COMPARATIVE STUDY OF VIRGIN AND ACID WASHED ACTIVATED CARBONS FOR ADSORPTION TREATMENT OF TEXTILE WASTEWATER

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A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Chemical Engineering with Honours

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May 2023

DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **"COMPARATIVE STUDY OF VIRGIN AND ACID WASHED ACTIVATED CARBONS FOR ADSORPTION TREATMENT OF TEXTILE WASTEWATER"** was prepared by **JOANNE LING SOON NING** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Chemical Engineering with Honours at Universiti Tunku Abdul Rahman.

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ABSTRACT

The production of textiles produces large volume of wastewater containing dyes, salts and heavy metals. The wastewater requires treatment before it can be recycled or discharged to any receiving water bodies. Adsorption is one of the commonly used methods to treat textile wastewater. It involves the binding of adsorbates that are present in the solution to the surface of the adsorbent used. In this study, the effectiveness of using virgin and acid washed activated carbons for adsorption to treat textile wastewater was investigated and compared. Four commercial activated carbons (ACs) include virgin coconut shell granular activated carbon (GAC), acid washed coconut shell GAC, virgin palm kernel shell GAC and acid washed palm kernel shell GAC were used as the adsorbents. Their surface morphologies were analysed using scanning electron microscopy (SEM). From the SEM images, it was observed that the virgin ACs had more porous structures while acid washed ACs showed collapsed structures with little pores. Following that, real textile wastewater was used to carry out batch adsorption to investigate the effect of retention time (20, 40, 60, 80, 100, 120 minutes) and pH (6, 7, 8, 9) on the removal efficiency of COD, colour, hardness, conductivity and turbidity. From the batch adsorption experiments, the removal performances of acid washed ACs were slightly better than that of virgin ACs. However, since virgin ACs were more economical than acid washed ACs, virgin ACs were selected for further adsorption study on the effect of pH. Overall, the optimum retention time and pH were 60 minutes and pH 7, respectively. Based on the effect of pH experiment, virgin coconut shell AC showed better colour removal efficiency than virgin palm kernel shell AC. Therefore, virgin coconut shell AC was used to carry out breakpoint analysis in a continuous system. A breakthrough time of 230 minutes was obtained. Lastly, a final set of batch experiment using both virgin ACs to treat two different textile wastewater samples was carried out, followed by a complete water quality test. In short, this study concludes that adsorption using commercial ACs made of virgin palm kernel shell and virgin coconut shell is feasible to treat textile wastewater.

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LIST OF SYMBOLS / ABBREVIATIONS

AC	activated carbon
As^{3+}	Arsenic (III) ion
As^{5+}	Arsenic (V) ion
b	Temkin constant related to sorption heat, J/mol
BOD	Biological Oxygen Demand
C	constant
C_e	concentration of adsorbate at equilibrium, mg/L
C_o	initial adsorbate concentration, mg/L
Cd^{2+}	Cadmium ion
Co^{2+}	Cobalt (II) ion
COD	Chemical Oxygen Demand
Cr^{6+}	Chromium (VI) ion
Cu^{2+}	Copper ion
D_e	effective diffusion coefficient, m^2/min
d_p	mean particle diameter, m
ε	Polanyi adsorption potential, kJ/mol
E_S	sorption mean free energy, kJ/mol
EDTA	Ethylenediamine tetraacetic acid
FAU	Formazin Attenuation Units
FTIR	Fourier Transform Infrared Spectroscopy
GAC	Granular Activated Carbon
H^+	hydrogen ion
Hg^{2+}	Mercuric ion
ICP-OES	Inductively coupled plasma optical emission spectrometry
K	constant related to adsorption energy of porosity factor, mol^2/kJ^2
K_F	Freundlich constant related to adsorption capacity, mg/g
K_L	Langmuir isotherm constant
K_M	Temkin isotherm constant, L/g
k_{WM}	Weber-Morris intraparticle diffusion rate constant, $mol \cdot kg^{-1} \cdot min^{-0.5}$
k_1	Pseudo-first-order adsorption rate constant, min^{-1}

k_2	Pseudo-second-order adsorption rate constant, g/mg/min
m	mass of activated carbon used, g
M	molarity
MB	methylene blue
n	Freundlich constant related to the strength of adsorption
OH^-	hydroxide ion
Pb^{2+}	Lead (II) ion
q_e	adsorption capacity at equilibrium, mg/g
Q_{max}	maximum adsorption capacity, mg/g
q_t	adsorption capacity at time t, mg/g
R_L	separation factor/equilibrium parameter
R	universal gas constant, J/mol/K
RSM	response surface methodology
SEM	Scanning Electron Microscope
T	temperature, K
t	time, min
V_o	initial adsorption rate (mg/g/min)
V	volume of the solution, L
Zn^{2+}	Zinc ion

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Textile industry is one of the leading global industries. It involves the production of textiles via a series of manufacturing processes such as processing stage, spinning, weaving and knitting, wet processing and manufacturing (Global Organic Textile Standard, 2021). Based on Uddin (2019), nowadays the rapid development of the textile industry is due to the consumers' growing demand to have better apparel and fashion styles.

The textile industry is an important manufacturing industry that contributes to the growth of the economy in Malaysia. According to Farhana, Mahamude and Mica (2022), the development of the Malaysian textile industry throughout the five years from 2017 to 2021 was flourishing. This is reflected in the revenue growth as shown in Figure 1.1. The overall textile industry increased rather steadily every year except for the substantial drop in 2020 due to the COVID-19 pandemic. As the textile industry is mostly driven by younger generations aged between 25 to 29, the rising trend in this market is expected in the next five years since their population is increasing over the recent years (Mordor Intelligence, 2022).

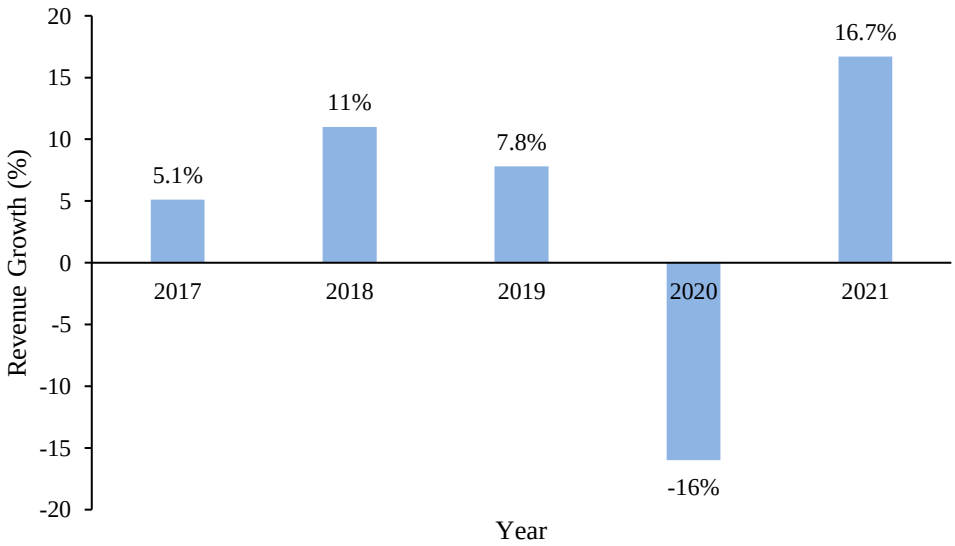


Figure 1.1: Growth in Revenue in the Malaysian Textile Industry from 2017 to 2021 (Mordor Intelligence, 2022).

Textile industry utilises various dyes in the wet processing stage which mainly involves the dyeing and printing processes. In the past, natural dyes were commonly used. According to Benkhaya, El Harfi and El Harfi (2017), natural dyes were derived from natural resources such as animals, plants and minerals. Nowadays, synthetic dyes are becoming increasingly popular as a replacement for natural dyes, mainly due to their lower cost. They also offer greater diversity of fabric colours to suit consumers' demand. During the wet processing stage, dye molecules diffuse through the aqueous solution and adsorb onto the fabric (Shang, 2013). Dyes which are not fixed onto the fabrics will be discharged along with water when the fabrics undergo the final washing process. In the study conducted by Senthilkumaar, et al. (2006), it was stated that about 10-15% of dyes were found in the effluent after the textiles undergo dyeing process. Figure 1.2 shows the discharge of dye effluent from various industries globally. It can be observed from Figure 1.2 that textile industry is the largest contributor to the dye effluent discharge (54%), followed by the dyeing industry (21%), paper and pulp industry (10%), tannery and paint industry (8%) and lastly dye manufacturing industry (7%).

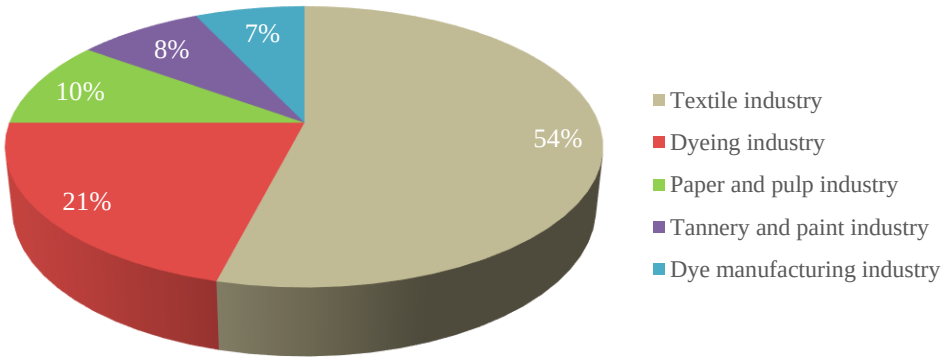


Figure 1.2: Dye Effluent Discharge from Different Industries Worldwide (Velusamy, et al., 2021)

Chequer, et al. (2013) explained that dyes have properties of being very stable and resistant to light, temperature, water, chemicals, and soap. They are non-biodegradable, so they would remain in the aquatic environment for a long time. Apart from textile dyes, salts and heavy metals are also found

in the textile wastewater discharge. According to Mirbolooki, Amirnezhad and Pendashteh (2017), the source of salts is from the addition of chemicals like sodium chloride to improve the stability and adsorption of dye molecules. Meanwhile, the presence of heavy metals is due to the addition of chemicals such as solvents, dyes and pigments during the production of textiles (Velusamy, et al., 2021).

If the textile effluent containing dyes, salts and heavy metals is discharged into any receiving water bodies, that would lead to water pollution and environmental health issues as the water would become toxic. The textile effluent can cause irritation of the skin, allergy and could lead to cancer. This can happen either through the evaporation of chemicals into the air or through the skin absorption after in contact with the polluted water (Kant, 2012). Besides, the textile effluent can affect aquatic plants as sunlight is unable to penetrate into the highly coloured dye-polluted water (Verma, Dash and Bhunia, 2011). This would then reduce the aquatic plants' ability to carry out photosynthesis, leading to a decrease in dissolved oxygen level the water. As a consequence, eutrophication may occur along with the growth of bacteria and viruses. Once the producer (aquatic plant) is affected, the other consumers in the food chain would naturally be affected too. Moreover, bioaccumulation of the toxic textile dyes would occur in the ecosystem. Subsequently, human health would be affected due to consumption of seafood from the contaminated water.

Since the textile wastewater contains toxic pollutants that can contribute to water pollution and health issues, appropriate wastewater treatment methods are necessary to treat the textile wastewater before they can be discharged to the water bodies. The treated textile wastewater also has to comply with the Standard A or Standard B of the Malaysian Environmental Quality (Industrial Effluent) Regulations 2009 before they can be safely discharged. Recycling is also another viable option where the textile wastewater is recycled back to the production line of the plant after the undergoing treatment process. In the study by Hussain and Wahab (2018), it was found that the amount of water consumed by a medium scale textile plant that manufactures 8000 kg/day of fabric is roughly 1.6 million litres on a daily basis. Thus, by recycling the treated textile wastewater, it can help to reduce

water consumption. The various applicable textile wastewater treatment methods include membrane filtration, coagulation and flocculation, adsorption, ozonation and biological aerobic treatment.

Among the textile wastewater treatment methods, adsorption is one of the widely used techniques to treat textile wastewater. It is a low-cost method with reliable ability to remove pollutants from the wastewater. In general, adsorption involves the mass transfer of solutes/adsorbates present in an aqueous solution to the solid surface of an adsorbent (Manchisi, et al., 2020). According to Rashid, et al. (2021), different types of adsorbents can be used to remove pollutants from the wastewater which include low-cost adsorbents, nano-adsorbents and bio-adsorbents. It can be made from organic resources like wood, coal, agricultural wastes and industrial wastes. Some examples of agricultural wastes include coconut shell and rice husk, whereas industrial wastes include fly ash and red mud. Among these activated carbons, coconut shell and palm kernel shell are commonly used absorbents for the adsorption process in the wastewater treatment industry. Besides, various conditions can affect the adsorption performance such as the nature of the adsorbent, pH, retention time, adsorbent dosage and temperature. Therefore, it is important to determine the optimum conditions in order to achieve maximum removal efficiency.

1.2 Importance of the Study

With the increment of population growth and the development of fashion industry, there will be a corresponding rise in the textile production to meet the demands of consumers. Consequently, larger amount of textile wastewater effluent will be produced. Therefore, there is a need to identify effective treatment method to remove pollutants present in the textile wastewater effluent. This study evaluates whether adsorption process is feasible to be applied for the treatment of real textile wastewater. The result of this present study may contribute to a better understanding of how adsorption can be applied to treat textile wastewater by utilising different commercial virgin and acid washed activated carbons. This study may also provide insight into the factors that could possibly affect the efficiency of adsorption, such as retention time and pH in batch system. Furthermore, this research may serve as a

foundation for conducting a breakpoint analysis in a continuous system, which can aid in determining the breakthrough time of the activated carbon. In addition, it can contribute to evaluate the practicability of using activated carbon adsorption in a continuous system for treating wastewater generated from textile dyeing and finishing processes.

1.3 Problem Statement

Water consumption is high during the textile production process, particularly in the wet processing stage. The washing of textiles and inefficient dyeing process would lead to large volumes of effluents containing dyes, salts and heavy metals to be released from the textile manufacturing industry. This has led to the production of textile waste effluent up to 280,000 tons/year globally (Berradi, et al., 2019). Furthermore, according to Pal (2017), textile wastewater is typically characterised by high COD, BOD, pH, colour, suspended solids, chlorides, nitrates and some heavy metals like iron, lead and copper. If the raw wastewater is discharged into the receiving water bodies, it would pose negative impacts towards the environment and human beings apart from being aesthetically unpleasant. Hence, wastewater treatment is essential in the textile industry to treat the raw wastewater before it is recycled or discharged to the water environment such as rivers, oceans or seas since the raw wastewater is unable to be reused directly (Badawi and Zaher, 2021). It is of interest to investigate the effectiveness of different commercial activated carbons (ACs) including virgin coconut shell granular AC, acid washed coconut shell granular AC, virgin palm kernel shell granular AC, and acid washed palm kernel shell granular AC for treating textile wastewater. Additionally, investigating parameters that affect the adsorption performance, such as retention time and pH, as well as the degree of adsorption efficiency across different qualities of wastewater, is also important. In this study, the textile wastewater parameters such as pH, COD, colour, hardness, conductivity and turbidity are mainly focused. This is because they provide the six most important pieces of information about the condition of the wastewater and the presence of contaminants, as well as reflect the efficiency of the treatment method.

1.4 Aim and Objectives

The aim of this study is to investigate the effectiveness of using virgin and acid washed palm kernel shell and coconut shell activated carbons for adsorption in treating textile wastewater. The objectives of this study are:

(i) To compare the adsorption ability of four types of commercial activated carbons (ACs) which include virgin coconut shell granular AC, acid washed coconut shell granular AC, virgin palm kernel shell granular AC and acid washed palm kernel shell granular AC towards textile wastewater.

(ii) To investigate the effect of retention time and pH on the removal efficiency of the activated carbons in batch system.

(iii) To determine the breakthrough time in a continuous system when the activated carbon needs to be replaced.

(iv) To determine the performance of activated carbons on different qualities of textile wastewater.

1.5 Scope of the Study

The scope of the study included comparing different types of activated carbons by carrying out characterisation analysis and adsorption test to understand their characteristics and adsorption ability. Characterisation were carried out using scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). After that, water quality test was carried out to determine the quality of the raw textile wastewater samples that were obtained from a textile manufacturing company in Johor, named Sincerely Dyeing and Finishing Sdn Bhd. Various water quality parameters such as pH, chemical oxygen demand (COD), colour, hardness, conductivity and turbidity were analysed to compare the adsorption ability of the activated carbons before and after the treatment.

Next, batch adsorption was carried out to optimize the adsorption process by determining the optimum retention time and pH for achieving high pollutant removal efficiency. Water quality test was then carried out after every batch adsorption experiment to determine the quality of the treated textile wastewater samples. Moving on, breakpoint analysis in a continuous system was carried out by using a fabricated adsorption column to mimic a

fixed bed column. The optimum results obtained from batch adsorption were used to carry out breakpoint analysis and identify the breakthrough time when the activated carbon needs to be replaced.

Subsequently, a final round of batch adsorption experiments was conducted to evaluate the performance of the activated carbons using the best conditions obtained from the previous tests and breakpoint analysis on two different textile wastewater samples. Lastly, the treated textile wastewater samples were subjected to a comprehensive water quality testing to assess the effectiveness of the activated carbon adsorption process in removing pollutants and to ensure compliance with regulatory standards.

CHAPTER 2

LITERATURE REVIEW

2.1 Textile Industry

Textile industry is an industry where fabrics are being manufactured in a large scale. Before the large-scale textile industry existed, textile was initially produced in small scale at homes using wools from their sheep livestock to make clothes. The growth of the textile industry was contributed by the industrial revolution in Britain in the 1700s with the invention of machines (Beck, 2022). According to BizVibe (2022), the three largest producers of textiles are China, India and United States (US), as illustrated in Figure 2.1. Although Malaysia is not one of the largest textile producers in the world, Malaysia has been a global competitor in this industry. Moreover, Farhana, Mahamude and Mica (2022) found that there will be a rise in the Malaysian textile industry as a result of the increase of the younger generation's fashion preference and apparel demand.

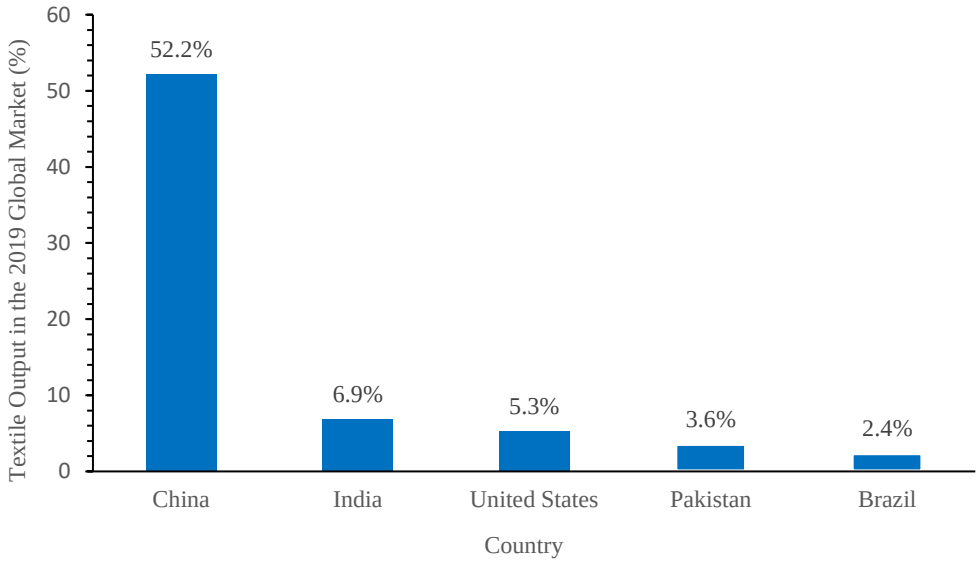


Figure 2.1: Top 5 Largest Textile Producers in 2019 (BizVibe, 2022).

2.1.1 Production of Textile

Textiles can be produced through five stages. They are processing stage, spinning, weaving and knitting, wet processing and manufacturing, as shown in Figure 2.2.

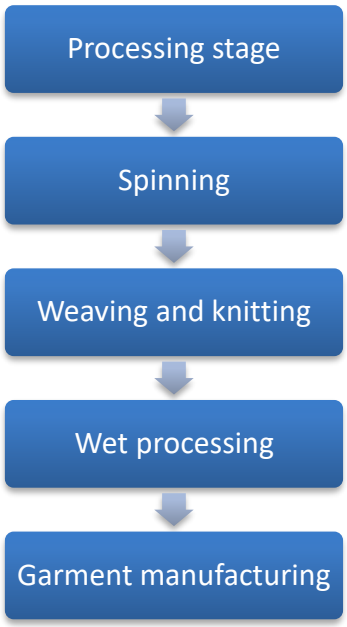


Figure 2.2: Textile Production Process (Global Organic Textile Standard, 2021).

In the processing stage, textile fibres such as cotton, wool, rayon, silk and polyester will be preliminarily processed. For instance, if cotton is used as the textile fibre, it will undergo a process called cotton ginning. In that process, soil, stems and debris will be removed from the cotton bolls, then followed by the removal of the cottonseed (Sharratt and Auvermann, 2014).

The second stage is spinning, whereby the textile fibres that have been processed in the first stage will be converted into yarns by using specialized nature machineries (Uddin, 2019). Textile fibres will be twisted and drawn continuously until yarns are formed. The third stage of textile production is weaving and knitting. In this stage, fabric will be produced from the yarns. The yarns would interlace one another to form different kind of fibrous structure. As a result, different types of fabric would be produced.

After that, the fabric will undergo wet processing. Textile wet processing is a textile improvement process, which involves pretreatment, colouration, and finishing (Kan, 2015). The pretreatment process is a fabrics preparation step to remove impurities on the textile materials and give the fabrics necessary properties such as strength and whiteness value. It can be carried out via bleaching, scouring, sizing, desizing, washing, heat-setting and mercerizing. After that, the fabrics are coloured according to the client's

demand by using either dyeing or printing. Both dyeing and printing require the usage of dyes as the colourant. Referring to the study by Shang (2013), adsorption and diffusion take place in the process of dyeing, where the dyes in the aqueous solution are transferred and diffused onto the fabric material. Meanwhile, printing involves the application and absorption of viscid dye paste onto the fabrics. The last process in wet processing – finishing, is the process where the fabrics are being modified or improved to enhance their quality and performance. According to Choudhury (2017), some of the examples of finishing are shrink proofing, softening, stiffening, calendaring and compressive shrinkage.

The last stage of the textile production process is garment manufacturing. It involves converting the finished textile fabrics into a garment or clothing. Conventional method or modern method can be applied in this stage. The conventional method generally covers cutting, sewing, washing and ironing while modern method uses modern technologies such as automation or Computer Aided Manufacturing to produce the final garment (Uddin, 2019).

2.1.2 Common Dyes Used in Textile Production

As aforementioned, dyes are used in the colouration step of the wet processing stage of textile production, be it dyeing or printing method. There are two major components in the structure of dyes, which are auxochromes and chromophores. Auxochromes are composed of various functional groups that include hydroxyl group (-OH), carboxyl group (-COOH), amino group ($-NH_2$) and sulphonate group ($-SO_3H$) that are responsible to give dyes their water solubility property. This property improves the attraction between the dye molecules and fibres. For example, the sulphonate group provides high solubility of dyes (Bhatia, et al., 2017). Auxochromes do not exhibit colour. However, when an auxochrome is attached to a chromophore, it helps to enhance the colour of the chromophore (Aziam, et al., 2021).

On the other hand, chromophores are composed of functional groups that provide dyes their individual unique colour such as nitro group ($-NO_2$), carbonyl group (-C=O) and azo group (-N=N-). The majority of the anionic and non-ionic dyes that contain chromophores belong to the azo groups or

anthraquinone groups (Abdelghaffar, 2021). Figure 2.3 illustrates the structure of an azo reactive dye where it is composed of the two major chromophore and auxochrome components. In this case, the chromophore has an azo group along with other water soluble groups.

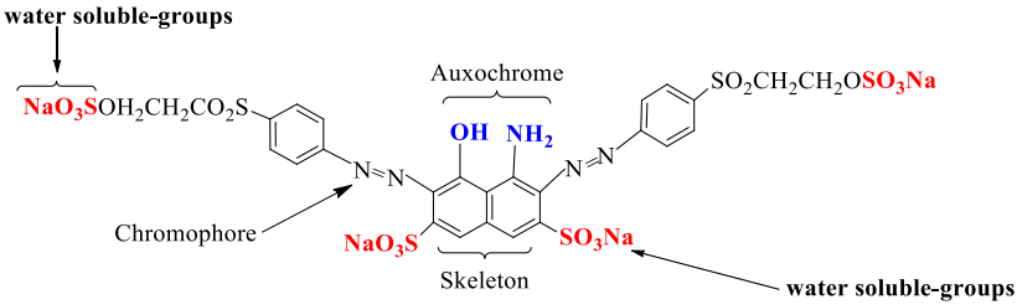


Figure 2.3: Chemical Structure of Azo Reactive Dye (Benkhaya, M'rabet and El Harfi, 2020).

Generally, textile dyes can be classified into natural dyes and synthetic dyes. Benkhaya, El Harfi and El Harfi (2017) explained that natural dyes implies that the dyes are derived and extracted from nature such as animals, plants and minerals. Before synthetic dyes were developed, natural dyes were solely used to give colours to textiles. Some natural dyes require a chemical known as dye fixative to bind the dyes with textile fibres. However, synthetic dyes have replaced most of the natural dyes in the current textile sector due to its enhanced manufacturing reliability and lower cost. Furthermore, a greater diversity of fabric colours can be produced from synthetic dyes compared to natural dyes, which would enhance the appearance of the textile. According to Samsami, et al. (2020), more than 700,000 tons/year of synthetic dyes are being manufactured in the global market while more than 10,000 dyes varieties are being used in the textile industry. These synthetic dyes can be named following their respective chemical structures of their chromophore groups, such as azo dyes, xanthene and diphenylmethane compounds (Shindy, 2017).

Abdelghaffar (2021) elaborated that textile dyes can have various chemical structures such as azo, xanthene, nitro, anthraquinone, phthalein, phthalocyanines, indigoid, diphenylmethane, triphenylmethane and the list goes on. Based on the study by Bhatia, et al. (2017), the most common dyes

which are used in the textile industry are azo dyes. Azo dyes are organic compounds that are composed of derivatives of aromatic hydrocarbon with at least one nitrogen double bond (-N=N-), which is also known as the azo group. Methyl red, methyl orange, direct blue dye and phenyl orange dye are some of the examples of azo dyes. Azo dyes are commonly used due to their appealing and favourable properties that include vast dye shades, good wash fastness, simple to use, form covalent bond with the fibres and cost effective (Abdelghaffar, 2021).

Dyes can be categorised in many ways based on their usage or the charge that is present on the molecules of the dyes. The examples of synthetic dyes that are categorised based on their usage include basic dyes, direct dyes, disperse dyes, acid dyes, vat dyes, reactive dyes, solvent dyes and sulphur dyes (Benkhaya, El Harfi and El Harfi, 2017). The properties and main usage of each dye class are presented in Table 2.1.

Table 2.1: Properties and Main Usage of Each Dye Class (Hunger, 2003).

Dye Class	Properties	Main Usage
Basic	• Water soluble cationic dyes	Polyacrylonitrile, paper, modified polyesters and modified nylons
Direct	• Water soluble anionic dyes	Paper, leather, dye regenerated cellulose, cotton and nylon
Disperse	• Water insoluble non-ionic dyes for hydrophobic fibers	Polyester, cellolose acetate, cellulose, acrylic fibers and nylon
Acid	• Water soluble anionic dyes	Nylon, silk, modified acrylics, wool, leather, paper, food, cosmetics and inkjet printing
Vat	• Water insoluble dyes • Good colour-fastness • Expensive	Cellulose fibres

Dye Class	Properties	Main Usage
Reactive	• Forms covalent bond between dyes and fibre • High colour-fastness	Cotton, wool, nylon
Solvent	• Water insoluble dyes but soluble in solvent	Colouring plastics, waxes, oil and gasoline
Sulphur	• Low cost • High colour-fastness	Cotton

In terms of the classification of dyes based on the charge that is present on the molecules of the dyes, they can be categorised into cationic dyes, anionic dyes and non-ionic dyes. The properties of all these categories of dyes are tabulated in Table 2.2, along with their respective examples.

Table 2.2: Properties and Examples of Dyes Based on the Charge Present (Abdelghaffar, 2021).

Dyes	Properties	Examples
Cationic dyes	▪ Has positive ion in the structure of the dye molecule ▪ Able to interact with anionic groups on the textile fibres ▪ Used to dye nylon, silk and wool ▪ Highly poisonous	Basic dyes, azo, methane, anthraquinone, diarylcarbenium, triarylcarbenium, phthalocyanine, polycarbocyclic dyes
Anionic dyes	▪ Has negative ion in the structure of the dye molecule ▪ Has low fixation properties	Acid dyes, direct dyes, reactive dyes
Non-ionic dyes	▪ Not ionised ▪ Used to dye acrylic, polyester and cellulose acetate hydrophobic fabrics	Vat dyes, disperse dyes, sulphur dyes

2.2 Characteristics of Textile Wastewater

The raw wastewater that is produced from the production of textile consists of high concentration in chemical oxygen demand (COD), biochemical oxygen demand (BOD), pH, colour, suspended solids, temperature, salts and metals (Yaseen and Scholz, 2018). If these parameters are released directly to the receiving water, they would impose pollution and hazard to living organisms. Hence, the concentration of these parameters has to be monitored and regulated through wastewater treatment process to meet local environmental legislation before the wastewater can be discharged into the water bodies or recycled to be re-used for the production of textile within the production plant.

The quality of the textile wastewater varies from one textile factory to another since it depends on the type of textile produced, chemicals employed and the process of textile production of the textile factory. According to the study by Grasso (2005), COD refers to the amount of oxygen required in the water to chemically oxidise organic matters via strong oxidizing agents such as potassium permanganate and potassium dichromate. Recalcitrant organics, colour, toxicants, salts, dirt, grease, and nutrients from the dye bath additives contributed to high COD. On the other hand, BOD is defined by the amount of oxygen that is required by microorganisms to degrade organic matter under aerobic conditions (Dey and Islam, 2015). High COD and BOD indicates great amount of organic matters are present in the wastewater. The dissolved oxygen level in the water body would then decrease significantly.

Next, based on the study of Araujo, et al. (2022), the source of the colour in the textile wastewater is from the release of unfixed dyes during the dyeing process. When the fabric is washed with water during the last stage of the textile manufacturing process, dyes which are not fixed onto the fibers will be washed out and released along with the raw wastewater. Visually, the water will look unpleasant. This scenario also affects the aquatic organisms as there would be inhibition of sunlight penetration for photosynthesis. As a result, food chain disruption will occur.

Apart from that, various chemicals such as acids, alkalis, salts and detergents are used in the textile manufacturing process. For instance, sodium

chloride and sodium nitrate are employed in the dyeing bath to improve the stability and fixation of dyes to the fibre. Salt enables neutralisation of the surface charge on the fibers, which would allow more dyes to be fixed to the fibres of the fabric (Mirbolooki, Amirnezhad and Pendashteh, 2017). The usage of salts will contribute to wastewater with high salinity content, as well as extreme pH conditions.

Furthermore, textile wastewater also contains heavy metal components such as copper, lead, chromium, zinc and antimony. Velusamy, et al. (2021) explained that the release of these heavy metals occurs during the wet processing stage of the textile manufacturing process. This is because some of the chemicals and complex dyes that are used contain metals. To illustrate, copper, lead, chromium and zinc are employed as catalysts to synthesise fibres. They also act as oxidising agents. Besides, to improve the resistance of polyethylene terephthalate (PET) fibres from changing the characteristics of its colour after dyeing, antimony is employed as the catalyst (Li, et al., 2021). The usage of heavy metals in the wet processing stage will lead to their emission to the water bodies.

2.3 Adsorption Mechanism

The raw textile wastewater needs to be treated before it can be discharged or recycled within the textile production plant. There are a variety of wastewater treatment methods which can be used to treat textile wastewater either via physical, chemical or biological method. The common methods for physical treatment include membrane filtration, adsorption, coagulation and flocculation. Chemical treatment includes ozonation, electrochemical oxidation and Fenton's oxidation whereas biological treatment involves the application of microorganisms to degrade pollutants (Rashid, et al., 2021). In the study conducted by Anil, et al. (2020), they stated that adsorption is categorised by the United States Environmental Protection Agency (USEPA) as one of the best treatment methods to treat wastewater.

According to Artioli (2008), adsorption takes place when there is adhesion of ions or molecules (adsorbate) from a gas or liquid onto the surface of a solid, known as the adsorbent. Generally, adsorption occurs at the interface of two phases. There is no diffusion of adsorbate into the adsorbent.

Adsorption is widely used in many applications such as water treatment, purification of air and wastewater treatment to remove pollutants. This is due to its simplicity in design, lower operating cost and effectiveness in eliminating organic pollutants. However, adsorbent regeneration or replacement is needed after a certain period of time when the adsorbent becomes saturated and it is unable to achieve the desired treatment efficiency (Sukmana, et al., 2021). Regeneration and replacement cost will then be imposed.

Sotelo, et al. (2013) further explained that in general, there are four steps which are involved in the adsorption process. The first step is the transfer of adsorbates from a solution to the adsorbent's boundary layer. Next, external diffusion takes place where the adsorbates diffuse through the boundary layer to the external surface of the adsorbent. Then, intra-particle diffusion occurs where the adsorbates diffuse to the active sites of the adsorbent. Lastly, the adsorbates adhere to the active sites of the adsorbent. Adsorption is then said to have taken place.

There are two types of adsorption mechanisms, namely physisorption and chemisorption. Referring to the study by Deng, et al. (2019), physisorption is known as the physical adsorption of the adsorbates onto the surface of the adsorbent as a result of dipole forces or Van der Waals forces. The interaction or binding force between the adsorbate and adsorbent is relatively weak. The adsorption energy is considerably low, in the range of 5-80 kJ/mol. This makes physisorption a reversible process if sufficient energy is provided to desorb the adhered substances. Physisorption can result in either a monolayer or multilayer of adsorbates on the surface of the adsorbent (Pashin, 2008).

Meanwhile, based on the study of Kwon, et al. (2011), chemisorption refers to the chemical adsorption via the mutual sharing of electrons between the adsorbates and surface of the adsorbent. Chemical bond or covalent bond which is a strong bond is formed. The adsorption energy of chemisorption is high, which is normally in the range of 200-400 kJ/mol. This makes chemisorption irreversible. If regeneration of adsorbent to remove adsorbates is required, high energy would be needed. The chemisorption also results in a single layer of the adsorbates that are adhered onto the adsorbent surface, called monolayer (Adeleke, et al., 2019).

Figure 2.4 illustrates the two adsorption mechanisms where the carbon particle surface acts as the adsorbent. For chemisorption, adsorbates bind together with the binding sites on the surface of the adsorbent only. On the other hand, for physisorption, adsorbates can bind on the surface of the adsorbent directly or on the surface of other adsorbates. That also explains the monolayer and multilayer adsorption phenomenon in chemisorption and physisorption, respectively as shown in Figure 2.5.

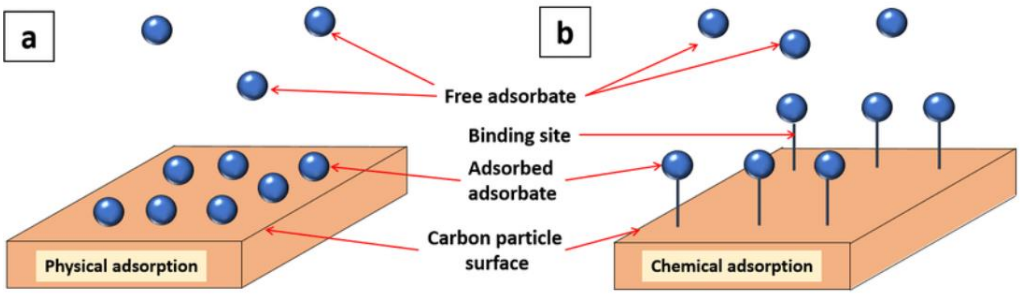


Figure 2.4: Adsorption Mechanisms: (a) Physisorption and (b) Chemisorption (Nandiyanto, et al., 2020).

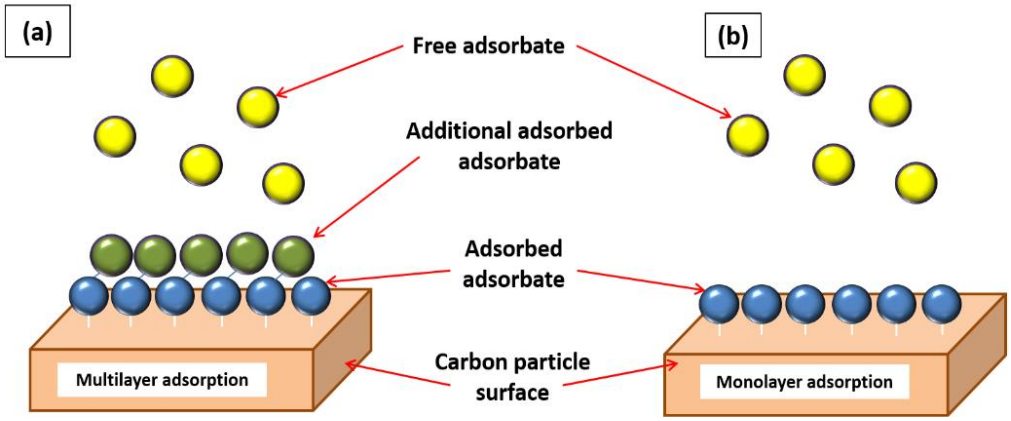


Figure 2.5: Multilayer Adsorption in (a) Physisorption and Monolayer Adsorption in (b) Chemisorption (Nandiyanto, et al., 2020).

2.4 Types of Adsorbents

Adsorbents should have sufficient binding sites so that dyes and other pollutants can adhere onto the sites and be removed from the wastewater (Rashid, et al., 2021). Various adsorbents exist and they can be categorised into three categories, namely low cost adsorbents, nano adsorbents and bio-adsorbents.

2.4.1 Low Cost Adsorbents

Low cost adsorbents are made from materials which exist naturally, or from agricultural and industrial wastes. Examples of natural adsorbents are zeolite, chitin, clay, wood and coal. According to Indarto, et al. (2019), zeolites are aluminosilicate crystals that has tetrahedral structure which are connected by alumina, oxygen and silica atoms. They have micropores network, making it suitable to be employed as catalysts, ion exchange mediums and adsorbents. Zeolites are normally used in the chemical industries that involves the separation or purification processes. The properties of zeolites such as porosity, surface area and thermal stability can be improved by modifying the zeolites via chemical activation using inorganic salts, surfactant modification, metal oxides modification and thermal oxidation (Krstić, 2021).

Next, based on Ribeiro and dos Santos (2019), chitin is a biopolymer that can be found in the exoskeleton of crustaceans like shrimps, lobsters, crabs, amphipods and crayfish. Chitin can be obtained from extractive processes and then undergo further deacetylation process to obtain chitosan. The source of raw material for chitin is abundant as it can be retrieved from seafood wastes which are valuable resources. One of the most easily obtainable seafood wastes is shrimp shell where it is made up of 15-20% of chitin. In the study by Anastopoulos, et al. (2017), the authors compiled the studies which were done by other researchers on the ability of chitin to remove toxic metals by adsorption process. For instance, the maximum adsorption capacity of Cd^{2+} by using chitin is found to be 90.1 mg/g, 32.4 mg/g and 58 mg/g from three different studies. Moreover, Cr^{6+} can also be removed by using different types of chitin adsorbents such as bargi scale, chitin derived from Bargi fish (*Heterotis Miloticus*) and polypryrrole-functionalized chitin to give the maximum adsorption capacity of 25 mg/g, 37.04 mg/g and 28.92 mg/g, respectively. This shows that chitin is a potential adsorbent to be used.

Besides, low cost adsorbents can also be obtained from agricultural wastes which are discarded such as banana peel, orange peel, rice husk, walnut shells, coconut shell, soybean hull and livestock manure. Instead of disposing these wastes, they can be re-used as valuable adsorbents. Some of the advantages of using agricultural wastes as adsorbents are they are less expensive, abundant, renewable and they help to reduce environmental

pollution. Agricultural wastes are classified as lignocellulosic biomass which is made up of lignin (aromatic polymer) as well as cellulose and hemicellulose (polysaccharides) (Zoghlami and Paës, 2019).

Dai, et al. (2018) further explains that the presence of carboxyl and hydroxyl functional groups in these agricultural wastes, along with their loose and highly porous structure makes agricultural wastes a suitable material for adsorption. For instance, lignin polymer has mainly methyl, hydroxyl and carbonyl groups whereas cellulose and hemicellulose have ether, carbonyl and hydroxyl groups. Organic contaminants and heavy metals will be binded onto the functional groups that are present in the agricultural wastes. In the study conducted by Módenes, et al. (2015), it was found that banana pseudostem, which was used as the adsorbent was able to adsorb reactive blue 5G dye by physical adsorption. Furthermore, it was discovered from the experiment which was conducted by Amer, El-Gendy and El-Haggar (2017) that by using raw rice straw, 94% of Pb^{2+} removal from water was obtained. This implies that rice straw showed good potential to adsorb Pb^{2+} heavy metal.

Apart from that, industrial wastes can act as adsorbents too. Industrial wastes are the by-products that are produced by from industrial processes. Some of the examples of industrial wastes are red mud, fly ash, blast furnace sludge, sugar beet pulp and tea industry waste. Based on Bhatnagar, et al. (2011), during the manufacturing of alumina, red mud is produced from the bauxite processing as a by-product. It has dense, fine and porous surface texture properties. Red mud is a potential adsorbent to be used to treat contaminants that are present in wastewater such as heavy metals, dyes and organic compounds, as well as for gas purification (Wang, Ang and Tadé, 2008).

Moreover, according to Aigbe, et al. (2021), fly ash is one of the by-products that is produced from firing coal to generate electricity in thermal power plants and factories. Fly ash is normally used in cement, concrete and brick production, construction works, as adsorbent to remove contaminants and so on. Fly ash is mainly composed of alumina and silica, so it can be used to produce zeolites which can be used as another type of adsorbent too. It also acts as a neutralising agent because of its alkaline properties. However, it is noted that the adsorption capacity of raw fly ash is considerably low. Thus, it

needs to be modified via physical or chemical treatment processes in order to improve its adsorption capacity (Ahmaruzzaman, 2011).

2.4.2 Nano Adsorbents

Referring to the study by Basheer (2018), nano adsorbents are very small particles that have a size range of 1-100 nm. They are the result of nanotechnology development. Some of the materials that are used to as nano adsorbents are carbon nanotubes, graphene and metal oxides. They possess good adsorption properties which can help to remove contaminants that are present in water. For instance, they are small in size, have high reactivity, catalytic potential and surface energy. They can be prepared through many methods such as ion sputtering, synthesis of thermal plasma, condensation of inert gas, sol-gel method, synthesis of flame and so on. Sharma, et al. (2009) further explained that the small size properties of nano adsorbents contribute to their large surface area as well as the large surface area to volume ratio. With that, they will have many available active sites to bind the pollutants that are present in the water such as Cd^{2+}, Cr^{6+}, Hg^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, As^{3+}, As^{5+}.

2.4.3 Bio-adsorbents

Bio-adsorbents are derived from biological sources such as living biomass, dead biomass and cellulosic materials (Wang and Chen, 2009). Lignocellulosic biomass such as palm kernel shell, coconut shell and walnut shell are also classified as bio-adsorbents. Microorganisms like algae, yeast and fungi can be used to treat wastewater that contains dyes. For example, Aragaw and Bogale (2021) found that the abundance of algae as well as the high bio-adsorption capacity of algae made them suitable bio-adsorbents. The authors also discovered that microalgae such as *Chlorella* and *Spirulina* species can remove 93.9-99% of textile dyes while brown algae such as *Sargassum* species are able to adsorb more than 90% of textile dyes from textile wastewater.

2.5 Activated Carbon

Adsorption requires an adsorption media or adsorbent for the solutes or adsorbates to adhere onto. There are many types of adsorbents that can be used

for adsorption such as activated carbon, zeolites, silica gel, metal oxides, synthetic ion exchange resins and activated alumina (Bakhtyari, Mofarahi and Lee, 2020). In the context of textile wastewater treatment, Hasanzadeh, Simchi and Far (2019) explained that activated carbon is favourable to be used as an adsorbent to remove pollutants due to its porous structure and large surface area.

Activated carbon can be produced in various forms such as powdered, granular and pellet forms. The raw materials to produce activated carbon can be derived from pyrolytic carbon or high carbon content materials (Aragaw and Bogale, 2021). In the recent years, there is an increase of interest in using high carbon content raw materials such as wood, coconut shell and palm kernel shell in the treatment of industrial wastewater. Not only do they possess good adsorption capacity, but also imply lower cost, since they are obtained from waste products.

2.5.1 Preparation of Activated Carbon

In the study by Bamdad, Hawboldt and MacQuarrie (2018), activated carbon is normally made of lignocellulosic biomass such as rice husk and saw dust, coals such as anthracite, lignite and bituminous, as well as industrial byproducts such as petroleum coke. They are generally made from high carbon content materials. There are two methods to produce activated carbon, which are physical activation and chemical activation.

Physical activation involves two steps to produce activated carbon. Based on Reza, et al. (2020), the high carbon content material will undergo carbonisation and activation process. The purpose of carbonisation is to obtain char or biochar. The high carbon content material will undergo pyrolysis during carbonisation in the absence of oxygen at a high temperature. The next activation process takes place, where the char is oxidised by oxidising gas that are present in the atmosphere such as carbon dioxide, nitrogen, steam and air mixtures at a temperature range of 800-1100 ˚C (Ozdemir, et al., 2014).

As for chemical activation, it is a one-step process where carbonisation and activation take place at the same time. It is normally applied for biomass materials that contain cellulose. According to Heidarinejad, et al. (2020), the high carbon content material is impregnated with oxidizing and

dehydrating agents. After that, it is heated to 400-900 ˚C to degrade cellulose, followed by washing to produce activated carbon.

2.5.2 Characteristics of Activated Carbon

Activated carbon is a substance that is highly porous. According to White, et al. (2009), the porosity of a material is defined as the interconnected empty voids that are filled with a gas or liquid within the material. The availability of numerous pores on the surface of the activated carbon increases the surface area that is available for ions and molecules (adsorbates) to adhere onto. This results in a cleaner gas or liquid that passes through the activated carbon as more adsorbates have been removed.

There are many ways where pore sizes can be classified. In general, there are three types of pore size in accordance to IUPAC (International Union of Pure and Applied Chemistry), as mentioned in the study by Ilomuanya, et al. (2017). They can be classified as macropores, mesopores and micropores. The pore diameter for each type of pore size are tabulated in Table 2.3 below. Meanwhile, in the study conducted by Mays (2007), the author has proposed another set of pore sizes classification where the pore sizes are categorised according to SI prefixes. They can be categorised into three major categories, such as nanopore, micropore and millipore. They can be further classified into sub, inter and super pores according to their pore diameter. This set of pore sizes classification is tabulated in Table 2.4.

Table 2.3: Classification of Pore Size According to Pore Diameter (Ilomuanya, et al., 2017).

Pore Size Classification	Pore Diameter
Macropores	> 50 nm
Mesopores	2-50 nm
Micropores	< 2 nm

Table 2.4: Proposed Set of Pore Size Classification (Mays, 2007).

Pore Size Classification	Pore Diameter
Nanopore	

Pore Size Classification	Pore Diameter
▪ Sub-nanopore	0.1-1 nm
▪ Inter-nanopore	1-10 nm
▪ Super-nanopore	10-100 nm
Micropore	
▪ Sub-micropore	0.1-1 μm
▪ Inter-micropore	1-10 μm
▪ Super-micropore	10-100 μm
Millipore	
▪ Sub-millipore	0.1-1 mm
▪ Inter-millipore	1-10 mm
▪ Super-millipore	10-100 mm

Based on the study by White, et al. (2009), strong electromagnetic field exists due to the close proximity of the pore width at the micropores of the activated carbon. The van der Waals intereaction within the micropores makes it suitable for gas or liquid phase adorption to take place. Furthermore, adsorption occurs with the help of capillary condensation at the mesopores of the activated carbon, where adsorbates will be adhered onto the mesopores until they form multi-layers of adsorbates. Capillary condensation is the phenomenon where vapour is adsorbed and condensed via the mesopores (Kikkinides, et al., 1999). This enables high loading and efficient diffusion and mass transfer of substrates at the mesopores. On the other hand, the surface of the macropores is analogous to flat surfaces, so macropores act as a filter and diffusion pathways for the transportation of adsorbates to the adsorption sites.

In the actual pore system of the activated carbon, a combination of pore sizes are present, which is illustrated in Figure 2.6. The adsorption of adsorbates onto the various pore sizes will depend on the size of the adsorbates. Very small adsorbates will diffuse further through the catalyst pores and adsorb onto the smaller pores such as micropores while bigger adsorbates can only adsorb onto the bigger pores such as mesopores or macropores due to the limitation to diffuse further into the vicinity of the pores. Figure 2.7 shows the pore structure of the activated carbon and the diffusion path of the adsorbates.

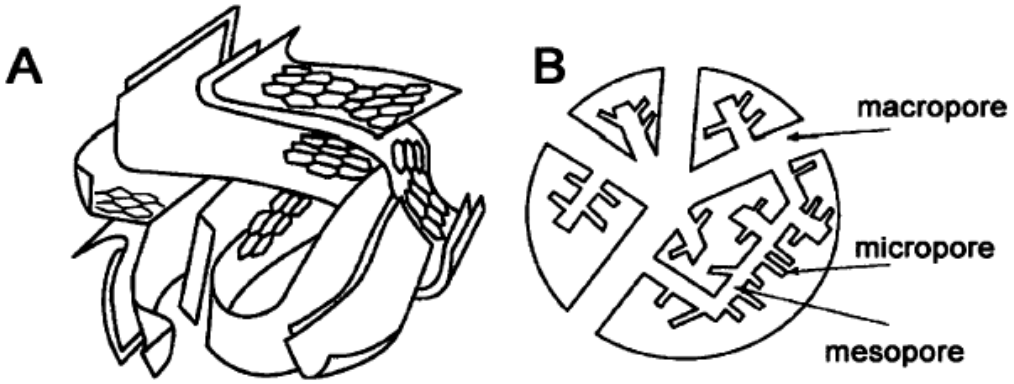


Figure 2.6: Schematic Diagram of Activated Carbon Structure in (a) 3D and (b) 2D (White, et al., 2009).

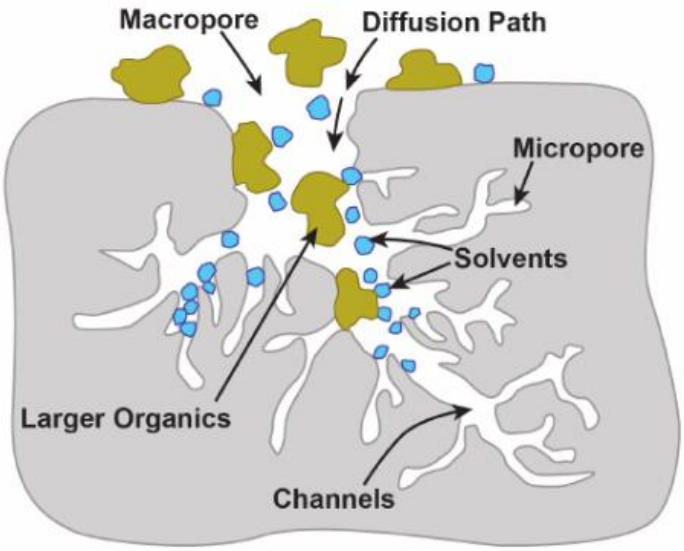


Figure 2.7: Schematic Diagram of the Pore Structure of the Activated Carbon (Kemp, 2017).

2.6 Factors that Affect Adsorption Process

There are various factors that could affect adsorption process, such as the nature of the activated carbon, pH, retention time and adsorbent dosage.

2.6.1 Nature of the Activated Carbon

The physical structure and surface chemistry of the activated carbon will affect its adsorption characteristics. The ability of adsorbate molecules to adsorb onto the surface of the activated carbon depends on the physical structure of

the activated carbon such as its pore size. As aforementioned, the pore size of the activated carbon can be categorised by various ways. If it is categorised based on the IUPAC, there are three types of pore sizes, which are macropores, mesopores and micropores. In the study conducted by Guo and Du, (2012), it was stated that adsorption mainly occurs at the mesopores and micropores while the macropores act as sieves to limit large molecules from adsorbing onto the pores of the activated carbon. Therefore, there will be a decrease in the adsorption capacity of molecules with larger diameters than the macropores. Meanwhile, the adsorption capacity of activated carbon with greater amount of mesopores and micropores will increase as more adsorption sites are available.

Next, the adsorption process is also affected by the surface chemistry which involves the functional groups on the activated carbon. According to Heidarinejad, et al. (2020), functional groups like carboxyl, lactone, phenol, carbonyl and so on help to adsorb pollutants. Atoms such as hydrogen, oxygen, nitrogen and sulphur are normally found in the functional groups. The activation method, raw material used and the treatment method can help to introduce or modify the functional groups on the activated carbon (Bhatnagar, et al., 2013). For example, functional groups that contain sulphur increases the adsorption capacity of carbon dioxide. This is because of the large sulphur that extends beyond the graphene plane, which causes straining to the framework. This results in the increase in charge localisation which favours carbon dioxide molecules to adsorb onto the activated carbon (Petrovic, Gorbounov and Soltani, 2022).

2.6.2 pH

The efficiency of the activated carbon to remove pollutants from the wastewater also depends on the pH of the adsorption media. In a solution containing dye, as pH is varied, the electrostatic interaction between the dyes and adsorbent will vary too. This is due to the change in the adsorbent's zeta potential that is dependent on the functional groups present on the adsorbent surface (Molavi, Pourghaderi and Shojaei, 2019). Al-Degs, et al. (2007) stated that the reactive dyes adsorption capacity will conceptually decrease with the increase in ionic strength due to the attractive electrostatic forces between the

reactive dyes and activated carbon. On the contrary, the reactive dyes adsorption capacity will increase with the increase in ionic strength due to the repulsive electrostatic forces.

In the study by Adeolu, Okareh and Dada (2016), it was found that the Cr^{6+} adsorption capacity increased along with the pH from pH 2 to pH 10. This is because when pH increases, the H^+ concentration is reduced so more metal ions can adsorb onto the adsorbent instead of protons. However, when the pH increased beyond pH 10, a decrease in adsorption capacity was observed. This is due to the precipitation of metal ions with the excess OH^- ions to form metal hydroxides instead of being adsorbed.

2.6.3 Retention Time

Adsorption is dependent on the retention time or contact time. Retention time is important because during that period of time, diffusion and adsorption of adsorbate molecules occur. Different adsorbate will give different optimum retention time to achieve maximum adsorption capacity using the same adsorbent. For instance, Kurniawati, et al. (2021) reported that the optimum retention time for rhodamine B dyes, methyl orange dyes and methylene blue dyes are 60, 90 and 150 minutes respectively. Nevertheless, there is a similar trend which can be observed among the three types of dyes studied. There would be an initial rapid adsorption rate, followed by a slow adsorption rate. This is because in the beginning of the adsorption process, there is plenty of adsorption site available for the adsorbate molecules. On the other hand, as adsorption proceeds for a period of time, the adsorption sites are slowly occupied and become saturated. As a result, the active sites can no longer bind anymore adsorbates, and the system is said to have reached equilibrium (Panda, et al., 2017).

2.6.4 Adsorbent Dosage

An increase in adsorbent dosage will promote more vacant active sites and effective surface area when the adsorbate molecules are kept constant (Wong, et al., 2020). Then, the adsorption capacity will increase since there will be less competition for active sites among the dye molecules. This is reflected in the study conducted by Sumalatha, et al. (2014) where the removal of indigo

carmine dyes increased as the activated carbon dosage increased. The same trend is observed in the study by Eletta, et al. (2018) using sawdust activated carbon to remove dye from textile wastewater, except the percentage of dye removal decreased after it reaches a certain activated carbon dosage. This can be explained by the accumulation of activated carbon that overlaps with one another which further reduces the available adsorption sites where dyes can adhere onto (Garg, et al., 2004).

2.7 Previous Studies on the Treatment of Textile Wastewater Using Various Adsorbents

Various batch adsorption studies have been carried out to treat textile wastewater using different adsorbents. For instance, Maroufi, Amirkhani and Zakryazadeh (2021) have utilised self-synthesised graphene oxide and response surface methodology (RSM) to conduct adsorption experiments for the removal of COD from actual textile wastewater. The RSM results gave the optimum pH, retention time and adsorbent dosage of pH 8, 25 minutes and 0.125 g/L, respectively. Based on the optimum conditions, graphene oxide demonstrated a high COD removal efficiency of 62.1%, indicating that it is a viable nano-adsorbent for treating actual textile wastewater.

A similar study was conducted by de Araujo, et al. (2018) using the same type of adsorbent material (graphene oxide) to remove dye. Different methods were used to synthesise various types of graphene oxide, which were subsequently tested in preliminary experiments using methylene blue solution. The most promising result was achieved using graphene oxide synthesised through the use of potassium permanganate oxidant, without the aid of sonication. It was subsequently used to treat actual textile wastewater at initial pH of 5.8, 30 minutes retention time and 0.04 g/L adsorbent dosage, which resulted in 60.4% removal of colour and 84.7% removal of turbidity. The result showed the potential application of graphene oxide as a dye removal adsorbent.

Furthermore, Assila, et al. (2020) investigated the ability of natural mineral M1 and M2 as adsorbents to treat actual textile wastewater. They conducted batch experiments to evaluate the effects of pH, retention time, dosage, and temperature on the removal of pollutants from the wastewater

using M1 and M2 as adsorbents. The results showed that the optimal conditions for M1 were pH 10, 90 minutes retention time, 1.5 g/L adsorbent dosage, and 55 ℃, while the optimal conditions for M2 were pH 10, 160 minutes retention time, 1.5 g/L adsorbent dosage, and 55 ℃. The use of M1 as an adsorbent resulted in the removal efficiencies of 88.68% for COD, 35.95% for cadmium, 39.43% for chromium, 28.27% for copper, and 39.53% for zinc. Meanwhile, the use of M2 as an adsorbent showed the removal efficiencies of 79.73% for COD, 19.42% for cadmium, 23.57% for chromium, 18.62% for copper, and 24.03% for zinc.

In addition, the feasibility of using low-cost activated carbon made from coconut shell waste to treat methylene blue solution was studied by Oribayo, et al. (2020). Based on the batch adsorption results, the researchers determined that the adsorption isotherm and kinetic models for the coconut shell activated carbon were the Langmuir isotherm and pseudo-second order model, respectively. They also identified the optimal conditions for methylene blue removal as pH 7, 270 minutes of retention time, 0.4 g/L of adsorbent dosage, and a temperature of 30 ℃. The coconut shell activated carbon demonstrated a high efficiency in removing methylene blue dyes, with a removal rate of 92.39% under these conditions.

Apart from that, Fito, Abrham and Angassa (2020) conducted a study on the utilisation of Parthenium hysterophorus stem as activated carbon to treat both synthetic methylene blue solution and actual textile wastewater. The batch adsorption experiments conducted using synthetic methylene blue solution showed that the optimum conditions for Parthenium hysterophorus stem activated carbon were pH 11, 20 g/L of activated carbon dosage, 100 minutes of retention time, and an initial methylene blue concentration of 100 mg/L. Under these conditions, a high removal efficiency of 93.8% was achieved. A further batch adsorption experiment was conducted on actual textile wastewater using the same optimal conditions. This resulted in a slightly lower, but still impressive, removal efficiency of 91.2% for methylene blue.

Overall, the previous studies have demonstrated the effectiveness of various adsorbents in treating textile wastewater. A summary of these studies is shown in Table 2.5.

Table 2.5: Summary of the Previous Studies on the Treatment of Textile Wastewater Using Various Adsorbents.

Adsorbent used	**Type of textile wastewater**	**Operating conditions**				**Result**	**Source**
		pH of solution	**Contact time (min)**	**Adsorbent dosage (g/L)**	**Temperature (˚C)**		
Graphene oxide	Real textile wastewater	8	25	0.125 g/L	Room temperature	1. 62.1% COD removal *($COD_{initial}$ = 2568 mg/L; COD_{final} = 973.5 mg/L)*	(Maroufi, Amirkhani and Zakryazadeh, 2021)
Graphene oxide	Real textile wastewater	5.8	30	0.04	Room temperature	1. 60.4% colour removal *($Colour_{initial}$ = 256 Hazen $Colour_{final}$ = 101.3 Hazen)* 2. 84.7% turbidity removal *($Turbidity_{initial}$ = 105 NTU; $Turbidity_{final}$ = 16.1 NTU)*	(de Araujo, et al., 2018)
Natural material (M1)	Real textile wastewater	10	90	1.5	55	1. 88.68% COD removal, *($COD_{initial}$ = 440 mg/L; COD_{final} = 49.8 mg/L)*	(Assila, et al., 2020)

Adsorbent used	Type of textile wastewater	Operating conditions				Result	Source
		pH of solution	Contact time (min)	Adsorbent dosage (g/L)	Temperature (˚C)		
						2. 35.95% cadmium removal, *(Cadmium$_{inital}$ = 0.0484 mg/L; Cadmium$_{final}$ = 0.031 mg/L)* 3. 39.43% chromium removal, *(Chromium$_{initial}$ = 0.2469 mg/L; Chromium$_{final}$ = 0.1499 mg/L)* 4. 28.27% copper removal, *(Copper$_{initial}$ = 0.1451 mg/L; Copperfinal = 0.1041 mg/L)* 5. 39.53% zinc removal *(Zinc$_{initial}$ = 1.2963 mg/L; Zinc$_{final}$ = 0.78 mg/L)*	

Adsorbent used	Type of textile wastewater	Operating conditions				Result	Source
		pH of solution	Contact time (min)	Adsorbent dosage (g/L)	Temperature (˚C)		
Natural material (M2)	Real textile wastewater	10	160	1.5	55	1. 79.73% COD removal (*$COD_{initial}$ = 440 mg/L; COD_{final} = 89.16 mg/L)* 2. 19.42% cadmium removal, *($Cadmium_{inital}$ = 0.0484 mg/L; $Cadmium_{final}$ = 0.039 mg/L)* 3. 23.57% chromium removal, *($Chromium_{initial}$ = 0.2469 mg/L; $Chromium_{final}$ = 0.188 mg/L)* 4. 18.62% copper removal, *($Copper_{initial}$ = 0.1451 mg/L; Copperfinal = 0.1189 mg/L)* 5. 24.03% zinc removal	(Assila, et al., 2020)

Adsorbent used	Type of textile wastewater	Operating conditions				Result	Source
		pH of solution	Contact time (min)	Adsorbent dosage (g/L)	Temperature (˚C)		
						($Zinc_{initial}$ = 1.2963 mg/L; $Zinc_{final}$ = 0.9894 mg/L)	
Coconut shell waste AC	Synthetic methylene blue solution	7	270	0.4	30	1. 92.39% methylene blue (MB) removal *($MB_{initial}$ = 450 mg/L; MB_{final} = 34.25 mg/L)*	(Oribayo, et al., 2020)
AC made from *Parthenium hysterophorus* plant stem	Synthetic and real textile wastewater	11	100	20	Room temperature	1. For synthetic wastewater: 93.8% MB removal *($MB_{initial}$ = 100 mg/L; MB_{final} = 6.2 mg/L)* 2. For real wastewater: 91.2% MB removal *($MB_{initial}$ = 86.5 mg/L; MB_{final} = 7.61 mg/L)*	(Fito, Abrham and Angassa, 2020)

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Flow Chart

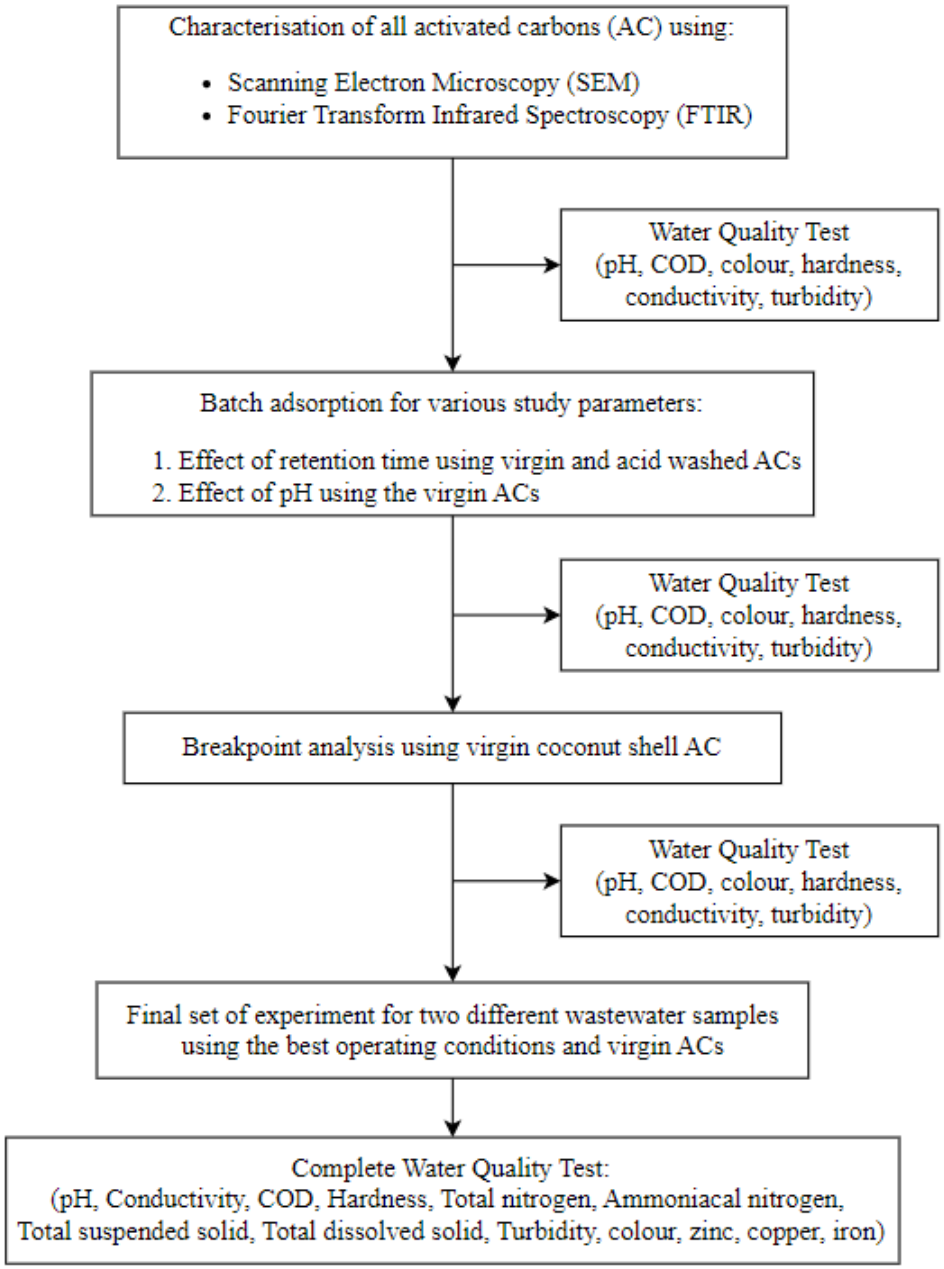


Figure 3.1: Flow Chart of the Work Plan.

3.2 Materials and Equipment

The textile wastewater samples were taken from a textile manufacturing company in Johor, named Sincerely Dyeing and Finishing Sdn Bhd. In that company, the raw textile production wastewater would be collected at the collection sump first. Next, the pH of the wastewater would be adjusted before it was directed to the flocculation tank to undergo flocculation. Subsequently, the wastewater would be channelled to an oxidising lagoon equipped with blower. Finally, the water would be channelled to the water lagoons before it was discharged as effluent. Therefore, the sampling point of the textile wastewater was at the end of the company's wastewater treatment processes, which was after the lagoons. The four types of activated carbons that were needed to carry out adsorption were purchased from KI Carbon Solutions Sdn Bhd. The list of materials and equipment used are shown in Table 3.1 and Table 3.2, respectively.

Table 3.1: List of Materials Used.

Materials	Purpose of usage
Activated carbon (AC): a) virgin coconut shell granular AC b) acid washed coconut shell granular AC c) virgin palm kernel shell granular AC d) acid washed palm kernel shell granular AC	As commercial adsorbents to adsorb dyes from the textile wastewater sample.
0.1 M hydrochloric acid solution	To adjust pH of textile wastewater to lower pH
0.1 M sodium hydroxide solution	To adjust pH of textile wastewater to higher pH
COD Digestion Reagent vials	To carry out COD test
10% Ammonia buffer, 0.02 N EDTA Solution, Solochrome Black indicator solution	To carry out hardness test

Materials	Purpose of usage
Filter papers	To filter the activated carbons from the treated samples after carrying out batch adsorption

Table 3.2: List of Equipment Used.

Equipment	Purpose of Usage
Scanning Electron Microscope (Hitachi S-3400N)	To carry out SEM characterisation to analyse the surface morphology of the activated carbons.
Fourier Transform Infrared Spectroscopy (FTIR) (Nicolet IS10)	To carry out FTIR characterisation to determine the functional groups present on the surface of the activated carbons.
DR3900 Spectrophotometer	To carry out water quality test analysis
Shaking incubator	To stir the mixture in the Erlenmeyer flask
Vacuum filter flask set and pump	To filter the activated carbons from the treated samples after carrying out batch adsorption
pH meter (Sartorius PB-10)	To measure the pH of the solution
Analytical balance	To measure adsorbent dosage
DRB200 Digital Reactor Block	To carry out COD and total nitrogen test
Benchtop multiparameter (HANNA HI 2550-02)	To carry out conductivity and total dissolved solid test
Filter nozzle and adsorption column	For breakpoint analysis set up
Inductively coupled plasma optical emission spectrometry (ICP-OES) (Perkin Elmer Optima 7000)	To carry out zinc, copper and iron test

3.3 Characterisation of Activated Carbons

All the four types of activated carbons were characterised before the batch adsorption test. The surface morphology of all the activated carbons were analysed using SEM. The model of the SEM used was Hitachi model S-3400N.

Besides, FTIR was employed to determine the functional groups present on the surface of the activated carbons. According to Song (2017), the absorption or emission infrared spectrum would be obtained by applying FTIR. The FTIR spectrum of the adsorbents were analysed within the range of 4000 – 400 cm^{-1} with a 4 cm^{-1} typical resolution. The model of the FTIR used was Nicolet IS10.

3.4 Batch Adsorption Test Using Various Types of Activated Carbons

Batch adsorption was carried out for the various studied parameters such as effect of retention time and pH. At the end of every batch adsorption, the treated samples were analysed for their respective parameters. Then, the removal efficiencies of the studied parameters were calculated using Equation 3.1.

$$R = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \qquad (3.1)$$

where

$R =$ removal efficiency (%)

$C_o =$ initial concentration of solution (mg/L)

$C_e =$ concentration of solution at equilibrium (mg/L)

3.4.1 Effect of Retention Time

All the four types of activated carbon were used to carry out the study of retention time. For every type of activated carbon, six 250 mL Erlenmeyer flasks were used. 250 mL of textile wastewater along with 1 g/L of activated carbon were added into each of the Erlenmeyer flasks (Ahmad, Loh and Aziz, 2007). The Erlenmeyer flasks were then placed in a shaking incubator where the stirring rate was fixed at 150 rpm at room temperature (25 ˚C). At every 20 minutes interval (20, 40, 60, 80, 100 and 120 minutes) for a total duration of 2

hours, the removal efficiency was determined. The activated carbon that gave the best results was chosen to carry out the study of pH and breakpoint analysis.

3.4.2 Effect of pH

The activated carbon that gave the best results from the previous study was chosen to carry out the study of effect of solution pH on the AC's adsorption performance. The pH of the textile wastewater was varied for pH 6, 7, 8 and 9 by adding 0.1 M hydrochloric acid solution or 0.1 M sodium hydroxide solution. After that, the pH of the solution was measured using a pH meter. As the pH was varied for each batch adsorption, other conditions such as retention time and activated carbon dosage were kept constant at the optimum retention time that is obtained from the study of retention time and 1 g/L, respectively. Four 250 mL Erlenmeyer flasks were used. 250 mL of the textile wastewater with different pH along with the activated carbon were added into each of the Erlenmeyer flask. The Erlenmeyer flasks were then placed in a shaking incubator where the stirring rate was fixed at 150 rpm at 25 ˚C. The effect of the pH was studied on the removal efficiency of the activated carbon.

3.5 Water Quality Test

Before the start of the batch adsorption experiment as well as after every batch adsorption experiment, the textile wastewater samples were tested for their respective water quality parameters, which include pH, chemical oxygen demand (COD), colour, hardness, conductivity and turbidity.

3.5.1 pH Test

A pH meter with the model of Sartorius PB-10 was used to measure the pH of the textile wastewater. The electrode of the pH meter was rinsed using deionised water and blotted-dry with a paper towel after every measurement.

3.5.2 Chemical Oxygen Demand (COD) Test

Hach Method 8000 was applied to test COD. Firstly, the DRB200 Digital Reactor Block was switched on and preheated to 150 ˚C. After removing the

cap from the COD Digestion Reagent vial, the vial was held at a 45˚ angle. Then, 2 mL of textile wastewater sample was added using a pipette. The same step was carried out to prepare the blank, except 2 mL of deionised water was added instead of the wastewater sample. Both vials were capped tightly. They were rinsed with water and wiped dry with a paper towel. Both vials were inverted gently a few times to mix the solution evenly.

After that, the vials were placed inside the preheated DRB200 reactor. The lid was closed, and the vials were heated for 2 hours. After 2 hours, the reactor was switched off and the lid was opened. Both of the vials were cooled to 120 ˚C or less inside the reactor for 20 minutes. They were inverted a few times while they were still warm. Then, they were placed onto a tube rack to let them cool to room temperature.

By using DR3900 Spectrophotometer, the program – 435 COD HR, was started. The blank sample cell was cleaned before it was placed into the cell holder. The ZERO button was pressed to set it to 0.0 mg/L COD. Next, the other sample cell was cleaned and placed into the cell holder. The READ button was pressed to get the result in mg/L COD. Finally, the results were recorded (HACH, 2021).

3.5.3 Colour Test

Hach Method 10048 was used to test for colour. Firstly, the program – 97 Colour ADMI 1 inch, was started on the DR3900 Spectrophotometer. 100 mL of the textile wastewater was poured into two 250 mL beakers, respectively. The pH of the wastewater sample in the first beaker was adjusted to pH 7.6 with a minimum volume of sulphuric acid or sodium hydroxide solution. If large pH adjustments were needed, 10 M solution was used while if small pH adjustments were needed, 0.1 M solution was used.

A blank sample cell was prepared by filling it with deionised water until it reaches the fill line. The second sample cell was filled with the wastewater sample that was pH-adjusted. Before inserting the blank sample cell into the cell holder of the DR3900 Spectrophotometer, it was cleaned. The ZERO button was pressed to set it to 0 ADMI value. The other sample cell was also cleaned before placing it into the cell holder. The READ button was pressed to get the result in ADMI value. The results were recorded. The steps

were repeated for the wastewater sample without adjusting its pH (HACH, 2019).

3.5.4 Hardness Test

Titration was carried out to test the hardness of the textile wastewater sample. Firstly, the burette was filled with EDTA solution to the zero level. Then, the burette was clamped onto a burette clamp and a retort stamp. The initial reading of the burette was recorded. Next, 50 mL of textile wastewater sample was poured into a conical flask. 1 mL of ammonia buffer, followed by 5 drops of solochrome black indicator solution were added to the wastewater sample. After that, titration was carried out until the end point was reached when the solution changed colour from wine red to blue colour. The final reading of the burette was recorded (Mohanlal Sukhadia University, 2022). The amount of hardness can be calculated using Equation 3.2.

$$Hardness\ (mg/L\ CaCO_3) = \left(\frac{EDTA\ Volume\ used,\ \ mL}{Sample\ Volume,\ \ mL}\right) \times 1000 \quad (3.2)$$

3.5.5 Conductivity Test

A benchtop multiparameter was used to measure the conductivity of the textile wastewater sample. Before placing the probe into the sample, the probe was rinsed with deionised water and the reading of the multiparameter was ensured to be at 0 μS/cm. After that, the probe was placed into the solution without touching the bottom or sides of the beaker. The reading of the multiparameter was allowed to stabilize before the reading was taken. Lastly, the probe was rinsed using deionised water and blotted-dry with a paper towel after every measurement.

3.5.6 Turbidity Test

Hach Method 8237 was used to test for the turbidity of the textile wastewater sample. Based on HACH (2013), the program – 745 FAU was started using the spectrophotometer. The blank was prepared by adding 10 mL of deionised water into a sample cell. The blank sample cell was cleaned before it was placed into the cell holder. The ZERO button was pressed to set it to 0 FAU.

After that, 10 mL of wastewater sample was added into another sample cell. It was cleaned and placed into the cell holder. The READ button was pressed to obtain the turbidity reading in Formazin Attenuation Units (FAU).

3.6 Breakpoint Analysis

After the experiments for the batch adsorption were carried out, the optimum pH condition at which maximum removal efficiency was achieved, was obtained. The optimum pH was then used to carry out breakpoint/breakthrough analysis using the best activated carbon that was found earlier. The purpose of the breakpoint analysis was to determine the breakthrough time at which the activated carbon should be replaced before the entire activated carbon bed became saturated.

The set up for the breakpoint analysis was as illustrated in Figure 3.2. Textile wastewater was pumped into the adsorption column at a flow rate of 0.0105 m^3/h. The surface loading rate of the adsorption column would be 2.5 $m^3/(m^2 \cdot h)$. The detailed design and dimension of the adsorption column were depicted in Figure 3.3. The surface area of the adsorption column was 0.004815 m^2. The bed height of the activated carbon was fixed at 27 cm. The filter nozzle was supported 5 cm above the base of the adsorption column.

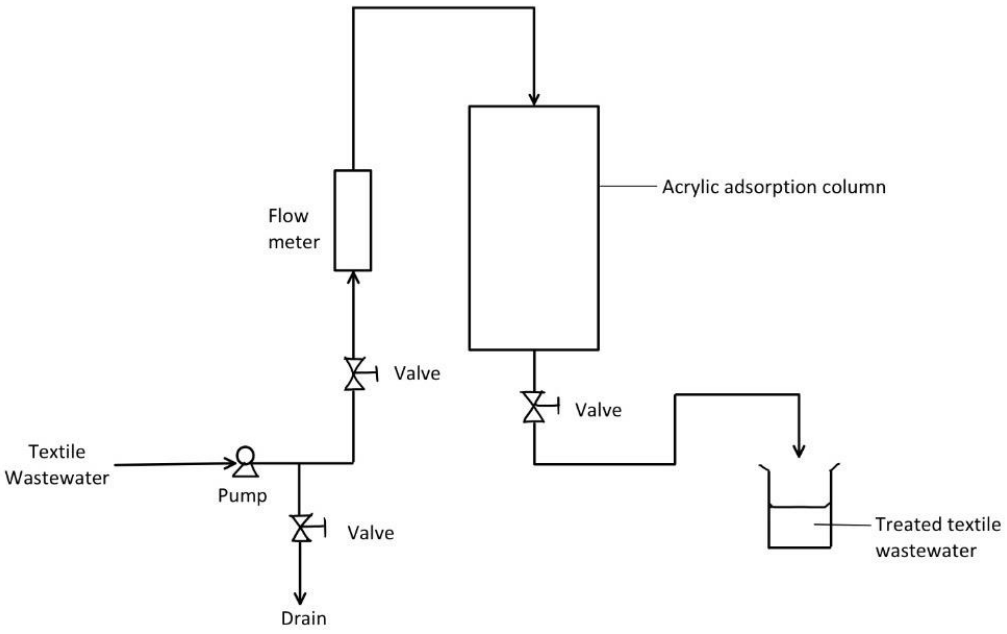


Figure 3.2: Continuous Flow System Setup for Breakpoint Analysis.

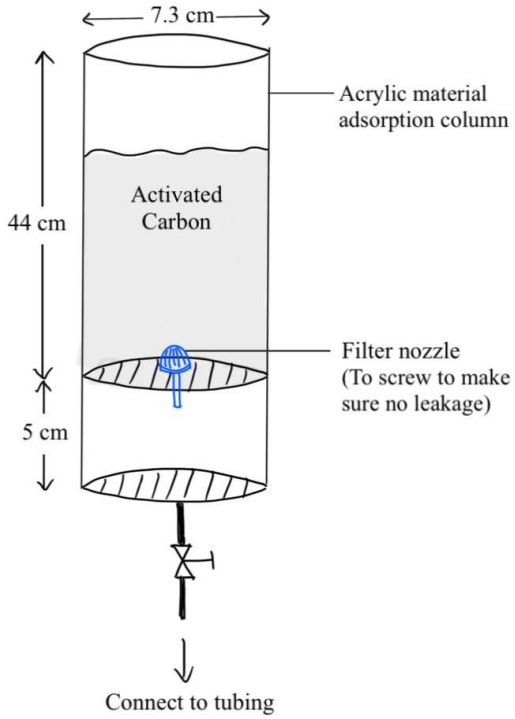


Figure 3.3: Design and Dimension of the Adsorption Column.

The textile wastewater was allowed to flow into the acrylic adsorption column and undergo adsorption to obtain the treated textile wastewater. The treated textile wastewater was collected in a beaker at regular intervals for the analysis of colour (ADMI). Based on the result obtained, a graph of the ratio of effluent concentration to inlet concentration (C_t/C_o) as a function of time was plotted. From the trendline of the graph, the breakthrough point was determined. The time at which the breakthrough point took place was called the breakthrough time.

3.7 Final Set of Experiment

Lastly, the best operating conditions of the batch adsorption (best activated carbon, optimum retention time and optimum textile wastewater pH) were used to carry out adsorption of two different textile wastewater samples. Then, the treated textile wastewater which was obtained would undergo a complete set of water quality testing. The parameters which were tested included pH, conductivity, COD, water hardness, total nitrogen, ammoniacal nitrogen, total suspended solid, total dissolved solid, turbidity, colour (ADMI), zinc, copper and iron.

3.8 Complete Water Quality Test

The complete water quality test comprised of pH, conductivity, COD, water hardness, total nitrogen, ammoniacal nitrogen, total suspended solid, total dissolved solid, turbidity, colour (ADMI), zinc, copper and iron. The method to test for pH, COD, colour, hardness, conductivity and turbidity had been stated in section 3.5. the rest of the water quality test would be listed in the following subsections.

3.8.1 Total Nitrogen

To test total nitrogen, Persulfate digestion method (HACH Method 10071) was applied. Firstly, the DRB200 Reactor was switched on and the temperature of the reactor was set to 105 ˚C. A funnel was used to add one packet of Total Nitrogen Persulfate Reagent Powder Pillow, respectively to two Total Nitrogen Hydroxide Digestion Reagent vials. 2 mL of sample was added to one of the vials while 2 mL of deionised water was added to the second vial. The vials were capped and shaken to mix the content of the vials. After that, the vials were placed into the reactor. The lid of the reactor was closed and both vials are left inside for half an hour. After 30 minutes, the vials were taken out to cool them to room temperature.

Then, the program 350 N, Total LR TNT was started. One packet of Total Nitrogen (TN) Reagent A Powder Pillow was added into every vial. Following that, they were capped and shaken for 15 seconds. A timer was started to let the content of the solution to react for 3 minutes. Next, one packet of TN Reagent B Powder Pillow was added into every vial and shaken for 15 seconds. A timer was started to let the content of the solution to react for 2 minutes. After that, 2 mL of the digested, treated sample was added into one TN Reagent C vial. On the other hand, 2 mL of the digested, treated blank was added into another TN Reagent C vial. The TN Reagent C vials were capped and inverted 10 times. The content inside the vials were allowed to react for 5 minutes. The treated blank vial was cleaned before it was placed into the cell holder. The ZERO button was pressed to set it to 0.0 mg/L N. Next, the other sample vial was cleaned and placed into the cell holder. The

READ button was pressed to get the result in mg/L N. Finally, the results were recorded (HACH, 2014b).

3.8.2 Ammoniacal Nitrogen

Salicylate Method (HACH Method 10023) was applied to carry out ammoniacal nitrogen test by using 342, Ammonia LR TNT program. To prepare the blank, 2 mL of ammonia-free water was added to one AmVer Diluent Reagent Test 'N Tube vial. On the other hand, to prepare the sample, 2 mL of sample was added to one AmVer Diluent Reagent Test 'N Tube vial. One packet each of Ammonia Salicylate Reagent Powder Pillow and Ammonia Cyanurate Reagent Powder Pillow were added to both vials and they were well shaken. A timer was started to let the content of the solution to react for 20 minutes. After that, the blank sample cell was cleaned before it was placed into the cell holder. The ZERO button was pressed to set it to 0.0 mg/L NH_3-N. Next, the other sample cell was cleaned and placed into the cell holder. The READ button was pressed to get the result in mg/L NH_3-N. Finally, the results were recorded (HACH, 2015).

3.8.3 Total Suspended Solid

Photometric method (HACH Method 8006) was used to determine the amount of suspended solids present in the sample by using program 630 Suspended Solids of the spectrophotometer. 10 mL of the sample was poured into a sample cell while 10 mL of deionised water was poured into another sample cell. The blank sample cell was cleaned before it was placed into the cell holder. The ZERO button was pressed to set it to 0 mg/L TSS. Next, the other prepared sample cell was swirled, cleaned and placed into the cell holder. The READ button was pressed to get the result in mg/L TSS. Finally, the results were recorded (HACH, 2014c).

3.8.4 Total Dissolved Solid

A benchtop multiparameter was used to determine the amount of total dissolved solids in the sample. Before placing the probe into the sample, the probe was rinsed with deionised water and the reading of the multiparameter was ensured to be at 0 ppm. After that, the probe was placed into the solution

without touching the bottom or sides of the beaker. The reading of the multiparameter was allowed to stabilize before the reading was taken. Lastly, the probe was rinsed using deionised water and blotted-dry with a paper towel after every measurement.

3.8.5 Zinc

The amount of zinc present in the sample was tested using ICP-OES. Before carrying out the ICP-OES analysis, 1, 2, 3, 4 and 5 mg/L zinc nitrate standard solution were prepared to obtain the calibration curve before testing the sample. After that, the sample was analysed.

3.8.6 Copper

The amount of copper present in the sample was tested using ICP-OES. Before carrying out the ICP-OES analysis, 1, 2, 3, 4 and 5 mg/L copper nitrate standard solution were prepared to obtain the calibration curve before testing the sample. After that, the sample was analysed.

3.8.7 Iron (ICP-OES)

The amount of iron present in the sample was tested using ICP-OES. Before carrying out the ICP-OES analysis, 1, 2, 3, 4 and 5 mg/L iron nitrate standard solution were prepared to obtain the calibration curve before testing the sample. After that, the sample was analysed.

3.8.8 Iron (HACH)

HACH Method 8008 was applied to test for the presence of iron in the sample by using program 265 Iron, FerroVer. 10 mL of sample was poured into a sample cell, followed by a packet of FerroVer Iron Reagent Powder Pillow. The sample cell was swirled to mix the content of the solution. After that, a timer was started to let the content of the solution to react for 3 minutes. If any of the samples show rust content, it is allowed to further react for at least 5 minutes. Following that, the blank can be prepared by pouring 10 mL of sample into a second sample cell. The blank sample cell was cleaned before it was placed into the cell holder. The ZERO button was pressed to set it to 0.00 mg/L Fe. Then, the other prepared sample cell was cleaned and placed into the

cell holder. The READ button was pressed to get the result in mg/L Fe. Lastly, the results were recorded (HACH, 2014a).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterisation of Activated Carbons

4.1.1 Scanning Electron Microscopy (SEM)

Figure 4.1 shows the surface morphology of the commercial virgin palm kernel shell granular AC, virgin coconut shell granular AC, acid washed palm kernel shell granular AC and acid washed coconut shell granular AC at 1000× magnification before they were being used to carry out adsorption.

By referring to Figure 4.1 (a) and (b), virgin palm kernel shell AC and virgin coconut shell AC show rough surface and porous structure. The porous structure has varying depth of pores. The virgin coconut shell AC shows rough and distinct honeycomb structures, where the pores are quite evenly arranged and spaced out. On the other hand, acid washed palm kernel shell AC (Figure 4.1 (c)) shows a rough surface with no well-developed porosity. There are only a few shallow pores and cracks on its surface. A very rough surface with many small holes could be seen on the surface of the acid washed coconut shell AC (Figure 4.1 (d)). Only a few big and well-developed pores are observed.

Both the virgin activated carbons that were made from palm kernel shell and coconut shell possessed porous structures. This would promote the adsorption of wastewater impurities onto the available porous surface area that served as adsorption sites (Liu, et al., 2021). Hence, their removal efficiencies of impurities were expected to be higher than that of the two other types of acid washed activated carbons.

On the other hand, from the observation of the SEM images of acid washed palm kernel shell AC and acid washed coconut shell AC, both of them showed a collapsed structure, where there were very few well-developed pores on the surface of the AC. Since they were commercially made, a few guesses were made to justify the collapsed carbon structures. According to Hagemann, et al. (2018), it could be due to the effect of chemical activation parameters such as the concentration of the activation chemical, duration of activation and activation temperature. For instance, the increase in the concentration of

activation chemical would lead to an increase in the number of pores on the AC until it reached a point where the number of pores no longer increased. Instead, the number of pores reduced, and the carbon structure collapsed due to the excessive chemical concentration (Budi, et al., 2016). This also implied that there would be a reduction in the available adsorption sites for both acid washed palm kernel shell AC and acid washed coconut shell AC.

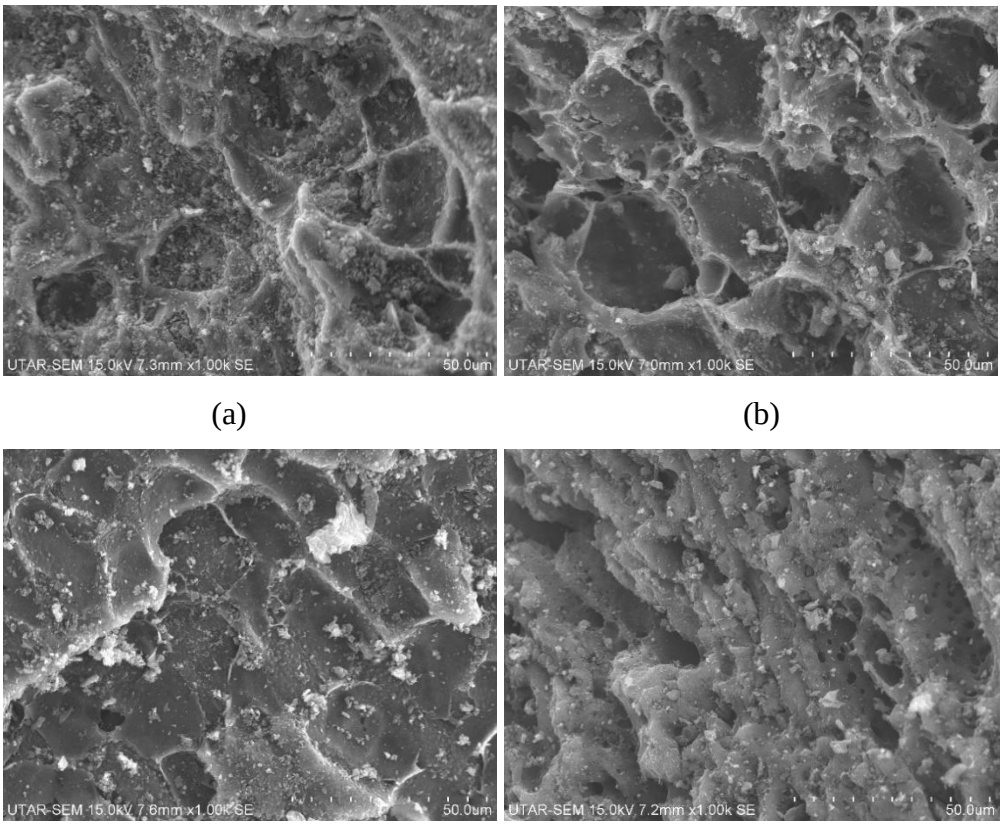
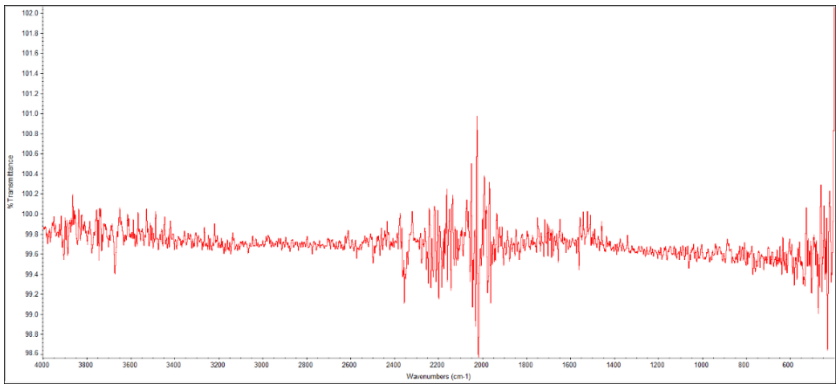


Figure 4.1: SEM Images of (a) virgin palm kernel shell granular AC, (b) virgin coconut shell granular AC, (c) acid washed palm kernel shell granular AC, and (d) acid washed coconut shell granular AC.

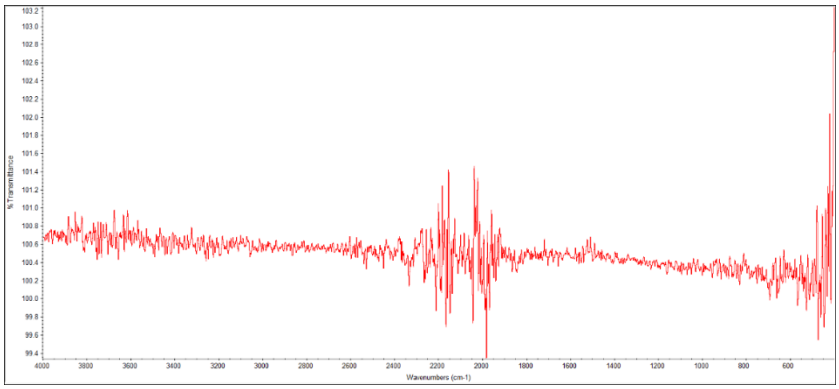
4.1.2 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 4.2 (a) to (d) show the FTIR images of all the commercial activated carbons before they were being used to carry out adsorption test. One common thing that was found from these images was the abnormal FTIR spectra displayed. They showed numerous peaks where the functional groups could not be identified. This implied that there were no functional groups present in all of the commercial activated carbons.

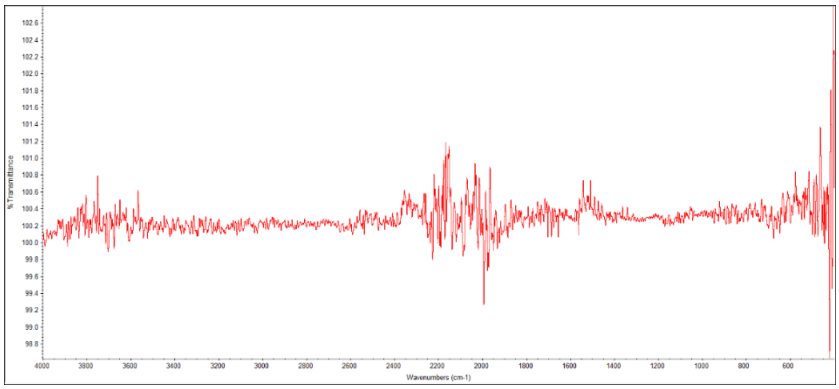
One of the possible reasons to that was the carbonisation temperature that was too high during the preparation of activated carbon. Yahya, et al. (1972) mentioned that during carbonisation, the organic materials present in the raw material would be thermally decomposed and volatile matters would evaporate to form pores. As carbonisation temperature increased, the drying of the raw material is promoted, followed by the increase in elemental carbon content and the decrease in volatile matters. This would also promote the formation of pores on the surface of the raw material. However, Hendrawan, et al. (2019) further explained that temperature greater than 1000 ˚C would increase the formation of ash that could lead to the closure of pores. This could explain why there were no functional groups detected by FTIR.



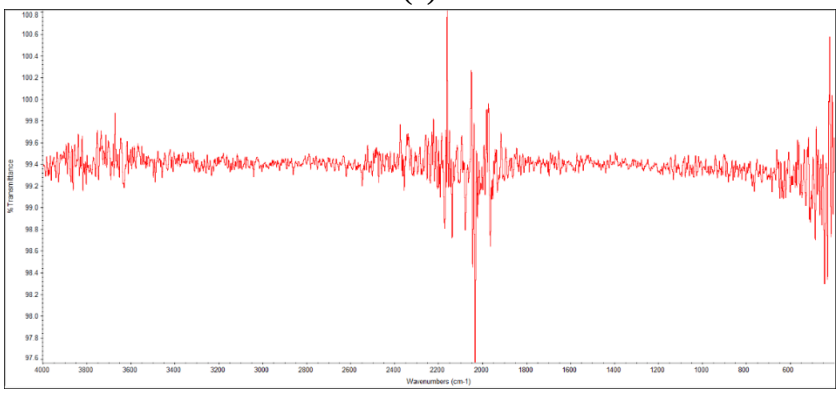
(a)



(b)



(c)



(d)

Figure 4.2: FTIR of (a) Virgin Palm Kernel Shell AC (b) Virgin Coconut Shell AC (c) Acid Washed Palm Kernel Shell AC (d) Acid Washed Coconut Shell AC.

4.2 Batch Adsorption Test Using Various Types of Activated Carbons

4.2.1 Effect of Retention Time

Figure 4.3 and Table 4.1 illustrate the effect of retention time on the overall removal efficiency of the respective parameters by using virgin palm kernel shell granular AC. The comparison of the treated wastewater samples across different retention time is shown in Figure A-1 in Appendix A. It was found that the COD and colour of the treated samples were able to comply with Standard A of the Environmental Quality (Industrial Effluents) Regulations 2009 – P.U. (A) 434/2009, as presented in Appendix C. Furthermore, by referring to Figure 4.3, the removal efficiency of COD was the highest among all the other parameters. Its removal efficiency was quite consistent at different retention time, while 60- and 100-minutes retention time shows the highest COD removal. Another significant parameter that was effectively removed is turbidity. Its removal efficiency fluctuated as retention time increased, giving the highest peak at 60 minutes retention time.

Meanwhile, the removal efficiency for colour (ADMI), hardness and conductivity were relatively low compared to the removal of COD and turbidity. The removal efficiency of colour (ADMI) gradually increased with a slight drop at 60 minutes retention time and then giving the highest removal efficiency at 120 minutes. Moving on, the removal efficiency of hardness fluctuated at the first half of the retention time before it remained constant at the second half of the retention time. It peaked at 20- and 60-minutes retention time. Lastly, the removal efficiency of conductivity was relatively constant with a slight increase at 120 minutes retention time. On average, the optimum retention time was 60 minutes.

As the retention time increased, the overall removal efficiency generally decreased. This result suggested that there were more vacant active sites available for adsorption at the beginning of the experiment. However, most of the surface sites had been occupied towards the end of the experiment, so the removal of the solute molecules decreased. Rolence, Machunda and Njau (2014) also stated that it could be due to the repulsion between the solute molecules in the liquid and the solute molecules that had been adsorbed onto

the solid. This would hinder the solute molecules in the liquid from adsorbing onto the remaining active sites.

Furthermore, the overall removal of colour, hardness and conductivity were much lower than that of COD and turbidity. This might be due to the competition among the mixed adsorbates that were present in the textile wastewater. In relation to that, it could be deduced that organic and inorganic matters that caused high COD and turbidity were the more dominant adsorbates, so they could be removed more easily. Besides, in the case of low colour removal, this might be due to insufficient amount of adsorbent dosage used. Jibril, et al. (2012) reported that at 60 minutes retention time, the optimum coconut shell AC and commercial AC dosage that was used to remove colour was 12 g/L, resulting in 74% and 44% of removal efficiencies, respectively. Their AC dosage was much greater than the AC dosage used in this experiment, which was 1 g/L. This could explain why the colour removal was low as the adsorption sites were limited.

In addition, according to Environmental Protection Agency (2022), conductivity indicates the presence of dissolved salts and inorganic compounds that are good electrical conductors. The common ways to remove conductivity of water effectively are via reverse osmosis, coagulation and flocculation, biological removal of phosphorus and nitrification (Levlin, 2007). On the other hand, water hardness is mainly caused by the presence of calcium and magnesium ions. To remove water hardness, water softening methods such as ion exchange, chemical precipitation and nano-filtration are commonly applied (Bibiano-Cruz, et al., 2016). Hence, adsorption using commercial virgin palm kernel shell might not be suitable to effectively remove conductivity and hardness.

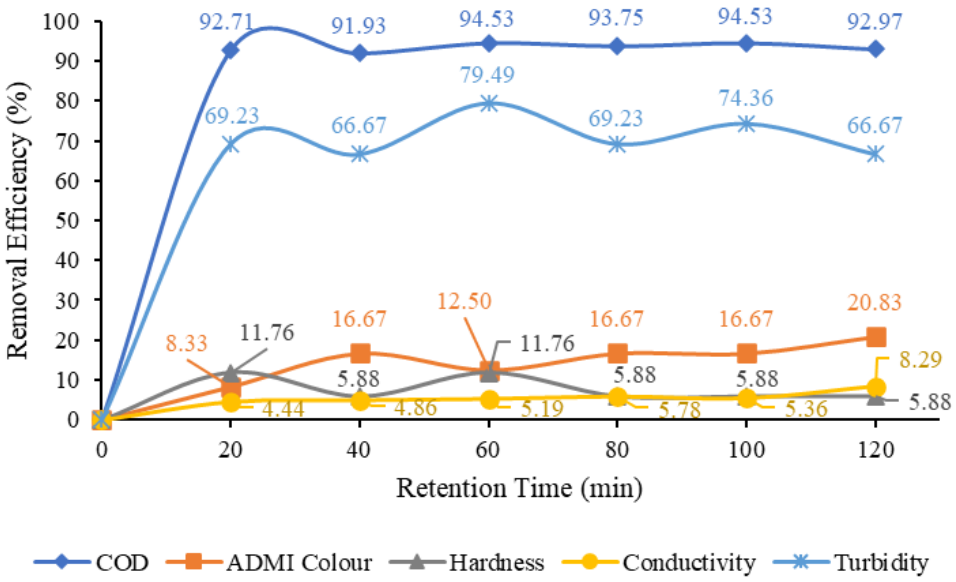


Figure 4.3: Effect of Retention Time on Removal Efficiency of Virgin Palm Kernel Shell Granular AC.

Table 4.1: Batch Adsorption Result of Virgin Palm Kernel Shell Granular AC at the Respective Retention Time.

Parameter	**Retention Time (min)**						
	0	**20**	**40**	**60**	**80**	**100**	**120**
COD	384	28	31	21	24	21	27
Colour (ADMI)	24	22	20	21	20	20	19
Hardness	34	30	32	30	32	32	32
Conductivity (µS)	1194	1141	1136	1132	1125	1130	1095
Turbidity (NTU)	39	12	13	8	12	10	13

Secondly, Figure 4.4 and Table 4.2 illustrate the effect of retention time on the overall removal efficiency of the respective parameters by using acid washed palm kernel shell granular AC. It was observed that the COD and colour of the treated samples were able to comply with Standard A of the Environmental Quality (Industrial Effluents) Regulations 2009 – P.U. (A) 434/2009, as presented in Appendix C. Furthermore, the overall removal efficiency of the graph was similar to that of virgin palm kernel shell granular AC, where the removal efficiency of COD and turbidity were much higher than that of colour (ADMI), hardness and conductivity. The comparison of the

treated wastewater samples across different retention time is shown in Figure A-2 in Appendix A.

Among all the tested parameters, COD removal efficiency of acid washed palm kernel shell AC was the highest. Its removal efficiency was rather constant over different retention time. As for turbidity, its removal efficiency increased and then dropped at the first half of the retention time, followed by a gradual increase until it reached its peak at 120 minutes retention time. Next, the removal efficiency of colour (ADMI) slightly increased over the retention time. On the contrary, the removal efficiency for hardness remained constant over the retention time, except for the drop at 100 minutes retention time. Lastly, the conductivity removal efficiency showed small fluctuation as retention time increases. Overall, its optimum retention time was found to be 120 minutes.

By comparing its removal efficiency to that of virgin palm kernel shell AC, the turbidity removal efficiency for acid washed palm kernel shell AC was significantly lower at the first half of the retention time and significantly higher at the second half of the retention time. For colour (ADMI), acid washed palm kernel shell AC showed lower removal performance at shorter retention time (20 min and 40 min). The ability of acid washed palm kernel shell AC to remove hardness was slightly higher while the COD removal efficiency was about the same.

Overall, the adsorption performance of acid washed palm kernel shell AC was not as efficient as that of virgin palm kernel shell. This could be due to the limited vacant active sites on the adsorbent. Based on the SEM image, virgin palm kernel shell AC showed many deep pores which allowed more adsorbates to bind onto its surface. On the other hand, there were limited number of well-developed pores on the surface of acid washed palm kernel shell AC. As a result, limited solute molecules could adsorb onto its surface.

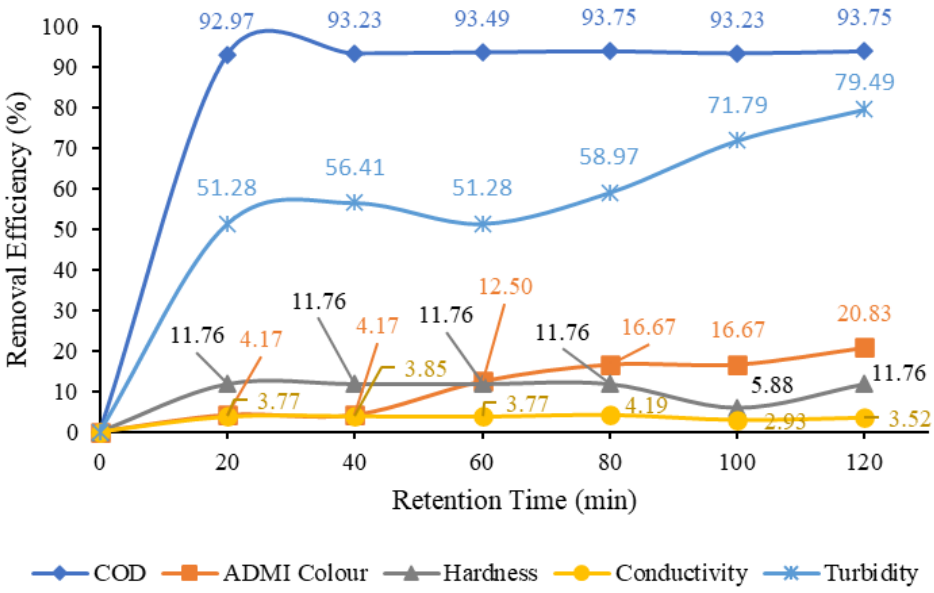


Figure 4.4: Effect of Retention Time on Removal Efficiency of Acid Washed Palm Kernel Shell Granular AC.

Table 4.2: Batch Adsorption Result of Acid Washed Palm Kernel Shell Granular AC at the Respective Retention Time.

Parameter	**Retention Time (min)**						
	0	**20**	**40**	**60**	**80**	**100**	**120**
COD	384	27	26	25	24	26	24
Colour (ADMI)	24	23	23	21	20	20	19
Hardness	34	30	30	30	30	32	30
Conductivity (µS)	1194	1149	1148	1149	1144	1159	1152
Turbidity (NTU)	39	19	17	19	16	11	8

For the third type of AC, the overall removal efficiency was similar to that of virgin palm kernel shell AC, where the removal efficiency of COD and turbidity were much higher than that of colour (ADMI), hardness and conductivity, as shown in Figure 4.5 and Table 4.3. The COD and conductivity removal efficiency showed a relatively constant trend while the turbidity and hardness removal efficiency showed a slight fluctuation as retention time increases. On the other hand, the removal efficiency of colour (ADMI) increased progressively before it dropped at 100 minutes retention time. As a whole, the optimum retention time was found to be 80 minutes.

In addition, it was discovered that the COD and colour of the treated samples were able to comply with Standard A of the Environmental Quality (Industrial Effluents) Regulations 2009 – P.U. (A) 434/2009, as presented in Appendix C. The comparison of the treated wastewater samples across different retention time is shown in Figure A-3 in Appendix A.

By comparing between virgin coconut shell AC and virgin palm kernel shell AC, the removal efficiency for all of the parameters were generally slightly higher for virgin coconut shell AC, except for conductivity. The conductivity removal efficiency was slightly lower across all the retention time. Both of their SEM images showed numerous rough and distinct pore structures so it was reasonable for them to have similar removal efficiency.

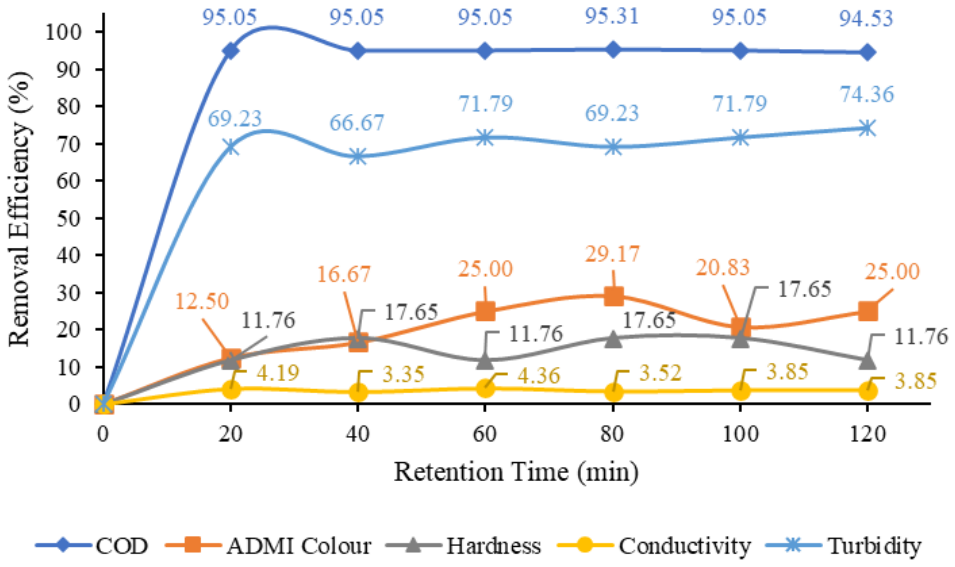


Figure 4.5: Effect of Retention Time on Removal Efficiency of Virgin Coconut Shell Granular AC.

Table 4.3: Batch Adsorption Result of Virgin Coconut Shell Granular AC at the Respective Retention Time.

Parameter	**Retention Time (min)**						
	0	**20**	**40**	**60**	**80**	**100**	**120**
COD	384	19	19	19	18	19	21
Colour (ADMI)	24	21	20	18	17	19	18
Hardness	34	30	28	30	28	28	30

Parameter	Retention Time (min)						
	0	**20**	**40**	**60**	**80**	**100**	**120**
Conductivity (µS)	1194	1144	1154	1142	1152	1148	1148
Turbidity (NTU)	39	12	13	11	12	11	10

The overall removal efficiency of the fourth type of AC was similar to that of virgin palm kernel shell AC, where the removal efficiency of COD and turbidity were much higher than that of colour (ADMI), hardness and conductivity, as illustrated in Figure 4.6 and Table 4.4. The COD and colour of the treated samples were able to comply with Standard A of the Environmental Quality (Industrial Effluents) Regulations 2009 – P.U. (A) 434/2009, as presented in Appendix C. The COD and conductivity removal efficiency showed a relatively constant trend while the turbidity removal efficiency showed a slight fluctuation as retention time increased. Meanwhile, the removal efficiency of colour (ADMI) increased progressively in the first half of the retention time, followed by a slight fluctuation. Conversely, there were no changes in the removal efficiency of hardness as retention time increased. Generally, the optimum retention time was observed to be 60 minutes. The comparison of the treated wastewater samples across different retention time is shown in Figure A-4 in Appendix A.

By comparing the removal efficiency of acid washed coconut shell AC with that of virgin coconut shell AC, virgin coconut shell AC showed better removal of COD, colour (ADMI), hardness and conductivity as compared to acid washed coconut shell AC. As for turbidity, its removal efficiency using acid washed coconut shell AC was higher across all the retention time, except at 120 minutes retention time. By referring to the SEM image, there were limited active sites on the surface of the acid washed coconut shell AC due to its collapsed structure. Naturally, less solutes could adsorb onto its surface and be removed from the textile wastewater.

In addition, between acid washed coconut shell AC and acid washed palm kernel shell AC, the removal efficiencies of COD and hardness using acid washed coconut shell AC were higher. Meanwhile, the removal performance of turbidity using acid washed coconut shell AC was higher across all the retention time, except for 120 minutes retention time.

Furthermore, acid washed coconut shell AC gave better removal of colour (ADMI) at the first half of the retention time. However, the removal of conductivity using acid washed coconut shell AC was lower than that of acid washed palm kernel shell. As a whole, acid washed coconut shell AC showed better removal performance than that of acid washed palm kernel shell AC.

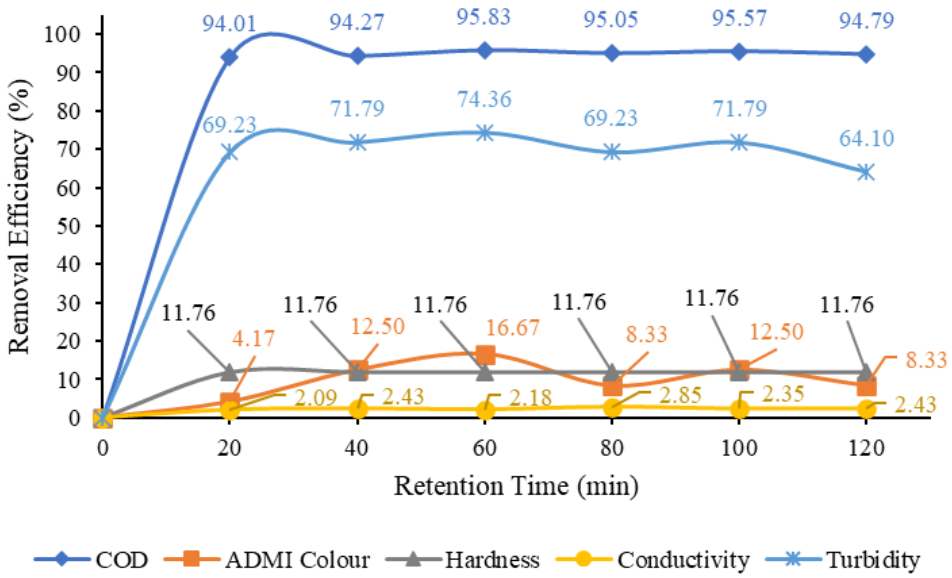


Figure 4.6: Effect of Retention Time on Removal Efficiency of Acid Washed Coconut Shell Granular AC.

Table 4.4: Batch Adsorption Result of Acid Washed Coconut Shell Granular AC at the Respective Retention Time.

Parameter	**Retention Time (min)**						
	0	**20**	**40**	**60**	**80**	**100**	**120**
COD	384	23	22	16	19	17	20
Colour (ADMI)	24	23	21	20	22	21	22
Hardness	34	30	30	30	30	30	30
Conductivity (µS)	1194	1169	1165	1168	1160	1166	1165
Turbidity (NTU)	39	12	11	10	12	11	14

Moving on, Table 4.5 tabulated the pH readings of the treated wastewater at the respective retention time for all the activated carbons. All the pH readings were in compliance with Standard A of the industrial effluent

in accordance to the Environmental Quality (Industrial Effluents) Regulations 2009 – P.U. (A) 434/2009 as they fell between 6.0 and 9.0. The Environmental Quality (Industrial Effluents) Regulations 2009 were shown in Appendix C Figure C-1. This implied that the treated wastewater could be safely discharged or recycled.

Table 4.5: pH Readings of the Treated Wastewater at the Respective Retention Time for All Types of Activated Carbon.

Type of AC	**Retention Time (min)**						
	0	**20**	**40**	**60**	**80**	**100**	**120**
Virgin PKS	6.54	7.14	7.24	7.24	7.25	7.31	7.36
AW PKS		7.17	7.32	7.57	7.73	7.84	7.96
Virgin CCS		7.93	8.05	7.99	8.02	8.02	8.03
AW CCS		7.42	7.50	7.61	7.65	7.72	7.74

4.2.2 Effect of pH

Based on the results obtained in section 4.2.1, it was observed that the removal performance of acid washed ACs was only slightly better than the virgin ACs. Furthermore, the cost of acid washed ACs was higher than the virgin ACs due to the additional washing or cleaning of ACs during the manufacturing process to reduce the total ash content in the carbon. The acid washed ACs costed RM30/kg while the virgin ACs costed RM25/kg. The selling price of acid washed ACs is 18.18% higher than that of the virgin ACs. The cost difference would be significant in a large-scale treatment plant. Taking these two factors into consideration, virgin palm kernel shell AC and virgin coconut shell AC were selected to proceed for further study on the effect of pH. Besides, retention time of 60 minutes was chosen to investigate the effect of pH since the removal efficiencies for most of the parameters were relatively high at that particular retention time.

Figure 4.7 and Table 4.6 illustrate the removal efficiency of virgin palm kernel shell granular AC at the respective initial pH. It was observed that the COD and colour of the treated samples were able to comply with Standard A of the Environmental Quality (Industrial Effluents) Regulations 2009 – P.U.

(A) 434/2009, as presented in Appendix C. Furthermore, among all the parameters, turbidity was the most effectively removed parameter from the textile wastewater whereas hardness was not removed at all. All the parameters showed similar removal pattern except for colour and hardness, where their removal efficiency peaked at pH 7 before they gradually decreased as pH increased. Meanwhile, the removal efficiency of colour (ADMI) remained constant at pH 6 and pH 7 before it dropped progressively until it reached pH 9. The comparison of the treated wastewater samples across different solution pH is shown in Figure A-5 in Appendix A.

Based on Rolence, Machunda and Njau (2014), the pH of the solution is related to the concentration of hydrogen ions present, which impacts the number of ions adsorbed onto the active sites of the adsorbent. The concentration of hydrogen ions is greater at lower pH, so more anions will be attracted to the vacant active sites while cations will be repelled and hindered from binding onto the active sites. Conversely, the concentration of hydroxide ions is greater at higher pH, so more cations will be attracted to the active sites while anions will be repelled and hindered from binding onto the active sites.

From the result, it was suggested that most of the solutes in the textile wastewater were best removed at neutral pH where the concentration of hydrogen and hydroxide ions were equal. It could then be deduced that there were almost a balance of anions and cations present in the textile wastewater, so carrying out adsorption at neutral pH would give a better removal performance than at acidic or alkaline pH.

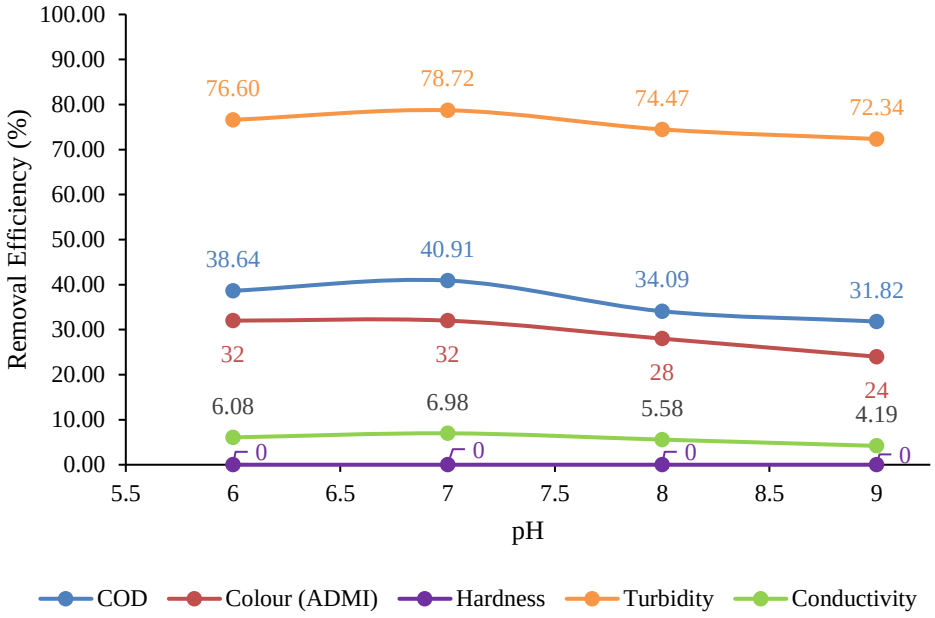


Figure 4.7: Effect of pH on Removal Efficiency of Virgin Palm Kernel Shell Granular AC.

Table 4.6: Batch Adsorption Result of Virgin Palm Kernel Shell Granular AC at the Respective Initial pH.

Parameter	**Initial**	**Solution pH**			
		6	**7**	**8**	**9**
COD	44	27	26	29	30
Colour (ADMI)	25	17	17	18	19
Hardness	30	30	30	30	30
Conductivity (µS)	1218	1144	1133	1150	1167
Turbidity (NTU)	47	11	10	12	13

Next, Figure 4.8 and Table 4.7 present the removal efficiency of virgin coconut shell granular AC at the respective initial pH. From the results obtained, the COD and colour of the treated samples were able to comply with Standard A of the Environmental Quality (Industrial Effluents) Regulations 2009 – P.U. (A) 434/2009, as presented in Appendix C. In addition, the parameter that adsorption could remove the most was turbidity. Its removal efficiency at pH 6 and 7 were constant, and the highest removal efficiency was achieved at pH 8 before it dropped at pH 9. As for COD and conductivity,

their removal efficiency increased and peaked at pH 7, followed by a gradual decrease from pH 7 to pH 9. On the other hand, the removal efficiency for colour (ADMI) increased and decreased uniformly from pH 6 to 9. Meanwhile, it was observed that hardness could not be removed by virgin coconut shell AC. The optimum pH for the removal of COD, colour and conductivity was at pH 7, while the optimum pH for the removal efficiency of turbidity was at pH 8. However, since the difference in the removal efficiency of turbidity at pH 7 and 8 was relatively small, neutral pH was chosen as the optimum pH. The comparison of the treated wastewater samples across different solution pH is shown in Figure A-6 in Appendix A.

In comparison with the removal efficiency of virgin palm kernel shell AC, the removal of turbidity and conductivity were lower for virgin coconut shell AC. On the other hand, the removal performance of COD and colour (ADMI) were higher using virgin coconut shell AC, which peaked at pH 7. Meanwhile, hardness was not removed for both virgin palm kernel shell and virgin coconut shell AC. Therefore, it was inferred that virgin palm kernel shell AC showed better turbidity and conductivity removal performance whereas virgin coconut shell exhibited better COD and colour removal performance.

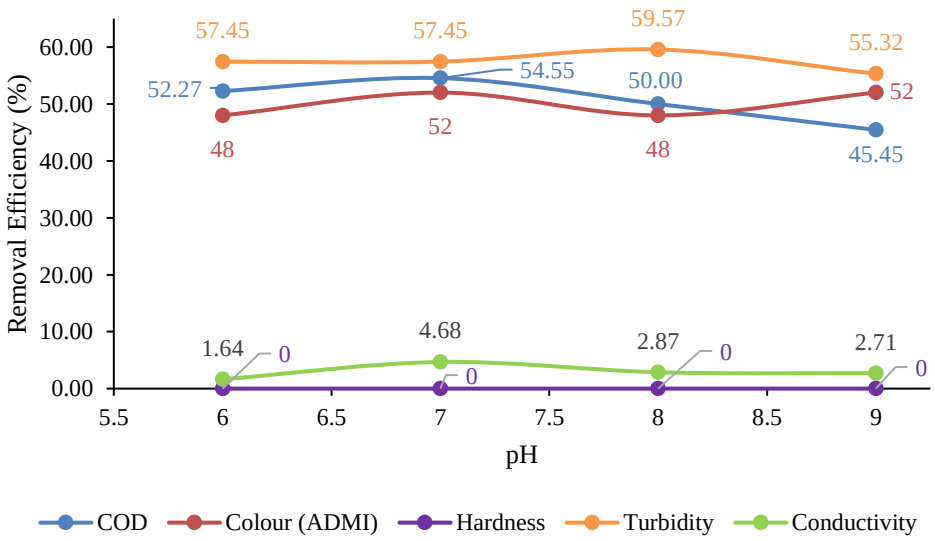


Figure 4.8: Effect of pH on Removal Efficiency of Virgin Coconut Shell Granular AC.

Table 4.7: Batch Adsorption Result of Virgin Coconut Shell Granular AC at the Respective Initial pH.

Parameter	Initial	Solution pH			
		6	7	8	9
COD	44	21	20	22	24
Colour (ADMI)	25	13	12	13	12
Hardness	30	30	30	30	30
Conductivity (µS)	1218	1198	1161	1183	1185
Turbidity (NTU)	47	20	20	19	21

Following that, the pH readings of the treated wastewater at the respective initial pH for virgin palm kernel shell AC and virgin coconut shell AC were shown in Table 4.8. Similarly, all the pH readings were in compliance with Standard A of the industrial effluent in accordance to the Environmental Quality (Industrial Effluents) Regulations 2009 – P.U. (A) 434/2009 as they fell between 6.0 and 9.0. The Environmental Quality (Industrial Effluents) Regulations 2009 were shown in Appendix C Figure C-1. This signified that the treated wastewater could be safely discharged or recycled.

Table 4.8: pH Readings of the Treated Wastewater at the Respective Initial pH for Virgin Palm Kernel Shell AC and Virgin Coconut Shell AC.

Type of AC	Initial	Solution pH			
		6	7	8	9
Virgin PKS	7.09	7.35	7.8	8.02	8.82
Virgin CCS		7.35	7.93	8.04	8.28

4.3 Breakpoint Analysis

Based on the results obtained from the batch adsorption of pH, both virgin palm kernel shell AC and virgin coconut shell AC had their own merits in terms of their removal performance. However, since the wastewater was from the textile industry, the main criteria when choosing the best adsorbent should

be its ability to remove colour. Thus, virgin coconut shell AC was chosen to carry out breakpoint analysis because its colour removal performance is better than that of virgin palm kernel shell AC, based on the effect of pH experiment. Then, its removal of colour (ADMI) was analysed. The actual setup of the continuous flow for breakpoint analysis was shown in Appendix D.

Table 4.10 tabulates the data of the breakpoint analysis in order to obtain the breakthrough curve that is shown in Figure 4.9. The breakthrough curve was plotted using the relationship of C_t/C_o ratio against the adsorption duration. Adsorption was carried out in a continuous manner for 6 hours 40 minutes (400 minutes) only due to the limited volume of textile wastewater available. The pattern of the breakthrough curve obtained in this experiment was similar as the breakthrough curve obtained by Samarghandi, Hadi and McKay (2014), where there is a steep increase in the ratio of C_t/C_o during the initial stage instead of the ideal S-shaped curve. This could be due to the presence of smaller sized solute molecules that had simpler molecular structures in the textile wastewater (Samarghandi, Hadi and McKay, 2014).

According to Patel and Vashi (2015), normally the breakpoint is taken as C_t/C_o ratio of 0.05 – 0.95, unless there is other fixed specification to adhere to. They also explained that the maximum operating limit of the activated carbon bed is when $C_t/C_o = 0.95$. In this experiment, C_t/C_o ratio of 0.5 was selected as the breakpoint since there was no fixed specification. Then, from the breakthrough curve, it was observed that the breakpoint time was achieved at 230 minutes in this fixed bed column. It could be interpreted that at 230 minutes, the activated carbon bed inside the fixed bed column should be replaced with another fresh activated carbon bed.

At less than 230 minutes, C_t/C_o was less than 0.5. After that, the C_t/C_o ratio increased progressively until it reached 0.6 C_t/C_o ratio at 400 minutes. This might be due to the reduced vacant sites available for solute molecules to bind onto. Although a complete breakthrough curve was not obtained in this experiment, it was expected that the breakthrough curve would continue to increase gradually until it reached saturation point at which $C_t/C_o = 1$. Once it had reached saturation point, the activated carbon inside the column would be completely exhausted.

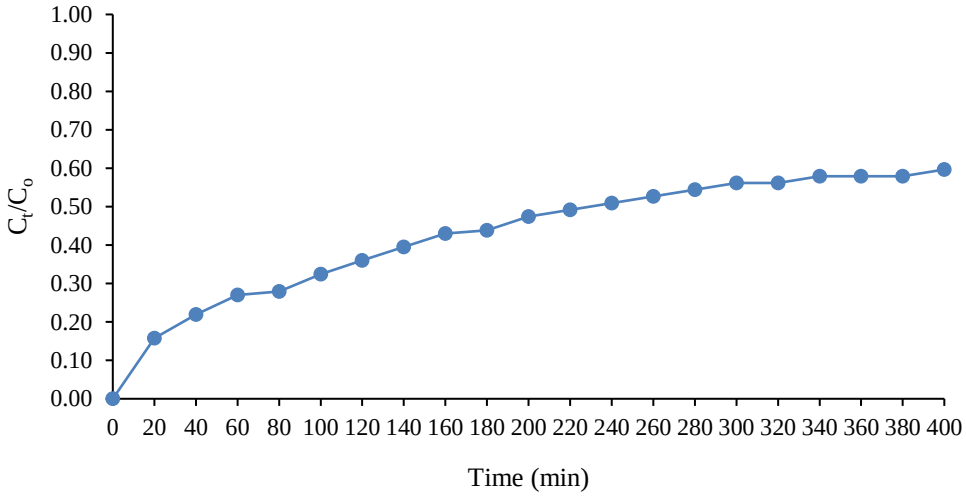


Figure 4.9: Breakthrough Curve.

Table 4.10: Breakpoint Analysis Data.

Time (min)	**Colour (ADMI)**	**C_t/C_o**	**Time (min)**	**Colour (ADMI)**	**C_t/C_o**
0	0	0.00	220	28	0.49
20	9	0.16	240	29	0.51
40	12.5	0.22	260	30	0.53
60	15.4	0.27	280	31	0.54
80	15.9	0.28	300	32	0.56
100	18.5	0.32	320	32	0.56
120	20.5	0.36	340	33	0.58
140	22.5	0.39	360	33	0.58
160	24.5	0.43	380	33	0.58
180	25	0.44	400	34	0.60
200	27	0.47			

4.4 Final Set of Experiment

Lastly, a final set of batch adsorption experiment using the optimum conditions (60 minutes retention time and pH 7) was carried out using both virgin palm kernel shell AC and virgin coconut shell AC. Two types of textile wastewater were provided by the company, namely Sample A and Sample B. Before treatment, Sample B was found to have two times higher colour than

Sample A. The full water quality test results for Sample A and Sample B were tabulated in Table 4.11 and 4.12. Both ICP-OES and HACH iron tests were carried out to standardize the iron results with the textile manufacturing company, instead of solely relying on ICP-OES.

From the results obtained, the removal performance of COD for both samples were much lower than the results obtained from the previous batch adsorption experiments. Furthermore, it was observed that the removal of colour and hardness for Samples A and B were much higher than the previous results. The presence of different adsorbates inside the textile wastewater which was obtained from different batches could have contributed to this. In the previous batch of wastewater, a higher adsorption capacity for organic material was demonstrated by the ACs, while in the current batch, better adsorption of colour and hardness was achieved.

Nevertheless, based on the overall results for Sample A and B, both types of AC were able to simultaneously reduce the mixed adsorbates that were present in the textile wastewater, but not all components could be removed effectively. In addition, they were able to comply with Standard A of the industrial effluent in accordance to the Environmental Quality (Industrial Effluents) Regulations 2009 – P.U. (A) 434/2009, as shown in Appendix C.

Table 4.11: Full Water Quality Test Result of Treated Wastewater Sample A.

		After treatment	
	Before treatment	**Virgin coconut shell AC**	**Virgin palm kernel shell AC**
pH	7.04	7.36	7.35
Conductivity (μS)	2273	2258	2268
COD (ppm)	55	51	52
Total nitrogen (ppm)	12.3	7	8.5
Ammoniacal nitrogen (ppm)	0.99	0.46	0.54
Total suspended solid (ppm)	76	24	29
Total dissolved solid (ppm)	1191	1135	686
Turbidity (NTU)	67.8	7.9	15

	Before treatment	After treatment	
		Virgin coconut shell AC	**Virgin palm kernel shell AC**
Hardness (ppm)	230	46	46
Colour (ADMI)	179	40	114
Zinc (ppm)	<0.0002	<0.0002	<0.0002
Copper (ppm)	0.117	0.116	0.116
Iron (ppm) (HACH reagent)	<0.02	<0.02	<0.02
Iron (ppm) (ICP-OES)	1.821	1.274	1.031

Table 4.12: Full Water Quality Test Result of Treated Wastewater Sample B.

	Before treatment	After treatment	
		Virgin coconut shell AC	**Virgin palm kernel shell AC**
pH	6.96	7.09	7.15
Conductivity (μS)	1938	1928	1931
COD (ppm)	85	77	74
Total nitrogen (ppm)	11.1	4.9	4.8
Ammoniacal nitrogen (ppm)	0.15	0.09	0.07
Total suspended solid (ppm)	89	40	39
Total dissolved solid (ppm)	1062	988	990
Turbidity (NTU)	25.8	21	22
Hardness (ppm)	182	58	54
Colour (ADMI)	425	156	193
Zinc (ppm)	<0.0002	<0.0002	<0.0002
Copper (ppm)	0.119	0.115	0.113
Iron (ppm) (HACH reagent)	<0.02	<0.02	<0.02
Iron (ppm) (ICP-OES)	2.079	1.33	1.331

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The effectiveness using four different types of commercial activated carbons, namely virgin coconut shell granular AC, acid washed coconut shell granular AC, virgin palm kernel shell granular AC and acid washed palm kernel shell granular AC for adsorption to treat the textile wastewater were investigated and compared. From the effect of retention time experiment, it could be concluded that most of the time acid washed activated carbons only showed slightly better removal performance than virgin activated carbons. Taking the removal performance into account along with the cost of the activated carbons, virgin activated carbons were chosen to proceed with the effect of pH experiment. The optimum retention time observed was 60 minutes. Next, from the effect of pH experiment, it could be deduced that virgin palm kernel shell AC and virgin coconut shell AC were both good adsorbents with their own merits. It was found that virgin palm kernel shell AC could remove turbidity and conductivity more effectively whereas virgin coconut shell AC could remove COD and colour more effectively. Furthermore, with the removal of colour as the main focus for the textile wastewater, virgin coconut shell AC was selected to carry out the breakpoint analysis. The breakpoint analysis showed that the breakthrough time was 230 minutes since C_t/C_o ratio of 0.5 was assumed. After 230 minutes of the continuous adsorption process, the activated carbon bed should be replaced with a fresh one. Finally, the final set of experiment using virgin palm kernel shell AC and virgin coconut shell AC in treating two different qualities of textile wastewater were able to comply with Standard A of the industrial effluent according to the Environmental Quality (Industrial Effluents) Regulations 2009 – P.U. (A) 434/2009, as shown in Appendix C.

5.2 Recommendations for Future Work

Repetitive experiments had to be conducted, which were time-consuming, due to the deviation of the obtained results from literature studies in this study. Due to time constraints and unexpected scenarios, this project could not be extensively explored. Thus, there are some recommendations for improvement of future studies.

The first recommendation is for different batches of raw wastewater containing single dye from the textile manufacturing company to be obtained instead of combined effluent, in order to further investigate the impact of these dyes on different types of ACs. Identifying the optimal AC for each dye and determining the appropriate adsorption conditions before conducting studies on combined effluent would be beneficial.

Besides, to facilitate continuous study, it is recommended that the textile manufacturing company supply more wastewater since the limited amount provided by the company prevented the completion of the continuous study of this project. Apart from that, as the laboratory is not accessible after office hours, it is recommended to carry out experimental work in the company's laboratory to allow for more flexible time.

In addition, it is recommended that a pilot-scale adsorption column be constructed in the vicinity of the company as the quality of the textile wastewater fluctuates after a period of time. This will enable more accurate water quality analysis results. Furthermore, continuous monitoring of the pilot-scale can be conducted by the operators since they operate in shifts.

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APPENDICES

Appendix A: Batch Adsorption Figures

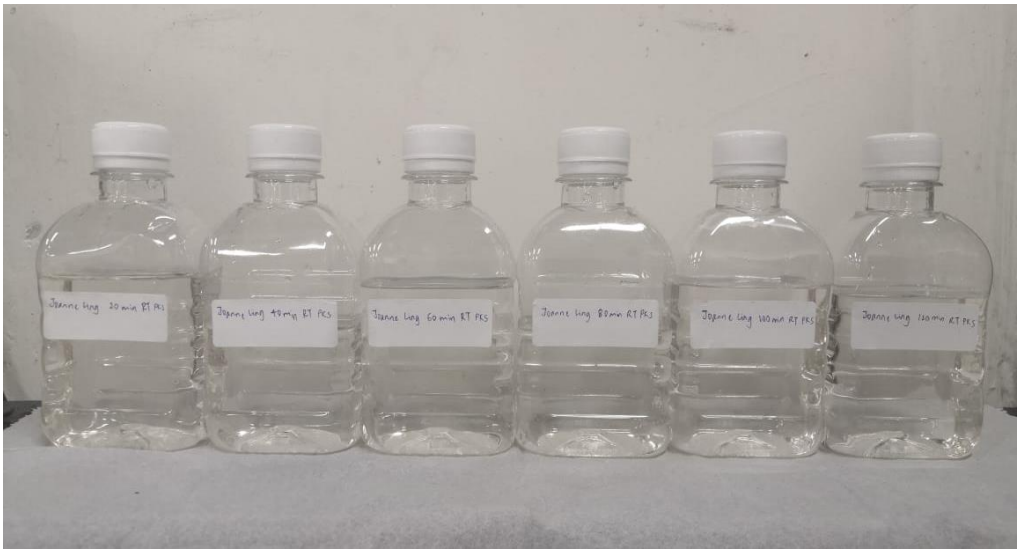

Figure A-1:Effect of Retention Time Using Virgin Palm Kernel Shell AC (From sequence of left to right: 20, 40, 60, 80, 100, 120 min).

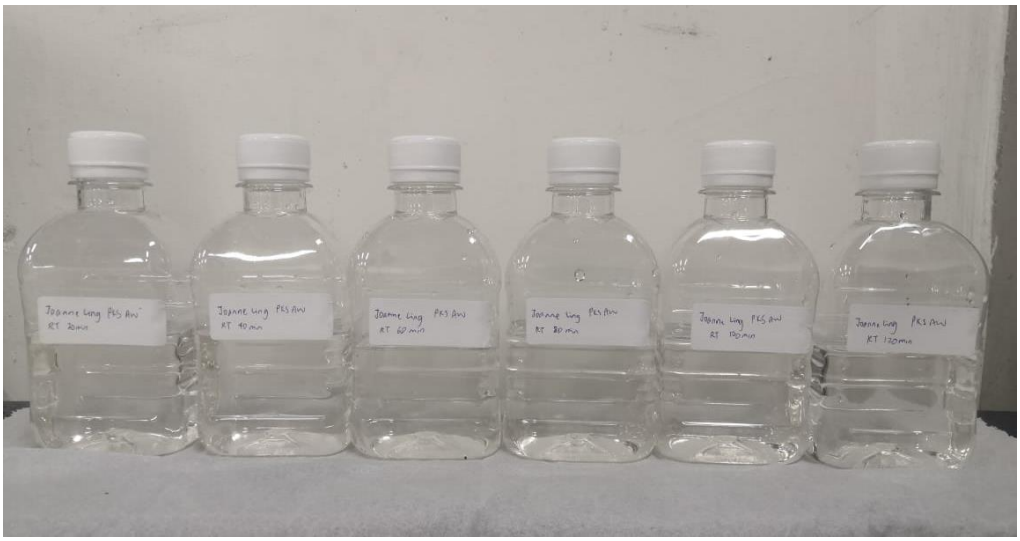

Figure A-2:Effect of Retention Time Using Acid Washed Palm Kernel Shell AC (From sequence of left to right: 20, 40, 60, 80, 100, 120 min).

Figure A-3:Effect of Retention Time Using Virgin Coconut Shell AC (From sequence of left to right: 20, 40, 60, 80, 100, 120 min).

Figure A-4:Effect of Retention Time Using Acid Washed Coconut Shell AC (From sequence of left to right: 20, 40, 60, 80, 100, 120 min).

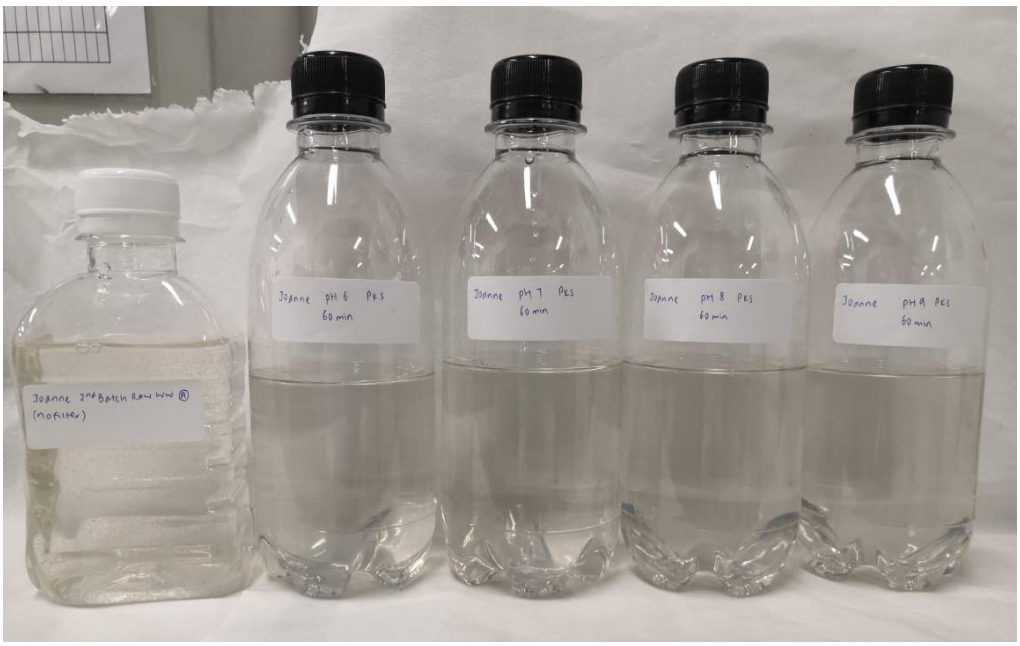

Figure A-5:Effect of Solution pH Using Virgin Palm Kernel Shell AC (From sequence of left to right: raw wastewater, pH 6, pH 7, pH 8, pH 9).

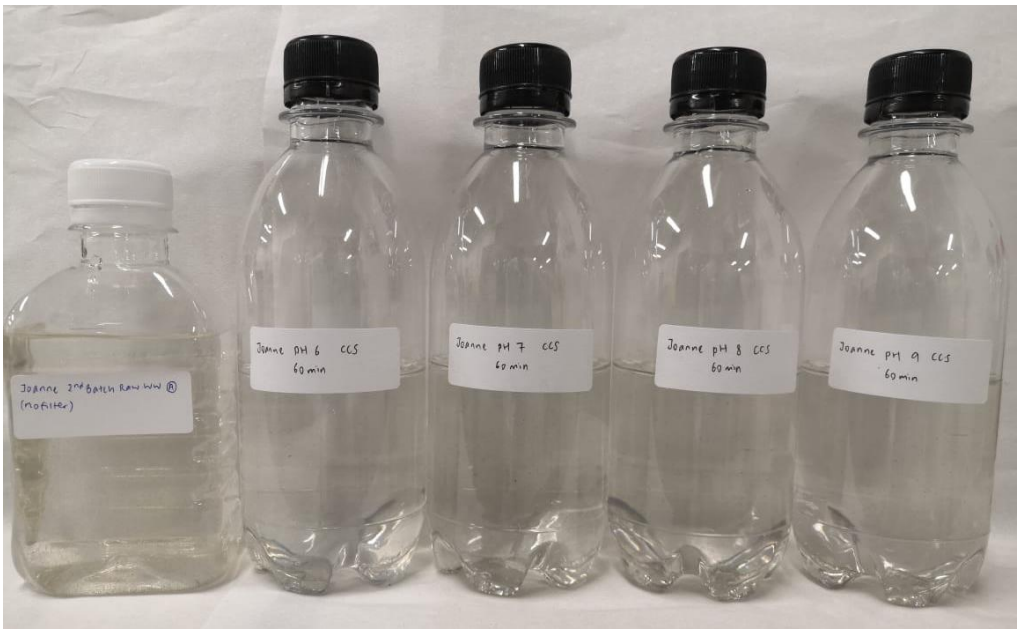

Figure A-6:Effect of Solution pH Using Virgin Coconut Shell AC (From sequence of left to right: raw wastewater, pH 6, pH 7, pH 8, pH 9).

Appendix B: Final Set of Experiment Figures

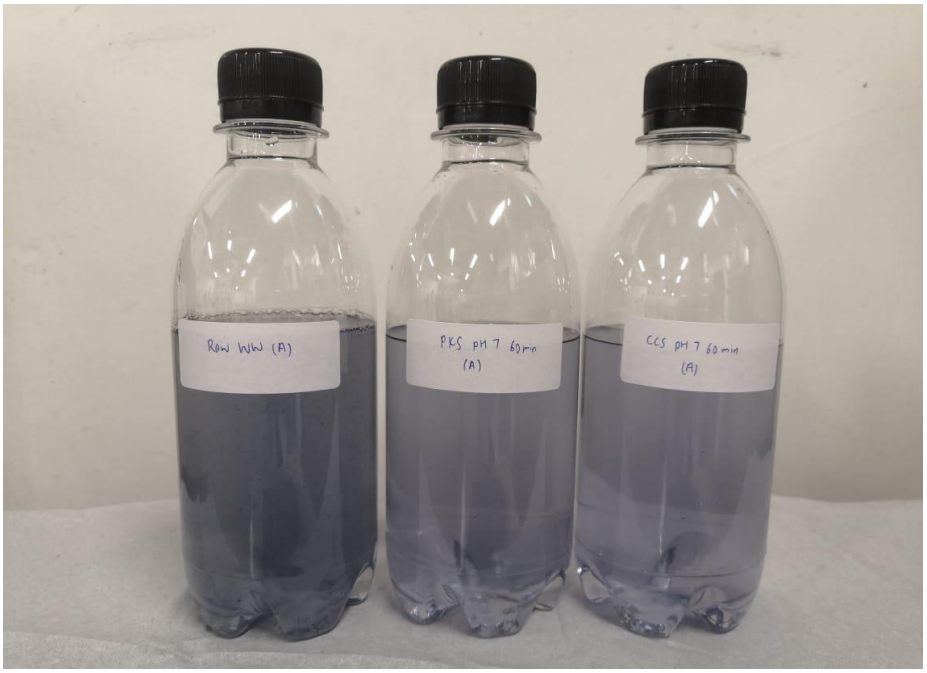

Figure B-1: Final Set of Batch Adsorption Experiment for Sample A Using Virgin Palm Kernel Shell AC and Virgin Coconut Shell AC.

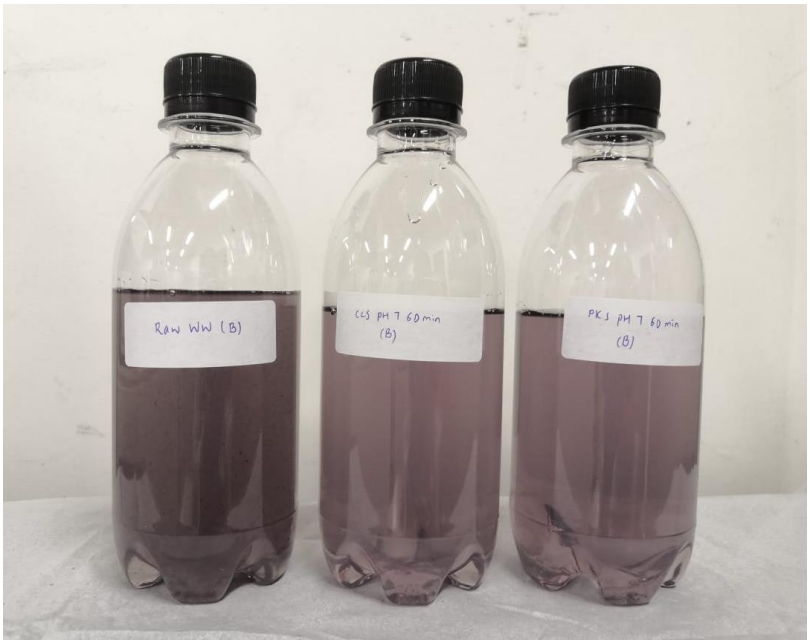

Figure B-2: Final Set of Batch Adsorption Experiment for Sample B Using Virgin Palm Kernel Shell AC and Virgin Coconut Shell AC.

Appendix C: Environmental Quality (Industrial Effluent) Regulations 2009

FIFTH SCHEDULE

[Paragraph 11(1)(*a*)]

ACCEPTABLE CONDITIONS FOR DISCHARGE OF INDUSTRIAL EFFLUENT OR MIXED EFFLUENT OF STANDARDS A AND B

	Parameter	Unit	Standard	
			A	B
	(1)	(2)	(3)	(4)
(i)	Temperature	°C	40	40
(ii)	pH Value	–	6.0-9.0	5.5-9.0
(iii)	BOD_5 at 20°C	mg/L	20	50
(iv)	Suspended Solids	mg/L	50	100
(v)	Mercury	mg/L	0.005	0.05
(vi)	Cadmium	mg/L	0.01	0.02
(vii)	Chromium, Hexavalent	mg/L	0.05	0.05
(viii)	Chromium, Trivalent	mg/L	0.20	1.0
(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)	Copper	mg/L	0.20	1.0
(xiii)	Manganese	mg/L	0.20	1.0
(xiv)	Nickel	mg/L	0.20	1.0
(xv)	Tin	mg/L	0.20	1.0
(xvi)	Zinc	mg/L	2.0	2.0
(xvii)	Boron	mg/L	1.0	4.0
(xviii)	Iron (Fe)	mg/L	1.0	5.0
(xix)	Silver	mg/L	0.1	1.0
(xx)	Aluminium	mg/L	10	15
(xxi)	Selenium	mg/L	0.02	0.5
(xxii)	Barium	mg/L	1.0	2.0
(xxiii)	Fluoride	mg/L	2.0	5.0
(xxiv)	Formaldehyde	mg/L	1.0	2.0
(xxv)	Phenol	mg/L	0.001	1.0
(xxvi)	Free Chlorine	mg/L	1.0	2.0
(xxvii)	Sulphide	mg/L	0.50	0.50
(xxviii)	Oil and Grease	mg/L	1.0	10
(xxix)	Ammoniacal Nitrogen	mg/L	10	20
(xxx)	Colour	ADMI*	100	200

*ADMI–American Dye Manufacturers Institute

Figure C-1: Standard A and B in the Fifth Schedule (Department of Environment Malaysia, 2023).

SEVENTH SCHEDULE

(Regulation 12)

ACCEPTABLE CONDITIONS FOR DISCHARGE OF INDUSTRIAL EFFLUENT CONTAINING CHEMICAL OXYGEN DEMAND (COD) FOR SPECIFIC TRADE OR INDUSTRY SECTOR

(1) Trade/Industry	(2) Unit	(3) Standard A	(4) Standard B
***(a)* Pulp and paper industry**			
(i) pulp mill	mg/L	80	350
(ii) paper mill (recycled)	mg/L	80	250
(iii) pulp and paper mill	mg/L	80	300
***(b)* Textile industry**	mg/L	80	250
***(c)* Fermentation and distillery industry**	mg/L	400	400
***(d)* Other industries**	mg/L	80	200

Figure C-2: Standard A and B in the Seventh Schedule (Department of Environment Malaysia, 2023).

Appendix D: Actual Setup of the Continuous Flow for Breakpoint Analysis

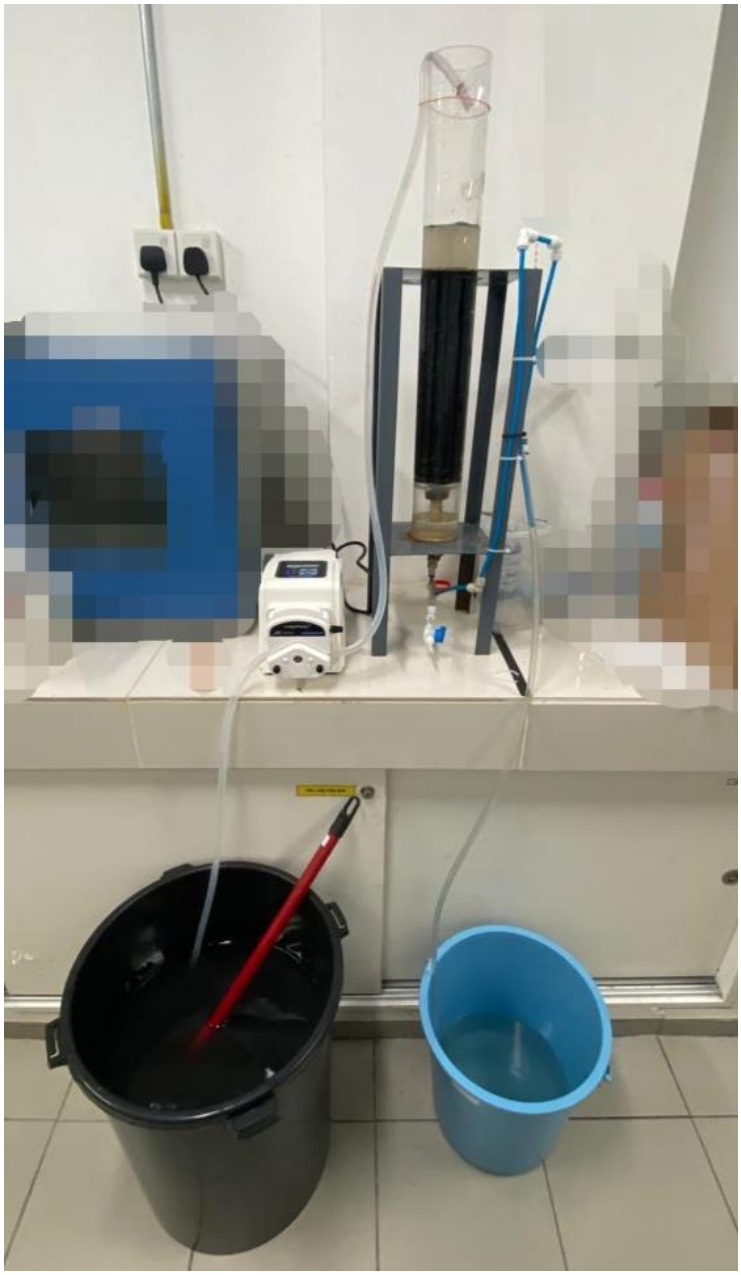

Figure D-1: Actual Experimental Setup of the Continuous Flow for Breakpoint Analysis.