

REMOVAL OF MALACHITE GREEN FROM AQUEOUS SOLUTION BY
USING DRIED WATER HYACINTH (*Eichhornia crassipes*)

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BORANG PENGESAHAN STATUS TESIS♦

JUDUL REMOVAL OF MALACHITE GREEN FROM AQUEOUS SOLUTION BY DRIED WATER HYACINTH (*Eichhornia Crassipes*)

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Many industries such as textile, leather tanning, paper and pulp, and food consume dyes extensively (M.Hasnain Isa *et al.*, 2007). The presence of dyes and pigments in water, even at very low concentrations, is highly visible and undesirable. It not only affects an esthetic merit, but also inhibits sunlight penetration and reduces photosynthetic action within ecosystem (Wen Cheng *et al.*, 2008).The dye under consideration is Malachite Green (MG), which is important water-soluble dye belonging to triphenylmethane family. MG is widely used to dye wool, silk, cotton, and leather materials. In agriculture, commercial fish hatchery and animal husbandry also acts as an antifungal therapeutic agent, while for human it is used as antiseptic and fungicidal.

Most of the dyes, including malachite green, are toxic and must be removed before discharge into receiving streams. Research has indicated that MG can be toxic to human cells and promotes liver tumor formation. This dye may enter into the food chain and could possibly cause carcinogenic, mutagenic and teratogenic (Wen Cheng *et al.*, 2008). MG has a complicated chemical structure it is resilient to fading on exposure to light and water. Therefore, MG is difficult to be removed from wastewaters by commonly used techniques. However, since it dissociates in aqueous solutions, it is prone to be strongly adsorbed into adsorbent such as dried water hyacinth (DWH).

There are various physical-chemical processes have been extensively used in effective treatment of the dye-containing wastewater. For example, most effective method to remove the dyes is adsorption on activated carbons which has been proven in removing dyes from aqueous solution. However, activated carbon is still considered expensive and currently the research is focused on the low-cost adsorbents for this purpose (K.Vasanth Kumar *et al.*, 2005). This process becomes economic if the adsorbent is inexpensive and does not require any expensive pretreatment. The use of biomaterials as adsorbents for the treatment of wastewaters will provide a potential alternate to the conventional treatment. Adsorption processes are being employed widely for large-scale in environmental recovery and purification applications (Mi-Hwa Baek *et al.*, 2009). As a consequence, considerable researches are recently being devoted to study the removal of dyes from aqueous solution using adsorption, chemical and also biological degradation methods.

In the present investigation, water hyacinth (*Eichhornia Crassipes*) was used as adsorption and evaluated to remove the MG dye. The water hyacinth (WH) is a free floating aquatic weed originated in Amazon in South America where it was kept under control by natural predators (Carina C. Gunnarsson *et al.*, 2007). It is found abundantly throughout the year in very large and drainage channel system and around the fields of irrigation. WH also has been listed as the most troublesome weed in aquatics systems. Recently, this plant has received attention because of its potential to remove pollutants such as heavy metals and dyes. The objective of this study was to evaluate the ability using WH for adsorption to remove MG including the effect of different parameters including adsorbent dosage, initial concentration of MG, contact time and pH of solution.

1.2 Problem Statement

Dye pollutants from various industries are an important source of environmental contaminations. Most industries use dyes and pigments to colour their products. Perhaps dyes are the serious polluters of our environment as far as colour pollution is concerned. The effluents from dye manufacturing and consuming industries are highly coloured coupled with high BOD, COD and suspended solids. The dyes are generally stable to light, oxidizing agents, heat and their presence in wastewaters offers considerable resistance to their biodegradation, and thus upsetting aquatic life. Colour affects the nature of water and inhibits the sunlight penetration into the stream and reduces photosynthetic activity. Some of the dyes are carcinogenic and mutagenic (Oaulid Hamdaoui *et al.*, 2008).

Most commercial treatment systems use activated carbon as adsorbent to remove dyes in wastewater because it has excellent adsorption ability. But its widespread use is limited due to high running cost. Many low-cost adsorbents, including natural materials waste materials from industry and agriculture have been proposed by several researches. These materials do not require any expensive additional pretreatment step and could be used as adsorbents for removal of dyes from solution (Runping Hun *et al.*, 2007). In this study, water hyacinth is chosen as adsorbent to remove the malachite green because according to K.S.Low *et al.*, 1995 the ability of WH to remove heavy metals in solution is well documented. This means that the root system could act as an adsorption medium for various materials which are soluble in water. As well known, MG is a water-soluble dye that commonly used nowadays.

Several researchers reported, water hyacinth grows and reproduces in a very high rate and is considered the worst aquatic plant. The characteristic of water hyacinth float on the water surface, blocking navigation and interfere with irrigation, fishing, recreation, and power generation. It is also prevent sunlight penetration and reduce the aeration of water, leading to oxygen deficiency, competitively exclude submerged

plants, and reduce biological diversity (Mohammad I. El-Khaiary *et al.*, 2007). Many researches have been conducted in efforts to create a use for dumped water hyacinth. This includes research on biogas generation fish feed and animal feed. In this study the waste WH, was used and evaluated as a possible adsorption for the removal of a cationic dye which is MG from aqueous solution.

In this study, dried water hyacinth (DWH) is chosen because it is environmental friendly which cannot lead to growth of mosquitoes' pest and not affect the spread of dengue fever to the residents nearby. It is also can prevent the bad odors. Another advantages using the DWH because this adsorbent easy to store and handling. Furthermore, we can reduce the space of transportation and the cost to transport itself as to commercialize this work. Based on the previous study, WH will be the good adsorbents chosen in adsorption of MG in industrial wastewater.

1.3 Objective

The objective of this study is to remove the Malachite Green from aqueous solution by using the dried water hyacinth (DWH).

1.4 Scope of Study

In order to achieve the objectives, the following scopes have been identified:

- i. Effect of dried water hyacinth dosage.
- ii. Effect of initial concentration.
- iii. Effect of pH of solution.
- iv. Effect of time.

1.3 Rationale And Significance

The purpose of this study is to remove malachite green which causes environmental and health problem because MG has complex structure that cannot be degraded or destroyed. It can cause dangerous because it can enter our bodies via food chain. In this study, we use dried water hyacinth (DWH) because there is evidence that, the weed of this plant has attracted worldwide attention due to its fast spread and congested growth.

By doing this study, we can also helps to improve the environment problems that caused by water hyacinth such as the blockage of canals and rivers that can even cause dangerous flooding. Besides that, water hyacinth is a low-cost, high efficiency of metal removal from dilute solutions and easily available material for adsorbent (Kaustubha Mohanty *et al.*, 2005). Moreover, using DWH have many advantages such as to prevent the dengue fever cause by aquatic WH and also can cut the cost of the commercialize process. WH also as a low cost adsorbent and high efficiency of removal dye in aqueous solution.

CHAPTER 2

LITERATURE REVIEW

2.1 Adsorption

2.1.1 Definition

Adsorption is a process in which atoms or molecules move from a bulk phase that is solid, liquid, or gas onto a solid or liquid surface. Adsorption is to be distinguished from absorption, a process in which atoms or molecules move into the bulk of a porous material, such as the absorption of water by a sponge. The term adsorption is most often used in the context of solid surfaces in contact with liquids and gases.

In simple terms, adsorption is the collection of a substance onto the surface of adsorbent solids. It is a removal process where certain particles are bound to an adsorbent particle surface by either chemical or physical attraction. Refer to Mohammad I.El-Khaiary *et al.*, 2007; adsorption is widely used to remove pollutants from waste water. Adsorption of dyes from wastewater has been studied before to find a suitable explanation of the mechanism and the kinetics.

Adsorption is one of the processes, which besides being widely used for dye removal also has wide applicability in waste water treatment. The term adsorption refers to a process wherein a material is concentrated at a solid surface from its liquid or gaseous surroundings. Figure 2.1, show that the attraction mechanism of adsorption process on to the medium with the present of positive and negative charge.

Gas phase adsorption is a condensation process where the adsorption forces condense the molecules from the bulk phase within the pores of adsorbent. The driving force for adsorption is the ratio of the partial pressure and the vapour pressure of the compound. The adsorption capacity for non-polar organics increases with the boiling point, molecular weight and concentration of the air contaminant. Low molecular weight (less than 50) and highly polar compounds such as formaldehyde, methane, and ethanol will not be readily adsorbed at low concentration. Liquid phase adsorption, the molecules go from the bulk phase to being adsorbed in the pores in semi-liquid state. The driving force for adsorption is the ratio of the concentration to the solubility of the compound.

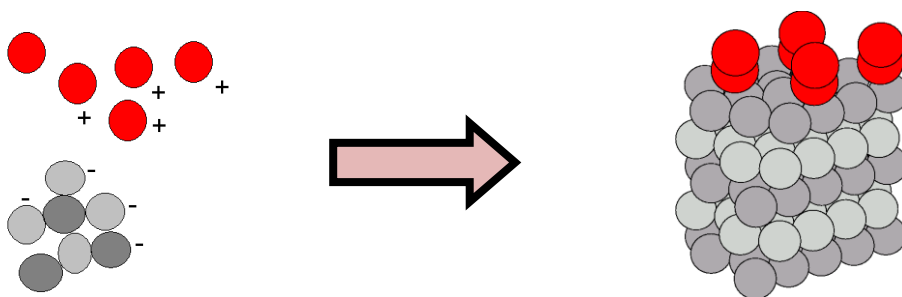


Figure 2.1: The Adsorption process.

2.1.2 Adsorbent

An adsorbent is a substance, usually porous in nature and with a high surface area that can adsorb substance onto its surface by intermolecular without changing the adsorbent physically or chemically. The most widely used adsorbent is activated carbon and usually prepared from coal, coconut shell, lignite and wood. However, this adsorbent is limited because it is expensive and hard to regenerate. Many researched have been done to produce the cheaper adsorbent to replace costly wastewater treatment methods such as chemical precipitation, ion exchange, electroflotation membrane separation, reverse osmosis, electrodialysis, solvent extraction and many others. Adsorption of low cost adsorbent is one of the physic-chemical treatment processes found to be effective in removing dyes in aqueous solution. According to Bailey *et al.*, (1999) an adsorbent can be considered as cheap or low- cost adsorbent if it is abundant in nature, requires little processing and a by-product of waste materials from waste industry.

Only at very low concentrations the adsorption isotherm linear, at higher concentrations the adsorption isotherm may be Langmuir or Freundlich in nature. Due to the fact that solutes can distribute between the adsorbent surface and a mobile phase, adsorbents are used as a stationary phases in gas-solid and liquid-solid chromatography. Adsorbents are also used for extraction purposes removing traces of organic materials from large volumes of water very efficiently. Typical adsorbents used in gas-solid chromatography are silica gel, alumina, carbon and bonded phases. These are mostly used in the separation of the permanent gases and the low molecular weight hydrocarbon gasses. Adsorbents used in liquid solid chromatography are mostly silica gel and various types of bonded phases. Adsorbents in liquid-solid chromatography have a very wide variety of application areas.

A review of the low cost adsorbent was well documented in the journal of Gupta *et al.*, 2009.

Table 2.1: List of LCAs intensively decolorizing synthetic dyes (Gupta *et al.*, 2009)

Species	Adsorbent	References
Malachite Green	Oil palm trunk fiber	Hameed and El-Khaiary <i>et al.</i> , (2008)
	AC-groundnut shell	Malik <i>et al.</i> , (2007)
	AC from pine sawdust	Akmil-Basar <i>et al.</i> , (2005)
	Sawdust carbon	Garg <i>et al.</i> , (2003)
	Neem sawdust, Sugarcane dust	Khatti <i>et al.</i> , (1999) and Singh <i>et al.</i> , (2000)
Acid blue 25	Saw dust-pitch pine	Ferrero <i>et al.</i> , (2007)
	Cane (bagasse) pith	Juang <i>et al.</i> , (2001)
	Water Hyacinth	Lee <i>et al.</i> , (1999)
Acid red 14	Soy meal hull	Arami <i>et al.</i> , (2006)
	Banana peel	Annadurai <i>et al.</i> , (2002)
	Orange peel	Annadurai <i>et al.</i> , (2002)
Acid yellow 36	Rice husk carbon	Malik <i>et al.</i> , (2003)
Methylene Blue	Fallen pheonix's tree leaves	Runphing Han <i>et al.</i> , (2007)
	Jackfruit (Artocarpus heterophyllus) leaf powder	Md. Tamez Uddin <i>et al.</i> , (2009)
	Biosolid	M. Sarioglu <i>et al.</i> , 2006
Phenol	Water hyacinth ash	M. T. Uddin <i>et al.</i> , 2007
Lead, Cadmium, Zinc, and Copper	Carbon developed from walnut, hazelnut, almond, pistachio shell, and apricot.	Maryam Kazemipour <i>et al.</i> , 2007

2.1.3 Adsorption Process

In the few years, many researchers have been done to prove that the kinetics studies have been very helpful to determine the process of adsorption. There is several equation of kinetics for adsorption can be used. It is showed that the results and graph plotted are almost all precise, undesirable and always can be interpreted easily. The most important for adsorption process to determine the mechanism of sorption for the design purpose. Generally, the adsorption dynamics is accepted to consist of the three consecutive steps:

- i. Transport of adsorbate molecules from the bulk solution to the adsorbent external surface through the boundary layer diffusion.
- ii. Diffusion of the adsorbate from the external surface into the pore of the adsorbent.
- iii. Adsorption of the adsorbate on the active sites on the internal surface of the pores.

As the general, adsorbability of a compound increased with the increasing molecular weight, a higher number of functional groups such as double bonds or halogen compounds and also increasing polarisability of the molecule. There are many studies conducted, proven that the boundary layer diffusion is the rate controlling steps in the system by dilute concentration of adsorbate, poor mixing, and small particle size of adsorbent. In addition, the interparticle diffusion controls the rate of adsorption in system by high concentrations of adsorbate, vigorous mixing and large particle size of adsorbent.

Usually, the layer diffusion is dominant at the beginning of adsorption during the initial removal, and then the rate of adsorption is regularly controlled by the intraparticle diffusion as the capacity of adsorbate has loaded the external surface of adsorbent. From the last step, adsorption is very rapid to be compare with the first two steps. For that

reason, it can be considered that the overall rate of adsorption is controlled by either the boundary layer or pore diffusion, or combining both.

Based on the previous study, the amount of dye adsorbed at time t , q_t was calculated from the mass balance equation (Q. Sun, L. Yang *et al.*, 2003):

$$q_t = \frac{(C_0 - C_t)V}{m} \quad 2.1$$

Where q_t is the amount of MG adsorbed (mg/g) at time, C_0 is the initial dye concentration in liquid phase (mg/L), C_t represents the liquid phase dye concentration at equilibrium (mg/L), V is the volume of dye solution used (L) and m is the mass of adsorbent used(g).

2.2 Water Hyacinth

The water hyacinth (*Eichhornia crassipes*) is a free-floating aquatic plant, which over the past century, has been spread around the world by human (Gopal *et al.*, 1987). Outside its native range is South America it can quickly grow to very high densities over 60 kg/m², thereby completely clogging water bodies. It has been listed as most troublesome weed in aquatic systems. When uncontrolled, the relatively high growth rate of this plant and the robustness of its seeds can disturb the aquatic ecosystem equilibrium, inducing environmental damages. It is a severe environmental and economical problem in many tropical and subtropical parts of the world. It forms dense mats that prevent river traffic, block irrigation canals.

As water hyacinth decays, there is a sharp increase in nutrient levels in water body, which ultimately creates the problem of eutrophication in aquatic system. Other effects of the fast growth are physical interference with fishing, obstruction of shipping

routes and losses of water in irrigation systems due to higher evaporation and interference with hydroelectric schemes and increased sedimentation by trapping silt particles (Carina *et al.*, 2006). Figure 2.2 shows the water hyacinth collected from Gambang Lake, Pahang.



Figure 2.2: Water Hyacinth habitat

2.2.1 Physical Characteristic

Figure 2.3 shows the common water hyacinth that consists of leaves, flowers, stems and roots. Water hyacinths are free-floating perennial plants that can grow varying in size from a few centimeters to over a meter in height (about 3 feet height). The dark glossy green, leathery leave blades are up to 20 cm long and 5 to 15 cm wide circular to elliptical in shape attached to a spongy, inflated petiole. Underneath the water is a thick, heavily branched, dark fibrous root system. The water hyacinth has striking light blue to violet flowers located on a terminal spike. Each flower has 6 bluish-purple petals joined at the base to form a short tube. One petal bears a yellow spot. The fruit is a three-celled capsule containing many minute, ribbed seeds. Water hyacinths are a very aggressive invader and can form thick mats. If these mats cover the entire surface of the pond they can cause oxygen depletions and fish kills. Water hyacinths should be controlled so they do not cover the entire pond.



Figure 2.3: Water Hyacinth aquatic plant.

2.2.2 Growth Habits

Water hyacinths regenerate prolifically from fragments of stems and the seed can remain viable for more than six years. These ways of regeneration make it very difficult to control the weed. The spreading of the water hyacinth is also thought to be enhanced by winds. The plant flourishes in nutrient-rich waters and on shallow shores with mud rich in nutrients. To estimate how much of a certain water hyacinth product can be produced, it is necessary to make approximations of how much biomass can be harvested. Thomas and Eden (2008) estimate the possible harvesting of water hyacinths to 320 ton of DM/ha (dry matter per hectare) and year. The water hyacinth mats are driven by the wind. The harvest possibilities will, therefore, depend on the local conditions and winds.

2.2.3 Environmental Impact

There are many reported of environmental impact that involving water hyacinth. As well documented by the previous studies, water hyacinth is listed as one of the most productive plants on earth and is considered one of the world's worst aquatic plants. It can double its size in 5 days and a mat of medium sized plants may contain 2 million plants per hectare that weigh 270 to 400 T. These dense mats interfere with navigation, recreation, irrigation, and power generation. Moreover, many large hydropower schemes have to devote significant time and money in clearing the weed in order to prevent it from entering the turbine and causing damage and power interruptions. The blockage of canals and rivers can even cause dangerous flooding. On the other hand, increased evapotranspiration due to water hyacinth can have serious implications where water is already scarce.

Water hyacinth can also present many problems for the fisherman such as decreased fish population, difficult access to the fishing sites and loss of fishing equipment, resulting in reduction in catch and subsequent loss of livelihood. Water hyacinth is blamed for the reduction of biodiversity as well. These mats competitively exclude native submerged and floating-leaved plants and its associated fauna, thereby causing an imbalance in the aquatic micro-ecosystem. Diversity of fish stocks is also affected. Low oxygen conditions beneath the mats create good breeding conditions for mosquito vectors of malaria, encephalitis and filariasis.

Lately the hyacinth has invaded many tropical lakes including Lake Victoria, East Africa where it caused several of the above described problems such as reduction in fish catch, interference with transportation and water supply and breeding of snails, mosquitoes and snakes. The density of snails *Biomphalaria sudanica* (hosts of the disease organism *Schistosoma mansoni*) was increased in the vicinity of water hyacinth in Lake Victoria, East Africa. In Zambia, extensive proliferation of water hyacinth in the Lower Kafue River has threatened the important economic infrastructure such as the

Kafue Road Bridge, which accounts for about 80% of Zambia's international trade through the south, and the Kafue Gorge Dam responsible for 60% of the country's hydropower requirements. Water hyacinth has apparently become a problem in different parts of the world due to its uncontrolled and rapid growth. Therefore, there is a need to manage its spread through suitable control measures.

2.2.4 Health impact

The increased growth rate of the water hyacinths has led to worsened health conditions for the people living in the affected areas. The floating water hyacinth mats can serve as a breeding ground for vector organisms carrying malaria, *bilharziosis* and river blindness. At some places precautions against water snakes, hippos and crocodiles need to be taken. The water hyacinths consume so much oxygen when decaying that it leads to less oxygen remaining in these waters. The decreased oxygen content in the water leads to less oxygen in the fish. This combined with fewer algae and other food sources for the fish cause the meat of the fish to go bad faster than before. Decreased possibility to store fish leads to lower income and food security.

This means that decreasing the amount of water hyacinths could hopefully improve the health situation. When working in water hyacinth infested areas, one of the problems is the risk of catching waterborne diseases, in the case of Lake Victoria especially *Schistosomiasis*. The problem is that the snails that serve as a host for the *bilharzia* parasites are very likely to be found in water hyacinths. If drying the water hyacinths is to be a successful way of eliminating the risk of catching bilharzias depends on if the water hyacinth can be harvested without snails.

2.2.5 Chemical Composition

Fresh plant contains 95.5% moisture, 0.04% N, 1.0% ash, 0.06% P_2O_5 , 0.20% K_2O , 3.5% organic matter. On a zero-moisture basis, it is 75.8% organic matter, 1.5% N, and 24.2% ash. The ash contains 28.7% K_2O , 1.8% Na_2O , 12.8% CaO , 21.0% Cl , and 7.0% P_2O_5 . The CP contains, per 100 g, 0.72 g methionine, 4.72 g phenylalanine, 4.32 g threonine, 5.34 g lysine, 4.32 g isoleucine, 0.27 g valine, and 7.2 g leucine (Matai and Bagchi, 1980). Water hyacinth roots naturally adsorb pollutants, including such toxic chemicals as lead, mercury, and strontium 90 (as well as some organic compounds believed to be carcinogenic) in concentrations 10,000 times that in the surrounding water.



Figure 2.4: Water Hyacinth

2.2.6 Harvesting

Harvesting the water hyacinths means a mechanical control of growth. Presently, the water hyacinths are only harvested to control their propagation where chemical or biological (e.g., introduction of water hyacinth eating insects) methods are prohibited or

unsuccessful. This is, according to Petrell and Bagnall 1991, because mechanical harvesting is too expensive and time-consuming. The advantages of mechanical control of water hyacinths are, according to Verbandt *et al.*, 1990:

- i. The removal of superfluous nutrients.
- ii. The immediate result without damage to the ecosystem.
- iii. Waterbodies can be used more widely (e.g., for irrigation of agriculture areas and drinking water supply).
- iv. Mechanical methods are possible in open flowing as well as in closed water systems.

Another advantage of harvest is that it makes it possible to use the water hyacinths in, for example, agricultural practice. A weed screen cleaner with continuously moving rakes is being developed in Belgium. The plan is to construct a back-raked screen that is mobile by being mounted on a converted military amphibian (Verbandt *et al.*, 1990). Another possibility might be to use agricultural harvesting machinery such as conveyor belts. In the Philippines they are reported to use barges with some kind of hand powered winch when harvesting open water hyacinths (Thore ´n *et al.*, 1997).

2.3 Malachite Green (MG)

Malachite green (MG) is an *N*-methylated diaminotriphenylmethanedyne, (CI= 42,000) is a dark green and crystalline solid prepared by condensing one part of benzaldehyde with two parts of diemethylaniline in the presence of concentrated sulphuric acid or zinc chloride. Malachite green is available in a number of forms, mainly as the oxalate or hydrochloride salt in a minimal 50% solution as a mixture of acetate and hydrochloride salts. Malachite green hydrochloride is an industrial grade variety which, during its manufacture, is precipitated by the addition of zinc chloride

and is, therefore, produced as a double zinc salt. This dye, like other triphenylemethanes, can exist in two ionic forms- as the dye salt and as the carbinol or pseudobase. Figure 2. 4 shows the Malachite Green purchased from Sigma Aldrich that used in this study.

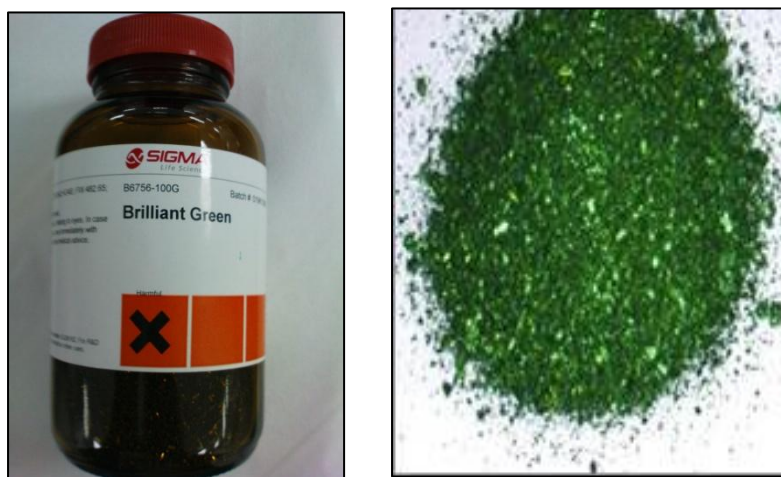


Figure 2.5: Malachite Green dye.

The chemical structure for malachite green shows in the table 2.2 and Figure 2.56 with the characteristic identification of MG.

Table 2.2: Identification of MG

Dye	Commercial name	IUPAC name	λ_{max}	Molecular wieght
Malachite green	Basicgreen, anilinegreen, fastgreen, Brilliant Green.	N-[4-[[4-(dimethylamino)-phenyl]phenylmethylene]-2,5-cyclohexadien-1-ylidene]-N-methylmethanaminium chloride	618	364. 92

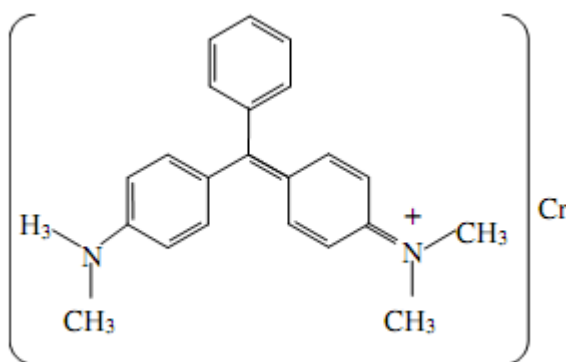


Figure 2.6: Chemical structure of MG

2.3.1 Toxicological effect of Malachite Green.

Malachite green is environmentally persistent and acutely toxic to a wide range of aquatic and terrestrial animals. It cause serious public health hazards and also poses potential environmental problem. Both clinical and experimental observations reported so far reveal that malachite green is a multi-organ toxin. Desciens and Bablet (1994) found renal changes in rabbit following repeated oral dosing of this dye. It decreases food intake, growth and fertility rates causes damage to liver, spleen, kidney and heart in flicts lesions on skin, eyes, lungs and bones and produces teratogenic effects in rats and mice. Apoptosis in the transitional epithelium of the urinary bladder and thyroid follicles was also observed in MG fed mice (Culp *et al.*, 1999). Clemmensen *et al.*, (1984) observed no systemic effects in rats following dermal application of the dye. However, long-term (28days) treatment with malachite green results in prominent weight loss and change in serum urea and aspartate aminotransferase levels in rats

Malachite green has been found to be mutagenic in rats and mice, and it causes significant developmental abnormalities in pregnant New Zealand white rabbits. It also produces chromosomal derangement in chironomid larvae and fruit fly. Malachite green is highly cytotoxic to mammalian cells (Fessard *et al.*, 1999) and carcinogenic to liver, thyroid and other organs of experimental animals (Sundarrajan *et al.*, 2000). Incidences

of tumours in lungs, breast and ovary have also been reported from rats exposed to malachite green. In the thyroid gland, leucomalachite green results in blockade of hormone synthesis, decreases T4 and increases TSH concentrations and causes tumors in thyroid follicle cells of rats.

2.3.2 Uses of Malachite Green

MG has been extensively used as a topical fungicide and ectoparasiticide in fish farming throughout the world. In African aquaculture, it has been used against infection by bacteria, protozoans, cestodes, trematodes, nematodes, crustaceans. MG also large used to prevent outgrowth of oomycete fungi on fish and fish eggs, both as a post infection therapy and prophylaxis. It was found to be the most effective fungicide among 49 compounds tested against a no oomycete fungus (S.Srivastava et al., 2004).According to Diggles *et al.*, 2001it has prevented the growth of Haliphthoros on rock lobster and salmon. Saprolegniasis has also been effectively controlled by MG in salmons channel catfish and rainbow trout. Aphanomyces invadis and Aspergillus flavus infection in Channa and some other fish have also been treated effectively with MG. Eggs of Cyprinus carpio and tench have been treated prophylactically to prevent fungal infection

CHAPTER 3

METHODOLOGY

3.1 Introduction

The purpose of this study is to understand and analyzed result according to the ability of water hyacinth to remove Malachite Green (MG) from aqueous solution and to study the effect of adsorbent dosage, initial concentration, pH of aqueous solution and time contact of adsorption of MG. The method use for this experiment was according to previous study done by Kaustubha Mohanty *et al.*, 2006. The experiment was conducted start from the preparation of adsorbent of dried water hyacinth, where the water hyacinth was randomly collect locally, wash thoroughly with water for several times to remove earthy matter and all the dirt particles, cut, dried, grind to obtain a fine powder and then it was stored at dry places. Next step is preparing the stock solution of MG dye solution. The MG stock solution is prepared by dissolving crystal MG in distilled water. This study was continued with the experiment to investigate the optimum condition for removing MG from aqueous solution with parameter dosage of adsorbent, initial concentration, and pH and time contact.

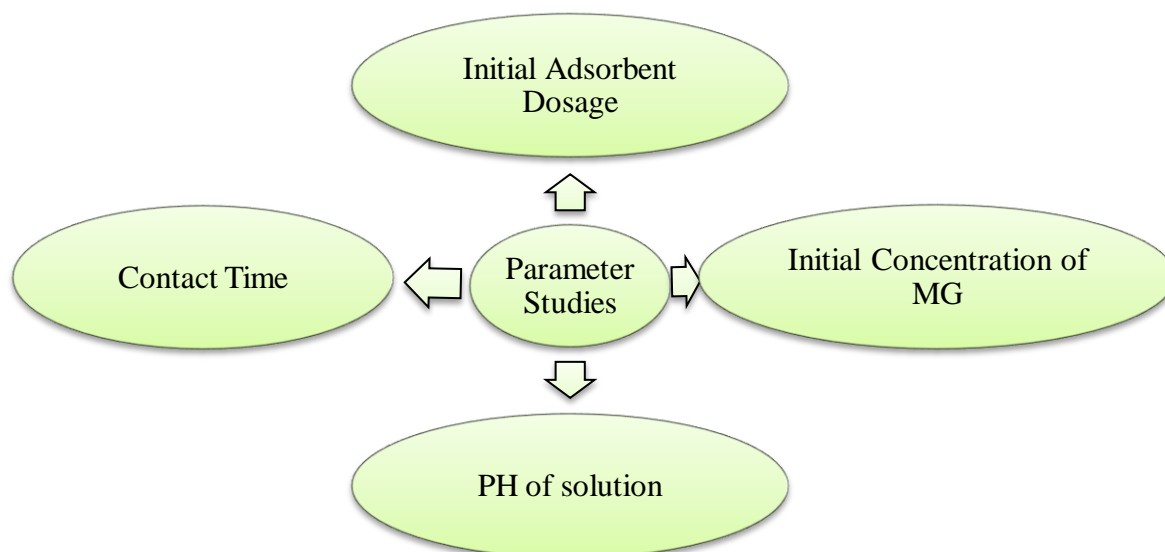


Figure 3.1 : Scope of Study

3.2 Equipments/Apparatus

In completing the study, some equipment is required. There are:

1. Oven (Memmert)
2. Fourier Transform Infra Red (FTIR)
3. UV-vis Spectrometer
4. Laboratory Blender
5. pH meter
6. Electric Balance Shimadzu
7. Conical Flask
8. Beaker
9. Orbital Shaker.

3.3 Reagents

In completing the study, some equipment is required. There are:

1. Adsorbent (Dried Water Hyacinth)
2. Malachite Green
3. Distilled water
4. 0.1M Sodium Hydroxide (NaOH)
5. 0.1M Hydrochloric Acid (HCl)

3.4 Adsorbent preparation

Water hyacinths were collected from Gambang Lake, Pahang. They were washed thoroughly with tap water to remove dirt and chopped into small pieces for ease of drying. It was then oven dried at 60°C to remove moisture. The dried samples were crushed and blended using dry blender into powder, then sieved to desire particle sizes of 45 μm and preserve in dry container for use. No further chemical or physical treatments prior to adsorption experiments.

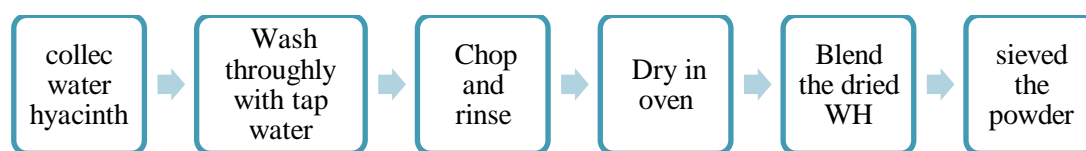


Figure 3.2 : Process flow for preparation dried water hyacinth



Figure 3.3 : Dried water hyacinth

3.5 Adsorbate preparation

The dye, MG (C.I =42000) has chemical formula, $C_{23}H_{26}N_2Cl$ with molecular weight 364.92 was supply by Sigma Aldrich Malaysia. The stock solution (1000 mg/L) of MG was prepared by dissolving accurately weihgt amount of the dye in distilled water. All working solution of the desired concentration were obtained by diluting the stock solution with distilled water. Figure 3.3 shows the stock solution of MG for this experiment.



Figure 3.4: Stock solution for Malachite Green.

3.6 Experimental Procedure

3.6.1 Effect of initial concentration.

For this parameter, different conical flasks containing 50 mL of MG solution with different initial concentration was prepared. The initial dye concentration of 20 to 100 mg/L was in conjunction with DWH sample of 0.2, 0.6 and 0.8 g. Contact time and pH were constantly at 120 minutes and 6, respectively. By using 0.1 M HCl and 0.1 M NaOH, the pH value of solution was adjusted. The conical flasks were sealed using aluminium foil and placed on the orbital shaker for 60 minutes shaking at 250 rpm. After that, the sample centrifuge for 30 minutes to separate the adsorbent with the dye. The supernatant were analyzing using UV-Vis spectrometer.

3.6.2 Effect of adsorbent dosage

For studying the effect of adsorbent dose, 0.1 to 1.0 g of DWH dosage was used with the initial concentration varied from 50 to 100 mg/L. All the other parameters were constant, at pH 6 and contact time 120 minutes. Flasks of sample were sealed using aluminium foil and shaken by using orbital shaker at 250 rpm. After centrifuging the sample, the supernatant was analyzed by using UV-Vis spectrometer. The adsorbent dosage was varied to observe the pattern of results obtained for optimum initial concentration. The value of optimum initial concentration is used for further parameters.

3.6.3 Effect of pH

The initial pH of solution was adjusted from pH 2 to 12 by using 0.1 M HCl and 0.1 M NaOH at different values of adsorbent dosage and initial concentration near the optimum condition obtained from previous experiments. This is done to observe the similar patterns of results for optimum pH value. The contact time is fixed at 120 minutes.

3.6.4 Effect of contact time

The effect of contact time is investigated for 20 to 160 minutes at pH 6 and at different values of adsorbent dosage and initial concentrations near their optimum values. The similar pattern of results for the optimum value is obtained.

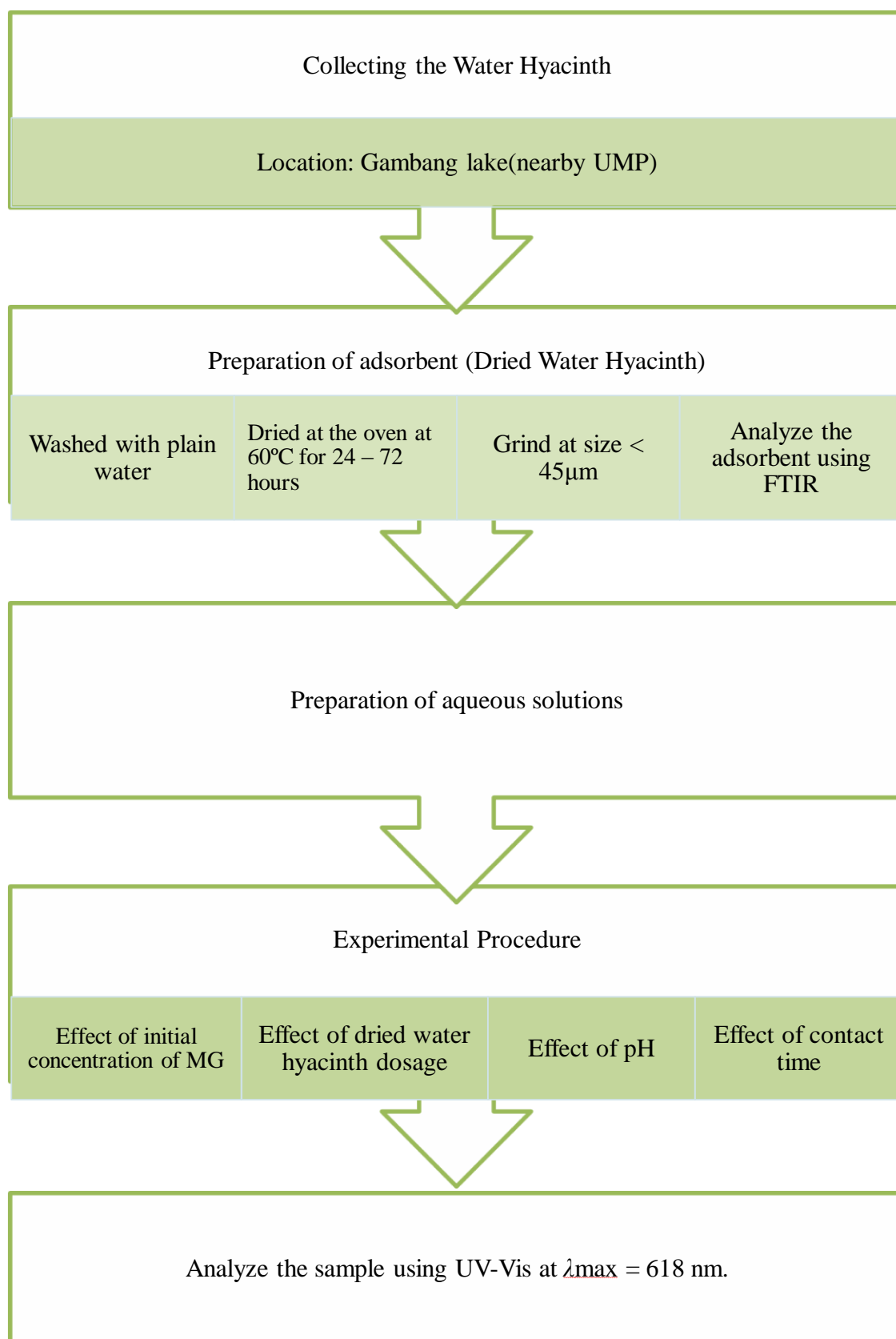


Figure 3.5: Flowchart of methodology

3.7 Analysis

The analysis was done by using the UV- Vis spectrometer (Model U-1800, Hitachi). Before doing the analysis, the standard MG solution was prepared to make the standard curve. The standard solution was prepared using distilled water.

3.8 Fourier Transform Infrared spectroscopy (FTIR)

Infrared spectral data obtained from Nicolet Avatar 370 DTGS spectrometer was utilized to determine the interaction between DWH with malachite green at room temperature. For this reason, powder of adsorbent was prepared. DWH and MG loaded were prepared at the optimum condition. The infrared spectra in the range $4000\text{-}400\text{cm}^{-1}$ were recorded.

CHAPTER 4

RESULT & DISCUSSION

4.1 Effect of Adsorbent Dosage

The effect of adsorbent dosage on the adsorptive removal of MG by DWH is shown in figure 4.1. In order to investigate the effect of initial dosage of adsorbent by using DWH, a series of adsorption experiments were conducted with different amount of adsorbent dosage range from 0.2g to 1.0 g while keeping the other parameters constant ($C_0=50\text{mg/L}$, $\text{pH}=6$, $\text{time}=60\text{ min}$). It was observed that the amount of MG adsorbed varied with varying amount of adsorbent dosage.

Result from the experiment shows that figure 4.1 (a) the percentage removal of MG increasing until it reached 0.6 g DWH dosage, the percentage considerably constantly. The optimum dosage was found to be 0.6 g as the percentage dye removal was 94.6%. Dye removal increase from 82.3% to 96.8% as the DWH dose was increased from 0.2g to 1.0g, however, figure 4.1(b) shows that the adsorption amount per unit mass of DWH decreased from 20.6 mg/g to 2.4 mg/g. The same pattern of result for this parameter was also show in the previous study done by J.Zhang *et al.*, 2008 by using *Arundo donax* root as the adsorbent.

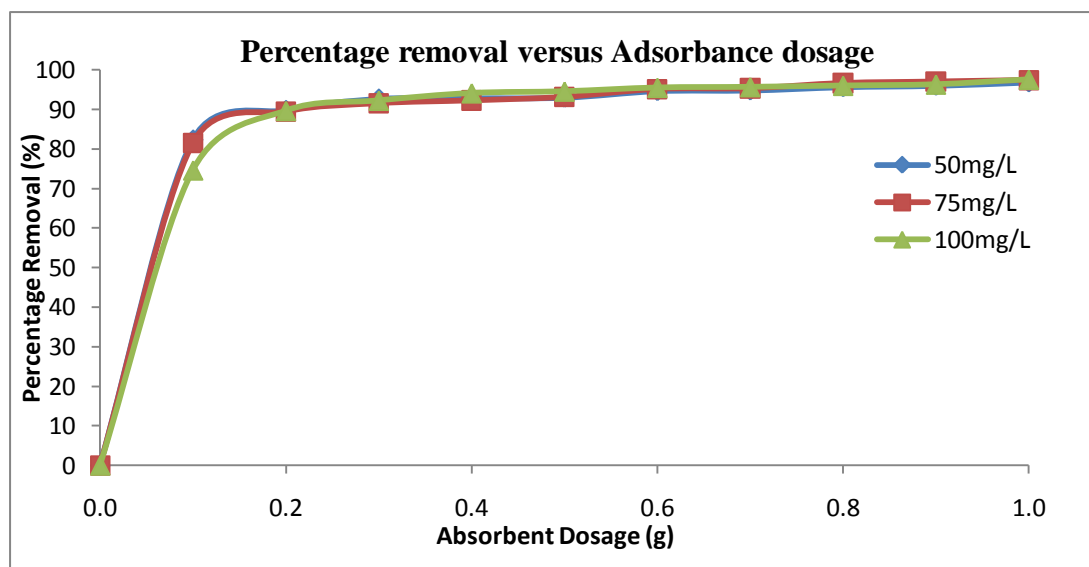


Figure 4.1 (a) : Effect of adsorbent dosage on removal percentage of MG by DWH. Speed shaker= 250 rpm, time=60 minutes, pH=6, dosage range=0.2g-1.0g, C_0 =50mg/L, 75MG/L, and 100mg/L

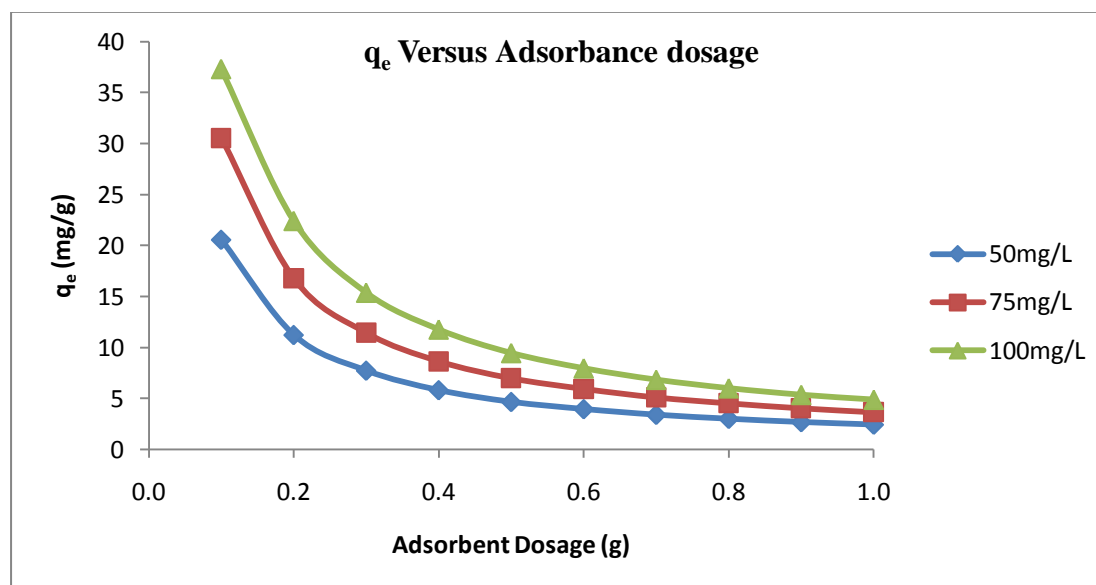


Figure 4.1 (b) : Effect of adsorbent dosage on adsorption per unit mass of MG by DWH. Speed shaker= 250 rpm, time=60 minutes, pH=6, dosage range=0.2g-1.0g, C_0 =50mg/L, 75MG/L, and 100mg/L.

As can be seen, adsorption of MG increased with increasing the amount of DWH and remained almost constant after increasing up to a certain limit. This can attributed to increased adsorbent surface area and availability of more adsorptions site (J.Zhang et al., 2008). For the adsorption amount per unit mass of DWH result decrease may be due to the decrease in total adsorption surface area available to MG resulting from overlapping or aggregation of adsorption sites in simple word, explain that the adsorbate were achieve the saturated condition. So that, the decrease in adsorption density with increase in adsorbent dose is mainly because of unsaturation of adsorption sites through the adsorption process (Ozacar and Sengil,2005;Yu et al., 2003; R.Malik et al., 2007).

The experiment was carried out by varying the value of initial concentration ($C_0=75\text{mg/L}$ and 100 mg/L) with other parameter remains constant. The purpose of this experiment to observe the pattern of percentage removal of dye. It is shown that the result of this pattern MG uptake is increased and decreased in adsorption per unit mass with increasing value of initial dosage of DWH as an adsorbent. The optimum value of initial adsorbent dosage can be determined to be at 0.6 g of DWH dosage.

4.2 Effect of Initial Concentration

The effect of initial concentration on the adsorptive removal of MG by dried water hyacinth (DWH) is shown in figure 4.2. The experiment conducted by varying the initial concentration of MG from range 20mg/L to 100mg/L . The other parameters keep constantly, ($\text{pH}=6$, $\text{time}=60\text{ min}$, $\text{speed shaker}=250\text{ rpm}$) at optimum adsorbent dosage 0.6 g . From the result of experiment, it can be observed that unit adsorption increased while the percentage removal can be considerable decreased with the increase in initial concentration of MG. The percentage removal of MG from 84.2% to 95.5% while the optimum initial concentration can be determine at 60 mg/L with the percentage uptake 96.4% . The result for dye adsorb per unit mass (mg/g) increasingly. The MG ions around adsorbent sites of adsorbent became much more with the increase

of initial MG concentration. Hence, the adsorption process was carried out more sufficient resulting in the increase of unit adsorption.

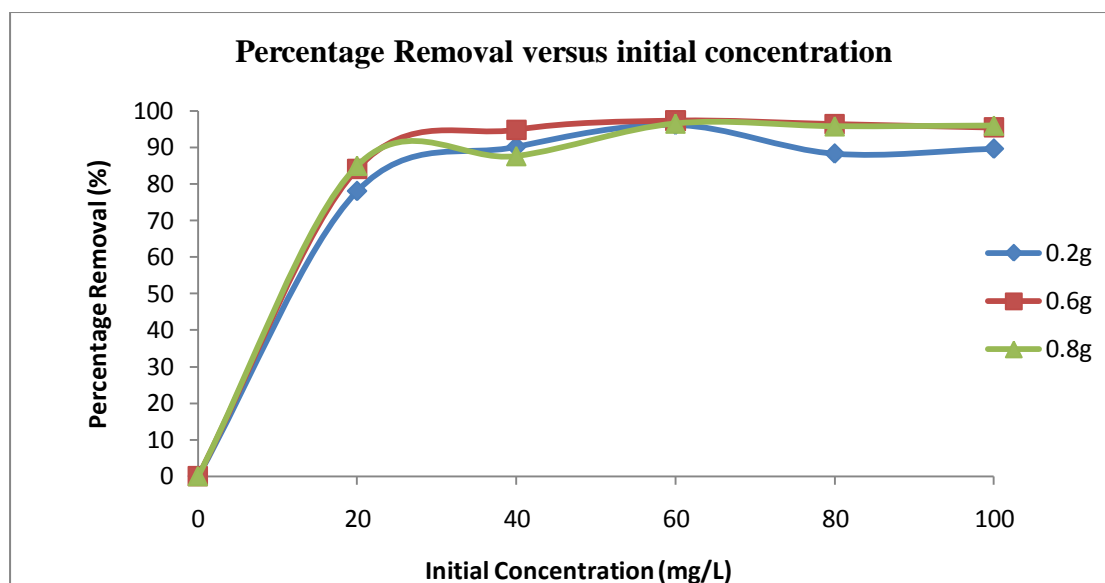


Figure 4.2 (a) : Effect of initial MG concentration on removal percentage of MG by DWH. Speed shaker= 250 rpm, time=60 minutes, pH=6, dosage=0.2g, 0.6g, 0.8g, $C_0=20\text{mg/L}$ to 100mg/L .

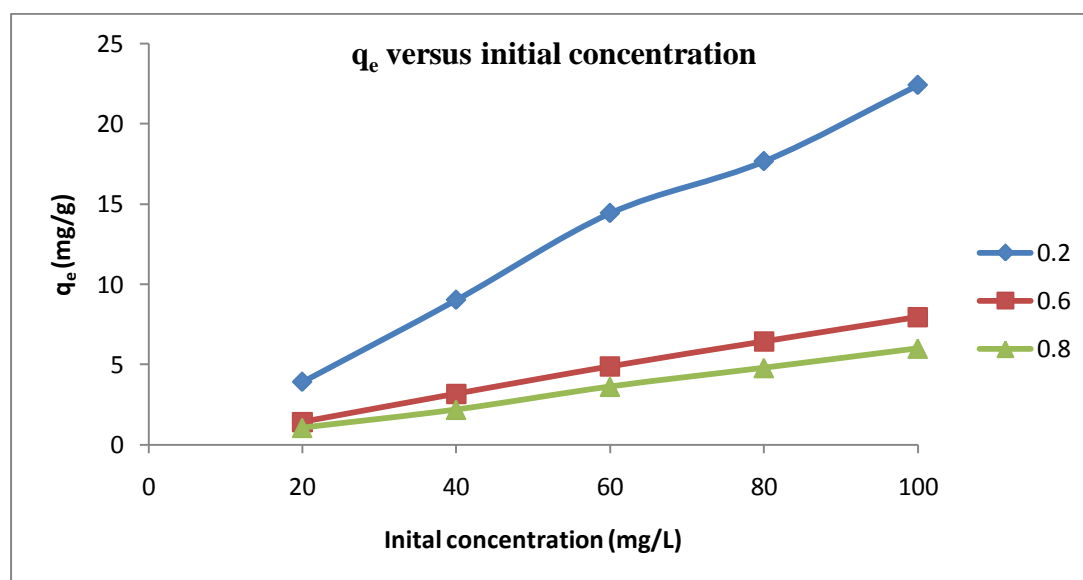


Figure 4.2 (b) : Effect of initial MG concentration on adsorption per unit mass of MG by DWH. Speed shaker= 250 rpm, time=60 minutes, pH=6, dosage=0.2g, 0.6g, 0.8g, $C_0=20\text{mg/L}$ to 100mg/L .

The increasing percentage of removal from lower initial concentration to the high concentration may be due to the stronger interactions between MG with DWH. The higher initial concentration of dyes provides an increasing driving force to overcome all mass transfer resistance of dyes between aqueous and solid phases. Moreover, it can accelerate the probable collision between dyes ion and adsorbent which result in higher dyes uptake. While the decrease in percentage adsorption at initial concentration 80mg/L may be because of lack of sufficient surface area to accommodate much more MG available in the solution. The percentage adsorption at higher concentration levels can considerably shows a decreasing trend whereas the equilibrium uptake per unit mass of MG displays on opposite trend. At lower concentration, all MG ions present in solution could interact with the binding sites, thus the percentage adsorption was higher than those at higher MG concentration. At higher concentration, lower adsorption yields are due to the saturation of adsorption site. This result also supported by previous study, that using rattan sawdust by B.H Hameed *et al.*, 2008.

The experiments were repeated at 0.2g and 0.8g of adsorbent dosage to show the pattern of result of dye uptake. The result of each graph show that the optimum initial concentration of MG can be determine at 60 mg/L. this may be can considered as the optimum condition for the removal of dye by using the dried water hyacinth.

4.3 Effect of pH

The effect of solution pH on the adsorptive removal of MG by using DWH is shown in figure 4.3. The experiment carried out at the optimum condition of initial adsorbent dosage (0.6 g), initial concentration ($C_0=60\text{mg/L}$) with the time (60 min) and the speed shaker at 250 rpm. As is known, pH can affect the structural stability of MG and therefore, its colour intensity (J.Zhang *et al.*, 2008). Based on the result obtain the colour of MG was found to be stable over the pH range of 4-7. This value also same with the previous research of J.Zhang *et al.*, 2008 in journal of hazardous material.

Dye removal by DWH was minimum at pH 3 (79.8%), which increased to 98.4% at pH 6. As it known, MG dye is the cationic dyes, the expected result of removal should be increased as the pH value increased. The DWH surface may contain large number of active sites and the MG uptake could be related to the active sites. At pH increase from range 1- 7, the percentage removals also increase. The maximum percentage is 98.4% at pH 6. This can be the optimum value for pH condition to remove the MG. while, at pH 8 to 12 the percentage of removal is decrease. As the initial solution pH increased, the number of negatively charge active sites increased and positively charged sites decreased. Therefore, the electrostatic repulsion between the absorbent site and positively charged dye cation was lowed, which may result in the increase of the adsorption. Also, lower adsorptive removal of MG at acidic pH was due to the presence of excess hydrogen ion competing with MG cation for adsorption.

In this study, the experiment repeated for 2 other trial to show the pattern of the result. The initial concentration of dye was varying to 80mg/L and 100 mg/L with the same optimum dosage 0.6 g of DWH. Based on the results, it shows the pattern of same result of the optimum value of pH solution at pH 6.0 .

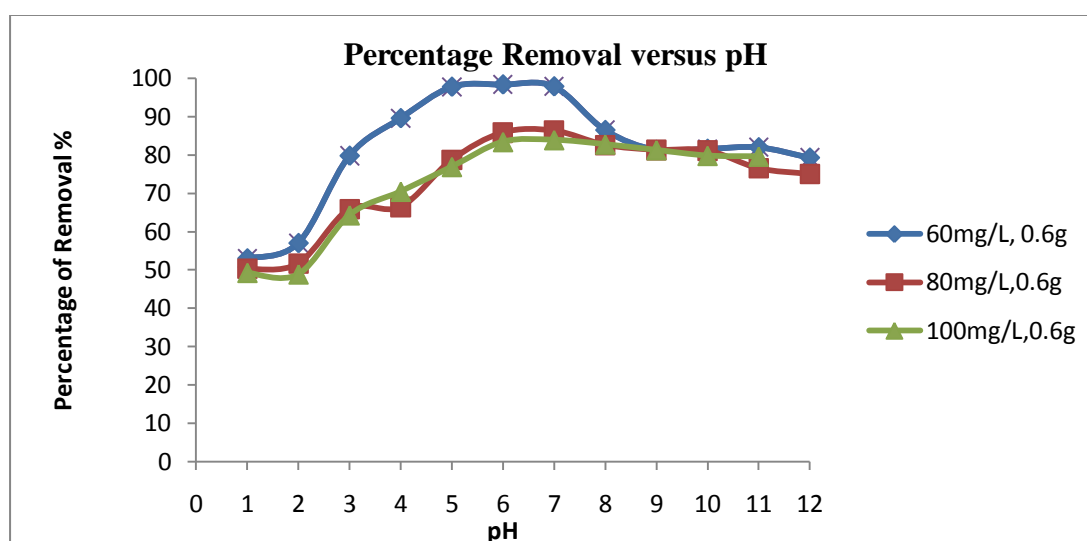


Figure 4.3 (a) : Effect of pH on removal percentage of MG by DWH. Speed shaker= 250 rpm, time=60 minutes, pH range =2.0-12.0, dosage=0.6 g, C_0 =60 mg/L,80 mg/L, 100mg/L

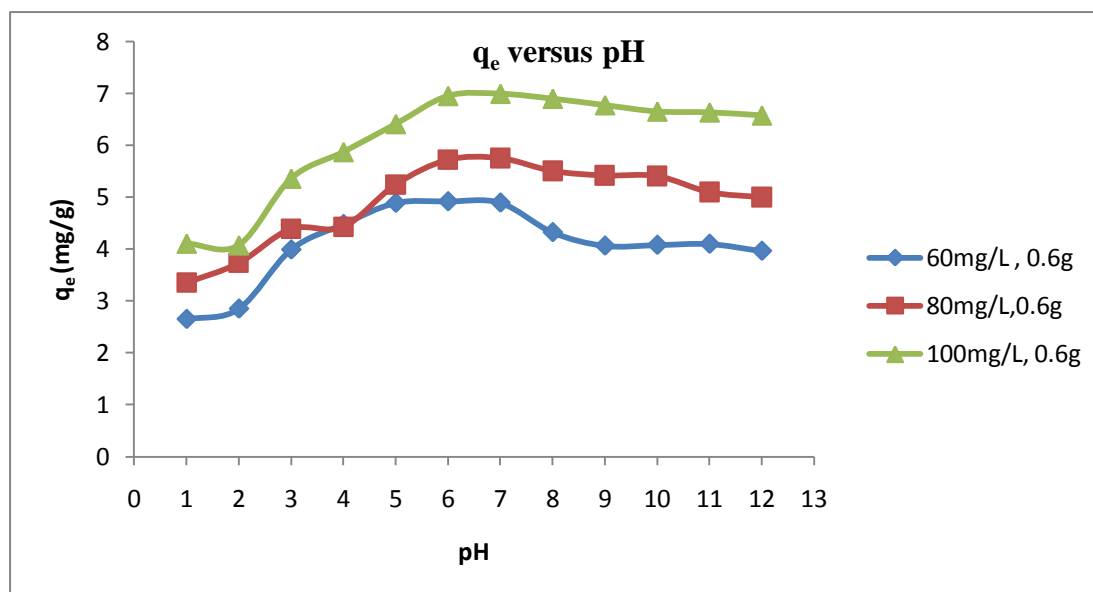


Figure 4.3 (b) : Effect of pH on adsorption per unit mass of MG by DWH. Speed shaker= 250 rpm, time=60 minutes, pH=6, dosage=0.2g, 0.6g, 0.8g, C_0 =20mg/L to 100mg/L.

The adsorption efficiency increased when the solution pH varied from 2 to 7. Little improvement was obtained above neutrality. As it is well established, pH affects the degree of ionization of the MG compounds. DWH material is composed of various functional groups, such as hydroxyl group and carboxyl, which could also be affected by the pH. When $\text{pH} = \text{pK}_a$, the anion and neutral forms will be 50% respectively. With the increase of the pH, the anion form increases while neutral form decreases. The neutral form can be neglected when $\text{pH} > \text{pK}_a$ more than 2 units. At higher pH values the concentration of the negatively charged increases. At lower pH values, the compounds are present as the acidic compounds. As shown in figure 4.3 (a), at low pH values, the rate of the sorbed MG compounds was very low. At higher pH, the adsorption increased and stabilized from pH 5 to 6. Thus high elimination of MG compounds in aqueous solution is achieved in a large pH zone. From a practical point of view, this will be of great interest, since it will not necessitate very accurate adjustment of the medium pH.

4.4 Effect of Time Contact

The percentage of MG removal as a function of time is shown in figure 4, with the optimum condition of initial concentration (60mg/L), initial dosage of DWH (0.6g), speed shaker (250 rpm) and pH at 6. The time contact varying in the range 20 min- 160 min. Based on the result obtain, the dye consider constantly percentage removal at 60- 160 minutes. It can be explain that the uptake of dye by adsorbent increase when the time increase until it reach equilibrium state. At the 60 minutes of time contact the dye uptake is 94% and the percentage continue with small change in percentage. While, the uptake of dyes per mass is 4.74 mg/g for this concentration. The experiments were conducted for more trials of initial concentration (80mg/L and 100mg/L) to show the pattern of dyes removal. The others parameter were constant as previous condition. As shown in the figure 4.4, the same curve obtained where the percentage increase when the time increase until it reach equilibrium state.

From then graph of the percentage of MG removal, it is show that the dye uptake rapidly at 1 minute to 40 minute, this is because the adsorption activity takes place at the outer surface of the adsorbent. The adsorption activities continue slower rate until achieve the saturated condition. This will be explain clearly that at the some point in time, when the amount of dye being adsorbed onto adsorbent was equal to the amount dyes being desorbed from adsorbent, the adsorption process reached a dynamic equilibrium and the adsorption amount remained approximately a constant.

The contact time necessary to reach equilibrium is about 60min. At this point, the sorbed amount of dye by DWH is in a state of dynamic equilibrium with the amount of the dye desorbing from the adsorbent. Additionally, the curve of contact time is single, smooth, and continuous leading to equilibrium. This curve indicates the possible monolayer coverage of dye on the surface of DWH.

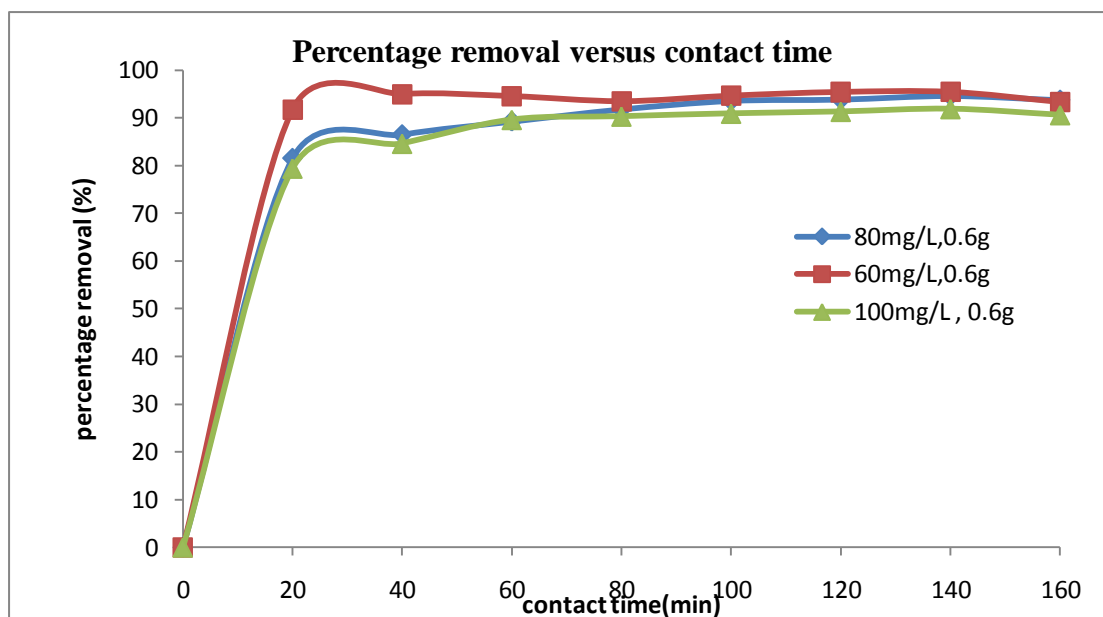


Figure 4.4 (a) : Effect of time contact on removal percentage of MG by DWH. Speed shaker= 250 rpm, time range =20-160 minutes, pH range =6.0 dosage=0.6 g, C_0 =60 mg/L, 80 mg/L, 100mg/L

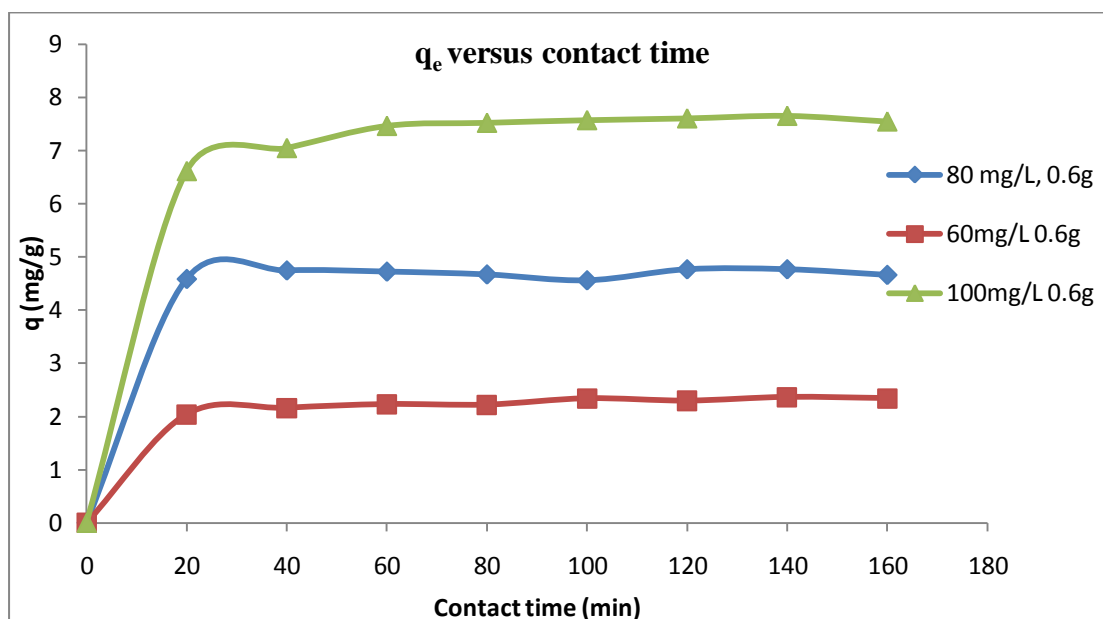


Figure 4.3 (b) : Effect of contact time on adsorption per unit mass of MG by DWH. Speed shaker= 250 rpm, time range =20-160 minutes, pH=6, dosage=0.6 g C_0 =20mg/L, 80 mg/L, 100mg/L.

4.5 Adsorption Isotherms

Various isotherms such as Freundlich, Langmuir, Dubnin–Radushkevich (D–R), Redlich-Peterson(R–P) and Temkin isotherm have been used to describe the equilibrium characteristics of adsorption in order to design the adsorption system and evaluate the applicability of sorption process. In this study, two most common isotherms, namely the Freundlich and Langmuir isotherm, were applied to analyze the adsorption equilibrium experimental data. The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. It based on the assumption of a heterogeneous surface with interaction between adsorbed molecules and a non uniform distribution of adsorption heat over the surface. The Freundlich isotherm equation is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \quad 4.1$$

where q_e is the amount of dye adsorbed at equilibrium(mg/g), C_e the equilibrium dye concentration in solution(mg/l), K_F the Freundlich constant((mg/g)(l/mg)^{1/n}) and $1/n$ is the heterogeneity factor which are related to the capacity and intensity of the adsorption, respectively. The linear form of Freundlich isotherm equation is

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad 4.2$$

Therefore, the values of K_F and $1/n$ can be obtained from the slope and the intercept of the plot of $\ln q_e$ versus $\ln C_e$.

Langmuir isotherm assumes that sorption occurs at specific homogenous sites within the adsorbent and the capacity of the adsorbent is finite. The equation of Langmuir is represented as follows:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad 4.3$$

Where q_m is monolayer adsorption capacity (mg/g), K_L is Langmuir isotherm constant related to the affinity of the binding sites and energy of adsorption (l/mg). A well-known linear form of Langmuir equation is written as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad 4.4$$

Therefore, the values of q_m and K_L can be calculated by plotting C_e/q_e versus C_e . The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L [36], which is defined by

$$R_L = \frac{1}{1 + K_L C_0} \quad 4.5$$

Where C_0 is the initial dye concentration (mg/l) and K_L is Langmuir isotherm constant (l/mg). The R_L values indicate the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

Figure 4.4 and figure 4.5 shows the plots of $\ln q_e$ versus $\ln C_e$ and the plots of C_e/q_e versus C_e for the adsorption of MG onto DWH according to the linear forms of Freundlich and Langmuir Isotherm. The constants value calculated from the linear forms of the two isotherms are given in the Table 4.1 below.

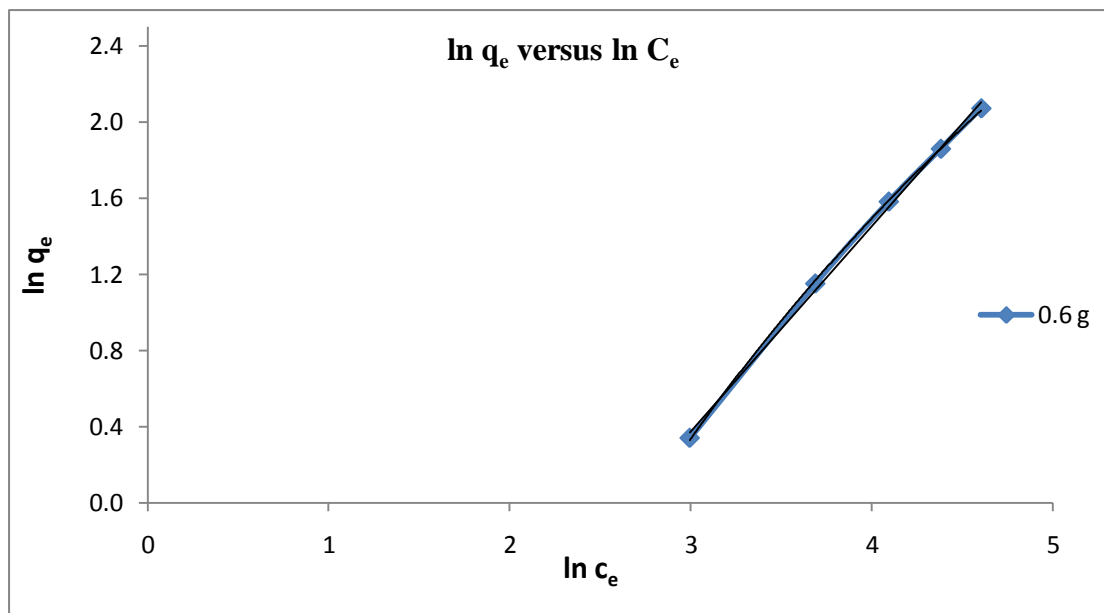


Figure 4.4: Freundlich isotherm using linear method for MG onto DWH ($C_0 = 20, 40, 60, 80$ and 100 mg/L, DWH dosage 0.6 g/50ml, pH=6, $t = 120$ min)

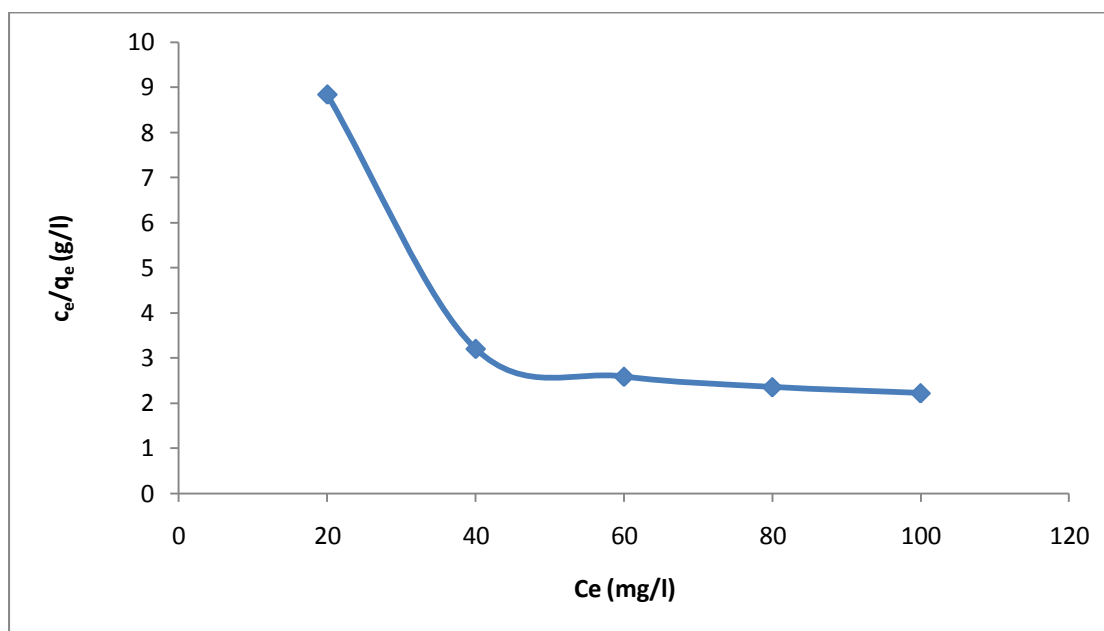


Figure 4.5: Langmuir isotherm using linear method for MG onto DWH; ($C_0 = 20, 40, 60, 80$ and 100 mg/L, DWH dosage 0.6 g/50ml, pH=6, $t = 120$ min)

Table 4.1: Isotherm parameters obtained by using linear method for the adsorption of Mg onto DWH.

Freundlich Isotherm Constant	
$K_F [(mg/g)(l/mg)^{1/n}]$	0.664
$1/n$	4.0277
R^2	0.9979
Langmuir Isotherm Constant	
q_m	14.184
K_L	0.123
R_L	0.119
R^2	0.9991

From the Table, the values of $1/n$ were found to be less than 1 indicating that the adsorption was favorable. This patent of results also reported in the previous study by J.Zhang *et al.*, 2008. The R_L value in the range 0-1 also confirmed the favorable adsorption uptake of dye process. Based on the value of R^2 calculated, it shows that the Freundlich Isotherm and Langmuir Isotherm with 0.9979 and 0.9991 respectively. The fact that Langmuir isotherm fits the experimental data very well suggest the monolayer coverage of MG onto DWH surface as well as the homogeneous distribution of active sites on the DWH surface. The assumption for the linear isotherm of Langmuir that the surface is homogeneous.

4.6 Fourier Transform Infrared study

Fourier Transform Infrared analysis was run to confirm the type of functional groups of the water hyacinth. For the FTIR study, finely ground biomass before treatment was used to prepare the translucent sample disks. The FTIR spectra of the native biomass displays a number of absorption peaks, indicating the complex nature of the biomass examined.

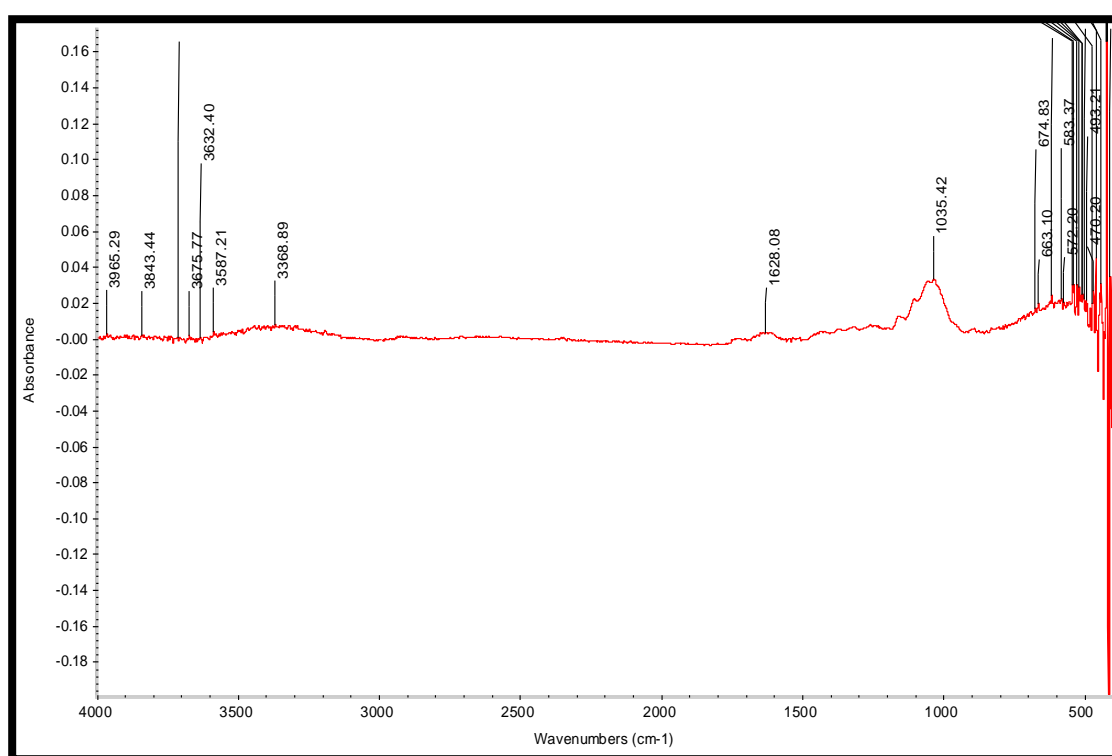


Figure 4.6: Fourier Transform Infra Red spectra of DWH before adsorption

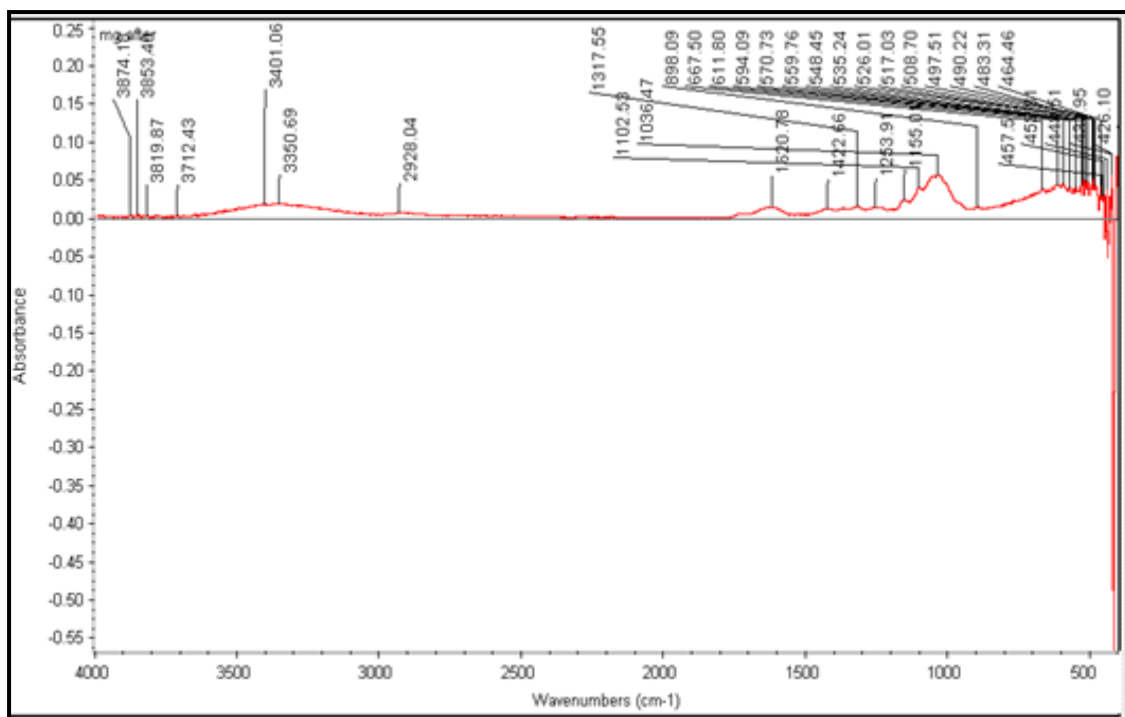


Figure 4.7: Fourier Transform Infra Red spectra of DWH-MG after adsorption

The FTIR of DWH before and after adsorption were shown in figure 4.6 and 4.7 respectively. The wide band at 3368.89 cm^{-1} shown in the spectrum of DWH is attributed to vibration of hydroxyl group of DWH. This band has shifted to 3350.69 cm^{-1} when MG was adsorbed. It may indicate a hydrogen bond between MG and -OH groups of DWH. The bands observe at 1628.08 cm^{-1} corresponds to N-H bending vibration. After adsorption process, these bands were shifted from 1628.08 cm^{-1} to 1620.78 cm^{-1} . It can be claimed that hydrogen bonding occurs between nitrogen and hydrogen of DWH and MG. As was indicated by Paulino *et al.*, 2008. From the spectrum, the band at 1035.42 cm^{-1} shows the vibration of C-O group and was shifted after process to 1036.47 cm^{-1} . There were a small different value and can be said that no interaction occurs between C-O groups of DWH with MG cation.

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 Conclusions

Detailed study on this paper has been carried out to investigate the performance of water hyacinth as adsorbent for removal of basic dyes, Malachite Green. Result and analyses obtained in this study proven that the adsorption process of Malachite green in aqueous solution using dried water hyacinth is successful. From the data collected, percentage of removal can be increased by adjustment of the parameter studied which are adsorbent dosage, initial concentration of dyes, pH solution and contact time. From result, it is shows that the optimum conditions to uptake the unwanted dyes were as follow, the initial dosage for removal process was 60 mg/L at the initial dosage of adsorbent 0.6 g. The optimum pH solution was at 6 and the time contact was at 60 minutes.

Based on the results obtained from the experimental, it proved that the DWH was good adsorbent to remove the MG from wastewater and also can be replace the conventional treatment methods because it was low cost adsorbent (LCAs), high efficiency of dye removal and can be applicable for industrial. As the results shows, there was some point of decreasing while it should increase as the expected due to some errors that might be had been occurs during the experiment such as contamination from

the equipment used. There were also some errors during the measuring of reading and preparing the sample.

In addition, the process is environment friendly and reduces the huge amount of indiscriminate effluent discharges around the small industry concerns. It may provide an affordable technology for small and medium scale industry. Thus, the biomass of water hyacinth (*Eichhornia Crassipes*) has the potential to be used as an ecofriendly and economic adsorbent material for the removal of MG from aqueous solution.

5.2 Recommendation

As recommendation for future study, we should consider this experiment of the removal continue by running it in an adsorption column. This can consider the adsorption process same as the industrial treatment. We also should be continue to run this experiment by using the industrial waste water such as textile, leather, silk and wool industry.

As reported by previous study on title “Kinetic studies for Ni (II) biosorption from industrial wastewater by *Cassia fistula* (Golden Shower) biomass”, the sorption equilibrium reached much faster in case of industrial wastewater samples in comparison to synthetic wastewater using same adsorbent. This variation was due to the presence of others ions in case of industrial effluents which were absent in case of synthetic wastewater. Due to presence of greater number of metal ions in industrial wastewater, the sorption equilibrium was reached much faster due to faster occupancy of sorption sites by metal ions. Relatively, in improving the efficiency of adsorption process, further study can use the actual waste water that taken from industries or stream but not synthetic wastewater such as aqueous solutions that were used in this study.

In order to develop better and effective process in removing dyes such as MG it is suggested to use smaller size of the adsorbent. According to the study by Muahammad Riaz and friends, it is evident that, smaller the granular size of adsorbent, larger the adsorption capacity (q). This also supported by statement from C.K Singh that indicated the smaller the particle size, the greater the rate of diffusion and adsorption. Intra-particle diffusion is reduced as the particle size reduces, because of the shorter mass transfer zone, causing a faster rate of adsorption. Likewise, to attain a better result it is suggested that the adsorbent should be used according to its particle sizes. This is because; the difference of particle sizes contributes to the inconsistency of the binding sites and pore distribution. It is best to consider the effects of a variety of dried water hyacinth particle sizes hence the sorption activity can be investigated at its optimum surface texture of the sorbent. With a constant condition of DWH surface, the results obtained are ensured to be at its best effectiveness value.

REMOVAL OF MALACHITE GREEN FROM AQUEOUS SOLUTION BY USING
DRIED WATER HYACINTH (*Eichhornia Crassipes*)

RUWAIDA BINTI AWANG

A thesis submitted in fulfillment
of the requirements for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang

APRIL 2010

I declare that this dissertation entitled “*Removal of Malachite Green from Aqueous Solution by Using Dried Water Hyacinth (Eichhornia Crassipes)*” is the result of my own research except as cited in the references. The Dissertation has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature :
Name : RUWAIDA BINTI AWANG
Date :

Special Dedication of This Grateful Feeling to My...

Beloved mother;

Mrs. Ramlah Binti Salleh

Loving brothers and sisters;

*Muhammad Wafi Akramin, Zamri & Ainun Azura, Muhammad Taqiuddeen &
Azmah, Syazwani, Mohammad Faiz and Muhammad Mustaqim.*

Adorable niece & nephew;

Zahra Aneesa and Zariff Akhmal

Understanding and helpful friends;

For Their Love, Support and Best Wishes.

ACKNOWLEDGEMENT

Assalamualaikum w.b.t....

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First and foremost, I wish to express my sincere appreciation to my Undergraduate Research Project supervisor, Madam Jun Haslinda Bt Hj Shariffuddin for her encouragement, guidance, critics and motivation. I am also very thankful to all my lecturers that directly or indirectly involves in this thesis for their guidance, and support. Without their motivation, this thesis would not have been same as presented here.

Special acknowledgement and grateful to all my family members for their support, understanding and encouraging throughout my research and study at University Malaysia Pahang (UMP). Also, special thanks to my special friend that always be with me all the time and for an invaluable support.

My sincere appreciation also extends to all my colleagues and others who have provided assistance at various occasions. Thank you for believing in me and helping me weather through my stormy weathers. The experiences and knowledge we gained throughout the process of completing this study would prove invaluable to better suit me for the challenges which lie ahead. Their views and tips are useful indeed. Unfortunately, it is not possible to list all of them in this limited space.

ABSTRACT

This paper shows a detailed study to investigate the potential of water hyacinth as adsorbent, to remove Malachite Green from aqueous solution and to identify the optimum condition for the parameter involved. There were four parameters that have been studied in this paper, they were effect of adsorbent dosage, effect of initial concentration of dye, effect of pH and effect of time contact. It was found that the optimum dosage for the adsorbent at initial dye concentration of 60 mg/L was 0.6 g, the optimum pH was at 6 and the optimum time contact was at 60 minutes for initial concentration 60 mg/L. At the optimum condition the removal of malachite green was increased as the initial concentration was increased. The optimum adsorption of malachite green was occurred at pH basic because the pH dependence of dye uptake could be related to functional group of the adsorbent and also to solution chemistry. The dye uptakes were analyzed by using UV-Vis Spectrometer. The result proved that dried water hyacinth is a good adsorbent to remove malachite green from waste water because it is economically feasible and high efficiency of dye removal from dilute solutions and also applicable for industrial.

ABSTRAK

Kajian ini dilakukan untuk mengkaji keupayaan keladi bunting sebagai penjerap untuk menyingkirkan Malachite Green dari larutan akuas dan untuk mengenalpasti keadaan optimum bagi faktor penghad yang terlibat. Terdapat empat faktor penghad yang telah dikaji iaitu kesan dos penjerap, kesan kepekatan awal, kesan pH dan kesan masa bersentuhan. Telah didapati bahawa dos yang optimum bagi penjerap pada kepekatan awal 60 mg/L ialah 0.6g, keadaan yang optimum bagi pH ialah pada pH 6 dan masa yang optimum ialah pada 60 minit untuk kepekatan awal 60 mg/L. Pada keadaan yang optimum penyingkiran Malachite Green meningkat apabila kepekatan awal meningkat. Penjerapan untuk Malachite Green berlaku pada pH alkali kerana kebergantungan pH untuk menyingkirkan adalah berkait dengan kumpulan berfungsi penjerap dan juga dengan larutan kimia. Hasil kajian membuktikan bahawa serbuk keladi bunting adalah penjerap yang baik untuk menyingkirkan Malachite Green dari air buangan kerana efektif dari segi ekonomi dan kecekapan penyingkiran pewarna yang tinggi dari larutan cair dan juga boleh digunakan untuk industri.

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LIST OF ABBREVIATION

MG	Malachite Green
WH	Water Hyacinth
DWH	Dried Water Hyacinth
FTIR	Fourier transform infra red
HCL	Hydrochloric Acid
NaOH	Sodium Hydroxide
rpm	Revolution per minutes
Ppm	part per million
LCAs	low cost adsorbents
mg/L	milligrams per liter
DM/ha	dry matter per hectare
q _e	uptake capacity
μ	Micro
g	Gram
L	Liter
m	Meter
⁰ C	Degree Celcius

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APPENDIX A

Apparatus/ Material



Figure A.1: Blender to blend water hyacinth to a smaller particle



Figure A.2: Fourier Transform Infra Red (FT-IR) to determine the functional group of water hyacinth

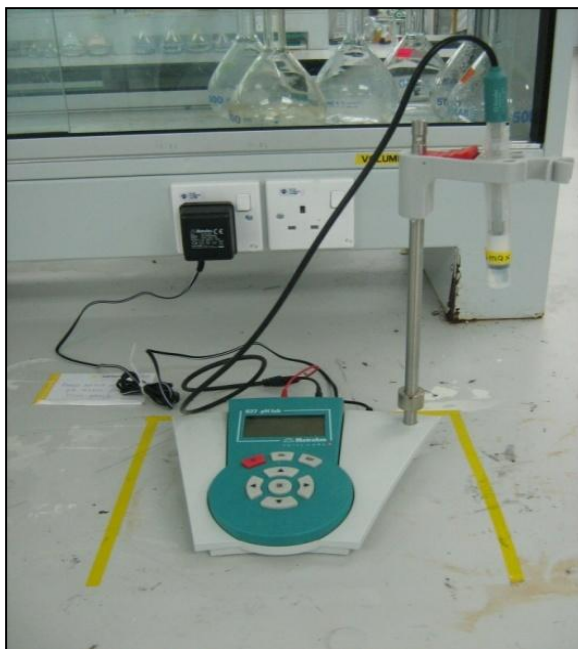


Figure A.3: pH Meter to adjust pH of the solution

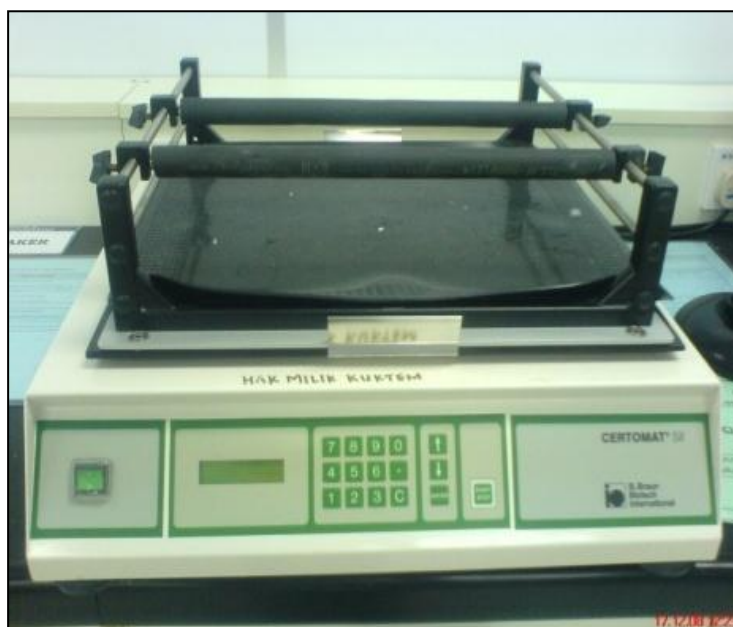


Figure A.4: Orbital Shaker for mixing the solution



Figure A.5: Oven to dry the water hyacinth



Figure A.6: UV-Vis Spectrophotometer for analysis of sample



Figure A.7: Refrigerated centrifuge to separate the supernatant



Figure A.8: Analytical balance to weight dye and DWH



Figure A.9: Dried water hyacinth



Figure A.10: Malachite Green/Brilliant Green

APPENDIX B

Methodology



Figure B.1: Preparation of Adsorbent

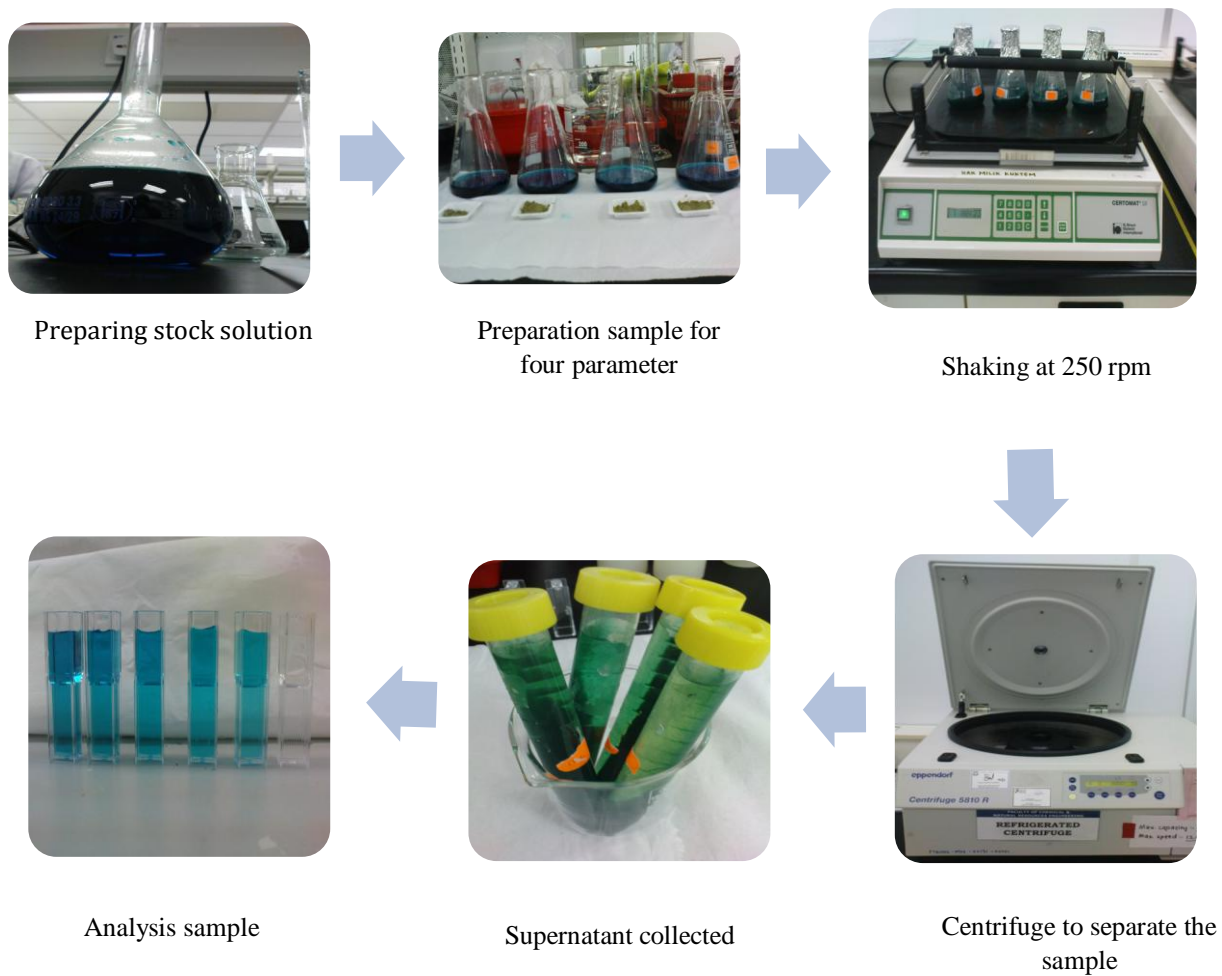


Figure B.2: Experimental procedure

APPENDIX C

Result

Table C.1: Result for Effect of Adsorbent Dosage

Dosage (g)	Removal (%)		
	50 mg/L	75 mg/L	100 mg/L
0.1	82.25	81.45	74.59
0.2	89.71	89.43	89.61
0.3	92.60	91.53	92.21
0.4	92.62	92.24	94.08
0.5	92.80	93.13	94.52
0.6	94.59	95.12	95.47
0.7	94.67	95.30	95.63
0.8	95.58	96.61	95.97
0.9	95.93	96.99	96.29
1.0	96.78	97.38	97.53

Table C.2: Result for Effect of Initial Concentration

Initial Concentration (mg/L)	Removal (%)		
	0.2 g	0.6 g	0.8 g
20	78.02	84.19	84.98
40	90.13	94.87	87.62
60	96.14	97.37	96.53
80	88.27	96.42	95.78
100	89.61	95.47	95.97

Table C.3: Result for Effect of pH

pH	Removal (%)		
	60 mg/L	80 mg/L	100 mg/L
1	53	50	49
2	57	52	49
3	80	66	64
4	90	66	70
5	98	79	77
6	98	86	83
7	98	86	84
8	86	83	83
9	81	81	81
10	82	81	80
11	82	77	80
12	79	75	79

Table C.4: Result for Effect of Contact Time

Time (min)	Removal (%)		
	30 mg/L	60 mg/L	100 mg/L
20	81.53	91.76	84.59
40	86.48	94.97	89.59
60	89.23	94.53	90.29
80	88.85	93.47	90.89
100	93.57	91.26	91.30
120	91.85	95.41	91.86
140	94.60	95.42	90.60
160	93.72	93.29	99.57

Table C.5: Equilibrium adsorption data for effect of adsorbent dosage

Dosage (g)	q _e (mg/g)		
	50 mg/L	75 mg/L	100 mg/L
0.1	20.56	30.54	37.2
0.2	11.21	16.77	22.40
0.3	7.72	11.44	15.37
0.4	5.79	8.65	11.76
0.5	4.64	6.98	9.45
0.6	3.94	5.95	7.96
0.7	3.38	5.11	6.83
0.8	2.99	4.53	5.99
0.9	2.67	4.04	5.35
1.0	2.42	3.65	4.88

Table C.6: Equilibrium adsorption data for effect of adsorbent dosage

Initial Concentration (mg/L)	Removal (%)		
	0.2 g	0.6 g	0.8 g
20	3.90	1.40	1.06
40	9.01	3.16	2.19
60	14.42	4.87	3.62
80	17.65	6.43	4.79
100	22.40	7.96	5.99

Table C.7: Equilibrium adsorption data for effect of pH

pH	q _e (mg/g)		
	60 mg/L	80 mg/L	100 mg/L
1	2.65	3.35	4.11
2	2.85	3.45	4.07
3	3.99	4.41	5.36
4	4.48	4.43	5.87
5	4.89	5.24	6.41
6	4.92	5.72	6.95
7	4.89	5.75	6.99
8	4.32	5.51	6.89
9	4.07	5.42	6.77
10	4.08	5.41	6.65
11	4.09	5.10	6.63
12	3.96	4.99	6.57

Table C.8: Equilibrium adsorption data for effect of contact time

Time (min)	q _t (mg/g)		
	30 mg/L	60 mg/L	100 mg/L
20	2.04	4.59	7.05
40	2.16	4.75	7.47
60	2.23	4.73	7.52
80	2.22	4.67	7.57
100	2.34	4.56	7.61
120	2.29	4.77	7.66
140	2.37	4.77	7.55
160	2.34	4.66	8.29