REMOVAL OF METHYL RED FROM AQUEOUS SOLUTION USING DRIED WATER HYACINTH *(Eichhornia Crassipes)*

NORIDAH ABDULLAH

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

ABSTRACT

Colouring effluent from industrial activities such as methyl red may affect environment and human health. Many methods have been used to decolourise such effluent including using low cost adsorbent. The objective of this study is to study the adsorption of methyl red from aqueous solution using dried water hyacinth. This study was focusing on the effect of decolourisation due to dosage of adsorbent, initial concentration of solution, pH, and the contact time. Adsorption isotherm was examined in this study and both the isotherms was found to be applicable in the case of dye adsorption using dried water hyacinth. The applicability of the pseudo first order and second order was also examined to conforms the adsorption kinetic. And it is fit well with pseudo second order. The effectiveness of the method was determined by measuring the percentage of removal the methyl red. It is found that the removal was directly proportional to the dosage and contact time. For the initial concentration the removal is inversely proportional and for the pH, it increase from pH 2-3 and decrease from pH 3-7. The higher percentage of removal is 88% and the optimum condition for this study was identified. For the dosage, 3.0 g is the optimum and 50 mg/L for initial concentration, pH 3 and 120 minutes for the contact time. As a conclusion dried water hyacinth can be used as a adsorbent to remove the methyl red.

ABSTRAK

Sisa berwarna daripada aktiviti industri seperti methyl red memberi kesan kepada persekitaran dan kesihatan manusia. Pelbagai kaedah telah digunakan untuk menyahwarna sisa ini termaksuklah kaedah yang menggunakan aplikasi penyerapan. Kajian ini dilaksanakan untuk menyelidik penyerapan larutan yang mengandungi bahan pewarna methyl red menggunakan keladi bunting yang kering. Fokus kajian ini menjurus kepada kesan penyingkiran oleh faktor jumlah serbuk keladi bunting, kepekatan larutan. pH dan masa bertindak balas. Isoterma penyerapan telah di kaji dan kedua-dua Lamgmuir dan Freundlich boleh digunakan dalam kes penyerapan warna menggunakan keladi bunting kering. Kesesuaian isoterma kinetik juga di kaji dan pseudo second order boleh digunakan dalam kes ini. Keberkesanan kaedah ini ditentukan melalui pengukuran peratusan penyingkiran warna. Sebagai hasilnya, penyingkiran warna berkadar langsung dengan jumlah keladi bunting dan masa. Untuk kepekatan larutan, penyingkiran berkadar songsang dan untuk pH, ia menaik dr pH 2-3 dan menurun dari pH 3-7. Peratusan tertinggi bagi kajian ini adalah 88% dan tahap maksimum juga telah dikenal pasti. Jumlah keladi bunting kering yang maksimum adalah 3.0 g, larutan kepekatan 50 mg/L, pH 3 dan 120 minit untuk masa bertindak balas. Sebagai kesimpulan keladi bunting kering boleh digunakan sebagai penjerap untuk menyingkirkan pewarna methyl red.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

%	-	Percentage
BOD	-	Biochemical oxygen demand
COD	-	Chemical Oxygen Demand
MTMA	-	Malaysia Textile Manufacturer Association
TSS	-	Total Suspended Solid
cm	-	Centimeter
g	-	Gram
h	-	Hour
L	-	Liter
min	-	Minute
ml	-	Milliliter
ºC	-	Degree celcius
MR	-	Methyl Red
rpm	-	Revolution per minute
DWH	-	Dried Water Hyacinth
DOE	-	Department of Environment
C.I.	-	Colour Index
TDS	-	Total Dissolved Solid
Al^{3+}	-	Aluminium
UV	-	Ultraviolet

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background

Water pollution is one of the most serious problems of today's civilization. The consumption of water has been doubling on every twenty years but the reduction of this period is expected if today's trends in water use continue (Velasevic and Djorovic, 1998). These two statements justify people's fear that whole areas of the world will remain without biochemical safe water suitable for drinking and other needs. One can say situation is already alarming if it is known that because of fresh water disposition on Earth only one third of its territory is well provide with water, and if drastic efforts in water protection are not made by year 2025, 2.3 billion people will live in areas with chronic water shortage (WHO, 2005). In order to overcome this problem, many processes in wastewater treatment plant are design.

Dyes is one of the pollutant in water. It is used in the cotton industry which makes up 50% of the world's fiber consumption. They are commonly used in the textile industry because of their bright colours, excellent colourfastness and ease of application (Ho *et al.,* 2001).

Methyl red is one of the pollutant in water. It is used in the cotton industry which makes up 50% of the world's fiber consumption. They are commonly used in the textile industry because of their bright colours, excellent colourfastness and ease of application (Gupta *et al.*, 2007). Methyl red, also called C.I. Acid Red 2, is an indicator dye that turns red in acidic solutions. It is an azo dye, and is a dark red crystalline powder.Methyl Red (MR) is a commonly used monoazo dye in laboratory assays, textiles and other commercial products; however, it may cause eye and skin sensitization (Hayes *et al.*, 2004) and pharyngeal or digestive tract irritation if inhaled or swallowed (Badr *et al.*, 2008). Furthermore, MR is mutagenic under aerobic conditions: it undergoes biotransformation into 2-aminobenzoic acid and N-N'-dimethyl-p-phenylene diamine (Chung *et al.*,1981). Of late, there has been increasing interest to develop low-cost means (Aksu *et al.*, 2003) of reducing the amount of, if not completely remove, MR in wastewater before being discharged into receiving water body.

The conventional wastewater treatment, which rely on aerobic biodegradation have low removal efficiency for reactive and other anionic soluble dyes. Due to low biodegradation of dyes, a convectional biological treatment process is not very effective in treating a dyes wastewater. It is usually treated with either by physical or chemical processes. However, these processes are very expensive and cannot effectively be used to treat the wide range of dyes waste (Grag, V.K *et al.*, 2004).The adsorption process is one of the effective methods for removal dyes from the waste effluent. The process of adsorption has an edge over the other methods due to its sludge free clean operation and completely removed dyes, even from the diluted solution. Activated carbon (powdered or granular) is the most widely used adsorbents because it has excellent adsorption efficiency for the organic compound. But, commercially available activated carbon is very expensive (Shaobin Wang *et al.*, 2005).

This had lead to further studies for cheaper substitutions. Nowadays, there are numerous number of low cost, commercially available adsorbents which had been used for the dye removal . However, as the adsorption capacities of the above adsorbents are not very large, the new adsorbents which more economical, easily available and highly effective are still needed. Water hyacinth is one of the low cost adsorbent that being used in this study to investigate the removal of methyl red in wastewater treatment.

1.2 Problem Statement

Dyes production industries and many others industries which use dyes and pigments generated wastewater, characteristically high in colour and organic content (Grag, V.K *et al.*, 2004). Dyes are widely used in industries such as textile, rubber, paper, plastic, and cosmetic. There are many of dyes exist in industries and one of them is methyl red which is to remove in this project.

In wastewater treatment plant, the cost of removal dyes is expensive. As chemical and mechanical removal is expensive and unaffectedly, the researchers is looking for the other alternative such as water hyacinth (*Eichhornia crassipes*) as a biological control agent. In this study, water hyacinth is used to investigate the removal of methyl red. Water hyacinth is chosen to be used in wastewater treatment due to their fast growth and ability to tolerate high levels of pollution. The water hyacinth is also easy to get according to their growth at any lakes. Water hyacinth thrive on sewage; they adsorb and digest wastewater pollutants, converting sewage effluents to relatively clean water (Gian Gupta, 1981). Dried water hyacinth are used in this research because it can decrease the area needed and to avoid the spreading of mosquito. It also used because of the easy handling and to avoid the odour.

The adsorption process is one of the effective methods for removal dyes from the waste effluent. The process of adsorption has an edge over the other methods due to its sludge free clean operation and completely removed dyes, even from the diluted solution (Shaobin Wang *et al.,* 2005).

1.3 Objective of study

This study is to achieve the following objectives:

1. To study the adsorption of methyl red by using dried water hyacinth.

1.4 Scope of study

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

1) Effect of initial concentration.
2) Effect of dried water hyacinth dosage.
3) Effect of pH.
4) Effect of contact time.

1.5 Rational and Significant

This research can help in minimizing the environmental impact cause by used water hyacinth as a adsorbent and can minimize the cost of treatment water. This research can also be used as a guideline and references in producing a new adsorbent for water treatment.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Surface water becomes coloured by pollution caused by highly coloured wastewater (Sawyer *et al.*, 1994). Coloured wastewater was waste from dyeing operation in paper, leather, and textile industry. In Malaysia textile industry is the largest industry that discharged highly coloured wastewater (Japan Consulting Institute, 1993). Coloured wastewater affecting environment and human health if directly discharge without treatment. That's make the treatment of dye wastewater are important. There are many treatment used to treat dyes effluent including using electricity. However, the performances of this process are not well defined.

2.2 Water pollution by textile industry

Water is so common that we take it for granted. Moreover, its covers nearly three-fourth of the surface of the earth. Water pollution problems in any part of world are far worse from day to day. Water that has been withdrawn, used for some purposed and returned will be polluted in one-way or another. Agricultural return water containing pesticides, fertilizer, and salt, municipal return water containing human sewage, industry returned water-containing chemical. All of this is due to human activity. When water was polluted, the water become unsuitable for drinking water and habitat for aquatic live. Wastewater discharged from textile industry characterized by high chemical demand (COD), low biodegradability, high salt content and is the source aesthetic pollution related to colour (Alinsafi *et al.,* 2004). Dyes formula contain numerous auxiliary ingredients for desizing, scouring and mercerising (Wu *et al.,* 1998). The salt and heavy metal from highly coloured wastewater are toxic to aquatic live (Wu *et al.*, 1998). While some of dye such as Azo dye is carcinogenic, this can cause serious health problem such as cancer (Maarit *et al.,* 2000). This caused the treatment of dye before discharged are important in order to ensure sustainable development able to achieve.

Based on report wrote by Japan Consulting Institute (1994), textile industry is the fifth major industry that become source of environmental problem (*table 2.1*). However, in term of colouring effluent textile industry is the largest industry discharging colouring effluent. So it is important to studies treatment process that is efficient to reduce the colour in the effluent. In order to ensure our water are safe for future generation. Japan Consulting Institute (1994) report wrote that, in Malaysia, textile industry is the second largest industry following the electric appliance industry in term of export. Since the domestic market for the product is small, so most of products are exported. The export amount reached 6433 million in 1992. Due to growth of the industry, textile companies has formed Malaysia Textile Manufacturer Association (MTMA). In 1994 number of member registered in MTMA was 290. All of this factories scattered around Selangor, Johor, Pulau Pinang, Terengganu, Kedah and Kelantan.

Table 2.1: Industrial sources of water pollution

Type of industry	Percentage, %
Palm oil	11.6
Raw natural rubber	8.6
Rubber and product	14.1
Food and beverage	40.5
Textile and leather	9.0
Paper	4.4
Chemical	11.8
Total	100

(source : Environmental Quality report 1991)

In accordance with the development of textile industry, the pollution of environment by the industry has become apparent. Especially coloured wastewater discharge from dyeing factory. Coloured wastewater caused serious environmental problems in various locations. Previously DOE has conducted investigation in the bigger textile company. Based on their report, bigger textile industry does equipped with treatment facilities. However, for coloured problem the factories not able to solve the problem of decolourisation. Many of factories discharge coloured wastewater without any treatment because colour is outside the scope of regulation. For small to middle size factory they don't even have treatment facilities to reduced pH, TSS, COD,BOD, temperature and all the hazardous chemical. This caused the pollution caused by textile industry become worst. To reduce water pollution caused by textile industry, study must be done to treat the textile effluent efficiently.

2.3 Dyes

Dyes can be classified on the basis of their solubility: soluble dyes which include acid, mordant, metal complex, direct, basic and reactive dyes; and insoluble dyes including azoic, sulfur, vat and disperse dyes. Though, the classification of dyes on basis of structure is an appropriate system and has many advantages, like it readily identifies dyes as belonging to a group and having characteristic properties. Besides these, both the synthetic dye chemist and the dye technologist use this classification most widely. However, the classification based on application is advantageous before considering chemical structures in detail because of the complexities of the dye nomenclature from this type of system. It is also worth to point that classification by application is the principal system adopted by the Colour Index (C.I.). Some properties of dyes classified on their usage (Christie, 2007; Hunger, 2003) are discussed in brief here.

Acid Dyes: An **acid dye** is a type of dye that is applied from an acidic solution. In textiles, acid dyes are effective on protein fibers—particularly animal hair fibers such as wool, alpaca, and mohair. They are also useful for dyeing silk. Acid dyes are thought to attach to fibers by ionic bonds, hydrogen bonds, and Van der Waals forces. The chemistry of acid dyes is quite complex. Dyes are normally very large aromatic molecules consisting of many linked rings. Acid dyes usually have a sulfonyl or amino group on the molecule making them soluble in water. Water is the medium in which dyeing takes place.

Cationic (Basic) Dyes: Any of the dyes which are salts of the colored organic bases containing amino and imino groups, combined with a colorless acid, such as hydrochloric or sulfuric. Used for paper, polyacrylonitrile, modified nylons, modified polyesters, cation dyeable polyethylene terephthalate and to some extent in medicine too.

Disperse Dyes: used mainly on polyester and to some extent on nylon, cellulose, cellulose acetate, and acrylic fibers. These are substantially water-insoluble nonionic dyes used for hydrophobic fibers from aqueous dispersion. They generally contain azo, anthraquinone, styryl, nitro, and benzodifuranone groups.

Direct Dyes: used in the dyeing of cotton and rayon, paper, leather, and, to some extent to nylon. They are water-soluble anionic dyes, and, when dyed from aqueous solution in the presence of electrolytes have high affinity for cellulosic fibers. Generally the dyes in this class are polyazo compounds, along with some stilbenes, phthalocyanines and oxazines.

Reactive Dyes: generally used for cotton and other cellulosics, but are also used to a small extent on wool and nylon. These dyes form a covalent bond with the fiber and contain chromophoric groups such as azo, anthraquinone, triarylmethane, phthalocyanine, formazan, oxazine, etc. Their chemical structures are simpler, absorption spectra show narrower absorption bands, and the dyeings are brighter making them advantageous over direct dyes.

Solvent Dyes: used for plastics, gasoline, lubricants, oils, and waxes. These dyes are solvent soluble (water insoluble) and generally nonpolar or little polar, i.e., lacking polar solubilizing groups such as sulfonic acid, carboxylic acid, or quaternary ammonium. The principal chemical classes are predominantly azo and anthraquinone, but phthalocyanine and triarylmethane are also used.

Overall at present there are more than 100,000 commercial dyes with a rough estimated production of 701246 tons per year (Christie, 2007; Hunger, 2003; Husain, 2006; Meyer, 1981; Zollinger, 1987). Of such a huge production the exact data on the quantity of dyes discharged in environment is not available. However, it is reported that

10–15% of the used dyes enter the environment through wastes (Hai *et al.,* 2007;Husain, 2006). The big consumers of dyes are textile, dyeing, paper and pulp, tannery and paint industries, and hence the effluents of these industries as well as those from plants manufacturing dyes tend to contain dyes in sufficient quantities.

Dyes are considered an objectionable type of pollutant because they are toxic (Bae and Freeman, 2007; Christie, 2007; Combes and Havelandsmith, 1982; Nemerow and Doby, 1958) generally due to oral ingestion and inhalation, skin and eye irritation, and skin sensitization leading to problems like skin irritation and skin sensitization and also due to carcinogenicity (Christie, 2007; Hatch and Maibach,1999; Rai *et al.,* 2005). They impart colour to water which is visible to human eye and therefore, highly objectionable on aesthetic grounds. Not only this, they also interfere with the transmission of light and upset the biological metabolism processes which cause the destruction of aquatic communities present in ecosystem(Kuo,1992; Walsh *et al.,* 1980). Further, the dyes have a tendency to sequester metal and may cause micro toxicity to fish and other organisms (Walsh *et al.,* 1980). As such it is important to treat coloured effluents for the removal of dyes.

Table 2.2: Typical characteristic of dyes used in textile industry

Dye class	Description	Fibers typically applied to	Typical pollutant associated with various dyes
Acid	Water-soluble anionic compounds	wool, nylon	Colour, organic acids, unfixed dyes
Basic	Water-soluble, applied in weakly acidic dye baths , very bright dyes	Acrylic, some polyesters	N/A
Direct	Water-soluble. Anionic compounds, can be applied directly to cellulosics without mordant (or metals like chromium and copper)	Cotton, rayon, other cellulosics	Colour, salt, unfixed dye, cationic fising agents, surfactant, defoamer, levelling and retarding agents, finish, diluents
Disperse	Not water-soluble	Polyester acetate, other synthetics	Colour, organic acids, phosphate, carriers, levelling, defoamers, lubricants, diluents
Reactive	Water-soluble, anionic compounds, largest dyes class	Cotton, other cellulosics, wool	Colour, salt, alkali, unfixed dye,, surfactant, defoamer, diluents, finish
Sulfur	Organic compounds containing sulphur or sodium sulphide	Cotton, other cellulosics	Colour, alkali, oxidizing agents, reducing agent, unfixed dye
Vat	Oldest dyes, more chemically complex, water insoluble	Cotton, other cellulosics	Colour, alkali, oxidizing agent, reducing agent

(Sources: DOE, 1997)

2.4 Methods of dye removal

Few decades earlier, the dyes selection, application and use were not given a major consideration with respect to their environmental impact. Even the chemical composition of half of the dyes used in the industry was estimated to be unknown. With the growing concern on health mainly on aesthetic grounds, it was more from 80s that people started paying much attention to the dye wastes too. In the last few years, however, more information on the environmental consequences of dyestuff usage has become available and the dye manufacturers, users and government themselves are taking substantial measures to treat the dye containing wastewaters.

Since initially there was no discharge limit the treatment of dye wastewater started just with some physical treatments such as sedimentation and equalisation to maintain the pH, total dissolved solids (TDS) and total suspended solids (TSS) of the discharged water. Later secondary treatments such as the use of filter beds for biodegradation and, more recently, the introduction of the activated sludge process (aerobic biodegradation) were used to treat the dye wastewater. Normally industrial-wastewater treatment processes (Perry *et al.*, 1997) consist of following steps like: Pre-treatment – industrial-wastewater streams prior to discharge to municipal sewerage systems or even to a central industrial sewerage system are pretreated doing equalisation, neutralization; then they undergo primary treatment and wastewater is directed toward removal of pollutants with the least effort.

Suspended solids are removed by either physical or chemical separation techniques and handled as concentrated solids; then they are given a secondary treatment usually involving microorganisms (biological treatment) primarily bacteria which stabilize the waste components. The third step is physical–chemical treatment or tertiary treatment and the processes included in this are adsorption, ion exchange, stripping, chemical oxidation, and membrane separations. All of these are more expensive than biological treatment but are used for the removal of pollutants that are not easily removed by biological methods. Though these are generally utilized in series with biological treatment, sometimes they are used as stand-alone processes too. The final step being the sludge processing and disposal.

Dye wastewater are also treated in more or less a similar way, nevertheless, there is no single standard methodology/treatment procedure used for all types of wastes. We are classifying the methodologies generally adopted to treat dye wastewater in four categories: (i) physical (ii) chemical (iii) biological and (iv) acoustical, radiation, and electrical processes. Some of the methodologies lying in above mentioned categories are discussed in brief in subsequent paragraphs.

Sedimentation is the basic form of primary treatment used at most municipal and industrial-wastewater treatment facilities (Cheremisinoff, 2002). There are a number of process options available to enhance gravity settling of suspended particles, including chemical flocculants, sedimentation basins, and clarifiers.

Filtration technology is an integral component of drinking water and wastewater treatment applications which includes microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. This has been investigated for colour removal (Avlonitis *et al.,* 2008; Cheremisinoff, 2002). Each membrane process is best suited for a particular water treatment function (Cheremisinoff, 2002). Among them, microfiltration is of not much use for wastewater treatment because of its large pore size, and though ultrafiltration and nanofiltration (Cheremisinoff, 2002; Marmagne and Coste, 1996) techniques are effective for the removal of all classes of dyestuffs, dye molecules cause frequent clogging of the membrane pores making the separation systems of limited use for textile effluent treatment. The main drawbacks are high working pressures, significant energy consumption, high cost of membrane and a relatively short membrane life which makes their use limited for treating dye wastewater. Reverse osmosis forces water, under pressure, through a membrane that is impermeable to most contaminants. The membrane is somewhat better at rejecting salts than it is at rejecting non-ionized weak acids and bases and smaller organic molecules generally molecular weight below 200. Reverse osmosis (Al-Bastaki, 2004; Marcucci *et al.,* 2001; Sostar-Turk *et al.,* 2005) is effective decolouring and desalting process against the most diverse range of dye wastes, and has been successfully employed for recycling. The water produced by reverse osmosis, will be close to pure H_2O.

Chemical treatment of dye wastewater with a coagulating/ flocculating agent (Shi *et al.,* 2007; Wang *et al.,* 2006a; Zhou *et al.,* 2008) is one of the robust ways to remove colour. The process involves adding agents, such as aluminum (Al^{3+}), calcium (Ca^{2+}) or ferric (Fe^{3+}) ions, to the dye effluent and induces flocculation. Besides these other agents (Mishra and Bajpai, 2006; Mishra *et al.*, 2006; Yue *et al.*, 2008) have also been used for the process. Sometimes combination (Wang *et al.*, 2007) of two may also be added to enhance the process. Generally, the process is economically feasible (but sometimes becomes expensive due to the cost of chemicals) with satisfactory removal of disperse, sulfur, and vat dyes. However, the main drawback of the process is that the final product is a concentrated sludge produced in large quantities also, besides this, the removal is pH dependent (Kace and Linford, 1975; Lee *et al.*, 2006). This process is not good for highly soluble dyes and the result with azo, reactive, acid and especially the basic dyes (Hai *et al.,* 2007; Raghavacharya, 1997) are generally not good.

Oxidation is a method by which wastewater is treated by using oxidizing agents. Generally, two forms viz. chemical oxidation and UV assisted oxidation using chlorine, hydrogen peroxide, fenton’s reagent, ozone, or potassium permanganate are used for treating the effluents, especially those obtained from primary treatment (sedimentation). They are among the most commonly used methods for decolourisation processes since they require low quantities and short reaction times. They are used to partially or completely degrade the dyes (generally to lower molecular weight species such as aldehydes, carboxylates, sulfates and nitrogen). However, a complete oxidation of dye