



**EFFICIENCY OF *MERETRIX LAMARCKII*
ACTIVATED CARBON IN MALACHITE GREEN
DYE REMOVAL**

by

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DECLARATION

I declare that this thesis entitled “Efficiency of *Meretrix Lamarckii* Activated Carbon in Malachite Green Dye Removal” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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Efficiency of *Meretrix Lamarckii* Activated Carbon in Malachite Green Dye Removal

ABSTRACT

Dyestuff manufacturing and consuming industry has led to water pollution through their discharge of untreated wastewater. Presence of dyes in water bodies may cause carcinogenic, mutagenic and caused harm to the entire aquatic ecosystem. This research has carried out to examine the adsorption efficiency of activated carbons derived from waste *Meretrix lamarckii* (*M. lamarckii*) shells towards Malachite Green (MG) dye removal. Activation with hydrochloric acid (HCl) and potassium hydroxide (KOH) were used for the conversion of seashells into AC 1 and AC 2 respectively. Following that, batch adsorption studies were carried out at 30°C by using AC 1 and AC 2 to study the effect of contact time, pH, initial concentration of adsorbate and adsorbent dosage on dye removal percentage. The optimized contact time for AC 1 was 210 minutes, with best performance in pH 10 aqueous medium, 10 mg/L initial concentration of MG and optimum dosage of 1.0 g. Whereas for AC 2, the optimized contact time was shorter than AC 1, which was only 90 minutes to attain equilibrium state. The optimized pH and initial concentration of adsorbate was the same as AC 1. While optimized adsorbent dosage for AC 2 was lower than that of AC 1, which was 0.8 g. Based on the results obtained, AC 2 was found to be more effective in MG dye removal than AC 1. High efficiency of AC 2 was due to the presence of alkyl halide group and its larger total surface area. From the study, it can be concluded that *M. lamarckii* activated carbons possess high adsorption efficiency and potentially to become a new introduce adsorbent in wastewater treatment technology.

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Kecekapan Cengkerang *Meretrix lamarckii* Karbon Teraktif dalam Penyerapan Pewarna Malakit Hijau

ABSTRAK

Industri penghasilan dan penggunaan pewarna telah menyumbang kepada pencemaran air melalui pelepasan air sisa yang tidak dirawat. Kewujudan pewarna dalam air boleh menyebabkan kesan karsinogenik, mutagenik dan mendatangkan kesan negatif kepada keseluruhan ekosistem akuatik. Kajian ini telah dijalankan untuk mengkaji kecekapan karbon teraktif yang dihasilkan daripada cengkerang *Meretrix lamarckii* (*M.lamarckii*) dalam penyerapan pewarna Malakit Hijau (MG). Kaedah pengaktifan dengan asid hidroklorik (HCl) dan kalium hidroksida (KOH) telah digunakan untuk menghasilkan karbon teraktif 1 (AC 1) dan karbon teraktif 2 (AC 2) masing-masing. Selepas itu, kajian penyerapan kelompok telah dijalankan pada suhu 30°C dengan menggunakan AC 1 dan AC 2, untuk mengkaji kesan masa sentuhan, pH, kepekatan larutan awal pewarna dan dos karbon teraktif terhadap penyerapan pewarna MG. Untuk AC 1, masa sentuhan yang optimum adalah 210 minit, dengan prestasi yang terbaik dalam medium pH 10, 10 mg/L kepekatan larutan awal pewarna MG, dan dos karbon teraktif yang optimum adalah 1.0 g. Bagi AC 2, masa sentuhan optimum adalah lebih pendek daripada AC 1, iaitu 90 minit untuk mencapai keadaan keseimbangan. Optimum pH dan kepekatan larutan awal pewarna adalah sama seperti AC 1. Manakala dos karbon teraktif untuk AC 2 adalah lebih rendah, iaitu 0.8 g. Berdasarkan keputusan yang diperolehi, AC 2 didapati lebih berkesan berbanding dengan AC 1 dalam penyerapan pewarna MG. Kecekapan tinggi ini adalah hasil daripada kewujudan kumpulan berfungsi alkil halide dan jumlah permukaan yang luas pada AC 2. Daripada kajian ini, ia dapat disimpulkan bahawa karbon teraktif yang dihasilkan daripada cengkerang *M.lamarckii* mempunyai kecekapan penyerapan yang tinggi dan amat berpotensi untuk menjadi penyerap yang baru dalam teknologi rawatan air sisa.

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LIST OF ABBREVIATIONS

SO ₂	Sulphur Dioxide
CO ₂	Carbon Dioxide
NO _x	Nitrogen Oxides
<i>M. lamarckii</i>	<i>Meretrix lamarckii</i>
HCl	Hydrochloric Acid
KOH	Potassium Hydroxide
NaOH	Sodium Hydroxide
MG	Malachite Green
DOE	Department of Environment
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
TOC	Total Organic Carbon
H ₃ PO ₄	Phosphoric Acid
ZnCl ₂	Zinc Chloride
Mg/g	Milligram per Gram
pH	Potential Hydrogen
Mg/L	Milligram per Litre
G	Gram
K	Kelvin
G/L	Gram per Litre
Pb ²⁺	Lead (II) Ion
CaO	Calcium Oxide
CaCO ₃	Calcium Carbonate
Ca(OH) ₂	Calcium Hydroxide
µm	Micrometre
ML	Millilitre
M	Molarity
Rpm	Revolutions per Minute
L	Litre
AC 1	Acid Activated Carbon (HCl Activation)
AC 2	Alkali Activated Carbon (KOH Activation)

LIST OF SYMBOLS

%	Percentage
K	Temperature (Kelvin)
°C	Temperature (Degree Celsius)
x	Multiply



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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Water is an essential element for all form of life on Earth planet. It is widely used in human daily life as drinking water, medical use, industrial applications and irrigation practises. From the total water resources on Earth, the only source of our drinking water – freshwater, is only accounts for less than 3% (World Wildlife Fund, 2017). Two-thirds of total freshwater is locked in iceberg and glaciers where they are not available to use, and only 1% remains assessible. Although freshwater is critical for human, but it continues to be threatened by various forces including overdevelopment, run-off from agricultural site, climate change, and etc (World Wildlife Fund, 2017). In general, water pollution can be defined as the degradation of water quality due to the entering of toxic substances into water bodies by dissolving into them, suspending in water bodies or depositing on the bed (Raúl, 2017). Some common causes that contribute to water pollution are mining activities, run-off from agricultural activities, untreated wastewater from industrial activities and so on (Rinkesh, 2009).

One of the main sources of water pollution in Malaysia is the discharge of dyes (Pang & Ahmad, 2013), and this pollutant can be traced back to the effluent from dyestuff manufacturing and consuming industry especially textile industry (Gaikwad & Kanawade, 2011). Presence of dyes in water bodies not only bring harmful impact

to the environment, but also human being and entire ecosystem. Many dyes and their by-products could bring toxic, mutagenic and carcinogenic effects to human and aquatic life (Akarslan & Demiralay, 2015). In addition, dyes can also block the penetration of sunlight into water bodies, reduce photosynthetic activities of phytoplankton and algae, and thus interrupt the food chain (Ayadi, Souissi, Jlassi, Peixoto, & Mnif, 2016). Hence, removal of dyes from industrial wastewater before discharging into municipal sewer or directly into natural stream become increasingly important and necessary (Jaiswal Rinku, Singh Shripal, & Pande Hemant, 2015). There are many different ways to perform this action including: coagulation/flocculation (Kim, Park, Yang, & Kim, 2004), ozonation (Ould Brahim, Belmedani, Belgacem, Hadoun, & Sadaoui, 2014), chemical oxidation (Oguz & Keskinler, 2007), and electrochemical treatment (Fan, Zhou, Yang, Chen, & Yang, 2008). However, most of these conventional treatment methods are costly, produce environment-threatening by-products, and consume large amount of energy (Yazdanbakhsh, Tavakkoli, & Hosseini, 2011; Tabari, Tavakkoli, Zargarani, & Beiknejad, 2012). Therefore, development of low cost, eco-friendly and efficient technologies become increasingly urgent in removing dye (Amuda, Olayiwola, Alade, Farombi, & Adebisi, 2014).

Adsorption is a widely used separation technique in dyes removal for its low-cost, simple design, sludge free clean operation and high removal efficiency (Pardeep Singh, Pathania Deepak, & Sharma Shikha, 2017). Due to the excellent adsorption effectiveness on organic compounds (dyes), activated carbons always been chosen as adsorbents (Gaikwad & Kanawade, 2011). Before the discovering of cheaper substitutions, there are three types of commercially available activated carbon: granular, powdered and pelleted activated carbon (Fabon, Legaspi, Leyesa, &

Macawile, 2013). However, these activated carbons are very expensive. Moreover, regeneration of activated carbon may produce additional effluent, and also results in 10% to 15% of adsorbent loss (Gaikwad & Kanawade, 2011). Therefore, a number of non-conventional, low-cost but more efficient adsorbents have been developed, such as sugarcane bagasse, rice husk, prawn shell, coconut shell, saw dust activated carbon and etc (Pardeep Singh et al., 2017).

Seashell is a type of seafood waste that can be used in producing activated carbon. It is a hard, protective outer layer of marine mollusc (Saha, Srivastava, & Chowdhury, 2013). After the soft part of marine mollusc has been consumed or rotten away, seashells will be left down and become unwanted waste. Waste seashells will normally be disposed at landfill sites, and this may lead to various environmental issues, such as generation of off-odours, air pollution and soil pollution. In addition, if they are dumped directly into the ocean, they may lead to water pollution and thus, harmful to the whole marine ecosystem (Hou et al., 2016). Several studies that have been conducted on waste seashells have shown that they are able to remove air pollutants such as carbon dioxide (CO₂), sulphur dioxide (SO₂) and nitrogen oxides (NO_x) (Jung, Lee, Lee, Yoo, & Shon, 2012), and also heavy metals from wastewater (Marinah Mohd Ariffin, Norhafiza Ilyana Yatim, & Sofiah Hamzah, 2017). Their important functional groups such as -CH₂, -CO₃, -OH and -PO₄, have contributed to their effective adsorbent properties in removing organic and inorganic pollutants from industrial wastewater (Saha et al., 2013). *Meretrix lamarckii* (*M. lamarckii*) is a type of commercial hard-shell clam that is always served as seafood. In this study, *M. lamarckii* shells were used as raw materials to produce activated carbon for dye removal. There were two types of activated carbon being prepared: acid activation activated carbon which used hydrochloric acid (HCl)

as activating agent (AC 1) and alkali activation activated carbon which use potassium hydroxide (KOH) as activating agent (AC 2).

1.2 Problem Statement

Dyestuff manufacturing and consuming industry has led to water pollution when untreated coloured wastewater directly discharge into water bodies (Bello & Ahmad, 2011). Presence of excessive dyes in water bodies will block the penetration of sunlight and reduce the photosynthesis rate of phytoplankton and algae, thus, affect the whole aquatic ecosystem (Yamin Yasin, Mohd Zobir Hussein, & Faujan Hj Ahmad, 2007). The dye molecules and their metabolic products can lead to serious human health problems as they bring toxic, mutagenic and carcinogenic effects (Ayadi et al., 2016).

Most dyes are made up of aromatic molecular structures which made them very stable and non-biodegradable in nature. Hence, conventional wastewater treatment methods such as coagulation or flocculation, ozonation, chemical oxidation and electrochemical treatment are not suitable for dye removal (Manoj Kumar Reddy, Krushnamurthy, Mahammadunnisa, Dayamani, & Subrahmanyam, 2015). Currently, activated carbon appeared to be the most suitable and effective method in dye removal for its high porous structure (Sartape et al., 2017).

In this study, *M. lamarckii* shells were chosen as raw material of activated carbon for malachite green (MG) removal due to its low cost, abundance and easily available especially at coastal area and seafood restaurant (Yao et al., 2014). Seashell waste that normally dispose at landfill site caused environmental problems such as bad odours, air pollution and soil pollution (Hou et al., 2016). Whereas for those which were

dumped back into the sea, they affected the aesthetic nature of coastal area, causing water pollution and harm to marine ecosystem (Rashidi, Mohamed, & Yusup, 2011).

1.3 Objectives

1. To prepare *Meretrix lamarckii* (*M. lamarckii*) activated carbon from acid and alkaline activation using hydrochloric acid (HCl) and potassium hydroxide (KOH).
2. To determine the optimum condition of contact time, initial pH of the solution, initial concentration of adsorbate and adsorbent dosage in dyes (malachite green) removal by using prepared activated carbon from *Meretrix lamarckii* (*M. lamarckii*).
3. To compare the efficiency of acid activated carbon (HCl activation) and alkali activated carbon (KOH activation) in dye (malachite green) removal.

1.4 Significant of Study

This study was conducted to investigate the potential of *M. lamarckii* shell activated carbon in dye removal. Optimization procedures were carried out to determine the optimum conditions that enable activated carbons attain the best adsorption performance. Several parameters that will affect the adsorption efficiency of activated carbons such as effect of contact time between adsorbent and adsorbate, initial pH of the solution, initial concentration of adsorbate and adsorbent dosage were optimized, in order to obtain the best combination. This combination is very important to provide optimum use of resources and time. In addition, it enables other researchers to use it as a reference in further study.

By using the waste seashells as raw materials in producing activated carbon, the amount of seafood waste can be reduced. Waste seashells that will be disposed to landfill or dumped directly into the sea can be minimize, and the waste can be converted into more useful products. Besides, utilization of seashells to produce activated carbon can also reduce cost in water treatment process. The high priced commercial activated carbon can be substitute by low-cost activated carbon, without affecting the efficiency of activated carbon in adsorption process. In addition, the utilization of waste *M. lamarckii* shells as raw materials to produce activated carbon is still very rare on market. This study may increase the public interest on *M. lamarckii* shell activated carbon, and more further studies may be carried out on this topic.

CHAPTER 2

LITERATURE REVIEW

2.1 Water Pollution

Water pollution can be defined as the existence of excessive amounts of pollutants in water bodies, which make the water no longer suitable for use (Owa, 2013). Globally, the growth of human population, industrialization and agricultural practises are the major causes that induced water pollution (Owa, 2013). Rapid growth of human population has increased the release of urban drainage and municipal wastewater into river basins (Liyanage & Yamada, 2017). This results in the degradation of water quality, which in turns affect the entire aquatic ecosystem (Liyanage & Yamada, 2017). In addition, discharge of toxic yet non-biodegradable effluent from various industries is the causal agent of water quality degradation (Eniscuola, 2011). It is estimated that million tonnes of heavy metals, solvents and toxic substances were dumped by various industries every year (World Water Assessment Programme, 2013). Besides, agricultural practises also result in water pollution by run-off of agro-chemicals, drug residues, saline drainage and organic matter into water bodies (United Nations Environment Programme, 2016).

Water pollution is inescapable in Malaysia as well. In past few decades, rapid urbanization and increasing population has increased the amount of wastes that has been produced, and most of them inevitably end up in water bodies (Huang, Ang, Lee, & Lee, 2015). According to Department of Environment (DOE), 7% of rivers in

Malaysia were polluted and 35% of them were slightly polluted out of 477 rivers monitored in 2015. The three significant contributors of water pollution in Malaysia were establishments of food services, sewage treatment plants, and manufacturing and agro-based industries (Huang et al., 2015).

Generally, industrial effluent is defined as the wastewater originated from human activities that involve processing and manufacturing of raw material (Ng, 2006). It can be categorized into two types: inorganic and organic. Inorganic wastewater largely came from coal, steel, non-metallic minerals, and surface metals processing commercial industries (iron picking and electroplating). Whereas for organic industrial wastewater, it originated from large scale chemical works and industries, such as cosmetic, pharmaceuticals, organic dye stuffs, pesticides, synthetic detergents, metal processing and paper production industries which often include organic materials for their chemical reactions (Shi, 2009). The treatment of organic wastewater is much complicated than inorganic wastewater. The organic substances contained in organic wastewater have various origins and characteristics, which can only be removed by special pre-treatment steps before biological treatment is carried out (Shi, 2009). Besides biological treatment technologies, there are some other methods to treat organic wastewater, include solvent extraction, incineration, photocatalysis, ultrasonic, chemical oxidation technologies, and adsorption technologies (Zheng, Zhao, Zhou, Fu, & Li, 2013).

2.2 Dyes

Among all the pollutants present in water bodies, dyes are a large and important group of organic industrial chemicals. They are organic compound that give colour to

a substance, which can be further categorized into two groups based on their structure: anionic dyes and cationic dyes. To date, the types of dyes are exceeding 100,000 with more than 700,000 tonnes of dyestuff generate annually (Robinson, McMullan, Marchant, & Nigam, 2001). They are widely use in various industries that involve dyestuff, such as textile, pharmaceutical, ceramics, cosmetic and paper industries (Moosa, Ridha, & Kadhim, 2016) which may generate high colour and organic contents wastewater (Sartape et al., 2017). Besides affecting the aesthetic nature of water bodies, release of the untreated effluents from those industries into water bodies may destroy aquatic life. This is due to the high concentration of dyes, variety of pH, high biochemical oxygen demand (BOD) and chemical oxygen demand (COD), total organic carbon (TOC), and total suspended solids in the effluents (Low, Teng, Norhashimah Morad, & Baharin Azahari, 2012). Besides that, presence of dyes in water bodies may block the penetration of sunlight into water bodies, reducing the photosynthesis process of aquatic plants and inhibit the growth of bacteria. The complex aromatic structures of dyes make them very stable to heat, light, microorganisms and oxidising agents, and thus, degradation of these dyes become more difficult. This has posed a threat to human health even if a small amount of dyes presents in drinking water (Bharathi & Ramesh, 2013) .

Malachite green (MG) is a cationic dye that readily soluble in water (Raval, Prapti, & Nisha, 2016). The molecular formula of MG dye is $C_{23}H_{25}ClN_2$, and its structural formula is shown in Figure 2.1. MG has been used extensively in the dyeing process of leather, silk, jute and wool (Sartape et al., 2017). Besides, it also used as an antifungal, anti-parasitical, and anti-bacteria therapeutic agents in animal husbandry and aquaculture industry to control fish parasites and diseases (Santhi, Kumar, & Muralidharan, 2015). High concentration of MG that released from industrial sites into

water bodies can cause serious effects on gill, gonads, kidney, intestine and liver of aquatic organisms (Santhi et al., 2015). It will also cause detrimental effects on human health, in which it has been reported to cause carcinogenesis, mutagenesis, teratogenicity, respiratory toxicity (Srivastava, Rangana, & Roy, 2004) and chromosomal fractures (Georgiadis et al., 2013). It can cause serious injuries to both human and animals through direct skin contact, inhalation and ingestion (Sudova, Machova, Svobodova, & Vesely, 2007). The use of MG has been banned in several countries, due to its properties of environmentally persistent and also toxic to major microorganisms. But it is still being used in many countries due to its easy availability, low cost, efficacy and lack of a proper alternative (Hameed & El-Khaiary, 2008; Papinutti, Mouso, & Forchiassin, 2006).

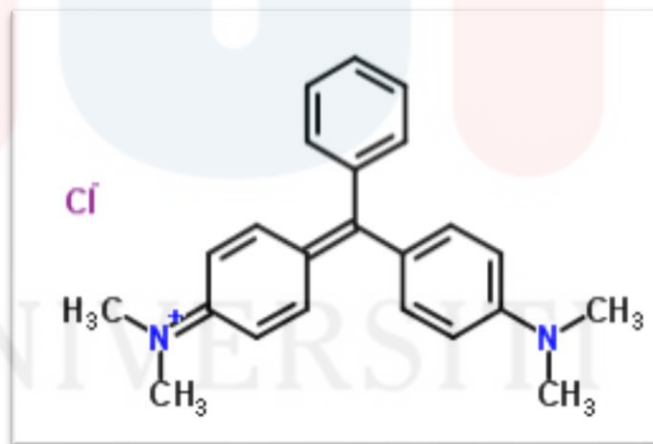


Figure 2.1: Structural formula of MG

Since MG can bring negative impacts to human and aquatic ecosystem, the discharging of untreated wastewater that contains MG become a great concern. Removal of MG before discharging into municipal sewer or directly into natural stream become necessary (Jaiswal Rinku et al., 2015). There are many different techniques has been used to remove dyes from industrial effluent including:

coagulation-flocculation (Kim et al., 2004), ozonation (Ould Brahim et al., 2014), electro chemical oxidation (Oguz & Keskinler, 2007), biodegradation, ion exchange (Fan et al., 2008) and adsorption by activated carbon. Among them, adsorption method appears to be the best technique for dye removal, due to its simplicity, low cost, eco-friendly and sludge free properties (Gaikwad & Kanawade, 2011). Activated carbon is the most effective adsorbent that used to perform this action because of its high adsorption capacity.

2.3 Activated carbon

Adsorption had been recognized as one of the most effective method (Carmen & Daniela, 2012) with potential application for dye removal from industrial effluent (Sarkheil, Noormohammadi, Rezaei, & Borujeni, 2014). It is an effective separation method in removing dissolved and suspended solid in wastewater, especially in terms of low initial cost, simple design, easy to be operated and insensitive to toxic substances (Pardeep Singh et al., 2017). Due to the presence of a large number of cavernous pores (Fabon et al., 2013) and high surface area (Egbuna, Mbah, & Okoye, 2015), activated carbon is found to be an effective adsorbent material. It is the most widely used adsorbent and usually exist in three forms: granular, powdered and pelleted activated carbon (Fabon et al., 2013).

Activated carbon is charcoal that has been enhanced to increase its microscopic pore network, which aid to its increased surface area (Alabadi, Razzaque, Yang, Chen, & Tan, 2015). This characteristic provides a greater adsorption power towards contaminants in water such as taste and odour compounds, natural organic compounds, and synthetic organic chemicals (Karanfil, 2006). However, commercially available

activated carbon can be very costly for its factors of intensive labour, energy, exchange rate, etc (Thomas & George, 2015). As cost is an important factor to consider when comparing the absorbents, substituting the source of activated carbon with low processing, natural, yet abundant wastes can be more economical while also help minimizing waste in the process.

2.4 Processing of Activated Carbon

2.4.1 Carbonization

Typically, the first step of activated carbon preparation is started by carbonization, followed by activation of this carbonaceous raw material (Leimkuehler, 2010). Carbonization is a thermo decomposition process of carbonaceous raw materials at temperature below 800°C in inert atmosphere, by which non-carbon species will be eliminated and a fixed carbon mass with rudimentary pore structure will be produced (Derbyshier et al., 1995). During carbonization, pyrolytic decomposition is first carried out, by which most of the non-carbon elements, hydrogen and oxygen will be removed in gaseous form, and followed by grouping of elementary carbon free atoms into an organized crystallographic formation called elementary graphite crystallite (Satish, 2003). This step is necessary and it helps to increase the strength of raw material and create an initial porous structure before it is being activated (Leimkuehler, 2010).

After the initial porous structure has been formed by carbonization process, activation is carried out to further create micropores (Beguin & Frackowiak, 2010). Besides raw materials and carbonization conditions, the characteristics of activated carbons largely depends on the activation method that used to activate them

(Hernandez, Aquino, & Capareda, 2007). Generally, there are two different methods that used to activate the activated carbon: physical activation and chemical activation (Bansal, Donnet, & Stoeckli, 1988).

2.4.2 Physical Activation

In general, physical activation consists of two major steps: carbonization process and activation process (Abechi, Gimba, Uzairu, Kagbu, & Ocholi, 2013).

Firstly, carbonization process will be carried out to break down the cross-linkage between carbon atoms and create an initial porous structure. This process is usually occurred at a relatively low temperature, which is below 800°C (Mui, E., Ko, D., & Mc Kay, G., 2004). After that, it is followed by activation process. A thermal treatment on carbonized product will be carried out in the presence of suitable oxidizing gases such as carbon dioxide (CO₂), air and steam, under the temperature of 800°C to 1000°C. This process is necessary because it enables the carbonized product develops porous structure of molecular dimension and extended surface area (Manocha et al., 2015). Generally, CO₂ always be chosen as activating gas, because it is cleaner, easier to handle, and it facilitates control of the activation process due to its slow reaction rate at high temperature (Zhang et al., 2004).

The largest advantage of physical activation is more environment friendly compare to chemical activation. Since it uses oxidizing gaseous as activating agents, it does not produce wastewater which contained chemicals (Viswanathan, Indra Neel, & Varadarajan, 2009). Waste generated can be minimized and thus, further treatment can be reduced. But it also possesses several disadvantages, such as high time consuming and higher energy required to produce activated carbon. In addition, a

relatively large amount of internal carbon mass is eliminated in order to obtain well-developed pore structure. This has limited the yield of activated carbon produced at the end of activation (Viswanathan et al., 2009).

2.4.3 Chemical Activation

Chemical activation is a single step process, in which carbonization of carbonaceous material and activation process will be carried out at the same time.

At the beginning, the carbonaceous material will be impregnated with a concentrated activating agent solution which act as oxidant and dehydrating agent (Ramakrishna, 2012). All these activating agents have dehydrating abilities which can influence the pyrolytic decomposition and inhibit tar formation (Tanmaya & Ankan, 2013). In addition, they also increase the yield of activated carbon, and reduced acetic acid and methanol formation (Tanmaya & Ankan, 2013). Zinc chloride ($ZnCl_2$), phosphoric acid (H_3PO_4) and potassium hydroxide (KOH) are some examples of the most commonly used chemical activating agents (Ramakrishna, 2012). Next, the chemical-impregnated product will then be pyrolyzed in the absence of air at temperature lower than $800^\circ C$ (El-Hendawy Alexander, Andrews, & Forrest, 2008). The lower activation temperature used in chemical activation process helps to improve the pore development in carbon structure (Sekirifa, et al., 2014). After pyrolysis, the remaining product is cooled down and washed to remove activating agents (Tanmaya & Ankan, 2013).

There are several advantages possess by chemical activation over physical activation, includes lower activation temperature (El-Hendawy et al., 2008), involve only a single activation step, produce a much higher yield of activated carbon, better

porous structure and shorter activation time needed (Nowicki, Pietrzak, & Wachowska, 2006). However, chemical activation also has some disadvantages, such as the corrosiveness of activation process and further treatment is required for wastewater generated during washing step (Davide, Toni, Henrik, & Ulla, 2018).

2.5 Adsorption Studies

2.5.1 Batch Adsorption Studies

In order to obtain the fundamental kinetic and equilibrium adsorption data for selected activated carbon, a laboratory batch adsorption study can be carried out. At equilibrium state, the amount of adsorbate that can be adsorbed by a particular adsorbent is a function of both temperature and adsorbate concentration. But, as the temperature keep constant, the resulting function is now referred as adsorption isotherm (Ruthven, 1984).

Adsorption isotherm is a graphical representation that used to show the relationship between the amount of adsorbate adsorbed by a unit weight of adsorbent, and the amount of remaining adsorbate at equilibrium state (Ng, Losso, Marshall, & Rao, 2002). There are three well-known isotherms, namely Freundlich, Langmuir and BET adsorption isotherm (Steve, Erika, Reynold, & Paul, 1998).

In theory, adsorption capacity of a particular adsorbent is achieved in equilibrium state when the adsorption rate equal to desorption rate. Different combinations of adsorbents with adsorbate require different time interval to achieved the equilibrium state.

2.6 Seashell

Seashell is a hard, protective outer layer owned by all marine mollusc which protect them from their predator (Saha et al., 2013). It is usually made up of 3 layers: the most outer layers of protein, intermediate layer of calcite and inner layer rich in calcium carbonate (Narayanan & Dutta, 2006). The seashell waste which rich in calcium-based materials such as CaO, CaCO₃, and Ca(OH)₂ are very suitable to be converted into adsorbent, due to their good reactivity (Yao et al., 2014). Their effectiveness in adsorption of organic and inorganic pollutants from industrial wastewater contributed by the existence of important functional groups such as –CH₂, –OH, –CO₃, and –PO₄ (Chowdhury & Saha, 2010).

Based on the study done by Saha, Srivastava and Chowdhury (2013), periwinkle shells, a type of seashell were used as adsorbents to treat phenol from industrial wastewater. According to their results obtained, periwinkle shells adsorbents showed excellent adsorption capacity, which is 175.27 mg/g at the pH of 4.0, initial phenol concentration of 50 mg/L, adsorbent dosage of 2 g and temperature of 293 K.

Besides periwinkle shells, another type of seashell waste - mussel shell biomass waste has showed their ability to remove dye from aqueous solution. Based on the study done by Mohammadine El-Haddad (2016), the adsorption capacity of calcined mussel shell for Basic Fuchsin dye removal is 141.65 mg/g. Another study done by Chrysi, Grigorios, Nikolaos and Argyris (2017) proved that mussel shells have high efficiency in removal of dye and heavy metal. Almost 100% of dye was removed by powdered mussel shells, while in the case of chromium and cadmium, their final concentrations reached below 1 mg/L.

According to a study conducted by Daniela et al. (2012), powdered waste shells of *Rapana* gastropod showed their high efficiency in removal of dyes from textile wastewater. Through batch experiment carried out, the authors found that the maximum percentage of dye removal was obtained at initial solution pH of 1.2, shells dose of 40 g/L, dye concentration of 50 mg/L and higher temperature.

On the other hand, according to the research that done by Marinah Mohd Ariffin et al. (2017), activated carbon prepared from bulk seashells able to remove 99.1% of Pb^{2+} ions. This study had showed their high potential to be used in heavy metal wastewater treatment. Besides, in a research done by Chowdhury and Saha (2010), they revealed that seashell powder has high potential in Basic Green 4 (malachite green) removal. This show that seashells can be used as an adsorbent for removal of various pollutants from aqueous solution, includes dye and heavy metals.

2.6.1 *Meretrix lamarckii* (*M. lamarckii*)

In this study, *Meretrix lamarckii* (*M. lamarckii*) shells was chosen as raw material of activated carbon in removal of dyes as it met the characteristics and basic requirements to become adsorbent. *M. lamarckii* is a type of bivalve molluscs which is more commonly known as Asian Hard Clams. They usually inhabit the estuaries, tidal flats, and sandy beach. They are commercially important fishery resources but only the flesh part can be consumed. After being consumed, their hard shells will be left behind as waste, either being disposed to landfill site or dumped back into the sea.

Seashell waste that normally dispose at landfill site will cause several environmental problems, such as production of bad odours, air pollution and soil pollution (Hou et al., 2016). Whereas for those seashell wastes which dumped back

into the sea, they will affect the aesthetic nature of coastal area, causing water pollution and harm to entire marine ecosystem (Rashidi et al., 2011). The physical appearance of *M. lamarckii* shells is shown in Figure 2.2.



Figure 2.2: *Meretrix lamarckii* shells

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials and Instruments

The chemicals and instruments that used in this study were listed in Table 3.1 and Table 3.2 respectively.

Table 3.1: List of chemicals used in this study

Chemicals	Brand
Hydrochloric acid (HCl)	R & M Chemicals
Potassium hydroxide (KOH)	System
Sodium hydroxide (NaOH)	R & M Chemicals
Malachite Green (C ₂₃ H ₂₅ ClN ₂)	Bendosen

Table 3.2: List of instruments used in this study

Instrument	Brand
Ultraviolet-visible spectrophotometer	HACH
Incubator shaker	IKA
Furnace	Wise Therm
Tube furnace	Carbolite

3.2 Sample Collection

Meretrix lamarckii (*M.lamarckii*) shells were collected from Café Kantin, which located at Tanah Merah, Kelantan with coordinate of 5°48'33.3"N 102°09'02.6"E. The location of Café Kantin on map was shown in Figure 3.1. After the collection had done, they were transported to laboratory for immediate use. They were first washed under

tap water to remove any dirt and sand. Any unwanted tissue attached to *M.lamarckii* shells were removed by using a sharp knife. After rinsed with distilled water, they were set aside and dried overnight at room temperature. After that, they were crushed by using commercial blender, mortar and pestle and later sieved with 250 μm sieve. The dried samples were then being kept in zipper bag at room temperature (Badmus, Audu, & Anyata, 2007).



Figure 3.1: Map of Café Kantin, Tanah Merah, Kelantan.

3.3 Preparation of Activated Carbon from Seashells

3.3.1 Acid Activation

About 200 g of *M.lamarckii* shell powder was carbonized at 700°C for 2 hours by using a furnace. Then, the sample was taken out and allowed to cool until its temperature was same as room temperature. Hydrochloric acid (HCl) was used as activating agent for acid activation process. About 200 g of carbonized *M.lamarckii*

shell powder was mixed with 250 mL of 5.5 M HCl, followed by boiling for 2 hours at 350°C with hotplate. After the slurry had cooled down, it was filtered, washed and rinsed away the acid by using distilled water until the residual liquid became pH 7, by using vacuum pump, buchner funnel and buchner flask. The activated carbon was then dried in oven at 110°C for 3 hours (Badmus et al., 2007).

3.3.2 Alkali Activation

About 200 g of *M.lamarckii* shell powder was first incinerated at 700°C for 1 hour under constant nitrogen flow inside a tube furnace. After that, it was soaked in potassium hydroxide (KOH) with impregnation ratio of 1:1 (KOH pellets : char). Then, it was dehydrated in oven at 105°C overnight. Dehydrated product was then incinerated in tube furnace under the flow of nitrogen gas at 850°C for 2 hours. Once the temperature reached 850°C, the nitrogen gas was replaced by carbon dioxide gas, and this process was continued for 2 hours (Bello & Ahmad, 2011).

3.4 Preparation of Adsorbate

In this research, Malachite Green (MG) was chosen as adsorbate. A stock solution of MG with concentration of 1000 mg/L was prepared by dissolving 1g of MG powder in 1L of distilled water (Enenebeaku, Okorocho, Enenebeaku, Okolie, & Anukam, 2016). The working solutions of desired concentrations were then prepared by dilution using a volumetric flask (Takute, Singh, & Yenkie, 2014). Volume of MG stock solution that needed for dilution was calculated by using formula:

$$M_1V_1 = M_2V_2 \quad (3.1)$$

where

M_1 = Molarity of MG stock solution

V_1 = Volume of MG stock solution

M_2 = Molarity of working solution

V_2 = Volume of working solution

To optimize contact time and initial pH, about 500 mL of MG working solution was prepared with concentration of 50 mg/L for each optimization experiment. The volume of MG stock solution that used for dilution process was calculated by using Eq. (3.1). Whereas for optimization process for initial concentration of adsorbate, about 100 mL of 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L and 50 mg/L MG working solutions were prepared separately. The volume of MG stock solution needed for dilution process was calculated by using the same formula. For optimization of the last parameter of this study, which was adsorbent dosage, the MG working solution with optimized concentration from previous step was prepared. By using the same formula, the volume of stock solution that needed for dilution process was calculated.

3.5 Optimization of Experiment

3.5.1 Effect of Contact Time

Eight different conical flasks containing 100 mL of 50 mg/L MG solution each with pH 7 were prepared. About 1 g of acid activated carbon (HCl activation) (AC 1) was added into each conical flask. After that, they were kept in the incubator shaker at constant speed of 150 rpm at 30°C, for time interval of 30 minutes, 60 minutes, 90

minutes, 120 minutes, 150 minutes, 180 minutes, 210 minutes and 240 minutes. After shaking, the solutions were filtered using filter paper.

The remaining MG solutions' absorbance were then measured by using UV-Vis spectrophotometer (Samal, 2014). The same steps were repeated by replacing AC 1 with alkali activated carbon (KOH activation) (AC 2).

3.5.2 Effect of initial pH of the solution

Five different conical flasks with 100 mL of 50 mg/L MG solution were prepared separately. About 1 g of AC 1 was added into each conical flask. The pH of the solutions was adjusted by using 0.1 M HCl and 0.1 M NaOH solution with pH meter. The pH values of the solutions were varying as 2, 4, 6, 8 and 10. The conical flasks were then being placed in incubator shaker with speed of 150 rpm at 30°C. The contact time of adsorbent with MG solution was taken from the previous optimization experiment. After shaking, the solutions were filtered by using filter paper.

The absorbance of remaining MG solutions was measured by using UV-Vis spectrophotometer (Amuda et al., 2014). The same steps were repeated by replacing AC 1 with AC 2.

3.5.3 Effect of Initial Concentration of Adsorbate (Malachite Green)

About 100 mL of MG solution with concentrations of 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L and 50 mg/L were prepared separately and taken into five different conical flasks. About 1 g of AC 1 was added into each conical flask. The pH of MG solution was adjusted to optimized pH as previous experiment. They were then being

placed in incubator shaker with speed of 150 rpm at constant temperature of 30°C, with the optimized contact time. After shaking, the solutions were filtered by using filter paper.

The remaining MG solutions' absorbance was measured by using UV-Vis spectrophotometer (Samal, 2014). The same steps were repeated by replacing AC 1 with AC 2.

3.5.4 Effect of Adsorbent Dosage

Five different conical flasks with 100 mL of optimized concentration of MG solution were prepared. Different dosage of AC 1 ranging from 0.6 g, 0.8 g, 1.0 g, 1.2 g and 1.4 g was added to each conical flask. The initial pH of the solutions was adjusted to the optimized pH as previous experiment by using 0.1 M HCl and 0.1 M NaOH. The conical flasks were placed inside incubator shaker with speed of 150 rpm and the temperature was maintained at 30°C. The contact time for adsorbent and adsorbate was fixed according to the optimized contact time obtained in previous experiment. After shaking process, the solutions were filtered by using filter paper.

The absorbance of remaining MG solutions was then being measured by using UV-Vis spectrophotometer (Samal, 2014). The same steps were repeated by replacing AC 1 with AC 2.

3.6 Analytical Method

Five sets of MG solutions with concentration of 10 mg/L, 20mg/L, 30 mg/L, 40 mg/L and 50 mg/L were prepared from stock solution. The volume of MG stock

solution needed for dilution was calculated by using Eq. (3.1). After that, the absorbance values of every prepared solutions were measured by using UV-Vis spectrophotometer for calibration curve purpose.

By using the calibration curved constructed, the unknown concentration of remaining MG solutions from every optimization process were determined.

3.7 Removal Efficiency

The removal efficiency of AC 1 and AC 2 was compared by calculated their MG dye removal percentage. The percentage of MG removal was calculated by using the Eq. (3.2).

$$\text{Removal (\%)} = \frac{C_o - C_e}{C_o} \times 100 \% \quad (3.2)$$

where

C_o = Initial MG dye concentration (mg/L)

C_e = Final MG dye concentration (mg/L)

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Preparation of Activated Carbon from Seashells

The physical appearance of raw seashell powder, acid activated carbon (HCl activation) (AC 1) and alkali activated carbon (KOH activation) (AC 2) were shown in Figure 4.1 as below. Originally, raw seashell powder was yellowish in colour (as shown in (a)), but then turned into grey colour after activated by hydrochloric acid (HCl) (as shown in (b)). While potassium hydroxide (KOH) activation turned raw seashell powder into white powder (as shown in (c)).

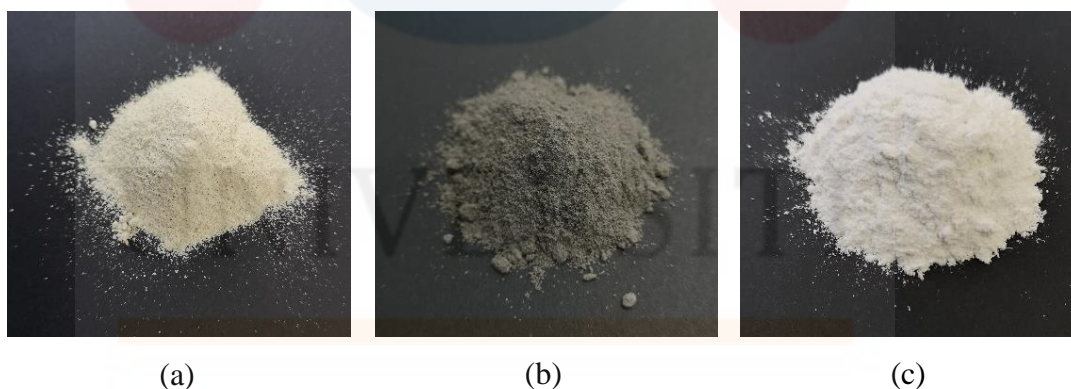


Figure 4.1: Physical appearance of (a) seashell powder (b) AC 1 (c) AC 2

4.2 Batch Adsorption Studies

4.2.1 Effect of Contact Time

The effect of contact time on the adsorption of Malachite Green (MG) by AC 1 and AC 2 was studied. The conditions such as adsorbent dosage, initial MG concentration and pH had been fixed at 1.0 g, 50mg/L and pH 7 respectively. Figure 4.2 shown the removal percentage of MG by AC 1 and AC 2 for duration of 4 hours which analysed for each 30 minutes by interval.

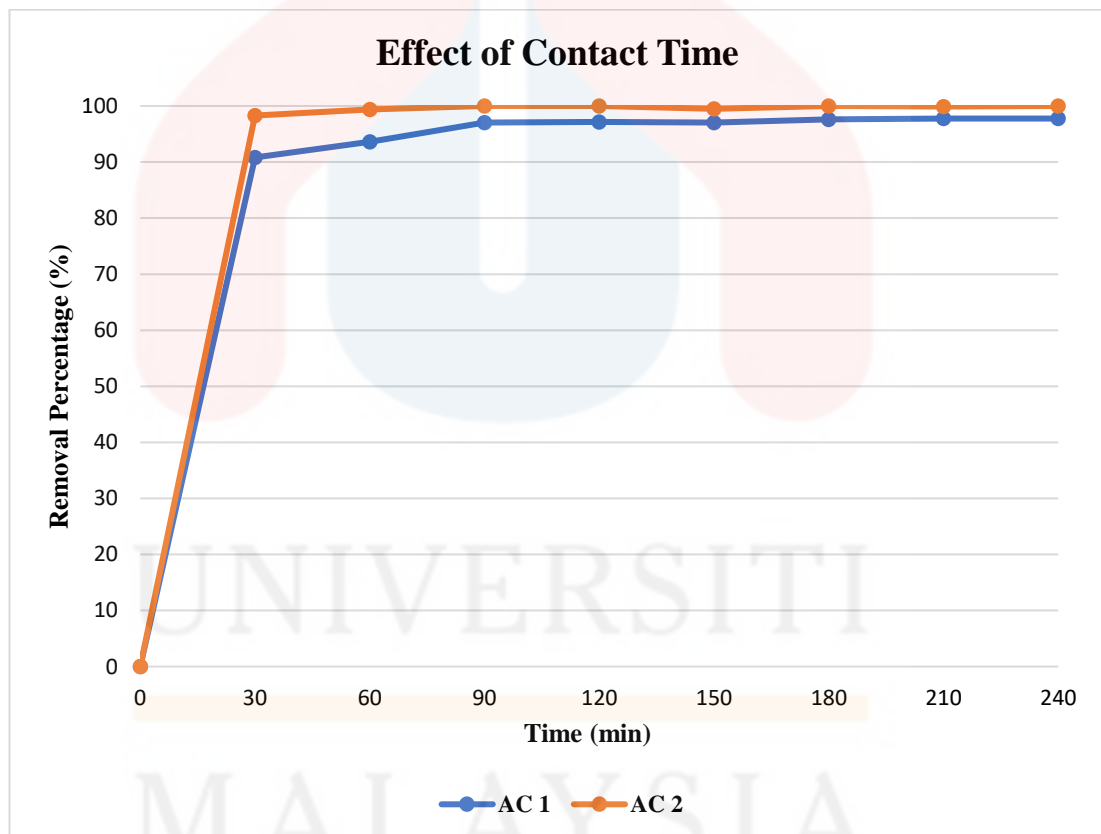


Figure 4.2: Effect of Contact Time

In the first 30 minutes, MG was rapidly adsorbed by both AC1 and AC 2. As time increased, the adsorption rate slow down, until the equilibrium state reached. At the beginning, the surface area of both types of activated carbon has not yet occupied.

MG molecules were adsorbed very fast at exterior surface of both AC 1 and AC 2. This caused the adsorption rate was very fast initially. After 30 minutes, the exterior surface of activated carbon was almost saturated and fully occupied by MG molecules. The dye molecules had to enter into the pores of activated carbon, and adsorb by the interior surface of activated carbon. This process took relatively long period of time until the both activated carbon attained equilibrium state (Allen & Koumanova, 2005; Marshahida & Erma, 2016). Besides, long contact time taken to reach equilibrium was also contributed by the repulsion force existed between the solute molecules of the solid and bulk phases (Idris & Ahmad, 2011).

Optimum contact time for MG dye removal recorded by AC 1 is 210 minutes, while for AC 2, the optimum time recorded was shorter, which was 90 minutes. The percentage removal by AC 1 and AC 2 are 97.76% and 100% respectively, after their optimum contact time with MG solution. This may due to the different functional groups that existed on both types of activated carbon. The existence of alkyl halides groups such as C-Cl and C-Br in AC 2 that cannot be found in AC 1 had contributed to better adsorption efficiency of AC 2, with shorter time needed to attain equilibrium state and higher removal efficiency.

After their optimum contact time, the colour of MG solution for both types of activated carbon changed significantly. For AC 1, the colour changed was from blue to pale blue, which indicated that a low concentration of dye was still remained in the aqueous solution. While for AC 2, the colour changed was from blue to colourless. This indicated that after adsorption process, all dye molecules were completely removed from aqueous solution. The colour change at each 30 minutes interval for AC 1 can be observed in Appendix A, while for AC 2, the colour change can be observed at Appendix E.

4.2.2 Effect of Initial pH of the solution

Another important factor that affect the MG dye removal is pH of the aqueous medium. It can affect the chemical characteristics of both activated carbon and MG dye molecules (Yamin Yasin et al., 2007). The effect of pH on the adsorption of MG by AC 1 and AC 2 was studied. The previously optimized contact time was bringing forward, which was 210 minutes for AC 1 and 90 minutes for AC 2. While other conditions such as adsorbent dosage and initial MG concentration had been fixed at 1.0 g and 50 mg/L respectively. Figure 4.3 shown the removal percentage of MG by AC 1 and AC 2, with varying initial pH ranging from 2 to 10.

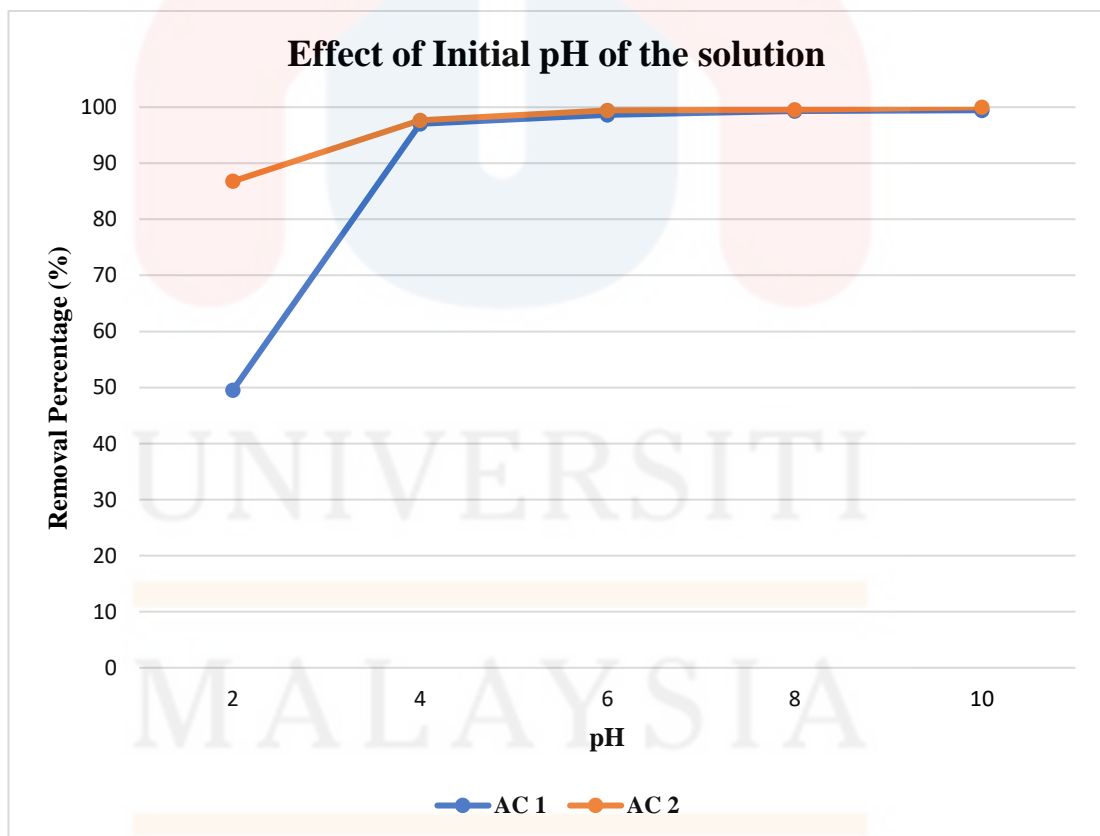


Figure 4.3: Effect of Initial pH of the solution

Activated carbon is amphoteric, by which its variable-charge surface can become positively charged or negatively charged depends on aqueous medium (Navasivayam & Kavitha, 2002). At lower pH or acidic medium, the surface of activated carbon will become positively charged, while at higher pH or alkaline medium, their surface will become negatively charged.

In this study, when the medium was at low pH such as pH 2, the removal percentage of MG was relatively low, which was 49.53% for AC 1 and 86.79% for AC 2. This probably due to the presence of hydrogen ions, H^+ in a large quantity in acidic medium. Since MG is a cationic dye, it is positively charge in aqueous medium. The large amount of H^+ ions competing with the cationic dyes for adsorption sites on activated carbon, causing a declination in the amount of MG adsorbed on activated carbon (Srinivasan, Sivakumar, & Raja, 2013). Besides that, in low pH medium, the surface of activated carbons was positively charged. The electrostatic repulsion between the same charge activated carbon and cationic dye was very high, which led to low adsorption rate of dye on activated carbon (Bao & Zhang, 2012).

In contrary, at high pH medium such as pH 10, the surface of both AC 1 and AC 2 became negatively charge, which lowered the surface charge density. This lowered the electrostatic repulsive force, and increased the electrostatic force of attraction between positively charged MG ions and negatively charge activated carbons, thus, results in increase of adsorption rate and removal percentage of dyes (Dermibas, Dizge, Sulak, & Kobya, 2008).

As the pH of MG aqueous medium increased, the removal percentage for AC 1 and AC 2 also increased (as shown in Figure 4.3). The optimum pH for AC 1 in dye removal was pH 10, with removal percentage of 99.46%; while for AC 2, the optimum

pH was same as AC 1, with slightly higher removal percentage, which was 100%. The studies done by Pan & Zhang (2009), Baek, Ijagbemi, SJ, & Kim (2010) and Sartape et al. (2017) had proved that when the pH values increase (more alkaline medium), the adsorption of MG to activated carbon will also increase.

Based on the colour change of MG solution, an inference can be drawn from those observations. For AC 1, the colour of MG solution reduced from blue to very pale blue, which indicated that very little MG molecules remained in the aqueous medium. While for AC 2, the blue colour of MG solution reduced to colourless, indicating there was no more MG molecules remaining in the aqueous solution. The colour change of MG solution at different initial pH can be observed in Appendix B for AC 1 and Appendix F for AC 2.

4.2.3 Effect of Initial Concentration of Adsorbate (Malachite Green)

Since there is a limit for a given amount of adsorbent to adsorb dye, the initial dye concentration become one of the most important parameters to be investigated (Benaissa, 2005). In this study, the experiment on effect of initial concentration of adsorbate (Malachite Green) on the removal efficiency by AC 1 and AC 2 was carried out. The previously optimized contact time was bringing forward, which was 210 minutes for AC 1 and 90 minutes for AC 2. The optimum pH for both AC 1 and AC 2 was pH 10, while the adsorbent dosage for both types of adsorbents was still fixed at 1.0 g. Figure 4.4 shown the removal percentage of MG by AC 1 and AC 2, for initial concentration varying from 10 mg/L to 50 mg/L.

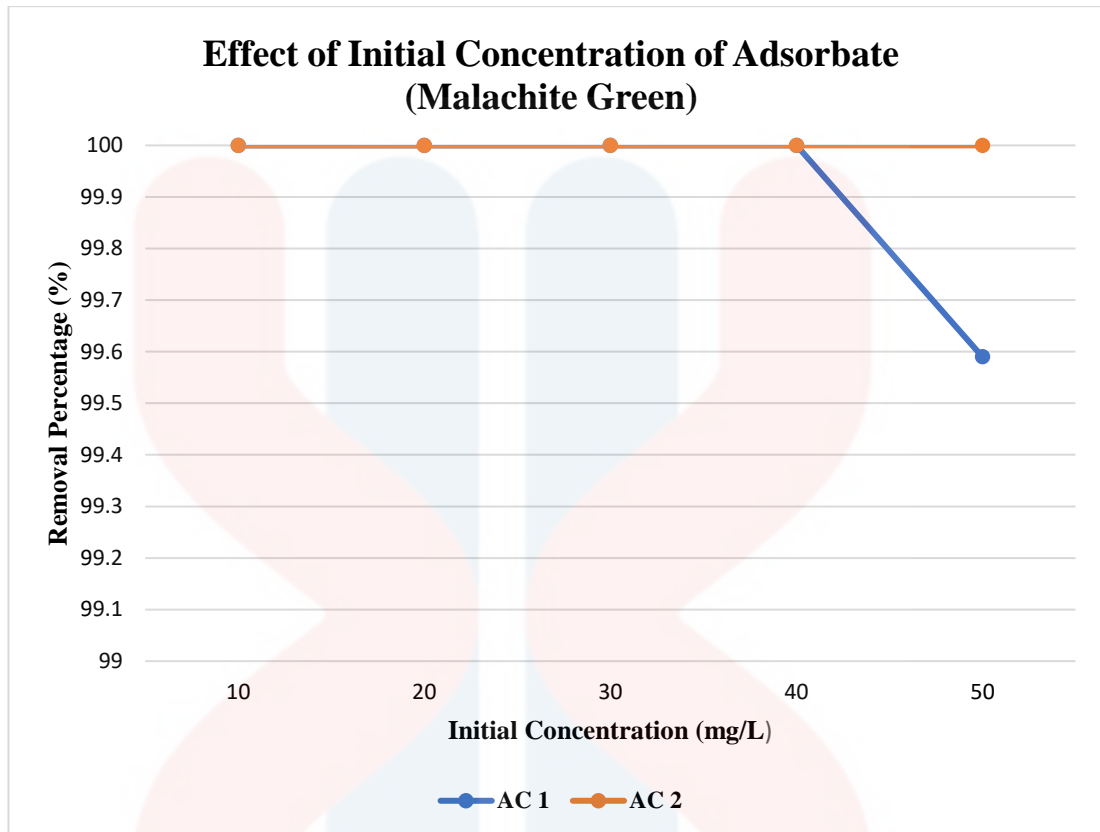


Figure 4.4: Effect of Initial Concentration of Adsorbate (Malachite Green)

The removal percentage of MG by both types of activated carbon is highly dependent on its initial concentration. It is depending on the immediate relation between the concentration of the dye and the availability of binding sites on surface of adsorbent (Ould Brahim et al., 2014). At low concentration of MG solution, there will be less amount of dye molecules present in the aqueous solution. A lot of unoccupied binding sites on activated carbon surface will exist, which enable dye molecules bind to them easier and faster. When the initial dye concentration increases, the amount of dye molecules present in solution will also increase. Therefore, lacking of binding sites required for the dye adsorption will happened. (Kannan & Sundaram, 2001). At very high concentration of MG solution, all the binding sites of activated carbon will be

fully occupied and become saturated, caused the excessive dye molecules remain “free” in the aqueous solution.

As shown in Figure 4.4, the removal percentage of MG found to decrease as initial concentration of adsorbate increased. For AC 1, the removal percentage for MG with initial concentration of 10 mg/L to 40 mg/L was 100%, and there was a slightly drop in removal percentage when the initial concentration increased to 50 mg/L, which was 99.59%. On the other hand, for AC 2, the removal percentage of MG maintained at 100% for the initial dye concentration of 10 mg/L to 50 mg/L. This result shown that AC 2 has a greater availability of surface area compared to AC 1. It had sufficient active sites for MG to bind on although the concentration of adsorbate was high.

Based on the observation of colour change in MG solution, an inference can be drawn – the removal efficiency of AC 2 was better than that of AC 1 even at higher adsorbate concentration. For AC 1, the colour of MG solution changed from blue to colourless when adsorbate concentrations were below 40 mg/L. But after the adsorbate concentration increased to 50 mg/L, the solution was remained pale blue. This indicated that at higher concentration of MG solution, AC 1 was almost fully occupied and unable to remove all MG molecules. In contrary, AC 2 was able to remove all dye molecules in all five-increasing concentration of MG aqueous solution. The colour of MG solution reduced from blue to colourless for all five sets of experiment. The detailed colour change of MG solution at different initial adsorbate concentration can be observed in Appendix C for AC 1 and Appendix G for AC 2.

4.2.4 Effect of Adsorbent Dosage

In the last part of this study, the experiment of effect of adsorbent dosage on MG dye removal was carried out. All the previously optimized parameters were combined to put into this last parameter. The conditions used were 210 minutes and 90 minutes of contact time for AC 1 and AC 2 respectively, and 10 mg/L of initial adsorbate concentration at pH 10 for both of them. Figure 4.5 shown the removal percentage of MG by AC 1 and AC 2, with varied adsorbent dosage in the range of 0.6 g to 1.4 g.

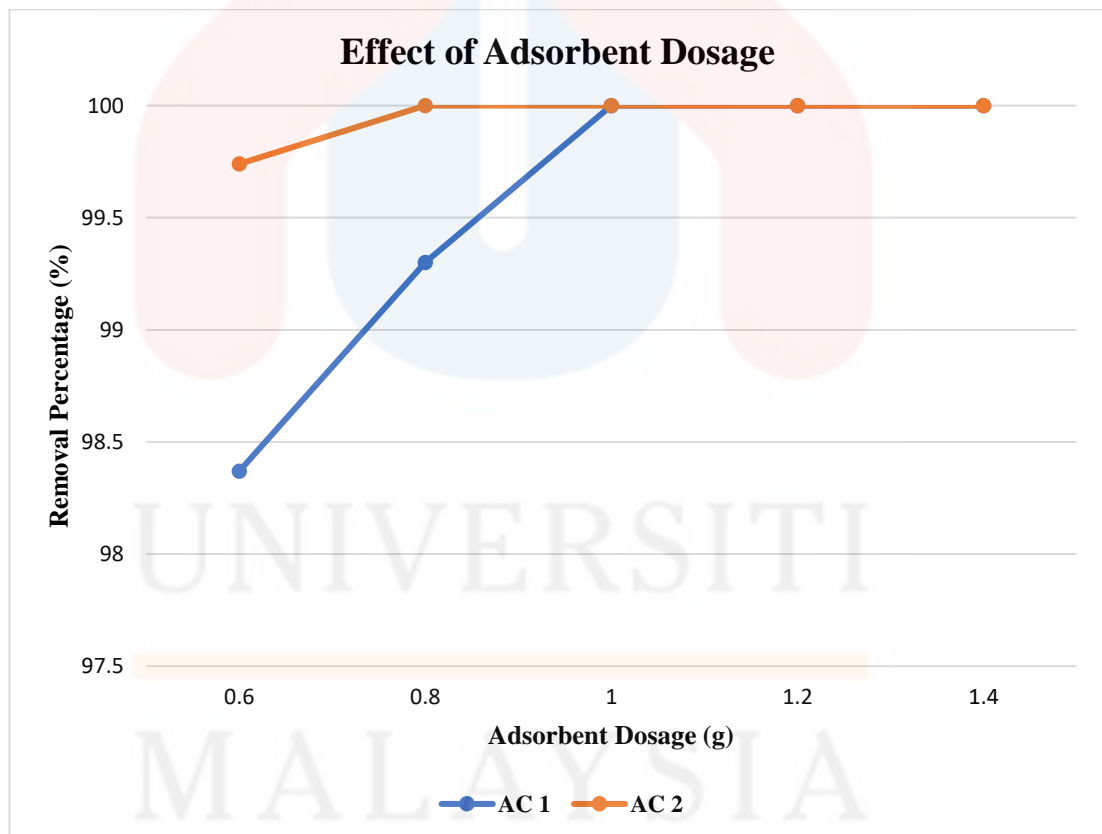


Figure 4.5: Effect of Adsorbent Dosage

As the amount of adsorbent increased, the removal percentage of MG was also increased, until they attained equilibrium state, which was 100% of removal percentage in this study. As illustrated in Figure 4.5, AC 1 required higher dosage (1.0 g) to remove all MG ions from aqueous solution, while AC 2 required less dosage, which was 0.8 g to achieve 100% removal percentage. As there was increment in adsorbent dosage, more surface area and active sites will be available (Garg, Gupta, Yadav, & Kumar, 2003). This increased the binding site that enable MG ions to bind on it (Marshahida & Erma, 2016). Since the binding sites were in excess and initial concentration of adsorbate was fixed, they remained unsaturated during adsorption reaction (Khattari & Singh, 2009). Thus, more dye molecules can be adsorbed by activated carbon and higher removal percentage of MG can be achieved.

Higher dye removal efficiency of AC 2 over AC 1 was contributed by the KOH and CO₂ activation method used. KOH that acted as activating agent for AC 2 enable more micropores to be formed on the surface of activated carbon, thus increasing the total surface area and pore volume (Okman, Karagoz, Tay, & Erdem, 2014; Hanna, Jan, & Marek, 2015; Bronislaw, 2016). In addition, CO₂ as an activation gas in the last step of activation process, functioned to widen the narrow submicropores and micropores formed by KOH beforehand, leading to microporous and mesoporous structures formation (Mohd Saufi Md Zaini & Syed Shatir A. Syed-Hassan, 2018). CO₂ able to penetrate the pores' structure and widen those submicropores and micropores, due to their special characteristic of low reaction rate even at high temperature (Zhang et al., 2004; Hanna et al., 2015). The formation of large quantity of micropores and mesopores provided a large total surface area for the MG adsorption to take place, thus increasing the removal percentage of dye by AC 2. As the

concentration of MG solution is kept constant (10 mg/L), AC 2 that had a larger total surface than AC 1, required only lesser dosage to achieved 100% removal percentage.

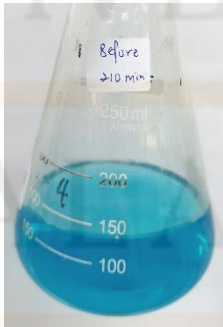
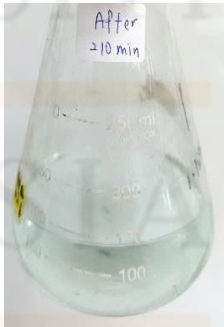
The MG solution shown changes in colour when being tested with different adsorbent dosage. For AC 1, the colour of MG solution was reduced from blue to pale blue when the adsorbent dosage less than 1.0 g. This indicated that there was low concentration of MG molecules still remain in the solution and cannot be completely removed by low adsorbent dosage. When the adsorbent dosage was increased to 1.0 g and above, the removal efficiency increased and the colour of MG solution turned colourless. While for AC 2, when the adsorbent dosage was less than 0.8 g, the colour of MG solution reduced from blue to pale blue. But as the adsorbent dosage increased to equal to or above 0.8 g, the colour of MG solution changed from blue to colourless. The colour change of MG solution by different dosage of AC 1 and AC 2 can be observed in Appendix D and Appendix H respectively.




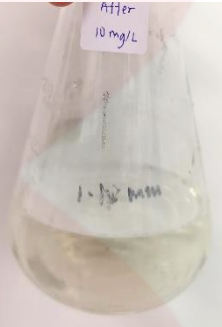
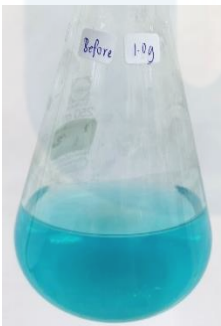
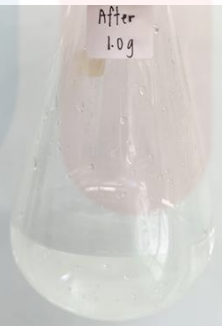
4.3 Optimized Conditions of Activated Carbons

4.3.1 Optimized Conditions of AC 1 in Removal of MG

After batch adsorption studies had been carried out, the optimized conditions for AC 1 were successfully found. The optimized contact time between AC 1 and MG solution was 210 minutes. While for the initial pH of the MG aqueous solution, the adsorption performance was the best in pH 10 medium. For the third parameter - initial adsorbate concentration, the optimization process shown that 10 mg/L was the best-performing concentration. Following that, the best adsorbent dosage was found to be at 1.0 g. Table 4.1 shown the optimized conditions for AC 1, with their respective colour change of MG solution and removal percentage. While the detailed colour change and removal percentage from ranges of contact time, pH, initial concentration of adsorbate and adsorbent dosage can be referred in appendix A, B, C and D respectively.

Table 4.1: Optimized Conditions of AC 1 in Removal of MG

Parameter	Colour Change of MG Solution		Removal Percentage (%)
	Before Adsorption Process	After Adsorption Process	
Optimized Contact time (210 minutes)	 <p style="text-align: center;">Blue</p>	 <p style="text-align: center;">Pale Blue</p>	97.76



<p>Optimized Initial pH of the solution (pH 10)</p>	 <p>Blue</p>	 <p>Very Pale Blue</p>	<p>99.46</p>
<p>Optimized Initial Concentration of Adsorbate (MG) (10 mg/L)</p>	 <p>Light blue</p>	 <p>Colourless</p>	<p>100.0</p>
<p>Optimized Adsorbent Dosage (1.0 g)</p>	 <p>Light Blue</p>	 <p>Colourless</p>	<p>100.0</p>

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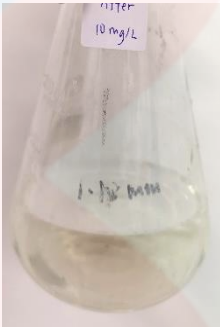

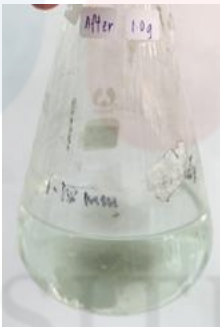
4.3.2 Optimized Conditions of AC 2 in Removal of MG

Through a series of experiments done, the optimized conditions for AC 2 to perform highest removal efficiency of MG had been found. The optimized contact time between AC 2 and MG aqueous solution was found to be 90 minutes. While the most suitable initial pH of MG solution for adsorption process to carry out was 10. On the other hand, the optimized initial adsorbate concentration was 10 mg/L. These optimized conditions were brought forward to be used in the last parameter and the adsorbent dosage was optimized at 0.8 g. Table 4.2 shown the optimized conditions for AC 2, with their respective colour change of MG solution and removal percentage. While the detailed colour change and removal percentage from ranges of contact time, pH, initial concentration of adsorbate and adsorbent dosage can be referred in appendix E, F, G and H respectively.

Table 4.2: Optimized Conditions of AC 2 in Removal of MG

Parameter	Colour Change of MG Solution		Removal Percentage (%)
	Before Adsorption Process	After Adsorption Process	
Optimized Contact time (90 minutes)	 <p>Blue</p>	 <p>Colourless</p>	100.0

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<p>Optimized Initial pH of the solution (pH 10)</p>	 <p>Blue</p>	 <p>Colourless</p>	<p>100.0</p>
<p>Optimized Initial Adsorbate (MG) (10 mg/L)</p>	 <p>Light Blue</p>	 <p>Colourless</p>	<p>100.0</p>
<p>Optimized Adsorbent Dosage (0.8 g)</p>	 <p>Light Blue</p>	 <p>Colourless</p>	<p>100.0</p>

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In this study, two types of activated carbon with different activation methods were prepared from *M.lamarckii* shells. By using both of them: acid activated carbon (HCl activation) (AC 1) and alkali activated carbon (KOH activation) (AC 2), batch adsorption experiments on removal of Malachite Green (MG) dye from aqueous solution has been carried out successfully. Some observations are made according to the experimental results.

Adsorption of MG by AC 1 and AC 2 tends to increase with contact time. The longer the contact time between adsorbents and adsorbate, the higher the removal percentage of MG from aqueous solution, until the equilibrium state has been achieved. At the beginning, the adsorption rate was very rapid due to the high availability of binding sites. The rate then slowed down after a period of time due to the saturation of activated carbons' exterior surface. Those MG molecules needed longer time to enter the interior surface of activated carbon. For AC 1, the optimum contact time was found to be 210 minutes, while for AC 2 was 90 minutes.

The optimum pH of both aqueous medium for AC 1 and AC 2 was at 10. The removal percentage of MG molecules tends to increase as pH increase. This phenomenon happened because MG dye is cationic dye which possess positive charge. High pH medium enabled activated carbons' surface to become negatively charged,

which increased the attraction force between activated carbon and MG molecules, make them easier to bind together. In addition, less H^+ ions are present in high pH medium, thus reduce the species that compete binding sites with MG molecules.

The optimum initial concentration of adsorbate (MG) for both types of activated carbon was found to be 10 mg/L. This is due to the high availability of binding sites at low concentration of MG solution. A lot of unoccupied binding sites enable dye molecules bind to activated carbon easier and faster.

Besides that, the optimum adsorbent dosage for AC 1 was found to be 1.0 g, while for AC 2, the optimum dosage was slightly lower than that of AC 1, which was 0.8 g. This happened due to the existence of larger pore volume and total surface area of AC 2 than AC 1, which enable lesser dosage of AC 2 to use in removing the same concentration of dye.

In conclusion, through comparison between AC 1 and AC 2, the removal efficiency of AC 2 is better than that of AC 1. This may due to the different functional group presented at the surface of both activated carbons. In addition, the formation of micropores and mesopores on AC 2 helps to increase its pore volume and total surface area. Thus, AC 2 need less contact time and less dosage to achieve 100% removal percentage, while AC 1 need longer contact time and slightly higher dosage to achieve 100% removal percentage. Both of them have high adsorption capability to remove MG from aqueous solution.

5.2 Recommendation

After the study had been completed, it is recommended that the carbonization temperature used to produce two types of activated carbon should be reduced. The

carbonization temperature of AC 1 was 700°C, while for AC 2, there was two times of carbonization, which was 700°C for the first time and 850°C for the second time. High carbonization temperature consumed large amount of energy, which in turn required high operating cost. Thus, some alternatives may come out with lower energy consumption without affect the adsorption capability of activated carbon produced.

On the other hand, nitrogen gas is not entirely necessary in carbonization process since it is very expensive. In future study, it is recommended to use muffle furnace instead of costlier tube furnace to cut down the cost of activated carbon production.

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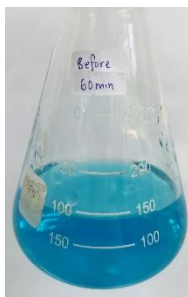
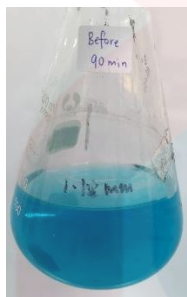
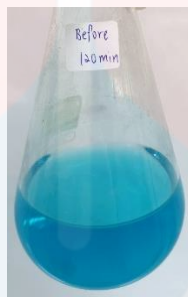
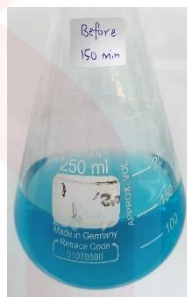
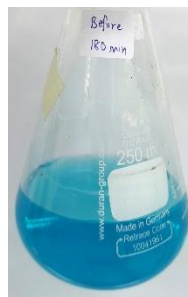
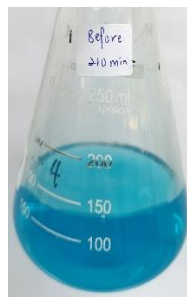
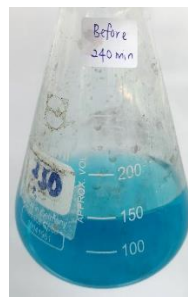
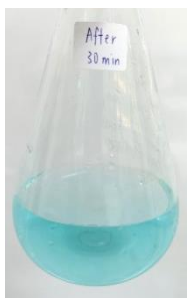

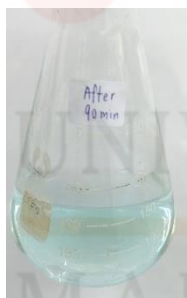

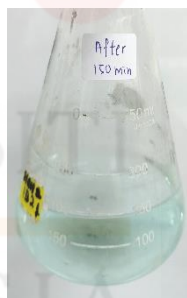
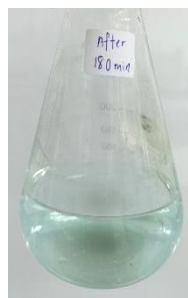


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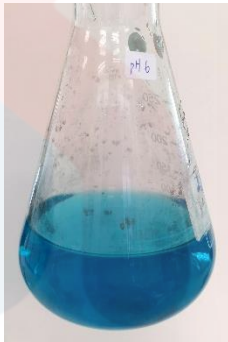

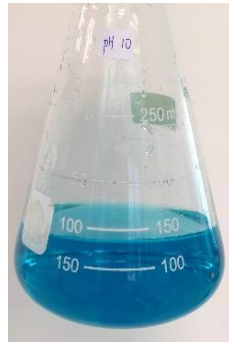

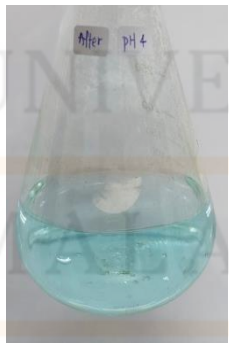

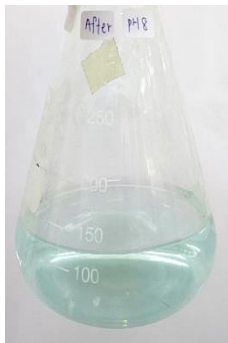

APPENDIX A

Table A-1: Optimization of Contact Time for AC 1

	Contact Time (min)							
	30	60	90	120	150	180	210	240
Before Adsorption Process								
After Adsorption Process								
Removal Percentage (%)	90.80	93.63	97.05	97.17	97.05	97.64	97.76	97.76



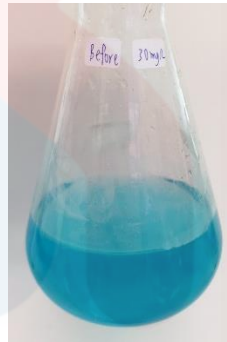


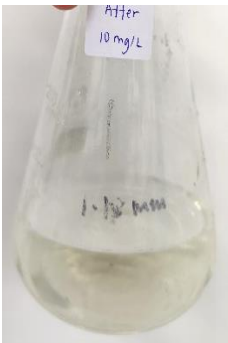
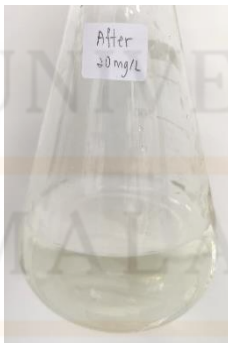


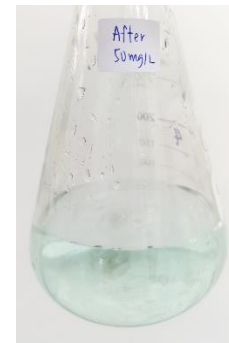
APPENDIX B

Table B-1: Optimization of pH for AC 1

	pH				
	2	4	6	8	10
Before Adsorption Process					
After Adsorption Process					
Removal Percentage (%)	49.53	97.04	98.65	99.34	99.46

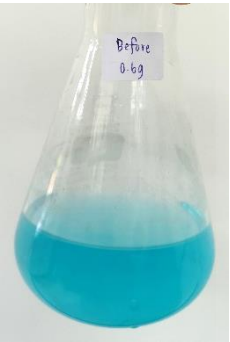

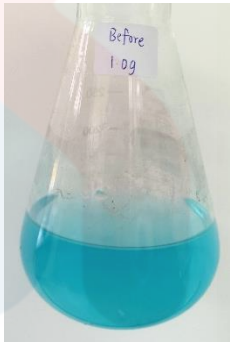
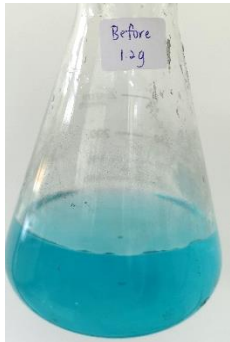
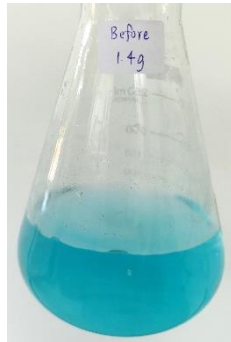


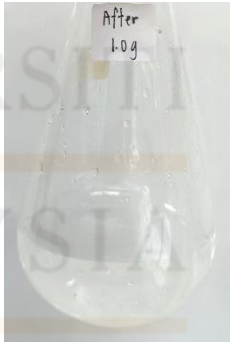
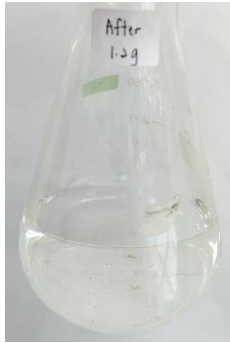
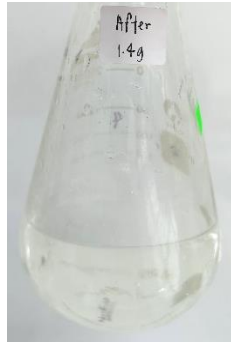
APPENDIX C

Table C-1: Optimization of Initial Concentration of Adsorbate (MG) for AC 1

	Initial Concentration of Adsorbate (MG) (mg/L)				
	10	20	30	40	50
Before Adsorption Process					
After Adsorption Process					
Removal Percentage (%)	100	100	100	100	99.59






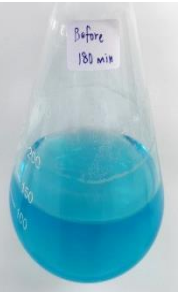
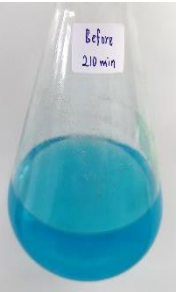





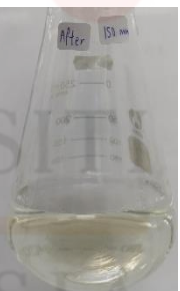


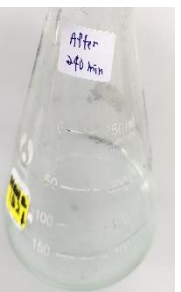
APPENDIX D

Table D-1: Optimization of Adsorbent Dosage for AC 1

	Adsorbent Dosage (g)				
	0.6	0.8	1.0	1.2	1.4
Before Adsorption Process					
After Adsorption Process					
Removal Percentage (%)	92.22	96.67	100.0	100.0	100.0

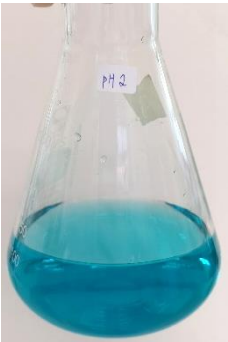

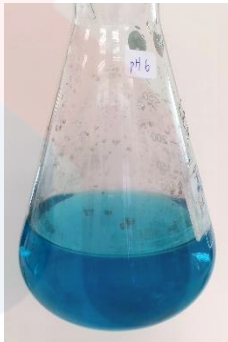

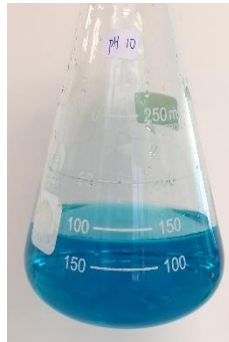





APPENDIX E

Table E-1: Optimization of Contact Time for AC 2

	Contact Time (min)							
	30	60	90	120	150	180	210	240
Before Adsorption Process								
After Adsorption Process								
Removal Percentage (%)	98.31	99.40	100	100	100	100	100	100






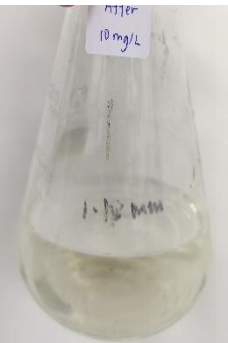


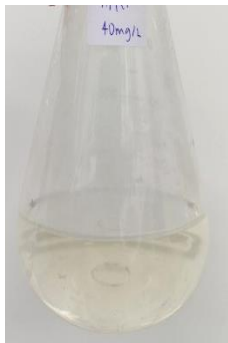

APPENDIX F

Table F-1: Optimization of pH for AC 2

	pH				
	2	4	6	8	10
Before Adsorption Process					
After Adsorption Process					
Removal Percentage (%)	86.79	97.68	99.42	99.54	100.0

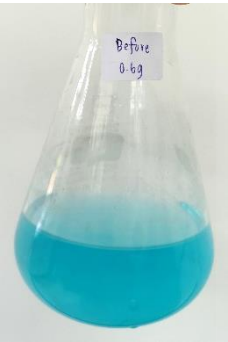

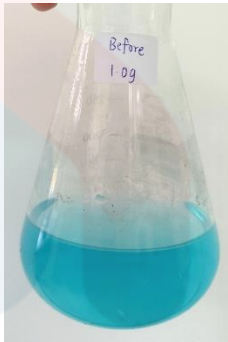
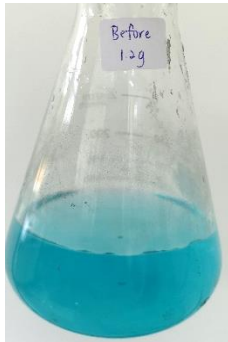
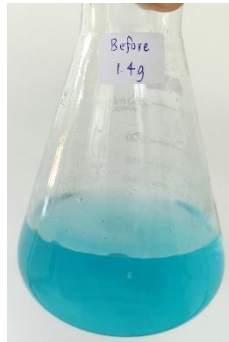



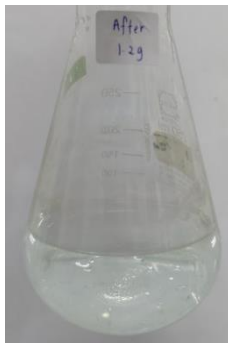

APPENDIX G

Table G-1: Optimization of Initial Concentration of Adsorbate (MG) for AC 2

	Initial Concentration of Adsorbate (MG) (mg/L)				
	10	20	30	40	50
Before Adsorption Process					
After Adsorption Process					
Removal Percentage (%)	100.0	100.0	100.0	100.0	100.0

APPENDIX H

Table H-1: Optimization of Adsorbent Dosage for AC 2

	Adsorbent Dosage (g)				
	0.6	0.8	1.0	1.2	1.4
Before Adsorption Process					
After Adsorption Process					
Removal Percentage (%)	98.86	100.0	100.0	100.0	100.0