As for recommendations, further study should be done to study whether the recycle lemon peel can be used for the treatment and to study the condition or experimental work procedure which is possible in finding the correct dosage of activated carbon to be used to get more effective result. The recommendations are:

- i. Research on the recycle lemon peels to be used for the activated carbon.
- ii. Increase the surface area of raw material by making the lemon peel into very fine powder.
- iii. Research on the other parameters such as dosage.
- iv. Research on different treatment method for heavy metal removal.

Research on the different type of variable, parameters and ways provides many opportunity wastewater treatment by using lemon peels.

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APPENDIX A
ACCEPTABLE LIMITS FOR DISCHARGE OF INDUSTRIAL EFFLUENTS
OR MIXED EFFLUENTS OR MIXED EFFLUENT OF STANDARDS A & B
PARAMETER UNIT STAND.

Parameter	Unit	Standard A	Standard B
(1)	(2)	(3)	(4)
(i) Temperature	°C	40	40
(ii) pH Value		6.0 - 9.0	5.5 - 9.5
(iii) BOD5 at 20°C	mg/l	20	50
(iv) COD	mg/l	50	100
(v) Suspended Solids	mg/l	50	100
(vi) Mercury	mg/l	0.005	0.05
(vii) Cadmium	mg/l	0.01	0.02
(viii) Chromium, Hexavalent	mg/l	0.05	0.05
(ix) Arsenic	mg/l	0.05	0.10
(x) Cyanide	mg/l	0.05	0.10
(xi) Lead	mg/l	0.10	0.5
(xii) Chormium, Trivalent	mg/l	0.20	1.0
(xiii) Copper	mg/l	0.20	1.0
(xiv) Manganese	mg/l	0.20	1.0
(xv) Nickel	mg/l	0.20	1.0
(xvi) Tin	mg/l	0.20	1.0
(xvii) Zinc	mg/l	1.0	1.0
(xviii) Boron	mg/l	1.0	4.0
(xix) Iron (Fe)	mg/l	1.0	5.0
(xx) Phenol	mg/l	0.001	1.0
(xxi) Free Chlorine	mg/l	1.0	2.0
(xxii) Sulphide	mg/l	0.50	0.50
(xxiii) Oil and Grease	mg/l	Not detectable	10

Sources : Environmental Quality (Industrial Effluent) Regulations 2009, Malaysia

APPENDIX B
INDUSTRIAL WASTEWATER TREATMENT FOR 1 MONTH

Date: 20 April 2017

treatment : week 1

Size / Parameters	1.18 mm	600 micron	Powder
pH	7.85	7.95	7.13
BOD (mg/l)	18.05	13.83	17.85
COD (mg/l)	154	143	130
TSS (mg/l)	95	91	83
Turbidity (NTU)	101	78	66
Colour (PtCo)	353	336	285
Ammoniacal Nitrogen (mg/L)	0.23	0.21	0.16
Heavy Metal (mg/L)	Cd – 0.280	0.250	0.150
	Zn – 0.041	0.038	0.022

Date : 26 April 2017

treatment : week 2

Size / Parameters	1.18 mm	600 micron	Powder
pH	6.98	8.07	6.83
BOD (mg/l)	11.03	10.4	9.65
COD (mg/l)	112	104	96
TSS (mg/l)	87	68	60
Turbidity (NTU)	95	63	42
Colour (PtCo)	336	316	256
Ammoniacal Nitrogen (mg/L)	0.20	0.15	0.13
Heavy Metal (mg/L)	Cd – 0.154 Zn – 0.032	0.147 0.024	0.119 0.014

Date : 3 May 2017

treatment : week 3

Size / Parameters	1.18 mm	600 micron	Powder
pH	6.55	7.32	6.53
BOD (mg/l)	7.5	4.98	2.15
COD (mg/l)	96	84	65
TSS (mg/l)	73	53	40
Turbidity (NTU)	42.2	53.6	32.1
Colour (PtCo)	319	267	214
Ammoniacal Nitrogen (mg/L)	0.16	0.13	0.09
Heavy Metal (mg/L)	Cd – 0.128 Zn – 0.021	0.107 0.016	0.093 0.008

Date : 12 May 2017

treatment : week 4

Size / Parameters	1.18 mm	600 micron	Powder
pH	6.26	6.81	6.83
BOD (mg/l)	5.4	3.67	1.87
COD (mg/l)	75	52	29
TSS (mg/l)	41	28	10
Turbidity (NTU)	36.2	29.7	13.9
Colour (PtCo)	289	215	162
Ammoniacal Nitrogen (mg/L)	0.13	0.09	0.04
Heavy Metal (mg/L)	Cd – 0.096	0.070	0.030
	Zn – 0.011	0.006	0.000

**APPENDIX C
STUDY AREA AND TEST (PHOTO)**



Figure C1: Site Area



Figure C2: Lemon Peels after dried



Figure C3: Take sample of wastewater treatment



Figure C4: Stir sample with activated carbon



Figure C5: Heavy metal test



Figure C6: Heavy Metal data analysis



Figure C7: Three different sample



Figure C8: Lemon peels after oven



Figure C9: Weight the activated carbon



Figure C10: Three different size activated carbon



Figure C6: Ammoniacal Nitrogen test



Figure C6: Total Suspended Solid test