REMOVAL OF MALACHITE GREEN FROM AQUEOUS SOLUTION BY ADSORPTION USING LUFFA SPONGE BIOMASS

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DISSERTATION SUBMITTED IN PARTIAL FULFILMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
BACHELOR OF SCIENCE WITH HONOURS

INDUSTRIAL CHEMISTRY PROGRAMME
SCHOOL OF SCIENCE AND TECHNOLOGY
UNIVERSITY MALAYSIA SABAH

APRIL 2007

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PUMS 99:1

UNIVERSITI MALAYSIA SABAH

BORANG PENGESAHAN STATUS TESIS@

JUDUL: REMOVAL OF MALACHITE GREEN FROM AQUEOUS SOLUTION BY ADSORPTION USING LUFFA SPONGE BIOMASS

Ijazah: SARJANA MUDA SAINS DENGAN KEPUJIAN (KIMIA INDUSTRI)

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DECLARATION

I hereby declare that this dissertation is based on my original work, except for the quotation and summaries each of which have been fully acknowledged.

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ACKNOWLEDGEMENTS

I wish to thank Assoc. Prof. Dr. Marcus Jopony for providing me so many helpful comments during the entire period doing this project. I also wish to thank all the lab assistants for assisting me in the lab. Besides this, I wish to thank also my family members for supporting me throughout the whole project.

ABSTRACT

The adsorption removal of malachite green from aqueous solution using luffa sponge biomass was determined by batch method under different contact time, initial dye concentration and adsorbent dosage. The residual dye concentration was analysed spectrophotometrically at λ=692nm. The results showed that the adsorption process was rapid with significant removal of malachite green from solution after 5 minutes. Equilibrium was, however, attained after 60 minutes. The adsorption confirms to pseudo-second-order kinetic model (R^2= 0.9996) as well as to both Freundlich and Langmuir isotherms (R^2= 0.9638 and R^2= 0.9789). The calculated maximum adsorption capacity was 10.46 mgg^{-1}. The effect of initial dye concentration and adsorbent dosage on removal of malachite green (more than 88% removal), was not very apparent for the range of concentrations and dosages studied. Overall, luffa sponge can potentially be used for the removal of cationic pollutants, including malachite green, from wastewater.

PENYINGKIRAN SECARA JERAPAN PEWARNA MALACHITE GREEN DARIPADA LARUTAN AKUES MENGGUNAKAN SERABUT PETOLA

ABSTRAK

Penyingkiran secara jerapan pewarna malachite green daripada larutan akues menggunakan serabut petola telah ditentukan berdasarkan kaedah kelompok pada keadaan masa, kepekatan awal pewarna, dan amaun penjerap yang berbeza. Kepekatan residu pewarna dianalisis secara spektrofotometrik pada λ*=692nm. Hasil kajian menunjukkan bahawa jerapan pewarna malachite green adalah cepat dan signifikan dalam masa 5 minit. Namun demikian, takat keseimbangan hanya dicapai selepas 60 minit. Proses jerapan mematuhi model kinetik tertib pseudo kedua (*R^2*= 0.9996), isoterma Langmuir dan isoterma Freundlich (*R^2*= 0.9638 dan* R^2*= 0.9789). Kapasiti jerapan maksimum yang didapati adalah 10.46mgg*$^{-1}$*. Kepekatan awal pewarna dan amaun penjerap tidak memberi pengaruh yang signifikan terhadap penyingkiran pewarna malachite green dalam lingkungan kepekatan dan amaun penjerap yang dikaji (lebih daripada 88% penyingkiran pewarna). Pada keseimbangan, serabut petola boleh digunakan untuk penyingkiran bahan pencemar kation, termasuk pewarna malachite green, daripada efluen.*

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LIST OF SYMBOLS

a_L	Langmuir isotherm constant(mgl^{-1})
C_e	equilibrium dye concentration in solution (mgl^{-1})
C_o	Initial concentration (mgl^{1})
K_L	Langmuir isotherm constant (gl^{-1})
K_F	Freundlich constant (gl^{-1})
k_1	equilibrium rate constant of pseudo-first-order sorption (min^{-1})
k_2	equilibrium rate constant of pseudo-second-order sorption (min^{-1})
m	mass of adsorbent (g)
M_1	concentration of stock solution (1000 mgl^{-1})
n_F	Freundlich isotherm exponent
M_2	concentration of the experimental solution
q_e	amount of dye adsorbed at equilibrium (mgg^{-1})
q_{max}	maximum adsorption capacity of the adsorbent (mgg^{-1})
q_t	amount of dye adsorbed at time t (mgg^{-1})
R^2	correlation coefficient
R_L	separator factor
t	time (min)
V	volume of dye solution (ml)
x	amount of dye adsorbed (mg)

CHAPTER 1

INTRODUCTION

1.1 CONTEXT AND RELEVANCE OF STUDY

Wastewaters from a number of industries can be highly coloured due to the presence of dyes. Examples of such industries include textile, leather, cosmetics, paper, printing, plastic, pharmaceuticals and food (Dilek *et al.*, 2005). The dye contaminants can be mainly synthetic dyestuff of varying types. The types of dyes that can be found in wastewaters can be acid dyes, azoic dyes, basic dyes, direct dyes, disperse dyes, reactive dyes, sulphur dyes, or vat dyes. The appearance of colour in dye is due to the presence of chromophores such as azo, anthraquinone, nitro, methane and quinoline-based structures (Steiner & Miskie, 1992).

Discharge of such coloured effluents to the surrounding aquatic environment can cause water to be highly coloured, coupled with high chemical and biological demands (COD and BOD) and suspended solids. It will also affect its aesthetic value. Colour interferes with penetration of sunlight into waters, retards photosynthesis, inhibits the growth of aquatic biota and interferes with gas solubility in water bodies. It also poses a problem because of its carcinogenicity and toxicity (Dilek *et al.* 2005).

Due to the environmental adverse impacts, such effluents need to be treated to remove the dyes prior to discharge. The conventional methods for treating dye-containing wastewaters include oxidation, ion exchange, membrane filtration, coagulation and flocculation, ozonation, photochemical, irradiation, electrokinetic coagulation, adsorption, and biological treatment (Chuah *et al.*, 2005). Overall, the most popular of these technologies is adsorption technique. However, the conventional carbon adsorbent need in this technique is expensive. Therefore, there is a growing interest in using low-cost, easily available materials as adsorbents for the adsortion of dye (Ayla *et al.*, 2005). Examples of low cost adsorbents that have been studied include algae (Vasanth *et al.*, 2005), hen feathers (Mittal, 2005), agro-industry waste (Garg *et al.*, 2004), wheat bran (Papinutti *et al.*, 2006), dead fungal (Dilek *et al.*, 2005), rice husk (Chuah *et al.*, 2004), and lemon peel (Vasanth, 2006). Biomass type of adsorbent are also known as biosorbents.

Luffa sponge is a locally widely available plant biomass. Due to it's promising properties, such as availability, biodegradability, and microcapillary structure, luffa sponge could be useful as adsorbent materials. However, the adsorption ability of this materials have not been fully explored (Tanobe *et al.*, 2005).

1.2 OBJECTIVE OF STUDY

The objectives of this study are

(a) To evaluate the efficiency of luffa sponge as biosorbent for the removal of dye from aqueous solution.

(b) To study the effects of operating conditions namely contact time, dye concentration and adsorbent dosage on dye removal efficiency.

1.3 SCOPE OF STUDY

In this study, the adsorbent used will be luffa sponge while the adsorbate is Malachite Green dye. Batch adsorption experiments will be carried out under different operating conditions. The final dye concentration in solution will be determined spectrophotometrically.

CHAPTER 2

LITERATURE REVIEW

2.1 DYE

Dyes usually have a synthetic origin and complex aromatic molecular structures (Fu & Viraraghavan, 2002). Dyes, unlike pigments, do dissolve during their application and in the process lose their crystal or particulate structure. There are more than 100,000 dyes available commercially today (Ayla *et al.,* 2005).

2.1.1 Classification of Dyes

Dyes can be classified into few classes as shown in Table 2.1. Its structural features serve as the basis for their classification and determine the substrates for which they have affinity (Steiner & Miskie, 1992).

Acid dyes owe their name to the fact that they are generally applied to textile fibres from dye-baths containing acid. Most have one or two sodium sulfonate (-SO_3Na) groups and consequently, are water soluble and capable of bonding with fibres having cationic sites. They give a wide range of bright colours on textiles, especially when monoazo and anthraquinone structures are used.

Table 2.1 Classification of dyes

Types of dyes	**Characteristics**	**Main Usage**	**Examples**
acid	Most have one or two sodium sulfonate (–SO_3Na) groups, water soluble	textile fibres dyeing	C.I. Acid Yellow 42 and C.I. Acid Red 151
azoic	Carry an azo function (-N=N-) between two sp^2 hybridized C atoms, water insoluble	cotton printing	Pigment Yellow 1
basic	presence of aromatic amino (basic) groups, cationic amino group	textile fibres dyeing	C.I. Basic Green 4
direct	based on four main chromophores: azo, stilbenzene, oxazine, and phthalocyanine	cotton dyeing	C.I. Direct Yellow 105, C.I. Direct Orange 39
disperse	vary in the type of chromophore present and include azo, anthraquinone, nitro, methine, benzodifuranone, and quinoline-based structures	dye acetate, triacetate, and nylon fibres	C.I. Disperse Red 177, , Disperse Red 156
reactive	water soluble due to the presence of one or more –SO_3Na groups	cotton dyeing	Reactive Blue 19, reactive Black 5
sulphur	presence of sulphide (–S_n–) bonds, water-insoluble	cotton dyeing	C.I. Sulphur Black 1
vat	have mainly anthraquinone (82 %) or indigoid/thioindigoid (9 %) structures, water-insoluble	cotton dyeing	C.I. Vat Blue 1

(Source: Steiner & Miskie, 1992)

Azoic dyes are mainly bright orange and red monoazo dyes for cotton, with dull violet and blue colours also possible. They are water insoluble and consequently give high washfastness (Steiner & Miskie, 1992). Azoic dyes are subdivided into monoazo and diazo pigments, having azo group (-N=N-) in common (Herbst &

Hunger, 1993). They are also referred to as azoic combinations rather than "dyes" because they do not exist as colorants until their constituent parts are combined inside the pores of cotton fibres and are quite useful for printing on cotton and often give good lightfastness in heavy depths. Azoic dyes are also known as naphthol dyes, since all employ a naphthol element in their formation, and can be produced in batch or continuous process.

Basic dyes were developed to dye negatively charged acrylic fibres, forming ionic bonds as shown in Figure 2.1. They owe their name to the presence of aromatic amino (basic groups), and in this case a cationic amino group is present. Generally, they have excellent brightness and colour strength, especially among triarylmethane types. Basic dyes include those containing mobile and fixed cations, examples of which are C.I Basic Blue 22, C.I. Basic Red 18 and C.I Basic Green 4.

$$\text{Acrylic-SO}_3^{-}\,{}^{+}\text{R}_3\text{N-Dye}$$

Figure 2.1 Ionic bond formation between an acrylic fiber and a cationic dye.

Direct dyes are anionic colorants that have affinity for cellulosic fibres. They were the first dyes with the ability to dye cotton in the absence of a mordanting agent, giving rise to the term *direct cotton dyes.* Like acid dyes, direct dyes contain one or more $-SO_3Na$ groups, making them water soluble. Unlike acid dyes, they interact with cellulose chains via secondary valency forces (H-bonding and dipole-dipole interactions). The combined effects of these rather weak forces and sulfonated structures cause direct dyes to have low intrinsic washfastness. Direct dyes are based on four chromophores- azo, stilbene, oxazine, and phthalocyanine. About 82 % of all direct dyes have diazo or polyazo structures, with stilbene and monoazo structures occupying about 5 % each and thiazole, phthalocyanne, and dioxazine structures covering the remaining few percent (Steiner & Miskie, 1992).

Disperse dyes were invented to dye the first hydrophobic fibre developed, namely cellulose acetate, and were initially called acetate dyes. Disperse dyes have extremely low water solubility and to be applied from this medium they must be milled to a very low particle size and dispersed in water using surfactant (dispersing agent). Disperse dyes vary in the type of chromophore present and include azo, anthraquinone, nitro, methine, benzodifuranone, and quinoline-based structures. These non-ionic, hydrophobic dyes can be used on acetate, triacetate, polyester, nylon, acrylic, and polyolefin fibres, and their mechanism of fixation involves solid-solid solution formation (Steiner & Miskie, 1992).

Sulfur dyes are water-insoluble dyes that are applied to cotton. Due to extremely low solubility, the precise structures of most sulfur dyes remain unknown. A key common feature of sulfur dyes is the presence of sulfide ($-S_n-$) bonds, and it is this feature that makes dye application from an aqueous medium possible. The reaction of sulfur dyes with sodium sulfide (Na_2S) at pH › 10 effects the reduction of the sulfide bonds, giving their water-soluble (leuco) forms (Steiner & Miskie, 1992).

Vat dyes are water insoluble colorants for cotton that must be reduced to their soluble "leuco" forms to be applied from and aqueous dyebaths. The term "vatting" is used to refer to the application of these dyes via chemical reduction followed by oxidation. Vats dyes have mainly anthraquinone (82%), or indigoid/thioindigoid (9%) structures, with the former having much better fastness properties. Vat dyes are brighter than direct and sulfur dyes but less so than reactive dyes. They are the colorants of choice when dye bleachfastness on cotton is important (Steiner & Miskie, 1992).

2.1.2 Colour Appearance of Dyes

The appearance of colour in a molecule is associated with electronic excitation caused by adsorption of incident electromagnetic radiation in the ultraviolet and visible regions of the spectrum. The hue is primarily defined by the pattern of chromophores (azo, stilbene, oxazine, anthraquinone, indigoid, thioindigoid, phthalocyanine etc.), a system of conjugated double bonds (π-electronic system) which is responsible for the adsorption of visible light (Herbst & Hunger, 1993).

Substituents with lone pairs, such as alkoxy, hydroxyl, alkyl, and arylamino groups, are known as electron donors. The CH_3 group, despite the absence of such free electron pairs, is also considered an electron donor. Functional groups with conjugated π-electron systems, such as NO_2, COOH, COOR, SO_2, or SO_2Ar act as electron acceptors Herbst & Hunger, 1993).

The chemical constitution of the pigment, especially the substitution pattern of the coupling component, determines the basic colour of a pigment; different shades within this colour are influenced by physical characteristics, such as crystal geometry, particle size and shape, particle size distribution, and polymorphic crystal modification (Herbst & Hunger, 1993)

2.2 MALACHITE GREEN

Malachite Green is also known aniline green, basic green 4, diamond green B, or victoria green B. Its IUPAC name is 4-[(4-dimethylaminophenyl)-phenyl-methyl]-N,N-dimethyl-aniline. Malachite Green is a cationic, basic dye. Its molecular formula is $C_{23}H_{25}ClN_2$ and has a molecular weight of 364.92 $gmole^{-1}$. Its chemical structure is shown in Figure 2.2. It has a pH of 1.4 when 1% of the solution is present in water. Furthermore, it is also soluble in alcohol, methanol, and amyl alcohol and very soluble in ethanol. The maximum adsorption wavelength of malachite green is 619 nm. When malachite green is heated to decomposition, it emits very toxic fumes of nitrogen oxide and hydrogen chloride (http://toxnet.nlm.nih.gov).

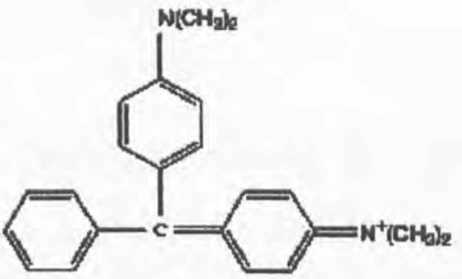

Figure 2.2 Chemical structure of Malachite Green

Malachite green has been widely used as a strong anti-fungal, anti-bacterial and anti-parasitical agent in fish farming. It is also an effective anti-protozoal agent. Malachite green is generally used for the dyeing of wool, silk, leather, cotton, jute, etc. (Indra *et al*., 2006).

Although malachite green is widely used in the industries, it has negative effects. Discharge of malachite green into receiving streams will affect the aquatic

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