BIOSORPTION OF METHYLENE BLUE FROM AQUEOUS SOLUTION USING DRIED WATER HYACINTH *(Eichornia crassipes*)

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SESI PENGAJIAN : 2008/2009

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NURUL SHAREENA AQMAR BTE MOHD SHARIF

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
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MAY 2009

DECLARATION

I declare that this thesis entitled “biosorption of methylene blue from aqueous solution using dried water hyacinth *(Eichornia crassipes*)” is the result of my own research except as cited in 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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Date	: 23th April 2009

DEDICATION

Special dedication to my beloved, Syahid for his never lack of love, kindness, supports and motivations, also to both my parents for their prayers and inspirations, my supervisor, my fellow friends, and everyone involved.

For all your love and care, I thank you and overwhelmed with gratitude.

ACKNOWLEDGEMENT

Praise be to Allah S.W.T for his help and guidance that finally I am able to complete this undergraduate research project as one of my requirement to complete my study.

First and foremost I would like to extend my deepest gratitude to all the parties involved in this research. A special thank you to my supervisor Mdm. Jun Haslinda binti Haji Shariffuddin for her time and dedications in guiding me throughout the research work right from the beginning until the end of it. All her advices and comments are most precious and bring nothing but perfection to the outcome of this research project.

Also, a thousand of appreciation to all my lecturers in the Faculty of Chemical and Natural Resources Engineering (FKKSA), for their help and support during this project development.

Not forgetting, to all my fellow friends, thank you for believing in me and helping me through the difficult times. The knowledge and experiences I gained along the process of completing this project would prove to be invaluable for the better to guide me for the challenges that lies ahead. And last but never the least to all my family members, I can never thank you enough for your love and prayers, and supporting me throughout my studies in University Malaysia Pahang.

ABSTRACT

In this study, dried water hyacinth (DWH), an abundant and freely available plant is proposed as a biosorbent for the biosorption of Methylene Blue (MB) dye from aqueous solutions. The effects of the biosorbent dosage, initial concentration, pH and contact time were studied in a batch experiments at room temperature (± 27^{o}C). Results show that the optimum condition is at 0.55g, 80 mg/L, pH 7.0 and 90 minutes of contact time, respectively. The functional group on the DWH surface is analyzed as well to observe the availability of binding sites for the sorption. Samples of MB after the uptake are analyzed with UV-Vis spectrophotometer. Langmuir adsorption isotherm model is used for the mathematical description to describe the biosorption equilibrium process and the maximum sorption capacity is determined to be 19.61 mg/g. The study is economically feasible and it is proven to be favorable. Also, water hyacinth is a potentially plant to be an effective biosorbent for the uptake of MB.

ABSTRAK

Keupayaan keladi bunting, tumbuhan akuatik terbiar dan mudah diperoleh telah dikaji sebagai agen bio-penjerap dalam memisahkan atau menjerap pewarna *Methylene Blue* dari larutan dalam skala makmal. Pengaruh jumlah dos agen bio-penjerap, kepekatan awal larutan pewarna, pH dan masa telah dikaji dalam eksperimen ini. Data paling optima yang diperolehi adalah 0.55 g, 80 mg/L, pH 7.0 dan 90 minit penggunaan, setiap satu. Kesemua kepekatan akhir larutan dianalisa menggunakan UV-Vis Spectrophotometer. Langmuir model telah dipilih untuk menerangkan proses penjerapan dari segi pengiraan matematik dan nilai jerapan maksima adalah 19.61 mg/g. Kajian ini telah terbukti bahawa penggunaan serbuk keladi bunting sebagai agen bio-penjerap adalah efektif dari segi ekonomi dan penggunaannya.

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LIST OF ABBREVIATIONS

DWH -	Dried water hyacinth
MB -	Methylene blue
Pb -	Lead
Cd -	Cadmium
U -	Uranium
Cu -	Copper
Zn -	Zinc
Cr -	Chromium

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Dyes are extensively used in many industries including printing processes, textile, plastics, cosmetics, etc. to add color for their final products. Most of the unspent dyes generate undesirable effluents and usually will be discharged to the environment with or without treatment. There are over 100,000 available dyes with more than 7 x 105 tonnes of dyestuff produced annually (X.S. Wang et al., 2008). Approximately 2% of dyes produced are discharged in effluent from manufacturing operations while 10% are discharged in effluent from textile and associated industries (X.S. Wang et al., 2008). The textile industry contributes about 22% of the total volume of industrial wastewater generated in the country (B.H. Hameed et al., 2008). The release of dyes into waters by industries is undesirable and causes serious environmental problems. It contains various organic compounds and toxic substances which are hazardous and harmful to aquatic organisms. The colored waste water in the receiving streams reduces the light penetration through the water's surface and therefore, reduces photosynthesis activity (Weisburger, 2002).

There are several techniques of removal of dyes from waste water. Some of them are, by flotation, precipitation, oxidation, filtration, coagulation, ozonation, supported

liquid membrane, and also biological process (A.S. Mahmoud et al., 2007). Meanwhile, a new and more environmental friendly method, the biosorption process is proven to be a promising process to remove dyes from effluent. It is stated by D.J Ju et al. in his research on 2006, biosorption is also known as the uptake or accumulation of chemicals by biomass. This process is similar to adsorbent process which it is cost-effective, easy to operate, simply designed and insensitivity to toxic substances. In this study, Methylene Blue (MB), known as strong adsorptions into solid, will be used as the biosorbate. MB is an important basic dye widely used for printing cotton and tannin, and dyeing leather. Even though it is not strongly hazardous, MB can cause harmful effects to human and other living organisms. Too much exposed of MB can cause eye burns and causes irritation to the skin.

Activated carbon is well known as the most widely used adsorbent and proven to be effective for removal of dye due to its large surface area, micro-porous structure, high adsorption capacity, etc, (X.S. Wang et al., 2008) but since it is high cost, this limits its usage in large scale production. Therefore, researches have investigated other alternatives adsorbent which is cost-effective, efficient and easily available materials for the biosorption process. Some of the proven efficiently adsorbent materials are *Posidonia Oceanica* (L.) fibre (M.C. Ncibi et al., 2007), orange and banana peels (Annadurai et al., 2002), peanut hull (Gong et al., 2005) and, pumpkin seed hull (B.H. Hameed et al., 2007). In this study, dried water hyacinth (DWH), an agricultural solid waste, is used as an alternative low-cost dye adsorbent. The water hyacinth is a relatively high growth rate plant and when uncontrolled, it can disturb the aquatic ecosystem equilibrium, thus inducing environmental damages (R. Bodo et al., 2004). To make better use of this cheap and abundant agricultural resource plant, it is used as an adsorbent to remove Methylene Blue from aqueous solutions.

1.2 Problem Statement

The expose of dyes into environment by various industries has been aesthetically undesirable and too much of it will eventually cause serious environmental effect, aquatic or non-aquatic. This is due to its properties which are mostly toxic, mutagenic, and carcinogenic (B.H. Hameed et al., 2008). Dyes are causing pollution to the environment, for example, dyes adsorb and reflect sunlight from entering water and thus interfere the aquatic ecosystem. Dyes when release can have acute and/or chronic effects (X.S. Wang et al., 2008). It is evidently, therefore, investigating the removal of dyes is significant environmental, technical, and commercially important.

Water hyacinth is a free-floating aquatic weed originating from tropical areas in so many countries. It is naturally a rapid and uncontrollable growth plant, thus it has become a major cause of water irrigation especially during raining season, where it can be found blocking the drains and water sources. It has caused high costs and labour requirements to control the plant, leaving only temporary removal of the water hyacinths and abundantly growing. This resulted in a major massive growth of mosquito's pest which will lead to serious health problems to the society. Therefore, in making this plant a better use, it is proposed as a biosorbent to remove dyes.

For this study purpose, the water hyacinth is better to be used in dried condition. This is because, in living condition, the plant needs a huge and somehow massive area for maintaining its growth. Therefore, it is better to dry the water hyacinth for it is more user-friendly and will maximize the place of work instead of place to grow the plant. Also, dried water hyacinth can lessen the usage of transportation and also reducing the cost to transport itself. With the plant is dried, the major problem that will occurred if it is living, that is growth of mosquito's pest, will be solved and also lead to a controlled, healthy and safe environment for living and for working.

1.3 Objectives

i) Investigate the biosorption of dyes by dried water hyacinth (DWH).
ii) Investigate the potential of dried water hyacinth as a low cost biosorbent.
iii) Identifying optimum condition in the removal of Methylene Blue (MB) dye ions by using dried water hyacinth.

1.4 Scope of study

This study investigates the biosorption abilities of dried water hyacinth (DWH) for the removal of Methylene Blue (MB) dye from aqueous solutions. There are four parameters to be studied which are the characteristic and effects of biosorbent dosage, initial concentration of MB, solution pH, and contact time.

1.5 Rational and Significant

Pollution caused by dyes had affected the society with serious environmental effect and health problems to human body. It is evident; therefore, removal of dyes from aqueous solutions is important. Problems caused by the rapid growth of water hyacinth in water sources can be solved by making use of the plant as a biosorbent to remove dyes. Also, water hyacinth is a low-cost, high efficiency of dye removal from dilute solutions and easily available material for adsorbent. Biosorption process is an effective alternative method to replace conventional method, which is high cost and more complicated compared to biosorption.

CHAPTER 2

LITERATURE REVIEW

2.1 Biosorption

2.1.1 Definition

Biosorption is a property of certain types of inactive, dead, microbial biomass to bind and concentrate heavy metals - or other types of molecules or ions - from even very dilute aqueous solution. Biomass exhibits this property, acting just as chemical substance, as an ion exchanger of biological origin. It is particularly the cell wall structure of certain algae, fungi and bacteria which was found responsible for this phenomenon. In similar meaning stated by D.J. Ju et al in his research, the uptake or accumulation of chemicals by biomass is known as biosorption. Opposite to biosorption is metabolically driven active bioaccumulation by living cells (Volesky, B. 2007). In that case, it takes a whole different approach for further exploration of the studies.

2.1.2 Biosorbent

There are a lot of efforts were made in many studies for the removal of dyes from either aqueous solutions or wastewaters. This includes the use of metal hydroxides, clays, sunflower stalks, bagasse pith, hardwood, fertilizers and steel wastes.

Suitable biomass comes as a waste material from fermentation industries or it is renewable, a certain abundant seaweeds growing in the oceans and ready to be collected. In either case, the costs of biomass raw materials are extremely low.

The use of microorganisms as biosorbents for dyes also offers a potential alternative to existing methods for detoxification. The cell wall of microorganisms, which consists essentially of various organic compounds such as chitin, lipids, amino acids and other cellular components, can provide a means for the passive uptake of reactive dyes (Z Aksu, 2001).

For example, as a basis for a metal biosorption processes, these biomass can accumulate in excess of approximately 25% of their dry weight in deposited heavy metals: Pb, Cd, U, Cu, Zn, even Cr and others. It is proven in many researches on biosorption which says that biosorption is sometimes a complex phenomenon where the metallic species could be deposited in the solid biosorbent through different sorption processes of ion exchange, complexation, chelation, microprecipitation, etc.

There are also new alternatives of suitable “formulated” biosorbents can be used in the process of metal removal and detoxification of industrial metal-bearing effluents. The most effective approach for the matter is the sorption packed-column configuration. It is stated that the recovery of the deposited metals from saturated biosorbent can be accomplished because they can often be easily released form the biosorbent in a concentrated wash solution which also regenerates the biosorbent for subsequent multiple reuse. This and extremely low cost of biosorbents makes the process highly

economical and competitive particularly for environmental applications in detoxifying effluents of e.g.

- Metal-planting and metal-finishing operations,
- Mining and ore processing operations,
- Metal processing, battery and accumulator manufacturing operations,
- Thermal power generation (coal-fired plants in particular),
- Nuclear power generation, (etc.)

2.1.3 Biosorption Mechanism

In many researches, it is proven that the kinetics studies have been very helpful in the effort to determine the process of biosorption. There are several equations can be used and the results and graphs are almost all precise, understandable and always can be interpreted easily. But it is also important to determine the mechanism of sorption for design purposes. Based on the observation of bare eyes, it is considerably that in a solid-liquid biosorption process, the biosorbate (dye) transfer to the biosorbent (biomass) can be illustrated by either boundary layer diffusion (external mass transfer), intraparticle diffusion (mass transfer through the pores), or by both. Generally, the biosorption dynamics is accepted to consist of three consecutive steps:

i) Transport of biosorbate molecules from the bulk solution to the biosorbent external surface through the boundary layer diffusion.
ii) Diffusion of the biosorbate from the external surface into the pore of the biosorbent.
iii) Biosorption of the biosorbate on the active sites on the internal surface of the pores.

Usually, the last step, biosorption, is very rapid to be compare with the first two steps. For that reason, it can be considered that the overall rate of biosorption is controlled by either the boundary layer or pore diffusion, or combining both. According to D. Mohan et al in his study on 2004, it is proven that the boundary layer diffusion is the rate controlling step in systems characterized by dilute concentrations of biosorbate, poor mixing, and small particle size of biosorbent. Whereas the intraparticle diffusion controls the rate of biosorption in systems characterized by high concentrations of biosorbate, vigorous mixing, and large particle size of biosorbent. Also, in many studies, the results similarly showed that boundary layer diffusion is dominant at the beginning of biosorption during the initial removal, and then the rate of biosorption is regularly controlled by the intraparticle diffusion as the capacity of biosorbate has loaded the external surface of biosorbent.

The intraparticle diffusion parameter, *k*i (mg/g min0.5) is defined by the following equation (W.J. Weber Jr. et al., 1963):

q . (2.1)

where q is the amount of MB adsorbed (mg/g) at time t, k_i the intraparticle diffusion constant (mg/g $min^{0.5}$), and c is the intercept. Theoretically, the plot of k_i versus $t^{0.5}$ should show at least four linear regions that represent boundary layer diffusion, followed by intraparticle diffusion in macro, meso, and micro pores (Y.S. Ho et al., 1998). These four regions are followed by a horizontal line representing the system at equilibrium.

2.1.4 Factors Affecting Biosorption

There are several factors that affecting the biosorption process. Studies have been done shows similar trends of results and observations for the same parameters investigated. Researches mostly investigate between these parameters to study its effect on biosorption process and how it can be improved to get the highest optimum uptake. This includes the biosorbent dosage, initial concentration of biosorbate, the solution pH, temperature, contact time between the sorbate and sorbent, particle sizes, and etc.

Generally, to explain the effect of biosorbent dosage, research on biosorption studies on Methylene Blue (MB) by tea waste done by M.T. Uddin et al., stated that the percentage removal of MB increased with the increase in adsorbent dosage. This can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase dosage of the adsorbent. But the adsorption density of MB decreased with increase in adsorbent dosage. Studies on other biomass such as guava leaf powder (V. Ponnusami et al., 2008), baggase (Raghuvanshi et al., 2004), papaya seed (B.H. Hameed, 2008) and fly ash (K. Rastogi et al., 2008) shows similar results.

As for the effect of time and initial concentration, it can be explained briefly in study done by Raghuvanshi et al., on baggase in 2004 which stated that the adsorption process was found to be very rapid initially, and a large fraction of the total concentration of dye was removed in the first 30 minutes. Though it was observed that adsorption of dye increased with an increase in dye concentration in the solution, which shows that removal of dye is dependent upon the concentration of dye solution. But as whole the percent removal decreases with the increase in dye concentration. Similar results have been obtained in research on other various biosorbent only the uptake value differs.

The effect of pH also shows similar results in research made by M. sarioglu et al., using biosolid, M.C. Ncibi et al., using *Posidonia oceanic*, B.H. Hameed et al., using pumpkin seed hull and many others using a varieties of biosorbent. Results obtained indicates that the effect of pH on the amount of dye removal was analyzed over the pH

range from 2 to 10 and the pH 6 to 8 is usually the optimum pH for the removal process. This trend might be explained by in such pH, the biosorbent combines both negatively and positively charged cells surface, which enhance the electrostatic attraction between anionic and cationic species of both sorbate and biosorbent.

Temperature also affected the process of biosorption and it is proven by previous studies where the results shows that the dye uptake increasing with the increasing of temperature. It is clear that biosorption equilibrium is a thermo-dependent process. This effect may be due to the fact that at higher temperatures, an increase in the movement of solute occurs (M.C. Ncibi et al., 2007).

In this study, only four parameters are selected which is biosorbent dosage, initial concentration of biosorbate, solution pH and contact time.

2.2 Water Hyacinth

Figure 2.1 is a picture of water hyacinth (*Eichhornia crassipes*) taken at local pond in Pekan, Pahang. From the figure, it is clearly shown that this plant is freely available and abundant with no use for any reasons.

Figure 2.1 Water hyacinths (*Eichhornia crassipes*)

2.2.1 Physical description

The picture of a water hyacinth is shown in Figure 2.2 where it consists of the flower, leaf, stem and roots of the plant.

Figure 2.2 Water hyacinth plant

The water hyacinth is a free floating aquatic weed originated in the Amazon in South America (Bolenz et al., 1990) where it was kept under control by natural predators (Lee, 1979). The plant has, through introduction by man, spread throughout the whole tropical zone (Aweke, 1993). At the beginning of its spread into many parts of the

world, water hyacinth started as an ornamental garden pond plant due to its beautiful large purple and violet flowers. Particularly, this plant is mostly suited to tropical and sub-tropical weather. Massive weed colonies can grow when introduced into areas that are conducive for their proliferation and for this reason, in a short period of time, it has become a problem plant in areas of the southern USA, South America, East, West and Southern Africa, South and South East Asia and Australia. Its spread throughout the world has taken place over the last 100 years or so, even though the actual course of its spread is poorly documented.

The plant is a perennial aquatic herb (*Eicchornia crassipes*) which originally belongs to the family Pontedericeae, closely related to the Liliaceae (lily family). The mature plant consists of long, pendant roots, rhizomes, stolons, leaves, inflorescences and fruit clusters. The plant can be up to three feet off the water's surface although 40 centimeters is mostly its usual height. The inflorescence grow at the top of a single stalk, bears six to ten lily-like flowers, each four to seven centimeters in diameter, in purplish blue or lavender with yellow color. The leaves are green, round to oval, four to eight inches in diameter, with gently incurved sides. Its leaf veins are dense and numerous so this helps the leaves stand erect. The stems and leaves contain air-filled tissue which create a bulbs and spongy effect help give the plant its considerable buoyancy. There is a mass of fine purplish black and feathery roots hangs in the water underneath the plant. Its vegetation reproduction is asexual and takes place at a rapid rate under preferential conditions (Herfjord, Osthagen and Saelthun, 1994).

2.2.2 Growth habit

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 (Lee, 1979). The number of plants can more than double in seven days in conditions of high temperature and humidity (Lareo and Bressmi, 1982, from

Tag El-Din, 1992) and up to 140 ton of DM/ha and yr are produced (Abdelhanid and Gabr, 1991). The plant normally forms cohesive floating mats and can cover large areas of the water surface. The spreading of the water hyacinth is also thought to be enhanced by winds (Gay, 1960, from Aweke, 1993). The plant flourishes in nutrient-rich waters and on shallow shores with mud rich in nutrients.

The mats can grow up to two meters thick which can reduce light and oxygen, change the water chemistry, affect flora and fauna, reduction of fish and cause significant increase in water loss due to its evapotranspiration. 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. It also restricts the possibilities of fishing from the shore with baskets or lines (Aweke, 1993) and can cause hygienic problems (Moursi, 1976a; Becker et al., 1987; Abdelhafiz, 1989, from Abdelhamid and Gabr, 1991).

The increased growth rate of the water hyacinths has led to worsened health conditions for the community in the affected areas. The floating water hyacinths mats can serve as a breeding ground for vector organisms carrying malaria, bilharziosis and river blindness (Moursi, 1976a; Becker et al., 1987; Abdelhaifz, 1989, from Abdelhamid and Gabr, 1991). 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 (Sunday Standard, Kenya, 12/1-1997). This means that decreasing the amount of water hyacinths could hopefully improve the health situation (C.C. Gunnarsson et al., 2007).

The major problem when working in the water hyacinth infested areas is the risk of catching waterborne diseases e.g.; malaria and diarrhea. Attempts to control the weed

have caused high costs and labour requirements, leading to nothing but temporary removal of the water hyacinths. Since the most favourable conditions for the growth of the water hyacinth often are found in developing countries, very limited resources have been put into curbing them. Fighting the water hyacinth generates neither food nor income, and the weeds are therefore left to cover the lakes. Fast growth is a feature valued in crops grown by man. The water hyacinth would, therefore, have a great potential if seen as raw material for industries or if incorporated into agricultural practice (C.C. Gunnarsson et al., 2007).

2.2.3 Roles of water hyacinth in the effluent from waste

Water hyacinth proliferate from tiny root fragments, which will eventually break off from the large plants and quickly develop leaf stalks and broad green leaves. Runners also grow along the water surface from the base of the petioles, thus resulting in a massively rapid spread of vegetative reproduction.

According to Evart in his writing about the weeds of Victoria in 1941, it stated that, the water hyacinth has always been used as manure, but is very bulky and rots quickly, so that it only has slight and temporary value in adding humus to the soil. Meanwhile, in Bengal, farmers were persuaded to turn the water hyacinth into composted manure. Analysis that been made at the time on random samples of the compost showed a nitrogen percentage of 1.12 on a dry condition.

It is said by G.C. Dymund that the potentialities of this plant were first fully recognized by Sir Albert Howard which in his recommendations to the Auckland Municipality, he emphasized the necessity for the complete utilization of all city wastes, particularly using the water hyacinth. The methods is described as screening of the solids, and thereafter drying and composting with city wastes, finally the sludge is filtered off, the clear effluent will contain valuable plant food in solution. This can be trapped by the water hyacinth. Then the clear sewage effluent, together with the storm

water, should be led into some local stream, river or low-lying area, where the water hyacinth can be cultivated as a crop, and the clear water will be allowed to escape freely into the sea. In later tests, it is found that an acre of water hyacinth could remove 2.4 tonnes of ammonium sulphate (nitrogen fertilizer) in one hour, and phosphorus just as efficiently. Many more studies have been made by researches, W. Zhou et al, M.I. El-Khaiary, M.T. Uddin et al, and etc., has found that water hyacinth can also remove toxic and heavy metals pollutants in effluent from waste.

In a research made by G.C. Dymund, it showed that the water hyacinth is a highly efficient absorber of fertilizer elements and in the conclusion, it stated that the plant provides a means of purification and of trapping vest amounts of fertile elements which are normally lost.

2.3 Methylene Blue

Figure 2.3 shows the Methylene Blue dye purchased from Fisher Scientific that is used in this study.

Figure 2.3 Methylene Blue dye

2.3.1 Characteristics

Methylene Blue (MB) is a heterocyclic aromatic chemical compound with its molecular formula $C_{16}H_{18}ClN_3S$. Particularly at room temperature it appears as a solid, odorless, dark green powder which become a blue solution when dissolved in water. The hydrated form has three molecules of water per molecule of MB. It is important not to confused MB with methyl blue, another histology stain, new methylene blue, nor the methyl violets where often used as pH indicators.

Moreover, MB IUPAC name is known as 3,7-bis(Dimethylamino)-phenazathionium chloride or Tetramethylthionine chloride. The molar mass is 319.85 g/mol and its melting point around 100 to 110^{oC}. When released into the soil or water, it is not expected to evaporate significantly. It is also stated that MB has an estimated bioconcentration factor (BCF) of less than 100 and it is not expected to significantly bioaccumulate. Other than that, MB is expected to be readily degraded by reaction with photochemically produced hydroxyl radicals and it ma be removed from the atmosphere to a moderate extent by wet deposition when it is released into the air.

2.3.2 Applications

Methylene Blue (MB) is an important basic dye widely used for printing calico, printing cotton and tannin and dyeing leather (X.S. Wang et al., 2008). Although not strongly hazardouse, MB can have various harmful effects. The MB is well-known as strong adsorption onto solids (B.H. Hameed et al., 2008). The applications and uses of MB includes chemically, biologically and also in medicine industries. These are some of its major uses.

In analytical chemistry, MB is widely used as a redox indicator. Solutions of this substance are blue when in an oxidizing environment, but will turn colorless if exposed to a reducing agent. It has been known that the redox properties can be seed in a classical demonstration of chemical kinetics in general chemistry, the “blue bottle” experiment. The technique is typical where a solution is made of dextrose, MB and sodium hydroxide. Upon shaking the bottle, oxygen oxidizes the MB, and the solution turns blue. The dextrose will gradually reduce the MB blut to its colorless, reduced form. Hence, when the dissolved oxygen is entirely consumed, the solution will turn colorless. Another use of MB, it is also a photosentizer where it is used to create singlet oxygen when exposed to both oxygen and light. It is used in this regard to make organic peroxides by a Diels-Alder reaction which is spinning forbidden with normal atmospheric triplet oxygen.

In biology application, MB is used as a dye for a number of various staining procedures, such as Wright’s stain and Jenner’s stain since it is a temporary staining technique, MB can also be used to wxamine RNA or DNA under the microscope or in a gel: for example, a solution of MB can be used to stain RNA on hybridization membranes in northern blotting to verify the amount of nucleic acid present. While MB is not as sensitive as ethidium bromide, it is surely less toxic and it does not intercalate in nucleic acid chains, thus avoiding interference with nucleic acid retention on hybridization membranes or with the hybridization process itself. Also, MB can be used as an indicator to determine if a cell such as yeast is alive or not. The blue indicator will turned colorless in the presence of active enzymes, thus indicating the present of living cells. However, if it stays blue it doesn’t mean that the cell is dead – the enzymes could be inactive or denatured. It must be noted that MB can inhibit the respiration of the yeast as it picks up hydrogen ions made during the process. The yeast cell cannot then use those ions to release energy. Another example of its application, in neuroscience, MB can also serve as a non-selective inhibitor of nitric oxide (NO) synthase.

The use of MB in the medicine world is surprisingly enormous. Generally, as stated by Gillman PK in his research on 2008, MB is a monoamine axidase inhibitor and if infused intravenous;y at doses exceeding 5 mg/kg, it may precipitate serious serotonin toxicity, and will lead to a serotonin syndrome if combined with any selective serotonin reuptake inhibitors (SSRIs) or other serotonin reuptake inhibitor, for example, deluxetine, sibutramine, venlafaxine, clomipramine, imipramine and etc. (Gillman PK, 2006). MB is a miraculously an effective treatment and alternatives for many disease which includes malaria, methemoglobinemia, cyanide poisoning, carbon monoxide poisoning, neurotoxicity and others, also is very useful in clinical trials. Another great use of MB is its used in aquaculture and by tropical fish hobbyists as a treatment for fungal infections. It can also be very effective in treating fish infected with *ich*, the parasitic protozoa *Ichthyophthirius multifiliis*. Usually it is used to protect newly laid fish eggs from being infected by fungus or bacteria.

2.3.3 Effects of Methylene Blue to environment and health

When exposed excessively, MB can be very harmful and toxic to the livings. It can cause eye burns, which will lead to permanent injury to the eyes of human and animals, irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea and also cause methemoglobinemia, cyanosis, convulsions, tachycardia, and dyspnea. Contact of MB with skin causes irritation (X.S. Wang et al., 2008).

MB can also cause problems in several other ways: MB can have acute and/or chronic effects on exposed organisms depending on the exposure time and dye concentration; they are highly visible and undesirable even at very low concentrations in effluent; dyes absorb and reflect sunlight entering water and so can interfere with growth of bacteria and hinder photosynthesis in aquatic plants (X.S. Wang et al., 2008).

Table 2.1 Summary of Literature Review

SPECIES	BIOSORBENT	REFERENCES
Phenol	Water hyacinth ash	M.T. Uddin et al., 2007
Basic dye	Pumpkin seed hull	B.H. Hameed et al., 2008
Basic dye	Agricultural by-product (rice bran, wheat bran)	X.S. Wang et al., 2008
Basic dye	Apricot stone activated carbon	E. Demirbas et al., 2008
Reactive Dye	Non-viable biomass of *Aspergillus Niger* & *Spiroyra* sp.	Mahmoud A. Khalaf, 2008
Reactive Dye	*Posidonia Oceanica* (L.) fibrous biomass	M. C. Ncibi et al., 2007
Heavy metals	Biomass	S. Senthilkumaar et al., 2000
Lead, Cadmium, Zinc, and Copper	Carbon developed from walnut, hazelnut, almond, pistachio shell, and apricot stone.	Maryam Kazemipour et al., 2007
Cr (VI)	*Eicchornia Crassipes*	Kaustubha Mohanty et al., 2005
Methylene Blue	Biosolid	M. Sarioglu et al., 2006
Methylene Blue and Iodine	Activated desert plant	B. Bestani et al., 2008
-	Water hyacinth	C.C. Gunnarsson et al., 2007
Reactive dye	Dried activated sludge	Dong-Jin Ju et al., 2006
Heavy metals	Sewage sludge-derived	F. Rozada et al., 2008
Arsenic	Bio-adsorbents	M.J. Islam et al., 2007
Esterifying citric acid	Rice straw	Renmin Gong et al., 2008

-	Water hyacinth	R. Bodo et al., 2004
Methylene Blue	Baggase	S.P. Raghuvanshi et al., 2004
Potassium	Water hyacinth	Wenbing Zhou et al., 2007
Dyes	Immobilised *Aspergillus niger* fungal biomass	Yuzhu Fu et al., 2003

Table 2.1 is the compilation of some of the references taken in the year 2003 until 2008 been used as the literature review for this study. It is proven that there are numbers of potential biosorbent can be used in removal of dyes, and heavy metals as well according to these successful investigations made recently. These previous studies are important to be made as indication of how effective is the dried water hyacinth as a biosorbent and to compare which biosorbent is the most effective to remove Methylene blue from aqueous solution.

CHAPTER 3

METHODOLOGY

3.1 Overall Methodology

The biosorbate particles were first analyzed with Scanning Electron Microscopy (SEM) and Fourier Transform Infra Red Spectrometer (FTIR, Thermo Nicolet). Biosorption experiments were carried out in a batch process using aqueous solution of Methylene Blue (MB) purchased from Fisher Scientific. Parameters studied were biosorbent dosage, initial MB concentration, solution pH and contact time. Stock solution of MB was prepared and standard solutions for the experiments were diluted from stock.

The experiments were conducted in a Stackable Incubator Shaker (Infors) at 120 rpm and at room temperature, 27^{o}C using 250mL conical flasks containing 50mL dye solution at different initial concentrations and pH values of MB solution. The initial pH values of the solutions were adjusted with 1.0M Sodium Hydroxide, NaOH or 1.0M Hydrochloric Acid, HCL before each experiment. The pH was measured by using a pH meter (Metrohm). A number of doses of Dried Water Hyacinth (DWH) were added to each flask, and then the flasks were sealed up with parafilm or aluminium foil to prevent any spilling that could change the volume of solution during the experiments. After shaking the flasks for a period of time intervals, the aqueous samples were taken and the

MB concentrations were measured by UV-Vis Spectrophotometer (Hitachi, Model U-1800) at its maximum wavelength, 664 nm. The percentage of MB removal from solution was calculated by

$$R\ \% \quad \text{——} \quad 100 \qquad (3.1)$$

where C_o is the initial MB concentration and C_t is the MB concentration (mg/L) at any time. The equilibrium amount of biosorption, q_t (mg/g), was calculated by

$$q \quad \text{———} \qquad ..(3.2)$$

where V is the volume of solution (L) and W is the mass of biosorbent used (g).

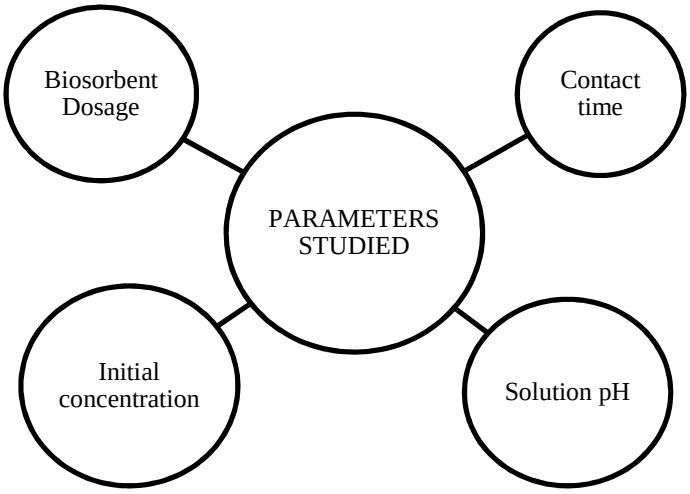


Figure 3.1 Scope of study

3.2 Biosorbent preparation

Water hyacinths were collected from local pond at Pekan, 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^{o}C for 24 hours to remove moisture. The dried samples were crushed and blended using dry blender, and then samples were placed in desiccator for 24 hours to remove moisture present in it and stored in seal plastic bag for further use. No further chemical or physical treatments prior to biosorption experiments.

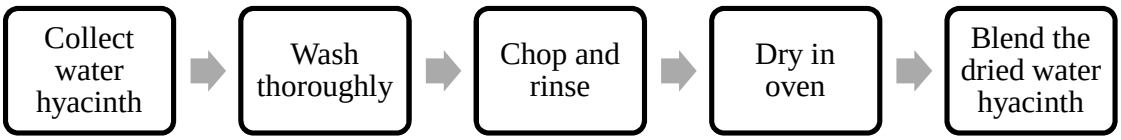


Figure 3.2 Process flow for preparation of dried water hyacinth

3.3 Biosorbate preparation

Methylene Blue, $C_{16}H_{18}ClN_3S.2H_2O$, is a cationic dye. The MB was chosen in this study because of its known strong biosorption onto solids. The maximum biosorption wavelength of this dye is 664 nm. The structure of MB is shown in Figure 3.1. In this study, MB was used without further purification. All of the MB solution was prepared with distilled water. The stock solution of 1000 mg/L was prepared by dissolving MB in 1000 mL distilled water. The experimental solution was gained by diluting the stock solution with distilled water.

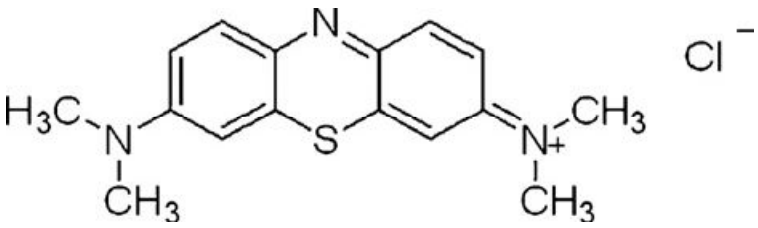


Figure 3.3. The structure of MB

Figure 3.4 Stock solution of Methylene Blue

3.4 Scanning Electron Microscopy & Fourier Transform Infra Red study

Scanning Electron Microscopy (SEM) analysis of the DWH was carried out to study its surface texture before and after the sorption process. Fourier Transform Infra-Red (FTIR) analysis was carried out on the DWH to determine its functional groups, by using FTIR Spectrometer (FTIR, Thermo Nicolet), with spectra were set from 4000 to 400 cm^{-1}.

3.5 Biosorption experiments

3.5.1 Effects of biosorbent dosage

For this parameter, initial dye concentration of 20 to 140 mg/L was used in 50 mL of solution in conjunction with DWH sample of 0.005 to 0.8 g. Contact time and pH were 120 minutes and & 7, respectively. The dye concentrations are varied to observe the pattern of results for optimum dosage. The value of optimum dose is used for other parameters.

3.5.2 Effects of initial MB concentrations

0.3 to 0.8 g of DWH dosage was used with the initial concentrations varied from 20 to 200 mg/L. Flasks of samples were shaken using rotary shaker at 120 minutes and pH 7. The biosorbent 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.

3.5.3 Effects of solution pH

The initial pH of solution was adjusted from pH 2 to 11 at different values of biosorbent 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.

3.5.4 Effects of contact time

The effect of contact time is investigated for 5 to 120 minutes at pH 7 and at different values of biosorbent dosage and initial concentrations near their optimum values. The similar pattern of results for the optimum value is obtained.

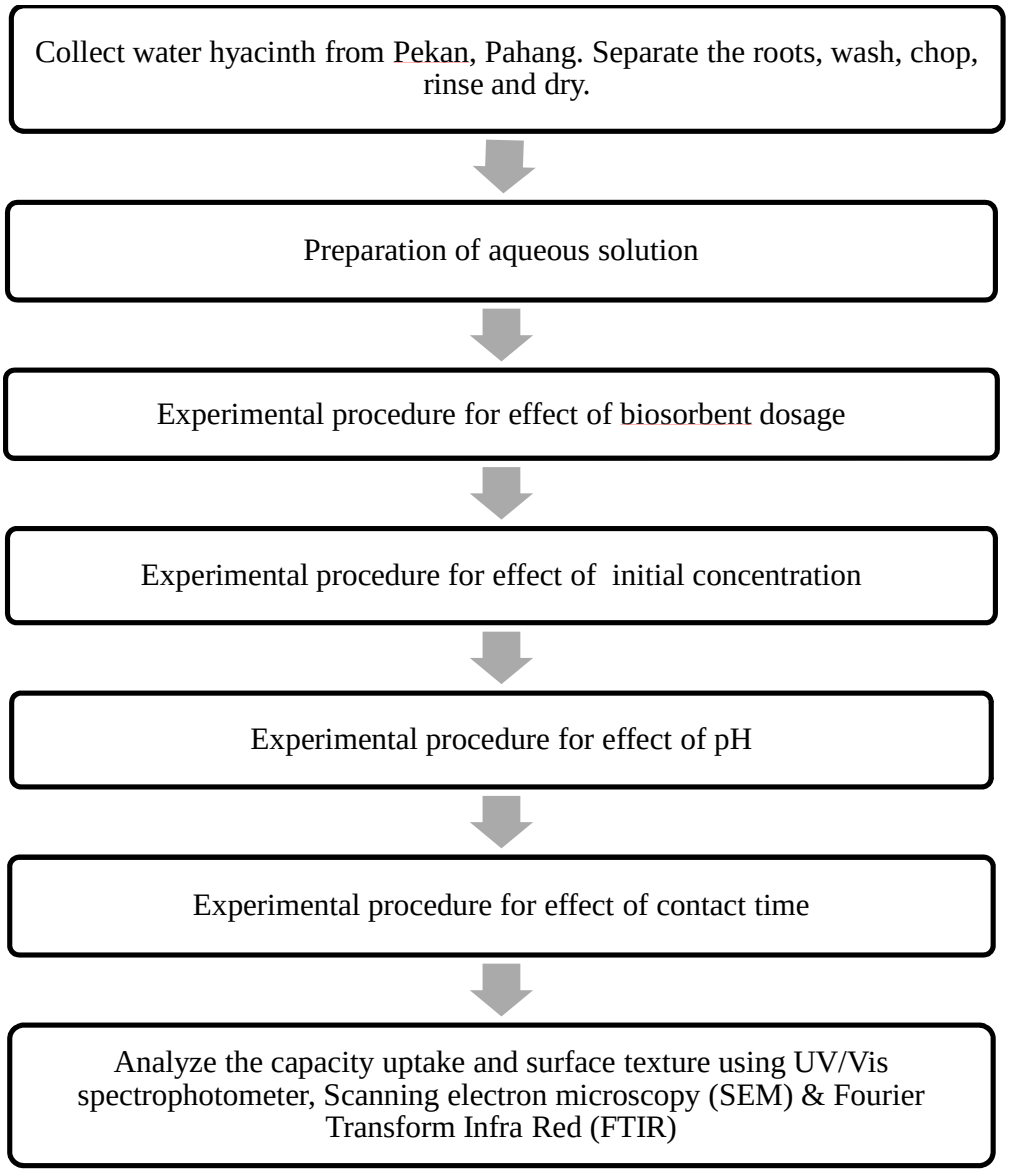


Figure 3.5. Flowchart of methodology

CHAPTER 4

RESULTS & DISCUSSIONS

4.1 SEM and FTIR of DWH

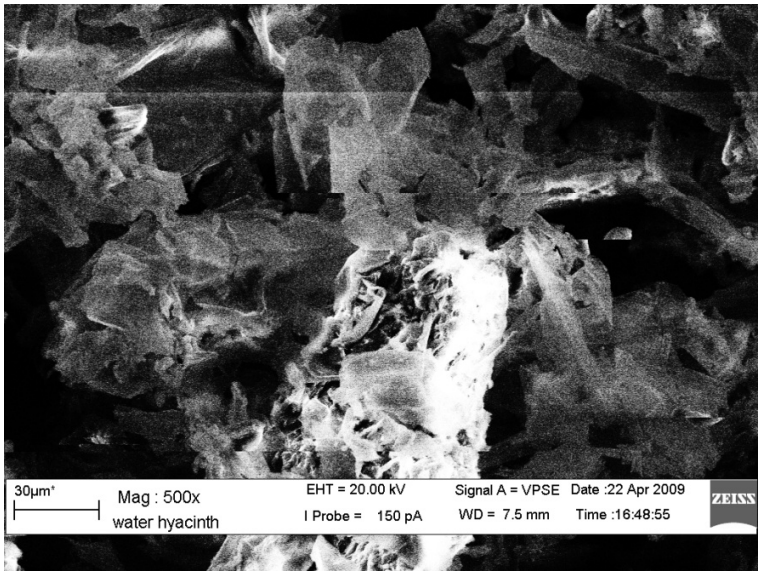
The structure of dried water hyacinth is investigated using scanning electron micrograph procedure where in this study, structure of DWH both before and after dye uptake is observe using ZEISS EVO Series with an operating condition of 500x magnification.

As a result, Figure 4.1 shows the micrographs of DWH surface texture before and after the dye sorption process obtained by SEM analysis. The surface of DWH before experiment in Figure 4.1 (a) clearly shows a considerable numbers of different sizes of heterogeneous pores with several cavities (macroporous) which are responsible for biosorptions to occur. With the present of these pores on the surface of sorbent, the claim that DWH could be a good biosorbent can be positively assured.

Meanwhile, Figure 4.1 (b) is the micrograph of DWH surface texture after the biosorption took place. There is an obviously significant change can be monitored. The observation of the fully loaded surface structure can be explained by the fact that the molecules of dye had been adsorbed on the surface and most likely to be trapped inside

the pores of sorbent, thus making the surface of DWH covered with a layer of dye, clearly.

(a)



(b)

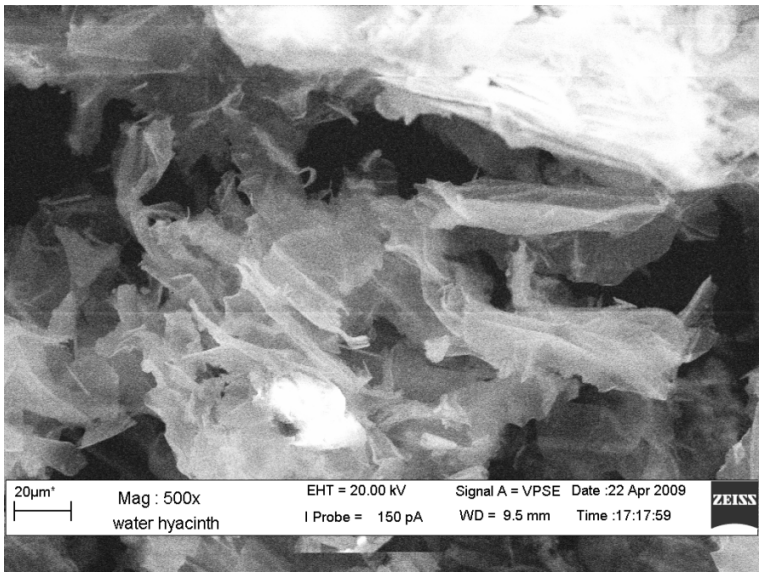
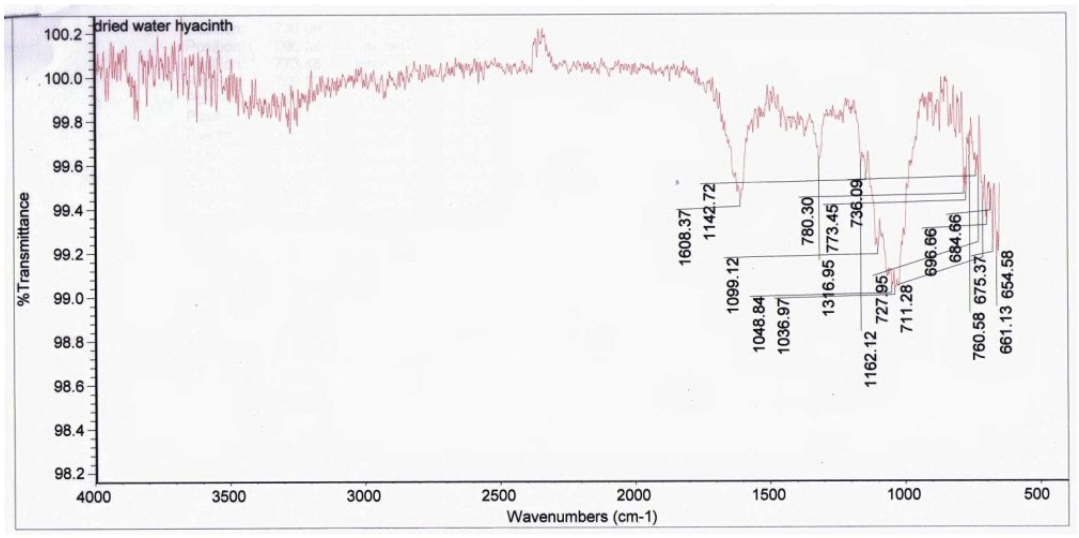


Figure 4.1 Scanning electron microscope of DWH particle: (a) before dye uptake and (b) after dye adsorbed

The FTIR vibrational spectrum of DWH before dye uptake is shown as illustrated in Figure 4.2 (a). It is clearly shown in the figure that there are a number of available adsorption peaks which allows the biosorption of dye molecules onto the biosorbate. The adsorption site indicated maximum wavenumber at 3200 cm^{-1} to 3400 cm^{-1}, representing stretching of –OH groups. Several peaks between 3300 cm^{-1} to 3700 cm^{-1} is due to the NH_2 stretching, confirmed the amine (R. Bodo et al., 2004) presence on the DWH particles. The band at approximately 2900 cm^{-1} was assigned to the stretching of C–H bonds. Also, the sharp intense peak at 1608 cm^{-1} was attributed to C–C bonds. Bands in the range of 1316 cm^{-1} to 1306 cm^{-1} referred to the presence of C–O phenols bonding.

On the other hand, the FTIR spectrum after 30 minutes of MB uptake onto biosorbate is shown in Figure 4.2 (b). The absorption sites and band peaks begins to form a straight line and there are less peaks left which confirmed the biosorption activities occurred between dye molecules and DWH and filled the initially available adsorption sites on the sorbent surface.

(a)



(b)

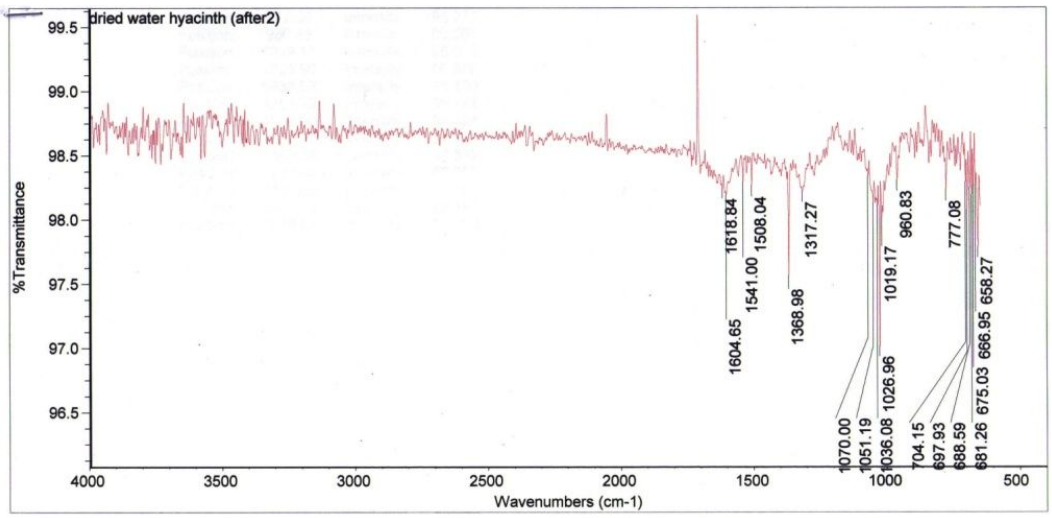


Figure 4.2 FTIR spectrum of dried water hyacinth: (a) before dye uptake and (b) after dye removal

4.2 Effects of biosorbent dosage

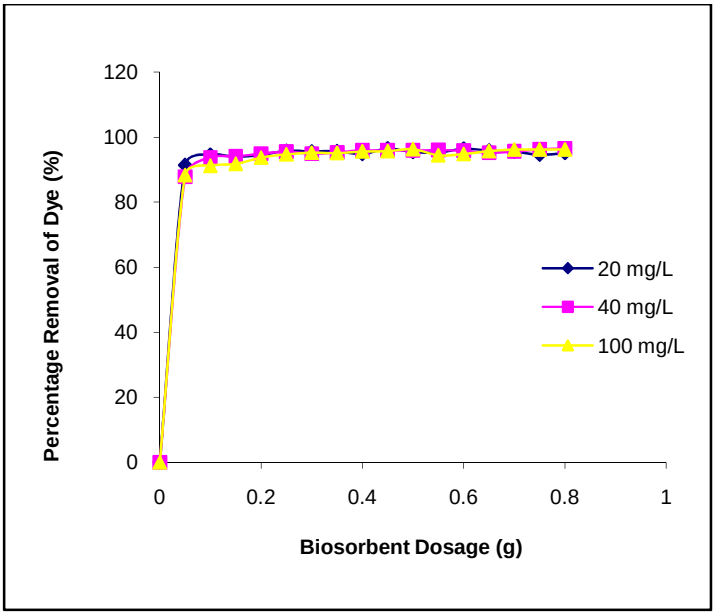
The study of biosorbent dosage effect on MB dye uptake can be observed in Figure 4.3. Experiment is conducted by using DWH doses range from 0.05 g to 0.8 g while keeping the other parameters constant (C_o = 40 mg/L, pH = 7.0, shaker speed = 120 rpm, time = 120 minutes). Results from the first experiment, as shown in Figure 4.3 (a) indicate that percentage removal of dye increase with the increase of biosorbent dosage accordingly. Until it reached 96 % of dye uptake at 0.55 g DWH dosage, the percentage removal of dye remain considerably constant even with the increase of dosage. However, as shown in Figure 4.3 (b), the amounts of dye sorbed per unit mass remain decreased from 34 to 2.5 mg/g along with the increasing of sorbent dosage.

The experiment was repeated by varying the value of initial concentration, C_o = 20 and 100 mg/L with other parameters constant. This is done to observe the pattern of percentage removal of dye and it is proved that each trial result in similar increase of dye

uptake and decrease of dye sorbed per unit mass with the same value of increasing biosorbent dosage. The optimum condition for the effect of biosorbent dosage in dye sorption is determined to be at 0.55 g of DWH.

The increasing value of percentage removal of dye uptake might be due to increase of surface area which means increasing of availability of sorption sites for removal of dye with the increase in biosorbent dosage. Whereas, the decreasing in dye sorbed per unit mass with increasing of DWH dosage can be because of reduction in effective surface area, or in other word, the biosorbate is saturated. This also can explained the constant value of percentage removal, where the dye had caused particles to aggregate and thereby resulting in unavailability of active sites for biosorption (M.M. Karim et al., 2006). Similar results for the effect of biosorbent dosage on MB removal is proven in other studies using pumpkin seed hull (B.H. Hameed et al., 2008), untreated coffee husk (L.S. Oliveira et al., 2008) and tea waste (Md.T. Uddin et al., 2008) as their potential biosorbent.

(a)



(b)

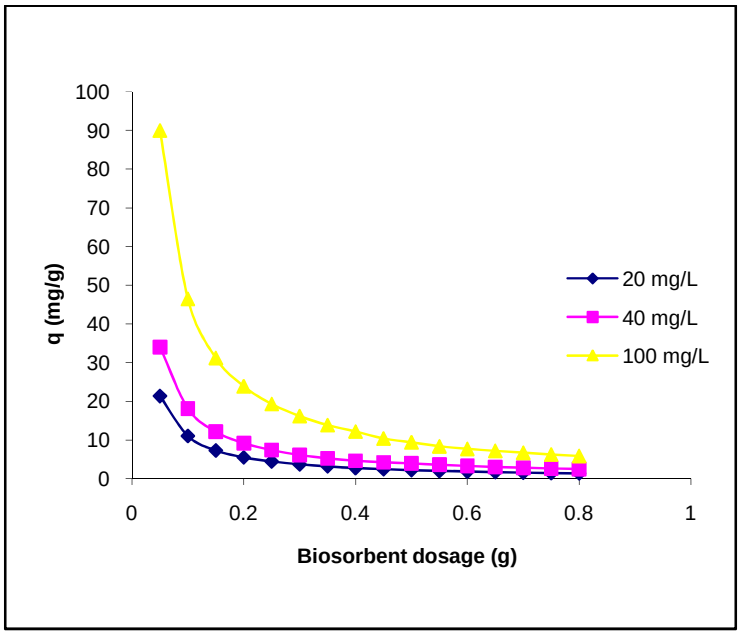


Figure 4.3. The effect of biosorbent dosage for the removal of MB. Speed=120 rpm, time=120minutes, pH=7.0, dosage=0.05-0.8g, Co=20-100mg/L: (a) Percentage removal and (b) Amount of dye sorbed

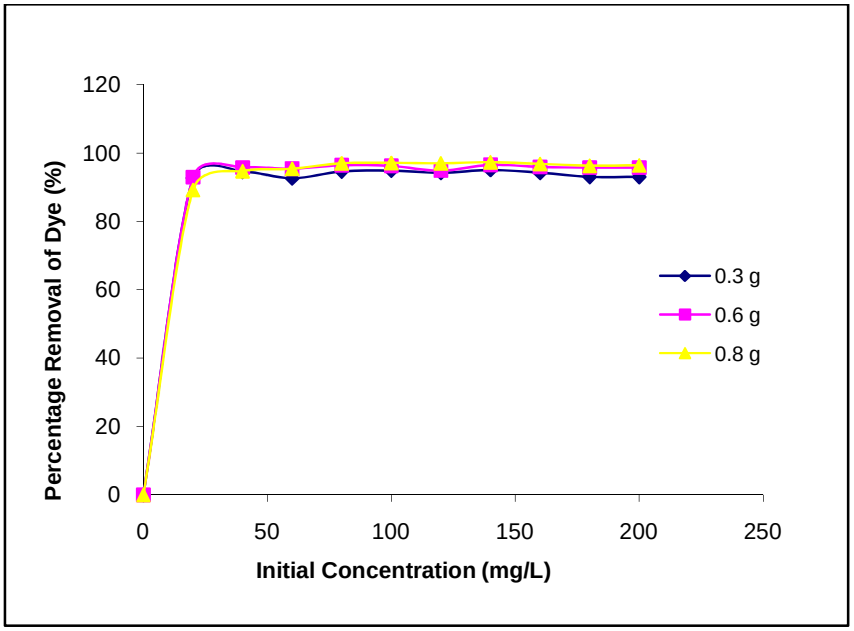
4.3 Effects of initial concentration

The effects of initial concentration for the removal of the dye were carried out by varying the value of initial concentration of MB solution from 20 to 200 mg/L with fixed value of other parameters (Dosage = 0.6 g, pH = 7.0, shaker speed = 120 rpm, time = 120 minutes). The result in Figure 4.4 (a) indicates that as the initial concentration increase, the percentage removal increased until it reaches equilibrium at 80 mg/L and after that the dye uptake started to decrease. However, for the result of dye sorbed per unit mass as shown in Figure 4.4 (b), the value of q_t continuously increasing with the increase of MB concentration.

Similar to the experiments for effect of biosorbent dosage, the study of this parameter is also done by repeating the same method with different values of sorbent dosage (Dosage = 0.3 g and 0.8 g) and other values were kept constant. The pattern of graph result from the repeated trials is observed and a similar pattern can be seen when compared to earlier experiment (Dosage = 0.6 g). The highest percentage removal is considerably 97% achieved at the value of 80 mg/L concentration of MB solution hence; it is selected as the optimum value of initial concentration for removal of dye.

Behavior of the percentage removal of dye where it increases with the increasing of initial concentration is probably due to the stronger interaction between MB and DWH. The concentration of dye provides a driving force to overcome the resistances to the mass transfer between solid and aqueous phases. Moreover, increasing the initial dye concentration increases the number of collisions between MB ions and the DWH, which enhances the biosorption process. Other studies made by B.H. Hameed et al., and R. Gong et al., both on 2008 have the same results about the initial MB concentration on biosorption capacity.

(a)



(b)

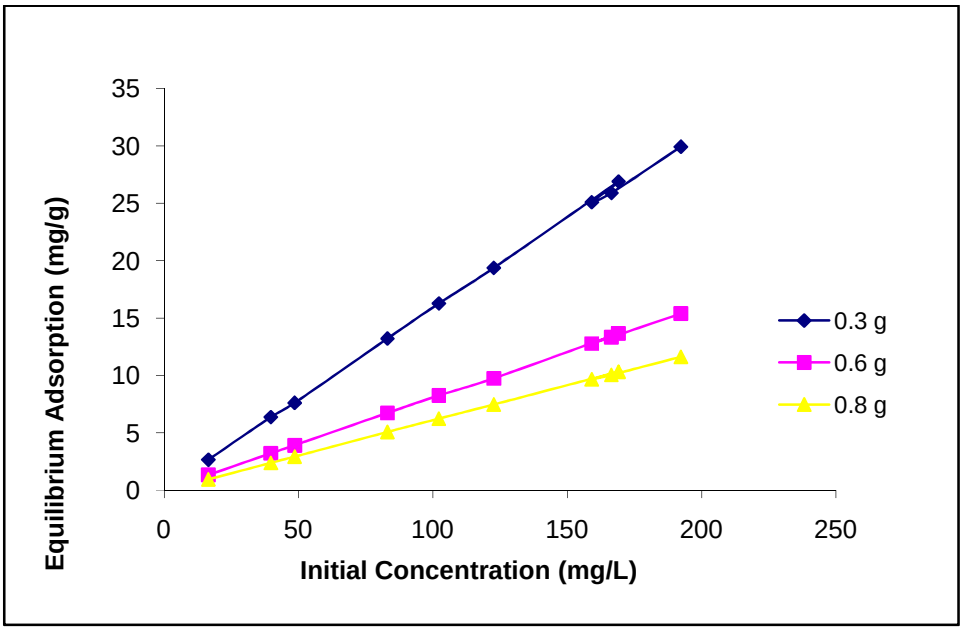


Figure 4.4. The effect of initial concentration for the removal of MB. Speed=120 rpm, time=120minutes, pH=7.0, dosage=0.3-0.8g, Co=20-200mg/L: (a) Percentage removal and (b) Amount of dye sorbed

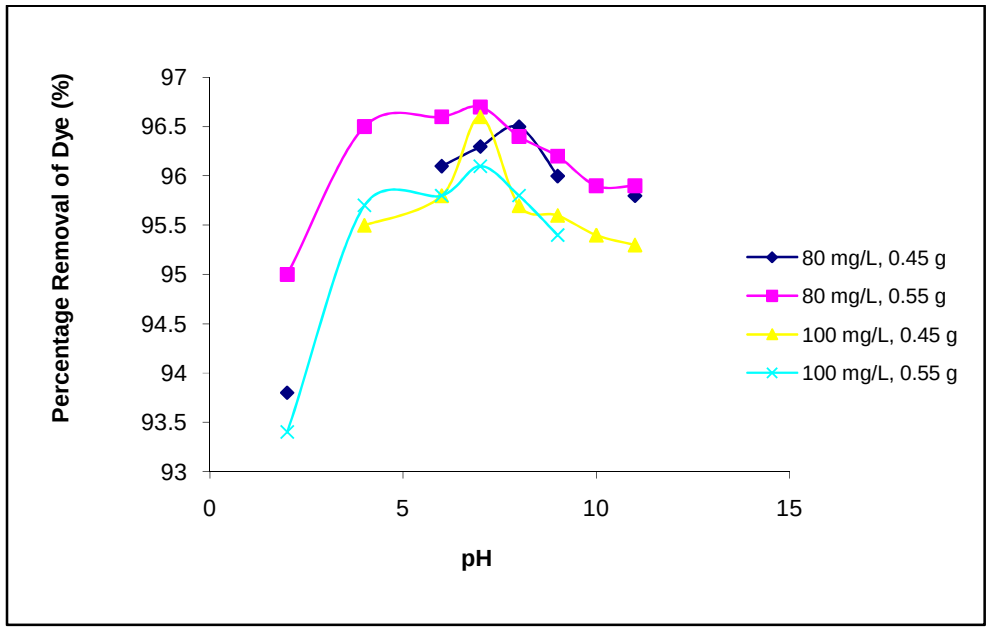
4.4 Effects of pH

The effect of pH is the most important factors controlling the biosorption ability on to the sorbent. Investigation is conducted by setting the MB initial concentration and DWH dosage at its optimum value which is 80 mg/L and 0.55 g, respectively and other parameters is fixed to 120 rpm shaker speed with 120 minutes of contact time. Meanwhile, the value of pH is varied from pH 2.0 to pH 11.0. Since methylene blue dye is a cationic dye, it is expected that dye uptake should be high at higher value of pH. Proven to be similar with previous studies using biosorbent such as biosolid (Sarioglu et al., 2006) and yellow passion fruit waste (F.A. Pavan et al., 2008), the result of dye percentage removal by DWH obtained from the study of pH effects is increasing with the increasing of pH values. At increasing pH in the range of 2.0 to 7.0, the value of

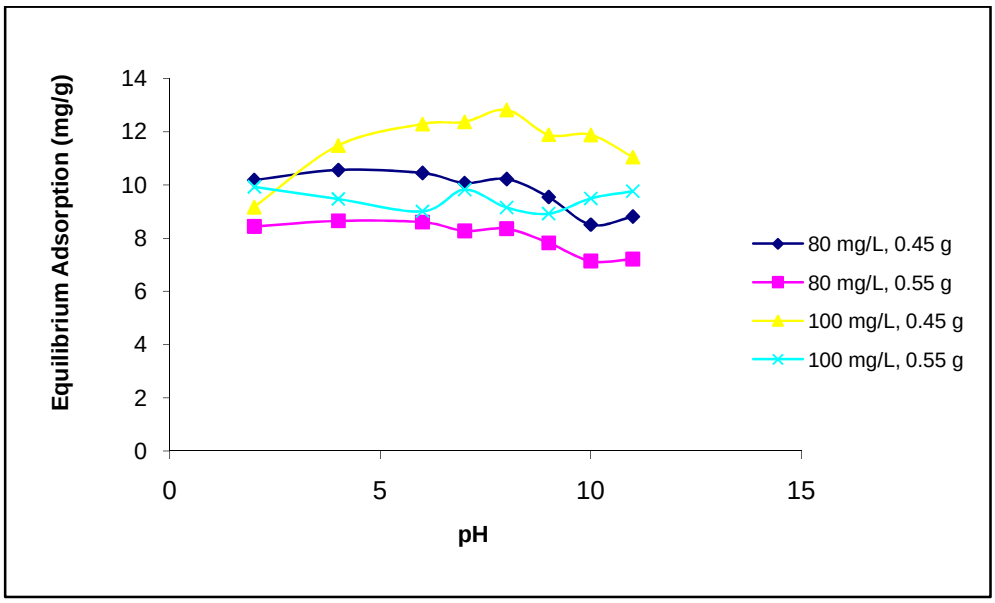
percentage removal and amount of dye sorbed were both increasing up to 97 % (Figure 4.5 (a)) and 10.2 mg/g (Figure 4.5 (b)). At pH 7.0 to 8.0, the uptake of dye is considerably constant but when proceeds to the higher pH value than 8.0, the percentage removal of dye as well as the amount of dye sorbed slowly decreasing with the increasing of pH value.

The procedure is repeated by varying values of dye initial concentrations (80 – 100 mg/L) and biosorbent dosage (0.45 – 0.55 g). Similar result is obtained where maximum uptake is clearly shown at pH 7.0 while low removal of dye is at pH lower and higher than 7.0. Hence, the optimum pH value for dye uptake is determined to be at pH 7.0.

At lower pH, which is in acidic condition, the removal of dye is low due to the excess of hydrogen ions, H+, competing with the molecules of dye cations to bind at the sorption sites at the surface of sorbent. Meanwhile, higher pH value caused the sorption sites on DWH surface to be more negatively charged thus enhance the capability of the binding activity between dye cations and sorbent surface through electrostatic forces of attraction. As the uptake value decreasing in the alkaline condition, it is because of the surface of dried water hyacinth become loaded with negatively charged ions that it attributed to solubilization of organic groups present on the surface of biosorbent (F.A. Pavan et al., 2008). This means that, the biosorption sites on the sorbent surface is decreasing hence, explained the reduction of dye removal.



(a)



(b)

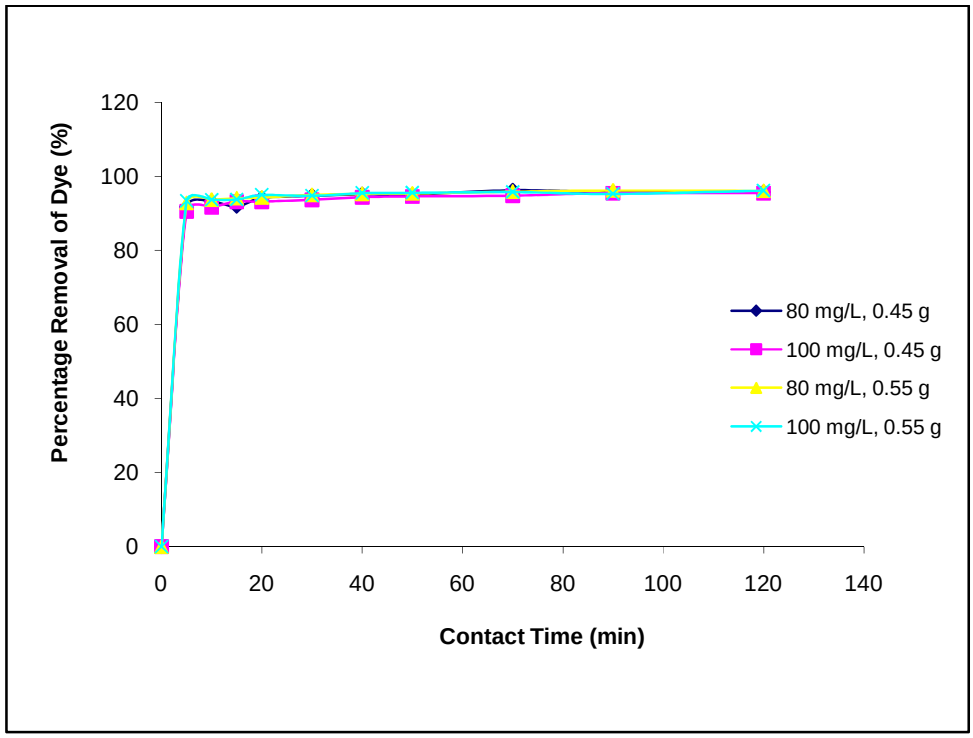
Figure 4.5. The effect of pH for the removal of MB. Speed=120 rpm, time=120minutes, pH=2.0-11.0, dosage=0.45-0.55g, Co=80-100mg/L: (a) Percentage removal and (b) Amount of dye sorbed

4.5 Effects of contact time

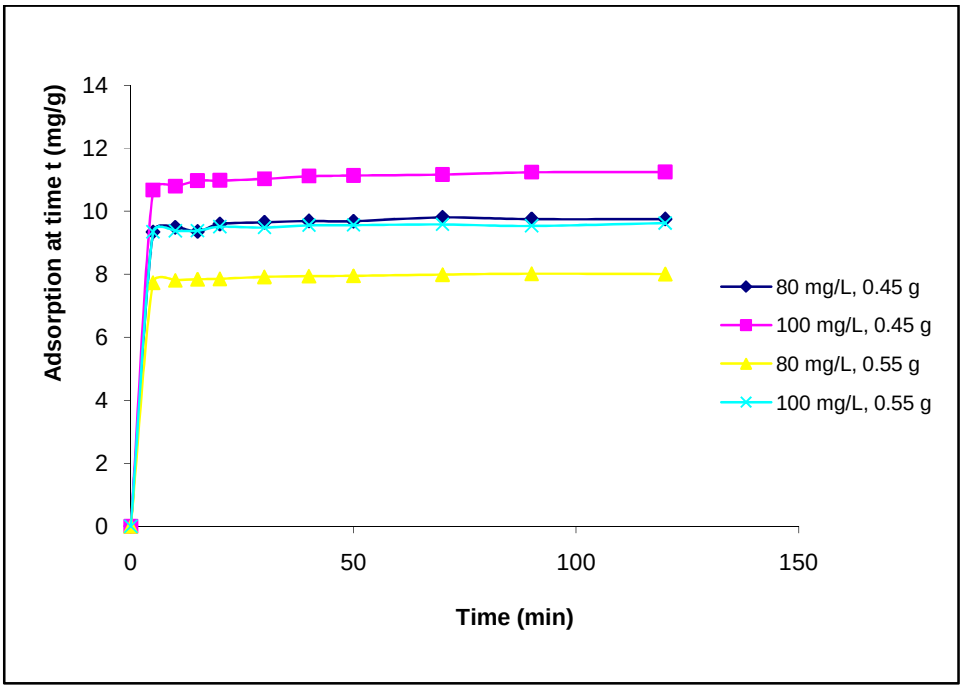
Biosorption rate can also be affected by varying the contact time during shaking the samples of MB solution. This parameter is done at the optimum dosage, initial concentration and pH for several different time intervals in the range from 5 to 120 minutes. The speed of shaker is kept constant at all time at 120 rpm. Figure 4.6 shows the result of this trial where (a) indicate the percentage dye removal and (b) is the sorption equilibrium. It can be explained clearly that the dye uptake increase with the increasing of time contact between the dye and biosorbent until it reached equilibrium at 90 to 100 minutes of experiment. Further extension of time contact results in constant value of removal which is at 96% percentage removal and 11.2 mg/g amount of dye sorbed approximately.

Trials are repeated with different value of initial concentration (C_o=100 mg/L) and biosorbent dosage (Dose=0.45 g) to observe the pattern of results. From Figure 4.6, similar curves are obtained where the dye uptake increased with the increasing of time until it reached equilibrium at 90 to 100 minutes and remained constant at further time extension.

Obviously, the dye uptake shows rapid removal of MB at the first 5 to 10 minutes and this is because the sorption activity took place at the outer surface of sorbent. Sorption process is followed by slower rate until it is attained from the 10^{th} to 100^{th} minute which can be explained by slow sorption activity inside the pores of DWH until it is saturated. Similar results are obtained from previous research using biosorbent such as biosolid (Sarioglu et al., 2006) and papaya seed (B.H. Hameed et al., 2008).



(a)



(b)

Figure 4.6. The effect of contact time for the removal of MB. Speed=120 rpm, time=5-120minutes, pH=7.0, dosage=0.45-0.55g, Co=80-100mg/L: (a) Percentage removal and (b) Amount of dye sorbed

4.6 Equilibrium isotherms

The Langmuir isotherm was tested for its ability to describe the experimental results. The derivation of the Langmuir isotherm is based on the assumption of ideal monolayer biosorption on a homogenous surface. A basic assumption is that sorption takes place at specific homogenous sites within the biosorbent. Once a dye molecule occupies a site, no further adsorption can take place at that site. The Langmuir adsorption isotherm has been successfully used to explain the adsorption of basic dyes from aqueous solutions (B.H.Hameed et al., 2008). It is expressed by:

q —— (4.1)

where C_e is the equilibrium concentration (mg/L), q_e the amount of dye adsorbed at equilibrium (mg/g), qm is q_e for complete monolayer adsorption capacity (mg/g), and K_a is the equilibrium adsorption constant (L/mg).

Figure 4.7 shows the experimental equilibrium data and the calculated Langmuir isotherms for the biosorption of MB onto DWH. The calculated isotherm constant is listed in Table 4.1. It can be seen from Figure 4.7 that Langmuir isotherm fits accordingly to the data which also confirmed by the high value of R^2 (0.996). This proves that the sorption of MB on DWH takes place as monolayer biosorption on a surface that is homogenous in biosorption affinity (B.H. Hameed et al., 2008). Table 4.1 indicates that the computed maximum monolayer biosorption capacity (q_m) of DWH for MB is accepted considerably, which is 19.61 mg/g.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by Equation 4.2 (B.H. Hameed et al., 2008):

R —— (4.2)

where C_o is the highest initial concentration of biosorbate (mg/L), and b (L/mg) is Langmuir constant. The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L values between 0 and 1 indicate favorable adsorption. For biosorption of MB onto DWH, R_L values obtained are shown in Figure 4.8. The R_L values for the biosorption of MB onto DWH are in the range of 0.0314–0.1412 which proves that the biosorption is a favorable process and at high initial MB concentrations the biosorption is nearly irreversible.

Table 4.1. Langmuir isotherm constant for MB sorption on DWH

Dosage 0.55g (Initial concentration=20,60,80,100 mg/L)						
C_o	C_e	q_e	C_e/q_e	q_m	K_a	R^2
22.43044	0.415065	2.001398	0.207388	19.60784	0.271277	0.996
63.68947	1.547271	5.649291	0.273888			
83.39431	2.195234	7.381734	0.297387			
113.761	3.873943	9.989732	0.387792			

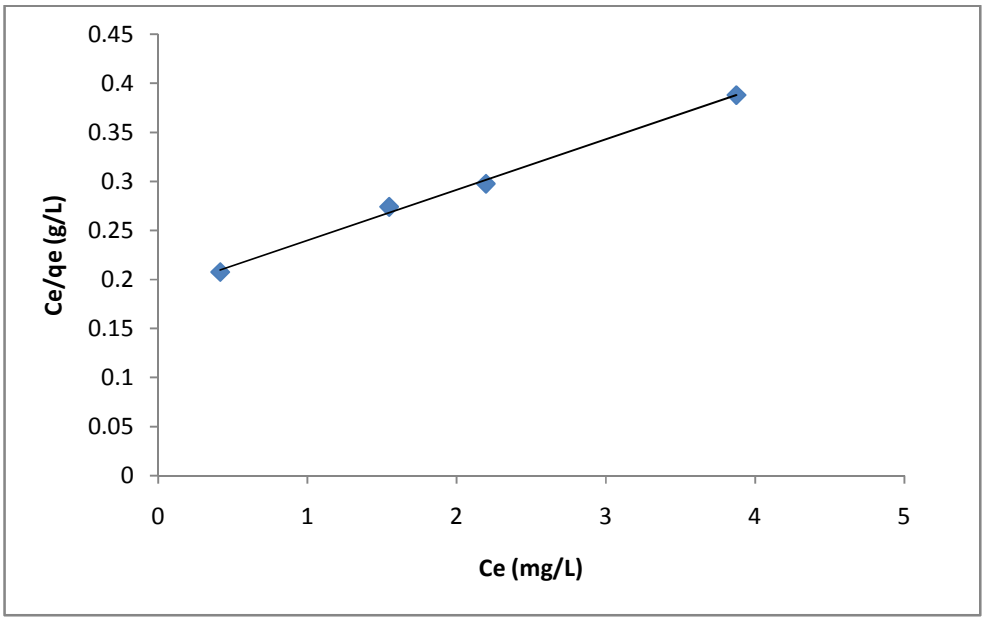


Figure 4.7. Langmuir isotherm plots for MB sorption on DWH

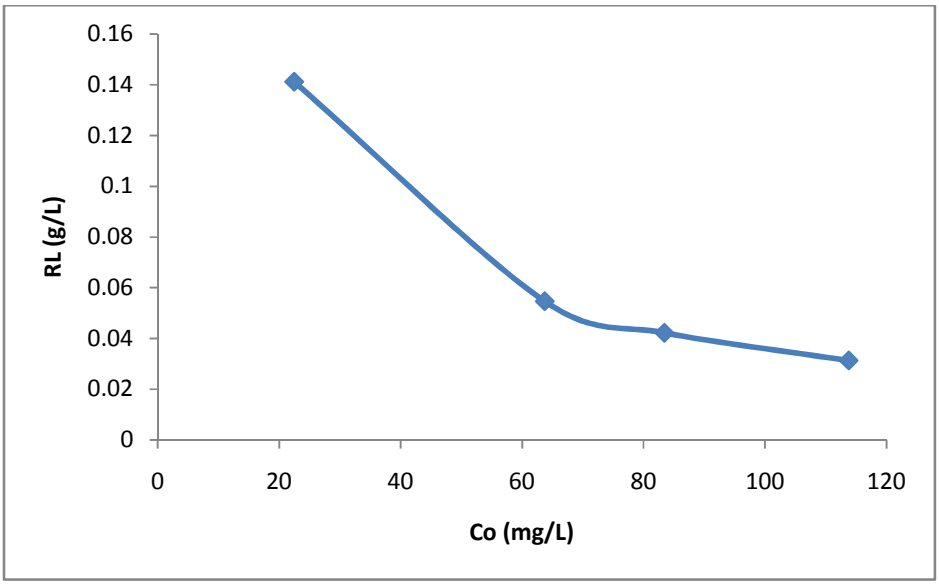


Figure 4.8. Separation factor for MB sorption on DWH

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Results and analyses obtained from this study proven that the biosorption of methylene blue from aqueous solution using dried water hyacinth is a success. The percentage removal of MB can be enhanced by the adjustments on the biosorbent dosage, initial concentration, pH solution and contact time where the results shows that the optimum conditions for the uptake of methylene blue are at 0.55g, 80 mg/L, pH 7.0 and 90 minutes, respectively.

Increasing of biosorbent dosage increased the dye removal because of the enhancement of the availability of sorption sites as the dried water hyacinth is added to the solution. Effects of initial concentration of dye is studied as well and the results shows that the uptake of dye rising when the concentration is increased. This is because of due to the stronger interaction between molecule of MB and DWH. The concentration of dye provides a driving force to overcome the resistances to the mass transfer between solid and aqueous phases. Solution pH affected the uptake by examined the biosorption at acidic, neutral and alkali condition and the data obtained indicates that in acidic condition, the removal of dye is low due to the excess of hydrogen ions, H+, competing with the molecules of dye cations to bind at the sorption sites at the surface of sorbent.

At higher pH caused the sorption sites to be more negatively charged thus enhance the capability of the binding activity between dye cations and sorbent surface through electrostatic forces of attraction. As the uptake value decreasing in the alkaline condition, it is because of the surface of DWH become loaded with negatively charged ions that it attributed to solubilization of organic groups present on the surface of biosorbent. Therefore, at neutral state (pH 7) is selected as the optimum condition. Meanwhile, the study of contact time between dye solution and sorbent shows that uptake is rapid initially as the sorption took place on the outer surface and followed by slower rate inside the pores of DWH and also the longer the time, the more removal is obtained until the sorption reached equilibrium which is due to the availability of sorption sites including the outer surface and pores of water hyacinth.

Moreover, the water hyacinth itself is proven to serve as a very potential biosorbent for the removal of MB. This can be explained by the determination of its functional group and binding sites available on the surface of the plant. The comparison of the availability of binding sites between before and after the biosorption clearly indicates that there are sorption activities occurring effectively.
The equilibrium data were well fitted to Langmuir model which shows that this sorption process takes place at specific homogenous sites within the biosorbent with its maximum monolayer biosorption capacity of 19.61 mg/g of DWH and also, the separation factor, R_L, values for the biosorption of MB onto DWH are in the range of 0.0314–0.1412 which proves that the biosorption is a favorable process.

As an addition, dried water hyacinths used in this study are abundantly available, does not require any further chemically pretreatment and possess high biosorption capacity for MB. Therefore, the biosorbent is likely to be economically feasible for removal of methylene blue dye from aqueous solutions.

5.2 Recommendations

In this study, only the stem part of the water hyacinth was taken as the biosorbent. This is because; the pore structures and physical appearance itself are different to be compared with the roots and other parts of the plant. Hence, it is strongly recommended that the water hyacinth is washed, dried and used separately to ensure the physical and chemical properties of the biosorbent is kept constant throughout the experiments. It is best to continue this study by using both stem and root (but separately) of the water hyacinth as the biosorbent to remove dye so that a comparison of which part contribute to the maximum biosorption capacity value can be determined.

Likewise, to attain a better result it is suggested that the biosorbent 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.

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APPENDIX A

EQUIPMENTS AND EXPERIMENTAL PROCESS

Figure A1. Collecting the water hyacinth at Pekan, Pahang

Figure A2. Washing the water hyacinth using tap water

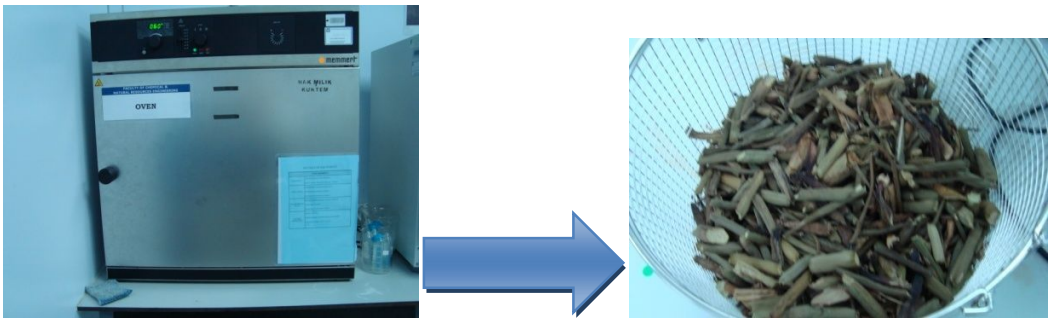

Figure A3. Water hyacinth is oven dried

Figure A4. Blending the dried water hyacinth

Figure A5. Filtration process and the sample to be analyzed

Figure A6. Stackable Incubator Shaker

Figure A7. Desiccator

Figure A8. pH meter

Figure A9. Samples in cuvettes

Figure A10. UV-Vis Spectrophotometer

Figure A11. Fourier Transform Infra Red

APPENDIX B

EXPERIMENTAL DATA

Table B1. Percentage removal experimental data for the effect of biosorbent dosage (C_o=20, 40, 100 mg/L, Dose=0.05-0.8 g)

Dose (g)	% Removal		
0.05	91.4	87.8	88.3
0.1	94.6	93.7	91.2
0.15	94	94.1	91.8
0.2	94.5	94.9	93.7
0.25	95.8	95.5	94.7
0.3	95.6	94.9	95.2
0.35	95.7	95.3	95.1
0.4	94.8	95.9	95.6
0.45	96.5	95.9	95.7
0.5	95.4	95.9	96.3
0.55	95.3	96	94.4
0.6	96.4	95.8	94.8
0.65	95.9	95.2	95.7
0.7	95.5	95.6	96.2
0.75	94.6	96.2	96.2
0.8	95.1	96.5	96.2

Table B2. Equilibrium adsorption data for the effect of biosorbent dosage (C_o=20, 40, 100 mg/L, Dose=0.05-0.8 g)

Dose (g)	qe (mg/g)		
0.05	21.34435	33.9854	89.93078
0.1	11.03843	18.14335	46.43234
0.15	7.316423	12.1381	31.18292
0.2	5.513451	9.190047	23.85856
0.25	4.472252	7.391546	19.29023
0.3	3.718806	6.125417	16.16615
0.35	3.190842	5.273087	13.83441
0.4	2.764796	4.63922	12.17649
0.45	2.479204	4.242805	10.37629
0.5	2.205919	3.968409	9.397079
0.55	2.001398	3.612536	8.369715
0.6	1.856393	3.305918	7.708109
0.65	1.704547	3.031514	7.184592
0.7	1.57659	2.82777	6.703031
0.75	1.457136	2.654625	6.257187
0.8	1.373559	2.496109	5.866593

Table B3. Percentage removal experimental data for the effect of initial concentration (Dose=0.3,0.6,0.8 g, C_o=20-200 mg/L)

Initial Concentration (mg/L)	% Removal		
20	92.7	92.9	89.2
40	94.5	95.7	94.7
60	92.6	95.4	95.4
80	94.6	96.4	97
100	94.8	96.2	97.1
120	94.2	94.8	97
140	95	96.5	97.3
160	94.2	95.9	96.8
180	93	95.7	96.3
200	93	95.7	96.4

Table B4. Equilibrium adsorption data for the effect of initial concentration (Dose=0.3,0.6,0.8 g, C_o=20-200 mg/L)

Initial Concentration (mg/L)	qe (mg/g)		
16.51038	2.65565	1.331284	0.958878
39.74865	6.371125	3.224635	2.392871
48.60338	7.607866	3.917499	2.937788
83.12529	13.21112	6.734563	5.082629
102.239	16.26915	8.254548	6.243611
122.6749	19.36933	9.745068	7.475692
169.0953	26.89342	13.6568	10.32653
159.1184	25.08365	12.76819	9.667083
166.4204	25.89585	13.32885	10.05366

192.2621	29.91635	15.38964	11.62519

Table B5. Percentage removal experimental data for effect of pH (Dose=0.45,0.55 g, C_o=80,100 mg/L, pH=2-11)

80 mg/L, 0.45 g ; 80 mg/L, 0.55 g ; 100 mg/L, 0.45g ; 100 mg/L, 0.55 g				
pH	% Removal			
2	93.8	95	79.2	93.4
4	96	96.5	95.5	95.7
6	96.1	96.6	95.8	95.8
7	96.3	96.7	96.6	96.1
8	96.5	96.4	95.7	95.8
9	96	96.2	95.6	95.4
10	95.5	95.9	95.4	95
11	95.8	95.9	95.3	94.6

Table B6. Equilibrium adsorption data for effect of pH (Dose=0.45,0.55 g, C_o=80,100 mg/L, pH=2-11)

80 mg/L, 0.45 g ; 80 mg/L, 0.55 g ; 100 mg/L, 0.45g ; 100 mg/L, 0.55 g				
pH	qe (mg/g)			
2	10.19131	8.445042	9.169015	9.935225
4	10.57059	8.652365	11.48347	9.48033
6	10.45726	8.605758	12.29055	9.014045
7	10.08037	8.278038	12.37228	9.831808
8	10.22803	8.360003	12.82407	9.161694
9	9.551371	7.829152	11.88974	8.926211

10	8.510547	7.143666	11.88718	9.503179
11	8.816039	7.217735	11.04817	9.769897

Table B7. Percentage removal experimental data for effect of time (Dose=0.45,0.55 g, C_o=80,100 mg/L, time intervals=5-120 minutes)

80 mg/L, 0.45 g ; 100 mg/L, 0.45 g ; 80 mg/L, 0.55 g ; 100 mg/L, 0.55 g				
Time (min)	% Removal			
0	0	0	0	0
5	91.8	90.6	92.8	93.4
10	93.2	91.7	93.7	93.7
15	91.9	93.2	94.1	93.8
20	94.2	93.2	94.3	95
30	94.8	93.7	95	94.8
40	95.2	94.4	95.3	95.5
50	95.1	94.6	95.4	95.6
70	96.3	94.8	95.9	95.8
90	95.8	95.5	96.2	95.3
120	95.8	95.5	96.1	96.2

Table B8. Equilibrium adsorption data for effect of time (Dose=0.45,0.55 g, C_o=80,100 mg/L, time intervals=5-120 minutes)

80 mg/L, 0.45 g ; 100 mg/L, 0.45 g ; 80 mg/L, 0.55 g ; 100 mg/L, 0.55 g				
Time (min)	qt (mg/g)			
0	0	0	0	0
5	9.344607	10.67469	7.733631	9.346444

10	9.49321	10.79708	7.808679	9.374884
15	9.359723	10.97216	7.84173	9.382291
20	9.596037	10.98019	7.854517	9.507369
30	9.65155	11.03254	7.917895	9.481795
40	9.693654	11.11623	7.939557	9.55237
50	9.687078	11.13955	7.950038	9.559357
70	9.807242	11.17064	7.989658	9.580739
90	9.75284	11.24263	8.017329	9.533503
120	9.753694	11.24947	8.007337	9.626439

APPENDIX C

PROCEDURE FOR SAMPLE ANALYSIS

Procedure using UV-Vis Spectrophotometer

1) Switch on the UV-Vis Spectrophotometer.
2) Wait until the equipment is calibrated completely.
3) Sample is diluted with minimum three times of dilution factor.
4) Place the diluted sample into the cuvette cell enough until it reach the margin on the cell.
5) Choose the characteristics to be analyzed on the screen and be sure to set the maximum wavelength of the sample before analyzing.
6) The data can be obtained at the 'Data Display' button.

Procedure using Fourier Transform Infra Red

1) Place the smart performer and switch on the FTIR.
2) Click on the software EZ OMNIC on the computer.
3) Follow the instructions given in the software.
4) Before placing the sample on the plate, it must be cleaned with acetone first.

5) Carefully handle the smart performer and the plate because it is a sensitive device.
6) Place the sample onto the cleaned plate.
7) Find the peaks according to the characteristics in the software.
8) Print out the data.