REMOVAL OF Cr (VI) CONTAIN IN TEXTILE DYE INDUSTRY EFFLUENT USING FOXTAIL PALM FRUIT AS ACTIVATED CARBON

by

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DECLARATION

I declare that this thesis entitled "Removal of Cr (VI) contain in Textile Dye Industry Effluent using Foxtail Palm Fruit as Activated Carbon" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ______________________________

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Date : 12/01/2020

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REMOVAL OF Cr (VI) IN TEXTILE DYE INDUSTRY EFFLUENT USING FOXTAIL PALM FRUIT AS ACTIVATED CARBON

ABSTRACT

Dyes are commonly used widely in many industries nowadays. The improper disposal of dyes could lead to negative effect to the water users and marine aquatic life. This is due to the properties of dyes which contain a lot of chemicals and heavy metals which can give harm to the environment and living organisms. One of the major industries that produce dye wastewater sources and contribute the negative effects to the environment is industry of textile. Industry of textile used a lot of chemicals which contain a lot of heavy metals such as chromium. As a consequence, the removal of heavy metals in dye wastewater by adsorption of activated carbon prepared from foxtail palm fruit was studied. The objectives of this study were to determine the chromium concentration contain in dye textile effluent, to study the influent pH on chromium removal and to study the effectiveness on adsorbent dosage and contact time towards the efficiency of prepared activated carbon. Activating agent that is nitric acid (HNO_3) was used in this experiment were left for overnight to impregnate at temperature of 500 ℃ for two hours and 30 minutes of carbonization. The adsorption capability of foxtail palm fruit activated carbon was determined with the use of a heavy metal called chromium. The chromium adsorption was identified based on range of the selected parameters which are adsorbent dosage, contact time and pH in order to investigate their effects in adsorption potential of foxtail palm fruit powder. The effectively parameters for adsorption of foxtail palm fruit activated carbon were at 5 g of adsorbent dosage, at 120 minutes of the contact time and at an acidic pH which was pH 2 with highest removal of Cr (VI) was 84.4 %.

PENYINGKIRAN Cr (VI) DALAM EFLUEN INDUSTRI TEKSTUR PEWARNA MENGGUNAKAN BUAH PINANG SEBAGAI KARBON AKTIF

ABSTRAK

Pewarna biasanya digunakan secara meluas dalam kebanyakkan industri pada masa kini. Pelupusan pewarna yang salah boleh menyebabkan berlakunya kesan negatif kepada pengguna air dan kehidupan akuatik laut. Ini disebabkan oleh sifat pewarna yang mengandungi banyak bahan kimia dan logam berat yang boleh memudaratkan alam sekitar dan organisma hidup. Salah satu industri utama yang menghasilkan sumber sisa air pewarna dan menyumbang kesan negatif kepada alam sekitar adalah industri tekstil. Industri tekstil menggunakan banyak bahan kimia dan mengandungi banyak logam berat seperti kromium. Oleh itu, penyingkiran logam berat dalam sisa air pewarna oleh penjerapan karbon aktif yang disediakan dari buah pinang telah dikaji. Objektif kajian ini adalah untuk menentukan kepekatan kromium yang terdapat dalam efluen tesktur pewarna, untuk mengkaji pH yang berpengaruh terhadap penyingkiran kromium dan untuk mengkaji keberkesanan pada dos penjerap dan tempoh masa terhadap kecekapan karbon aktif yang dihasilkan. Ajen pengaktifan iaitu asid nitrik (HNO_3) yang digunakan dalam eksperimen ini dibiarkan selama semalaman untuk impregnasi pada suhu 500 °C selama dua jam 30 minit untuk proses pengkarbonan. Keupayaan penjerapan buah pinang karbon aktif ditentukan dengan menggunakan logam berat yang dipanggil kromium. Penjerapan kromium (VI) telah dikenalpasti berdasarkan pelbagai parameter yang dipilih iaitu dos penjerap, tempoh masa dan pH untuk mengkaji keberkesanannya dalam keupayaan penjerapan serbuk buah pinang. Parameter yang berkesan untuk penjerapan karbon aktif buah pinang adalah pada 5 g dos penjerap, 120 minit tempoh masa dan pada pH berasid iaitu pH 2 dengan penyingkiran tertinggi Cr (VI) adalah sebanyak 84.4%.

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LIST OF ABBREVIATIONS

AC	Activated Carbon
Cr (VI)	Chromium
UV-Vis	Ultraviolet-Visible Spectrophotometry
HNO_3	Nitric Acid
rpm	Revolutions per minute
HCl	Hydrochloric Acid
H_2SO_4	Sulphuric Acid

LIST OF SYMBOLS

°C	Degree Celsius
%	Percentage
g	Gram
mL	Millilitre
nm	Nanometre

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Activated carbon is defined as a carbonaceous and highly porous adsorptive medium that have a complex structure that primarily composed of carbon atoms (HAYCARB, 2019). Activated carbon can be produced from many sources such as foxtail palm fruit, rice husk and coconut husk. (HAYCARB, 2019). In this study, foxtail palm fruit has been chosen to produce an activated carbon.

Foxtail palm fruit or their scientific name is *Wodyetia bifurcata* is a palm tree with symmetrical shape, rounded, smooth, tufted foxtails and grey trunk that is similar with foxtails. The characteristics of this plant is very fast in growing, adaptability and has amazing beauty which are very famous in landscape industries and nursery. Foxtail palm fruit has been found that can be formed into activated carbon which can be very useful in order to reduce the contamination of heavy metals in the wastewater.

Contamination of heavy metals in the wastewater basically come from anthropogenic sources such as discharge of industrial wastewater and untreated domestic, spills of chemical accidentally, soil waste directly dumping, and residues from some agricultural inputs that present in water, sediments and air (Anticó et al., 2017). Due to their toxicity at very low doses, all those elements have been associated with the environmental degradation, different human diseases and poor water quality (Anticó et al., 2017). The toxicity effects of heavy metals can be divided into two categories which are acute and chronic effects. Acute effects will happen immediately or after short time of exposure, while chronic effect may happen after many years of exposure and their etiological origins are often difficult to trace (Anticó et al., 2017). Heavy metals from the industrial wastewater can be generated from chemicals industry, steel and iron industry, pulp and paper industry, mines and quarries industry, oil and gas industry, food industry (Watermark, 2019).

Textiles dye is a common contributor to the contamination of heavy metals in wastewater. Their toxic nature have become a significant matter to the environmentalist. On all forms of life, the use of synthetic dyes could give and adverse impact whether to the living things or non-living things. From the textiles dye industry, it uses more than 2000 types of chemicals and more than 7000 types of dyes (Halimoon & Yin, 2010). Due to that, there are a lot of chemicals that presence in the textiles dye wastewater which are chromium, sulphur, soaps, nitrates and heavy metals such as mercury, lead, cadmium which make the effluent are highly toxic (Rita Kant, 2012). Dyeing was included of combination process which were colouring and bleaching that contribute high volume of wastewater and causing the environmental degradation (Balakrishnan et al., 2008). Even though most of the colours stay on the fabrics, but 30 to 40 percent of the colour will be washed out and flushed whether directly to the environment such as rover or land, or into the drainage system.

In Malaysia, batik fabric are very popular due to the traditional fabric that are handmade textile craft. In the past time, Malaysian batik can be found on the east coast of Malaysia which are Terengganu, Pahang and Kelantan but now it was already spread throughout the whole Malaysia. In result, the textiles dye wastewater become increasing from day to day due to increasing in production of batik fabric every day.

To overcome the environmental pollution problems, a lot of research were conducted to explore the most effective and suitable method to remove the contamination in that textiles dye effluent. Activated carbon adsorption, ion exchange, electrolysis, chemical treatment and chemical coagulation were various method that were developed to remove contaminants from the wastewater before it is release into the environment (Geçgel et al., 2013).

From the various method, the foxtail palm fruit that act as an activated carbon were used to treat the effluent that has been released from the textiles dye industry and at the same time it can reduce or minimize the contamination of heavy metals in the water sources.

The research study were done to determine the Chromium (VI) concentration that contain in dye textiles industry effluent. This research also were conducted to produce the activated carbon from foxtail palm fruit. With that, the waste of foxtail palm fruit can be reduced. Next, this research also to determine the effectiveness of produced activated carbon in removing Chromium (VI) concentration based on effect of adsorbent dosage, contact time and pH.

Figure 1.1: Foxtail Palm Tree

Figure 1.2: Foxtail Palm Fruit

1.2 Problem Statement

Nowadays, activated carbon are becoming very popular with their potential that can treat and reduce the contamination of heavy metals that contain in the wastewater. Many research have been done that used activated carbon to treat the heavy metals such as foxtail palm fruit, rice husk, tropical wood, coconut shells, palm shells, durian peel, walnut shells, corncobs, watermelon, tobacco stems, bean husks, hazelnut shell, banana peel and many more (Tadda et al., 2016). All these sources of activated carbon are widely used throughout the world but for foxtail palm fruit, their usage to treat the heavy metals have not being found yet. From the previous research that has been done, foxtail palm fruit has been removed the dye methylene blue up to 97.13% of the removal. This shows that, foxtail palm fruit are very effective activated carbon in order to use on removing the heavy metals in the wastewater. From that previous research, it is expected that foxtail palm fruit can also be very effective to treat and reduce the contamination of heavy metals that contain in the textiles dye industry effluent. Because of the commercial activated carbon are very costly, the alternative ways has been taken that is by using agricultural waste. So, this will be another starting point for foxtail palm fruit to be converted into activated carbon and used to treat the heavy metals in wastewater and at the same time, it will help in reducing the foxtail palm fruit waste products.

1.3 Objectives

There are three objectives for this research study. The objectives are

i. To determine the chromium (VI) concentration contain in textile dye industry effluent.

ii. To study the influent of pH on chromium (VI) removal.

iii. To determine the effectiveness of produced activated carbon in removing chromium (VI) concentration based on effect of adsorbent dosage and contact time.

1.4 Scope of Study

This research study were focusing on the using of agriculture waste that is foxtail palm fruit that act as an activated carbon. This activated carbon were used to remove the heavy metals in the textiles dye industry effluent. Textiles dye effluent is a real waste that comes from wastewater that have been released from Adnan Batik Industry Kota Bharu, Kelantan. The foxtail palm fruit were collected at the surrounding area in Jeli, Kelantan where there were the plant that has been planted around those areas. This research were conducted from August 2019 until December 2019. By using Ultraviolet-Visible Spectrophotometry (UV-Vis), the heavy metals from textiles dye industry effluent were analysed.

1.5 Significance of Study

This study are very important especially in textiles dye industry and foxtail palm fruit. From this study, the foxtail palm fruit can be utilize from agricultural waste product into something that valuable that is activated carbon which is very useful. Next, this study can help on minimizing or reducing the total textiles dye industry effluent at the selected industry from being discharged into the river, streams or any other water sources.

CHAPTER 2

LITERATURE REVIEW

2.1 Activated Carbon

Activated carbon is a porous carbon material or known as char which has been subjected to reaction with gases, sometimes with addition of chemicals such as $ZnCl_2$ before, during or after carbonization in order to increase its adsorptive properties (Jackson, 2014). Have large adsorption capacity, preferably for small molecules, and are used for purification of liquids and gases are some properties of activated carbon. Activated carbon can available in three forms which are pellet, granular and powdered forms, but the most frequently used are powdered and granular (Tadda et al., 2016). As a result of its high surface area, activated carbon is found to be very useful in removing many contaminants from both wastewater and potable water.

Activated carbon can be formed from many sources such as foxtail palm fruit, maize corncob, cornelian cherry, apricot stones, mango kernel and almond shells (Tadda et al., 2016). From the previous research that used cornelian cherry as activated carbon, the removal of Cr (VI) in wastewater can up to 99.99% at 25 ℃ of the temperature (Demirbas et al., 2004). While, from another previous study that use mango kernel as activated carbon, the removal of Cr (VI) in wastewater can up to 78% (Rai et al., 2016). Next, the previous research use maize corncob as activated carbon with the removal of Cr (VI) can up to 75% with the adsorbent dosage 3g (Azad, 2014).

Activated carbon can be synthesized by some methods which are chemical and physical activation process (Tadda et al., 2016). For the chemical activation, the raw materials which is the starting materials are impregnated with a strong dehydrating agent, then were followed by pyrolysis at high temperature to prepare activated carbon. While, for the physical activation method, it consist of carbonization of the precursor which is raw material in an inert atmosphere and gasification of the resulting char in the presence of air, steams, or carbon dioxide (Ossman et al., 2014). Because of limited sources of all materials here, foxtail palm fruit are been chosen to form activated carbon as Jeli are very popular with this tree as this tree normally were planted at any garden such as at school's garden, public's garden and many more.

2.2 Foxtail Palm Fruit

For this research, foxtail palm fruit were used as activated carbon. Foxtail palm fruit or their scientific name is *Wodyetia bifurcata* is a palm tree with symmetrical shape, rounded, smooth, tufted foxtails and grey trunk that is similar with foxtails. Foxtail palm tree have acknowledged famous attention in landscape industries and nursery because of their fast growth, adaptability and amazing beauty characteristics. Foxtail palm tree is a monocot plant that has a solitary growth habit, with trunks that are delicate, bloated at the base and surround with leaf scars. It has a pale green crown shaft and a crown of 8-10 leaves that range in length from 8 to 10 feet (Palm et al., 2014). The characteristics of the plant that is their leaves are pinnately compound or also known as feather-leaved, with few hundred fishtail leaf-lets attached together with rachis, or leaf rib, allowing them to look alike foxtail appearance. This plants reached their maturity at about 12 years of their age which at that time, they are able to produce inflorescences. The inflorescences, which grow up at the base of crown shaft, bears with white flowers. Foxtail palm tree can grow very fast in the full sun to partial shade. They also relatively easy going and can adapt easily with salt and wind.

High surface area are one of the characteristics that make this fruit are very suitable to form an activated carbon. With high surface area, the adsorption of heavy metals in the textiles dye industry effluent can be very effective. As previous research that found that, this fruit are very effective in removing dye methylene blue in the wastewater. So, it was expected that, this fruit would give the same result in removing heavy metals that is Chromium (VI) from the textiles dye industry effluent.

2.3 Textiles Dye Industry

Textiles dye industry is one of the most vital and important industry for the present and the future as it is one of the asset of a nation. Effluent is generated in large quantity in textiles dye industry. It may contains many undisclosed substances, chemicals and many dissolved substances in their effluent. Textiles dye industry will produce effluent and sludge during different industrial processes. Treatment for effluent from textiles dye industry is a matter of alarming for us, where scientist and expertise throughout the world now are struggling to develop innovative technologies to treat the effluent (Sinha et al., 2014). Textiles dye industry is a significant contributor to the pollution of environment. Because of that, it needs to produce more cleaner and efficient technologies to minimize its environmental footprint and to make sure the long term of sustainability of the industry (SEAISI, 2008).

Textiles dye industry mostly produce batik fabric. It needs large amount of dye to produce batik fabric. As a consequences, production of batik fabric give significant amount of residues, air pollutants, and solid by-product, together with waste water sludge. Based on biological system, heavy metals can contribute to affect cellular components and organelles such as mitochondrial, endoplasmic reticulum, cell membrane, lysosome and others enzymes that involved in detoxification, damage repair and metabolism (Tchounwou et al., 2012). Source of heavy metals has reported in the environment including agricultural, pharmaceutical, industrial, atmospheric sources and domestic effluents (Tchounwou et al., 2012).

Next, air pollution could happen where there are a lot of emission of particulate matter that contain in the air such as chromium. Besides that, there are also metals in emission of particulate matter such as cadmium, lead, copper, arsenic, zinc, nickel and iron. Also the other pollutants that contain in emission of particulate matter are nitrogen oxide, sulphur dioxide, and polycyclic aromatic hydrocarbons (SEAISI, 2008). Textiles dye industry also one of the factors that generates amount of carbon dioxide emission into the atmosphere where it forms during the dyeing making process.

Furthermore, textiles dye industry effluent is the waste that is generating from drainage of that industry and flow into the water sources such as drainage system and directly flow into streams and river which contribute to water pollution. Some of them were dissolved into groundwater system. To produce one ton of dyes, it is effectively use more than 10, 000 of dyes and over 2000 types of chemicals. In the textiles dye effluent, it may contains many dissolved, undissolved substances, and chemicals that are very poisonous. Heavy metals toxicity from this water pollution can contribute to lower of energy levels, damage the functioning of brain, lungs, liver, blood composition, kidneys and other important organs (Jaishankar et al., 2014). For long-term exposure, it can contribute to gradually progressing of muscular, physical and neurological degenerative processes that imitate disease such as Parkinson's disease, muscular dystrophy, multiple sclerosis and Alzheimer's disease (Jaishankar et al., 2014).

Besides, textiles dye industry also contribute to the sound or noise pollution that comes from the machineries and other accoutrements. By exposing to the loud in a long time period, it will cause the injuries on the ears (Oni, 2016).

2.4 Heavy Metals

There are a lot of heavy metals that can be found in the dye textile industry effluent which can give negative impacts to the environment including humans, animals and plants. Chromium was one of the very dangerous heavy metals that can be found in the textiles dye industry effluent. To manufacture the textile fabric, one of the important step that should be done was dyeing process. Throughout this process, the colour were mixed with the fibres and to improve the adsorption process between fibres and colour, a lot of different chemicals have being used (Scholz, 2019). When the final product was formed after the finishing process, some of those chemicals and dyes became a part of the textile industry effluent. All those chemicals and dyes would undergo breakdown process which resulted to be very toxic and may contaminate the surface water, ground water, soil and sediment that near to the industry and contributed to the very serious environmental pollution (Scholz, 2019).

Chromium, one of the dangerous heavy metals that can be found in textiles dye industry effluent. Chromium can be formed in many oxidation states but there were three form of valence states that common and mostly in stable state which were Cr (0), trivalent chromium (III) and hexavalent chromium (VI) (Rollinson, 1973). Chromium (VI) was more toxic compared to Cr (III) due to the present of high solubility, high oxidizing potential and high in the mobility across the membrane in the environment and living organisms (Oliveira, 2012). Cr (III) was considered less toxic because it is insoluble in water, has lower mobility and most bound to the organic matter in aquatic environments and soil (Oliveira, 2012). However, Cr (III) can be oxidized and formed Cr (VI) when the concentration of Manganese oxides or oxygen is high in that water samples (Oliveira, 2012). The concentrations range that should be in the industrial wastewater were between 0.5 to 270.00 mg/l (Berihun, 2017). Besides, for discharge into inland surface water and in potable water, the tolerance limit for Cr (VI) both of sources were 0.1 mg/l and 0.05 mg/l respectively (Berihun, 2017).

Adnan Batik industry that located in Kota Bharu, Kelantan which this state were very well known with the usage of underground water in their daily life. Due to that, people that live near to Adnan Batik Industry might have a high risk to get affected after being consumed the polluted underground water. Cr (VI) was considered as a powerful epithelial irritant and was a human carcinogen (Oliveira, 2012). It is also toxic to aquatic animals, microorganisms and many plants (Sneddon, 2016). Due to that, foxtail palm fruit was considered to form as activated carbon that undergo chemical activation in order to reduce and remove all these pollutions.

2.5 Chemical Activation

Chemical activation process has been chosen to form the activated carbon from foxtail palm fruit. In the chemical activation process, it involves multiple two steps that occur simultaneously, where chemical activating agents were mixed together with precursor that act as oxidants and dehydrates (Tadda M.A. et al., 2016). During chemical activation process, the activation and carbonization were perform simultaneously at the lower temperature in order to have better result of porous structure of activated carbon but due to concern of environmental protection, it may limit the use of chemical agents for activation (Tadda M.A. et al., 2016). Next, some chemicals that are very popular used as activating agents are potassium carbonate (K_2CO_3), potassium hydroxide (KOH), zinc chloride ($ZnCl_2$), nitric acid (HNO_3), trihydroxidooxidophosphorus, and phosphoric acid (H_3PO_4) (Tadda M.A. et al., 2016).

2.6 UV-Vis Spectrophotometry

Term for spectrophotometry refers to the technique where an analyte at a certain wavelength uses the absorbance of light in order to determine the analyte concentration (Protik, 2016). UV-Vis spectrophotometry uses the light in UV and visible part of the electromagnetic spectrum. The light of the wavelength are able to effect the excitation of electrons in the molecular or atomic ground state to higher energy levels which will arise to an absorbance at wavelengths specific to each molecule (Protik, 2016). Some of the light may be absorbed and the rest are transmitted through the sample when a beam of radiation or light are passing through a solution or a substance (Protik, 2016). This concept states that the absorption of ultraviolet radiation by the energy is literally same to the energy difference between the ground state and the higher energy state (Ankur, 2017).

UV-Vis Spectrophotometry principle follows the Beer-Lambert Law. This law shows that when beam of monochromatic light is passed through a solution together with an absorbing substance, the rate of radiation intensity will decrease together with the thickness of the absorbing solution is basically proportional to the incident radiation and the concentration of the solution (Ankur, 2017).

Beer-Lambert Law is show through this equation:

$$A = \log (I0/I) = ECI$$

From the equation, A is represent a absorbance, I0 is represent the intensity upon a sample cell, I is represent the intensity of light differing the sample cell, C is represent the concentration of the solute, L is represent the length of the sample cell and E represent the molar absorptivity (Ankur, 2017). Referring to the Beer-Lambert Law, it has been found that the greater the number of molecules that are able to absorb light at a certain wavelength, the greater the amount of the absorption of light (Ankur, 2017)

The principle and concept of UV-Vis Spectrophotometry have many applications. For example, this instrument can be used to detect a functional group. It can be used to identify the presence or the absence of chromophore in a complex compound (Ankur, 2017). It also can be used to identify the amount of conjugation in polyenes (Ankur, 2017). For example, when there are an increasing in double bonds, the absorption would shot to the longer wavelength. Besides, UV-Vis spectrophotometry can be used to find out the unknown compounds (Ankur, 2017). The spectrum of an unknown compound were compared with the spectrum of a reference compound. Those unknown compound will be successfully identified when both of the spectrum are matched each other. Lastly, this instrument also can be used to decontaminate the substance (Ankur, 2017). To decontaminate the substance, the absorption rate of the reference solution were compared with the absorption rate of the sample solution. To calculate the contamination of a substance, the intensity of the absorption were used.

CHAPTER 3

MATERIALS AND METHODOLOGY

3.1 Materials

The raw materials used are Foxtail Palm fruit. The reagent used are nitric acid (HNO_3), hydrochloric acid (Hcl), sulphuric acid (H_2SO_4) and 1, 5-Diphenylcarbohydrazide. (1, 5-DPC). The instrument used are UV-Vis Spectrophotometry.

3.2 Collection of raw materials

For this research study, *Wodyetia Bifurcata I.K Irvine* fruits or also known as foxtail palm fruit is the raw materials that were used to make the activated carbon. The fruits were collected at surrounding area in Jeli, Kelantan, Malaysia.

3.3 Carbonization of Foxtail Palm Fruits

Firstly, Foxtail Palm fruits were collected at the surrounding area in Jeli. Then, the fruits were cleaned and washed thoroughly by using distilled water in order to remove the dirt and the impurities at the surface of the fruits. Next, the fruits were dried in the oven at the temperature of 100 ℃ for overnight and then were cooled down at the room temperature. For the further usage, the dried foxtail fruits were kept in the tight polyethylene bag and put them in the desiccators. For exactly 2 hours, the dried foxtail fruits were carbonized at 300 ℃ in the furnace. After that, the dried foxtail fruits again were cooled down at the room temperature. By using the pestle and mortar, the fruits were crushed into small pieces and sieved them through 250 µm. The weight of the crashed fruits were recorded. Next, the sieved fruits were stored again in tight polyethylene bag and were kept dry in desiccators.

3.4 Preparation of Activated Carbon Using Nitric Acid as Chemical Activation Agent

With the chemical activation process, the foxtail palm fruit activated carbon was prepared. For about 40 g of oven dried foxtail palm fruit were soaked and impregnated in the beaker that contained 100 mL of concentrated HNO_3. The mixture were mixed vigorously for about 30 minutes until it become paste with constant stirring. The paste were left impregnated overnight in the fume hood to let the chemicals to fully dissolve and react. Next, the slurry were weighed and were placed in the dry crucibles and were carbonized at 500 ℃ for about 2 hours and 30 minutes in the furnace. The activated carbon were washed by using hot distilled water and the pH were adjusted until it reach natural value of pH that is 7. After that, the activated carbon were dried at 150 ℃ for 3 hours in the oven. Then, the activated carbon were kept in the tight polyethylene bag and were stored in the desiccator for the next usage.

3.5 Sampling of Textiles Dye Industry Effluent

The textiles dye industry effluent have being sampled at Adnan Batik Kota Bharu, Kelantan. Five PTFE bottles have being used to keep the textiles dye industry effluent. By wearing the glove, the effluent have slowly poured into the PTFE bottles. Three drops of concentrated hydrochloric acid (HCl) have being added into the PTFE bottles as a preservation method. It is also to make sure that all the samples were preserved evenly as soon as collected. Next, the PTFE bottles were put in the ice box that was full with ice to minimize the potential of biodegradation or volatilization of the sampling and analysis process. In the laboratory, the PTFE bottles that full with samples were refrigerated at 4℃ before they have being analysed.

3.6 Adsorption Test

3.6.1 Effect of Adsorbent Dosage

The adsorption study were conducted on the effect of adsorbent dosage on the efficiency of Cr (VI) removal from the textiles dye effluent. To achieve the equilibrium adsorption time of 30 minutes at room temperature that followed by intermittent stirring, 50 mL of the adsorbate which is textiles dye effluent were measured and contacted with 1 g of the adsorbent which is foxtail palm fruit activated carbon (Aji, Gutti, & Highina, 2015). The mixture was shaken at 200 rpm in an isothermal shaker to obtain the equilibrium state. Next, the textiles dye was filtered by using 0.45 µm Whatman filter paper. Then, the UV-VIS spectrophotometer was used to identify the optical density of adsorbed Cr (VI) by the foxtail palm fruit activated carbon at the maximum absorbance of 540 nm wavelength after being react with 1, 5-DPC reagent. The same steps were repeated with different adsorbent dosage which are 2 g, 3 g, 4 g, and 5 g.

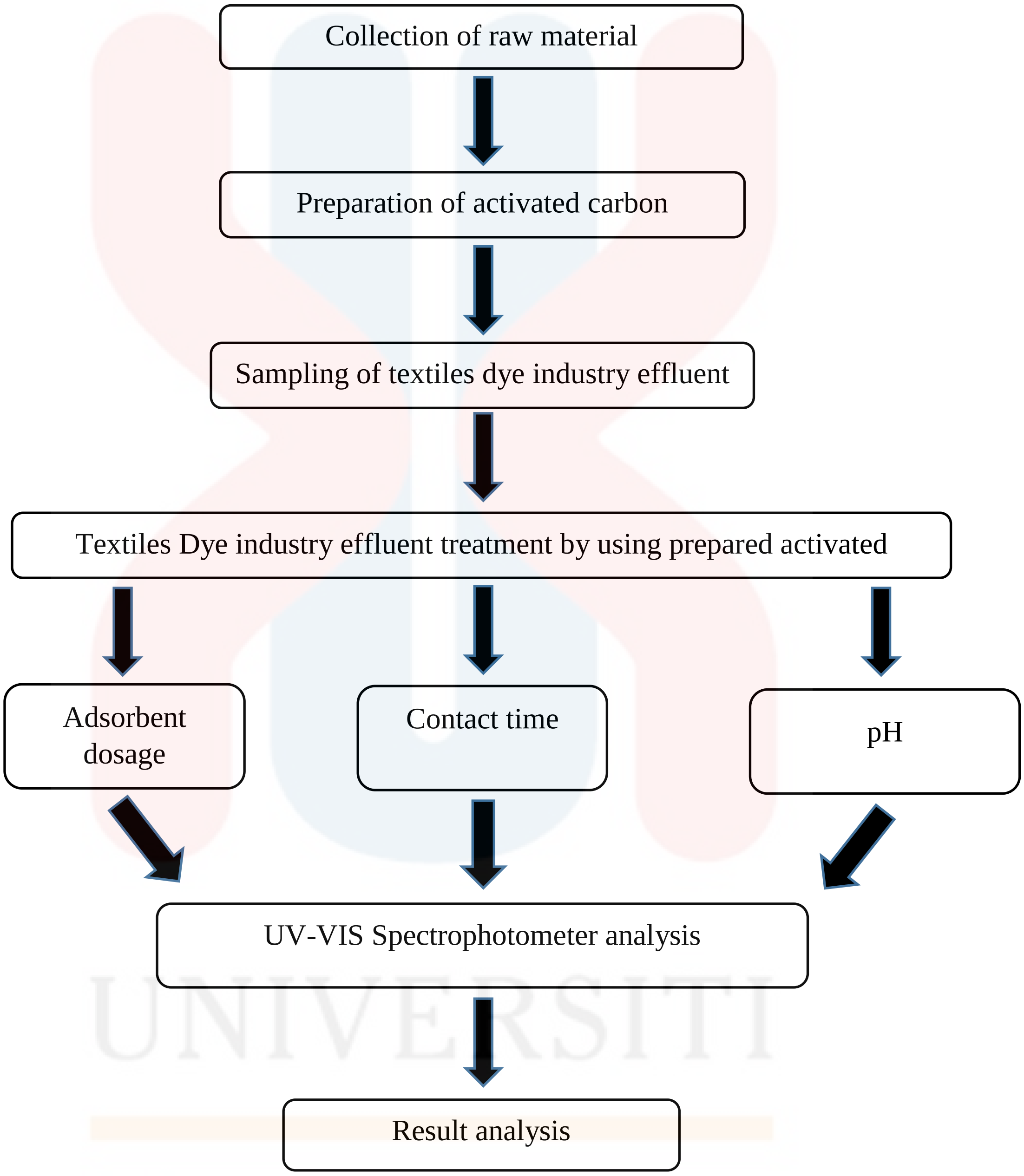
3.6.2 Effect of Contact Time

The determination of residence time is an important characteristic in the definition of the efficiency of an adsorbent (Shafiq et al., 2018). The adsorption study were conducted on the effect of contact time on efficiency removal of Cr (VI) from textiles dye effluent. This adsorption test were performed by mixing 50 mL of textiles dye effluent with optimised adsorbent dosage which is 5 g of foxtail palm fruit activated carbon into the 250 mL of Erlenmeyer flask set with 60 minutes of contact time at room temperature. The mixture were placed and kept for optimum adsorbent dosage and at 200 rpm in an isothermal shaker to obtain the equilibrium state. Then, the textiles dye effluent were filtered by using 0.45 µm Whatman filter paper. The UV-VIS spectrophotometer was used to identify the optical density of adsorbed Cr (VI) by the foxtail palm fruit activated carbon at the maximum absorbance of 540 nm wavelength after being react with 1, 5-DPC reagent. The same steps were repeated by using different contact time which are 90, 120, and 150 minutes. 1 mL of the mixture was pipette out at the different time intervals which are 90, 120 and 150 minutes until equilibrium reach (Aji et al., 2015).

3.6.3 Effect of pH

The pH has a large impact in governing the mechanism of the adsorption process (Shafiq et al., 2018). The adsorption study were conducted on the effect of pH solution on efficiency removal of Cr (VI) from textiles dye effluent. This adsorption test were performed by mixing 50 mL of pH 2 textiles dye effluent with optimised adsorbent dosage which is 5 g of foxtail palm fruit activated carbon and optimised contact time which is 120 minutes into the 250 mL of Erlenmeyer flask at room temperature. The mixture were placed and kept for optimum adsorbent dosage and contact time and at 200 rpm in an isothermal shaker to obtain the equilibrium state. Then, the textiles dye effluent were filtered by using 0.45 µm Whatman filter paper. The UV-VIS spectrophotometer was used to identify the optical density of adsorbed Cr (VI) by the foxtail palm fruit activated carbon at the maximum absorbance of 540 nm wavelength after being react with 1, 5-DPC reagent. The same steps were repeated by using different pH of dye textiles effluent which are pH 4, pH 6, pH 7 and pH 8 that including three types of pH that are pH for acid, pH for neutral and pH for alkaline. With decreasing the initial pH, the removal efficiency of heavy metals will increase and it will reach the peak value of pH which is around pH 2 (Ossman et al., 2014).

Methodology Flow Chart



3.6.4: Methodology flow chart

3.7 Percentage of Removal

The Cr (VI) removal's percentage is calculated by using the following equation:

The percentage of removal of Cr (VI) = $\frac{Ci-Cf}{Ci}$ × 100%

Where:

C_i = Initial concentration of Cr (VI)

C_f = Cr (VI) concentration after being treated with foxtail palm fruit (activated carbon)

CHAPTER 4

RESULT AND DISCUSSION

4.1 Effect of Adsorbent Dosage

Adsorbent dosage was the parameter that mainly important to determine the amount of removal Cr (VI) in textiles dye effluent (Fatemeh Gorzin et al., 2017). At the first stage of optimization with foxtail palm fruit activated carbon, the different amount of foxtail palm fruit activated carbon which were 1 g, 2 g, 3 g, 4 g, and 5 g were used to examine the effect of adsorbent dosage on Cr (VI) adsorption. The contact time and initial pH were fixed with 30 minutes and 10.77 of textiles dye effluent respectively. Figure 4.1 shows the effect of adsorbent dosage on Cr (VI) adsorption.

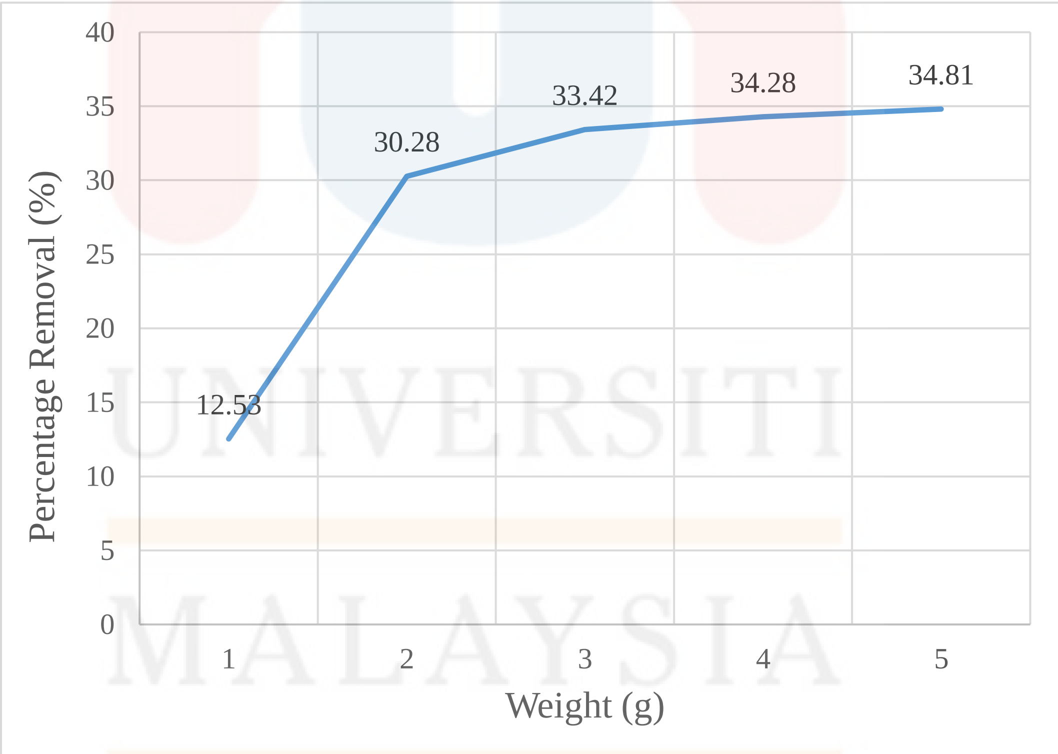


Figure 4.1: Effect of Adsorbent Dosage

Figure 4.1 shows the graph pattern from the result obtained between adsorbent dosage and percentage removal of Cr (VI) in textiles dye effluent. From the graph, it shows that there was a drastically increased in percentage removal from 1 g to 2 g of foxtail palm fruit activated carbon that showed 12.53% to 30.28% of total removal respectively. As the adsorbent dosage increase from 3 g to 4 g, the percentage removal were slightly increased from 33.42% to 34.28% each. It continue increased to 34.81% at highest adsorbent dosage which was 5 g of adsorbent dosage removal. The result indicated that the percentage removal of Cr (VI) were slightly increased with the adsorbent dosage. More adsorption sites were available for Cr (VI) ions when the adsorbent dosage were higher.

Here, it was showed that as the adsorbent dosage increased, the percentage removal of Cr (VI) also increased.

4.2 Effect of Contact Time

One of the effective factors for adsorption process was contact time. All the parameters in this stage exclude contact time, which are adsorbent dosage (5 g) and pH (10.77) were kept constant with isothermal shaker (200 rpm). The contact time were adjusted for 30, 60, 90, 120 and 150 minutes. Figure 4.2 showed the efficiency of Cr (VI) adsorption based on contact time.

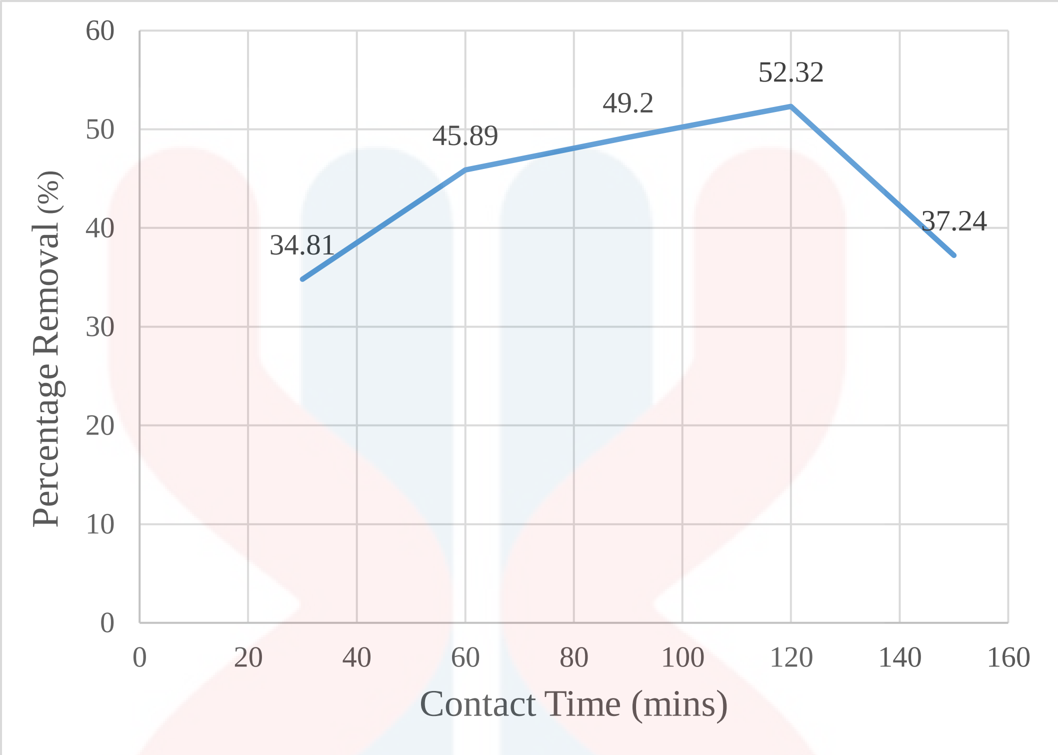


Figure 4.2: Effect of Contact Time

In figure 4.2, it was shown that there was slightly increase at the initially of the adsorption rate and within 120 minutes, the optimal removal efficiency was reached. It was clearly showed that there was directly proportional relationship between percentage removal of Cr (VI) from the effluent with the contact time at the equilibrium state which was 120 minutes and started to decrease gradually after the equilibrium state (Fatemeh et al., 2017). When the number of available site are much longer than the number of metal species to be adsorbed, the adsorption process start to proceed (Panda et. al., 2017). The rate binding of hexavalent chromium ions with the surface of activated carbon is significant that caused by a lot of the availability of adsorption sites make the metal adsorption became slow (Fatemeh et al., 2017). There was a decreased in adsorption rate from 52.32% of removal to 37.24% between 120 and 150 minutes of contact time.

This showed that, at 120 minutes of contact time, the adsorption process reached the optimum value. With that, 120 minutes of contact time was decided to be used for all experiments.

4.3 Effect of pH

The pHs of the solution were one of the important parameter that controlled the adsorption process (Panda et. al., 2017). At this stage, the experiment were done at the constant condition of parameters which were adsorbent dosage (5 g) and contact time (120 minutes). The pH of the effluent were adjusted for pH 2, pH 4, pH 6, pH 7, pH 8 and self pH which is 10.77 and the removal of Cr (VI) were observed. In figure 4.3 was the experimental results at this stage were presented.

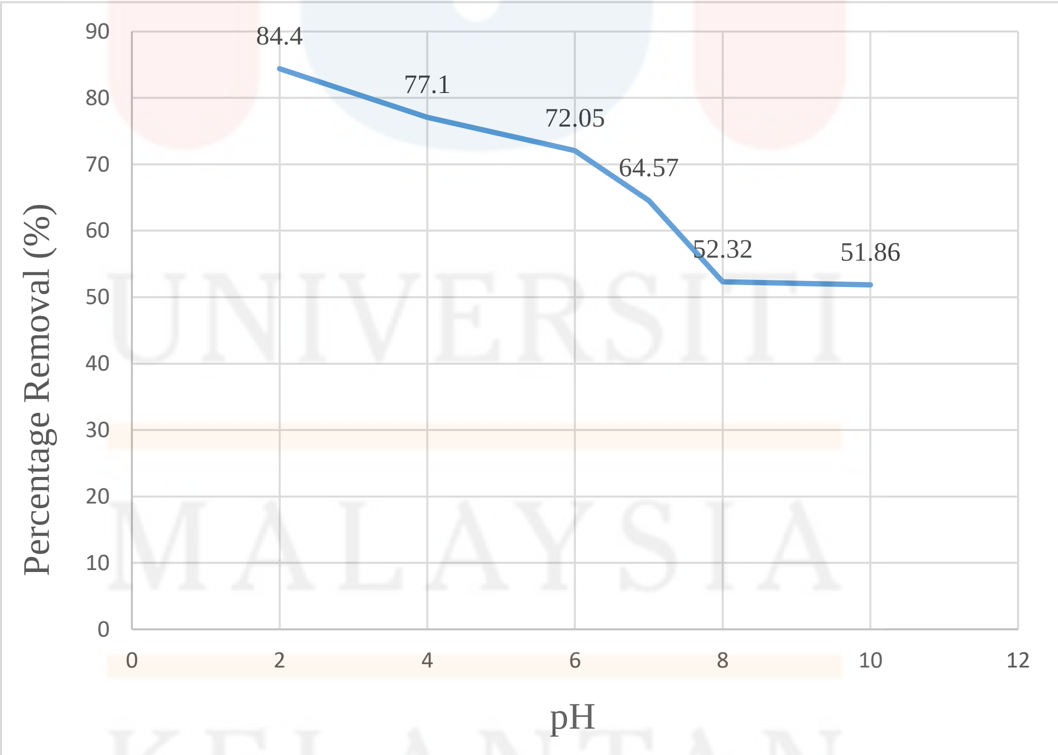


Figure 4.3: Effect of pH

From the figure 4.3, it shows the effect of pH effluent in removing Cr (VI). The optimum pH of effluent was obtained at pH 2. A drastic decrease were observed in adsorption percentage when the pH was increased. The reduction in sorption capacity were caused by the weak attraction of electrostatic force between the opposite charge of adsorbent and adsorbate (Panda et al., 2017). With that, pH 2 was selected as the optimum value of pH for more adsorption of Cr (VI) experiments in order to achieve the best removal efficiency and the capacity of uptake Cr (VI).

Due to the high of protonated adsorbent surface, the efficiency of removal were increased at the low pH which was pH 2. Electrostatic attraction between oxy-anion and the positive charged of foxtail palm fruit activated carbon surface (Gupta et al., 2010) become strong where it was affected by the high protonated adsorbent surface (Fatemeh et al., 2017). There was declination in percentage removal of Cr (VI) when the pH increase from 2 to 8. This can be affected when repulsive force between negative charged of adsorbent surface and the oxy-anion of chromium were improved when the OH^- ions on the surface of activated carbon were increased (Selvaraj et al., 2003).

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

As a conclusion, to study the capacity of adsorbent and adsorption efficiency to remove Cr (VI) from aqueous solution, the adsorption process on the liquid phase was constructed. To prepare the activated carbon from foxtail palm fruit, it must be prepared with HNO_3 aqueous solution. In this experiment, concentrated HNO_3 act as activating agent was undergone carbonization process where it has been through 1:2 of soaking ratio, soaking for overnight period, and also with 2 hours and half at 500 °C. Those process was generated more sites of pore for adsorbent to able AC to adsorb high amount of pollutants in the wastewater. Plus, with the ability to remove some contaminants that attached on the surface of activated carbon became the main reason the usage of HNO_3 in this experiment which resulting a better performance of activated carbon.

Foxtail palm fruit that act as a good raw substance was became an efficient adsorbent on removing the heavy metals which was Cr (VI) in the textiles dye wastewater. Parameters that have being used in this experiment including adsorbent dosage, contact time and pH were investigated by using a low cost adsorbent. It was found that adsorption was high with 37% percentage removal that affected by adsorbent dosage which was 5 g of activated carbon, 50% percentage removal that affected by contact time which at 120 minutes and adsorbent dosage of 5 g and 89% percentage removal that affected by pH which at pH 2, adsorbent dosage of 5 g and contact time for 120 minutes. Thus, from the obtaining result of this study, the activated carbon from foxtail palm fruit that have being utilized could act as prospective precursor to treat the contamination of textiles dye industry wastewater effectively. The effectively parameters for foxtail palm fruit activated carbon were at 5 g of foxtail palm fruit activated carbon, at 120 minutes of the contact time and at an acidic pH which was pH 2 with highest removal of Cr (VI) was 84.4 %.

5.2 Recommendations for future research

The application of *Wodyetia bifurcate I. K Irvine* materials to remove Cr (VI) in textiles dye industry effluent was studied. The result indicate that the foxtail palm fruit was an effective adsorbent material for the dye wastewater treatment. However, some recommendations need to be addressed for future research in order to improve the efficiency of the foxtail palm fruit activated carbon based on their surface area value. The research can be done by experimenting other parameters such as particle size, temperature, and initial Cr (VI) concentration. All those parameters can be optimized the efficiency of the foxtail palm fruit activated carbon. Besides, the researcher also can study other heavy metals such as lead, mercury and dyes such as methylene blue, congo red and malachite green in order to study the effectiveness of activated carbon to remove all those pollutants.

Next, other chemicals can be used during the process chemical activation of the foxtail palm fruit activated carbon. This is one of other alternative chemicals that the researcher can be used instead of using the HNO_3 such as HCl and H_2SO_4 (Ademiluyi & David-West, 2012). The result might be different from this obtained result due to the different usage of chemicals. Chemicals itself play a vital role that act as a catalyst for the adsorbent to elevate the adsorption capacity efficiency.

Lastly, the preparation of foxtail palm fruit activated carbon should be done thoroughly in order to get the best production of the activated carbon. Activated carbon that have a large surface area are one of the good properties to adsorb all the particles, contaminants and pollutants on the sample.

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APPENDIX A

Percentage removal on Adsorbent Dosage

Table A1: Co: 77.65

Weight (g)	Final Concentration (mg/L)	Percentage Removal (%)
1	67.92	12.53
2	54.14	30.28
3	51.70	33.42
4	51.03	34.28
5	50.62	34.81

Table A1: Percentage removal on adsorbent dosage

Percentage removal on Contact Time

Table A2: Co: 77.65

Contact Time (mins)	Final Concentration (mg/L)	Percentage Removal (%)
30	50.62	34.81
60	42.02	45.89
90	39.45	49.20
120	37.02	52.32
150	48.73	37.24

Table A2: Percentage removal on Contact Time

Percentage removal on pH

Table A3: Co: 77.65

pH	Final Concentration (mg/L)	Percentage Removal (%)
2	12.11	84.40
4	17.78	77.10
6	21.70	72.05
7	27.51	64.57
8	37.02	52.32
10	37.38	51.86

Table A3: Percentage removal on pH

APPENDIX B

Preparation of Foxtail Palm Fruit into Activated Carbon

Figure B1: Foxtail Palm Fruit.

Figure B2: Soaked and impregnated foxtail palm fruit with HNO3.

Figure B3: After 24 hours of Chemical Activation (impregnation process).

Figure B4: Ready to be carbonized at 500 °C for 2.5 hours.

Figure B5: Production after carbonization process.

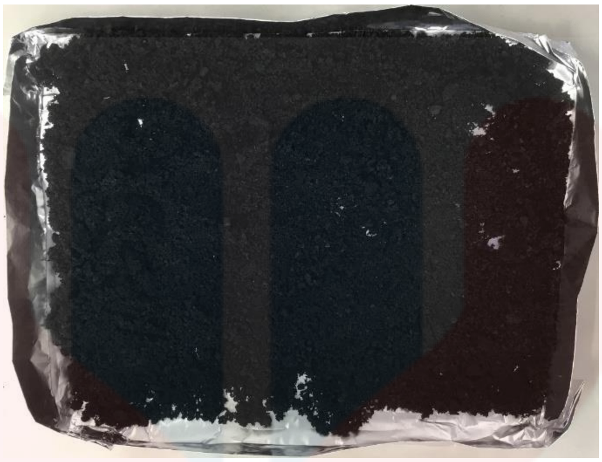

Figure B6: Ready to be dried at 150 ℃ for 3 hours.

Figure B7: Production of Foxtail Palm Fruit Activated Carbon.

APPENDIX C

Adnan Batik Textiles Dye Industry

Figure C1: Location on processing of batik textiles dye.

Figure C2: Textiles dye for batik's soaking process.

Figure C3: Textiles dye wastewater.

Figure C4: Sampled
textiles dye wastewater.