DEGRADATION OF DYES (METHYLENE BLUE) USING NATURAL RUBBER INCORPORATED WITH SILVER NANOPARTICLES IN WATER TREATMENT TANK

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By

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I hereby declare that all corrections and comments made by the supervisor(s) and examiner have been taken into consideration and rectified accordingly.

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ABSTRAK

Air sisa daripada industri tekstil biasanya menghasilkan jumlah air yang banyak kaya dengan warna yang mengandungi sisa pewarna dan sisa toksik. Dalam usaha untuk merendahkan pewarna dari efluen sebelum melepaskan kepada alam sekitar, membran getah asli digabungkan dengan nanopartikel Argentum (NR-Ag) mesra alam telah dikaji. Dalam kajian ini, model pewarna yang telah digunakan adalah Metilena Biru (MB) dan membran-membran bola NR-Ag telah disediakan dengan menggunakan bola memancing apungan yang disalut dengan NR-Ag. Membran-membran bola NR-Ag telah dihasilkan menggunakan rawatan haba yang sederhana dan telah dicirikan menggunakan Spectrophotometer UV-Vis dan Spektroskopi Serapan Atom (AAS). Aktiviti pemangkinan membran bola NR-Ag untuk menyahwarnakan pewarna MB adalah dikaji menggunakan kalium borohydride (KBH4) sebagai agen penurunan. Laporan ini menekankan kesan kuantiti bola NR-Ag, kesan tekanan udara dan kesan kepekatan KBH4 pada kadar penyahwarnaan MB oleh KBH4. Kadar penyahwarnaan didapati meningkat dengan jumlah bola NR-Ag, serta dengan peningkatan tekanan udara. Jumlah optimum bola NR-Ag adalah 10 dan kadar tekanan udara yang terbaik adalah 0.6 bar. Tambahan lagi, proses penyahwarnaan meningkat dengan kadar kepekatan KBH_4 yang tinggi.

ABSTRACT

Wastewater from textile industries commonly produce large amount of water often rich in colour containing residues of dyes and toxicity. In order to degrade dyes from the effluent before releasing to the environment, the natural rubber incorporated with silver nanoparticles (NR-Ag) were studied. In this work, the dye that used as a model of dye was methylene blue (M) and the NR-Ag ball membranes have been prepared using fishing float ball coated with NR-Ag. The NR-Ag ball membranes were formed using mild heat treatments and characterized using UV-Vis Spectrophotometer and Atomic Absorption Spectroscopy (AAS). Catalytic activity of the NR-Ag ball membranes for the degradation of MB dye was studies using potassium borohydride (KBH_4) as reducing agent. The report emphasizes the effect of quantity of NR-Ag balls, the effect of air pressure and the effect of KBH_4 concentration on decolourization rate of MB by KBH_4. The rate of decolourization was found to increase with increasing amount of NR-Ag balls and with increasing of air pressure. The optimum amount of NR-Ag ball was 10 and the best air pressure rate was 0.6 bar. Furthermore, the process of decolourization increased with higher concentration of KBH_4.

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LIST OF ABBREVIATIONS

AAS	**A**tomic **A**dsorption **S**pectroscopy
Ag	**S**ilver
CB	**C**ork **B**ark
EY	**E**osin **Y**ellow
MB	**M**ethylene **B**lue
NR	**N**atural **R**ubber
GS	**G**rape **S**talk
PACI	**P**olyaluminium **C**hloride
PFCI	**P**olyferrous **S**ulphate
PAFCI	**P**olyaluminium **F**erric **C**hloride

NOMENCLATURES

KBH_4	Pottasium Borohydride
TiO_2	Titanium Dioxide
$AgNO_3$	Silver Nitrate

CHAPTER 1

INTRODUCTION

1.1 Background

Dyes are used to colour a materials for the fabrication of products that we use throughout the day. Today there are more than 100000 dyes available commercially with a total yearly production of 7×10^5 tonnes per year (Yagub et al. 2014). Most dyes are used extensively in many industries such as food, rubber, paper, cosmetics, carpets, plastics and textiles (Bedin et al. 2016). The extensive use of dyes often poses a pollution problems in the form of coloured wastewater discharge into water bodies. Even small quantities of dyes can colour large water bodies (Zhao et al, 2011).

Moreover, textile industries are the most industry that consumes large quantities of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes (Verma et al. 2012). Wastewater from printing and dyeing units is often rich in colour as it contains dye residues and chemicals (Wang et al. 2011). Hence, the main contributors to environmental pollution are from textile industry (Anisuzzaman et al. 2015).

Basically, dyes can be classified based on the method of application onto fabric. It can be divided into 3 categories which are cationic, anionic and non-ionic dyes. Cationic dyes are basic dyes while the anionic dyes include direct, acidic and reactive dyes and disperse dye are neutral molecule (Asgher 2012). Cationic dyes are widely used in acrylic, wool, nylon and silk dyeing. They are considered as toxic colorants and can cause harmful effects (Eren et al. 2009). Cationic dyes are water soluble and can carry a positive charge in their molecule, and yield coloured cations in solution (Salleh

et al. 2011). Generally, the most common used among all other dyes for dyeing cotton, wool and silk is Methylene Blue (MB) which include in cationic dyes (Islam et al. 2015). Hence, in this study MB was chosen as a model of dye for its absorption efficiency onto Natural Rubber Silver (NR-Ag) under different experimental conditions.

1.2 Problem Statement

Environmental pollution, particularly water pollution has been the main concern in many countries. Therefore, the released of dye-bearing wastewater into natural streams and river from textile, paper, painting and printing and also food industries causes severe environmental problems. Dyes in wastewater are not only toxic to aquatic life but are also detrimental to aesthetic features of the environment (Utara & Phatai 2014).

The effluent coming out from dyeing industries result in water pollution since they produce pollutants such as water-colouring agents produced by the small amounts of dyes (Anisuzzaman et al. 2015) and toxic heavy metals such as zinc, cadmium, copper, lead, chromium and mercury that are extremely harmful to the environment even at low concentration (Emamjomeh & Sivakumar 2009). Discharging them into water resources also can affect the aquatic life, food web as well as human health. Dyes can also cause allergic dermatitis, skin irritation, mutations and cancer (Ramesh 2013). Some dyes have been reported to carcinogenic for aquatic organisms and humans (Sinha et al, 2012). Therefore, the removal of dyes from waste effluents becomes environmentally important.

The removal of dyes in effluents from industrial plants is crucial in order to provide good quality of water resources to living organism. The effluents require proper treatment before it is discharged into any water body (Sivamani & Leena 2009). Several physical, chemical and biological treatment approaches have been used to remove these dye residues from wastewater. Hence, one of the method is via using activated carbon which is a widely used adsorbent due to its high adsorption abilities in removing organic pollutants from wastewaters. However, the regeneration is difficult which limits its usage in dye waste treatment (Deiana et al. 2009).

Besides that, other methods are degradation, for example using TiO_2 which is used to degrade the dye contamination from effluents (Ahmed et al. 2013). Many types of adsorbent materials have been employed in water treatment such as orange peel (Abdurrahman, et al, 2013), fly ash ((Agarwal et al, 2015), sand (Olugbenga Solomen Bello et al, 2013) and onion membrane (Saber-Samandari & Heydaripour 2015). Thus, many researchers have conducted research to find low cost and biodegradable substitutes made from natural resources such as cork bark and grape stalk as a mechanistic approach to removes dyes from wastewater (Àngels Olivella et al. 2012).

1.3 Objectives

This study is conducted with the following objectives:

a) To determine the adsorption capacity of natural rubber incorporated with silver nanoparticles to degrade MB dye.

b) To determine the optimum amount of NR-Ag balls, rate of air pressure and KBH_4 concentration in water treatment tank.

1.4 Scope of Study

This study explores the optimum adsorption conditions for the methylene blue removal using low cost material. In this case, the low-cost, renewable, biodegradable and easily available adsorbent material which is natural rubber (NR) and silver (Ag) nanoparticles were the main focus of this study. The study focused on methylene blue removal specifically the best conditions for the adsorption of MB in terms of agitation time and quantity of NR-Ag balls to be used.

1.5 Benefits of Study for Civil Engineering

Presently, Malaysia was in rank 6 between the leading natural rubber producing countries in the world (Oishimaya Sen Nag, 2017). Hence, it has been used for various purposes such as manufacturing tyres, gloves, tubings and others. It is important to continuously find new applications for this natural polymer. Hence, the aim of this study is to investigate the effectiveness of adsorption onto MB by using NR.

NR based membrane is developed to degrade dye via a dual mechanism which are adsorption and degradation. The NR acts by adsorbing the dye while the Ag incorporated in NR acts as a catalyst for the degradation of dye. It is fast and easy preparative method and flexible that can be designed according to various needs. In addition, it is a lightweight material and renewable. Therefore, by using NR, this study may develop a new method for dye treatment which is green and renewable also an effective low cost water treatment product.

1.6 Dissertation Outline

This dissertation consist of five chapters which are organized in the following manner:

Chapter 1 provides an overview on dyes used in various sectors, characteristic of dyes and its category. The introduction describes including the background of the study, problem statement, objective, scope and benefit of this study for Civil Engineering. Chapter 2 presents the literature review which covers the general introduction, classification of dyes, methylene blue, and dyes wastewater treatment studies. Chapter 3 presents the procedures, materials and methods of the research undertaken. Chapter 4 describes the results and discussion of the experiments. Chapter 5 gives the conclusions and recommendations based on the results obtained.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

Environmental pollution has been concerned in Malaysia. Production activities such as cosmetics, plastics, food, planting, mining and textile from industrial result in water pollution. Pollutants that produce such as water-colouring agents and toxic heavy metals are extremely harmful to people and the environment even in small amount of concentrations (Saber-Samandari & Heydaripour 2015). The main contributor to environmental pollution are from textile industry that caused by the use of dyes (Anisuzzaman et al. 2015). It consumes large quantities of water and produces large volumes of wastewater from different steps in the dyeing and finishing processes (Wang et al. 2011).

Generally, dye can be defined as a coloured substance that has an affinity to substrate to which it is being applied. Synthetic dyes are man-made, that are made from synthetic resources such as petroleum by-products and earth minerals. *Mauveine* is the first human-made organic aniline dye. It was discovered by William Henry Perkin in 1856 (Saratale et al. 2011). Others synthetic dyes also known as aniline dyes have since been prepared such as fuchsine (Ali 2010) which is magenta dye and safranine (Salleh et al. 2011) which is also known as basic red 2. In addition, synthetic dyes are fabricated of complex aromatic molecular structures purposely constructed to resist fading on exposure to sweat, soap, water, light and oxidizing agents (Asgher 2012).

Furthermore, dye might cause toxicity to aquatic life. The release of coloured wastes into streams from industries may present hazards so that it introduce the

potential danger of bioaccumulation which may affect man through the food chain (Àngels Olivella et al. 2012).

2.2 Classification of Dyes

Dyes can be classified into two categories which are according to their solubility and chemical properties. There are a few types of dyes that can be classified according to how they are used in the dyeing process. Acid dyes are water soluble anionic dyes that are applied to fibres such as silk, wool, nylon and modified acrylic fibres using neutral to acid dye baths. Most synthetic food colours are included in this category. Basic dyes are water soluble cationic dyes that are mainly applied to acrylic fibres. These types of dyes are also used in the coloration of paper. While direct dye are used on cotton, paper, leather, wool, silk and nylon also as pH indicators and as biological stains (Rafatullah et al. 2010) .

In contrast, reactive dye are a class of that are used in tinting textile. It can also be used to dye wool and nylon besides it can applied under weakly acidic conditions. Besides that, mordant dyes are used for wool also very useful for black and navy shades. The direct, acid and reactive dyes are in the group of anionic dyes while basic dye is cationic dyes. Other classes of dyes includes azo dyes, insoluble dyes, vat dyes, disperse dyes and sulphur dyes (Wang et al. 2011).

2.3 Methylene Blue Dye

Methylene blue (MB) is a basic aniline dye with the molecular formula $C_{16}H_{18}N_3SCI$. MB is a compound consisting of dark green powder or crystalline powder having a bronze-like lustre that yields a blue solution when dissolved in water

at room temperature (Netai Muchanyereyi et al, 2014). It has many uses in a number of different fields such as chemical, biological, medical, agriculture and production. For instance, chemist use it to detect oxidizing agents while biologist use it to stain tissue samples and detect nucleic acids.

In contrast with medicine, which use it as a treatment for various illnesses and disorders including kidney stones, herpes infection, methemoglobinemia and schizophrenia. In agriculture, MB is used to protect aquatic life to prevent freshwater fish eggs from being infected by bacteria and fungi. Other than that, MB has also been used as a dye for temporary hair colorants, cotton, wool, leather and paper (New World Encyclopedia, 2014)

2.4 Hazards of Dyes

Water pollution due to discharge of effluents containing dyes from textile dyeing, painting and printing industries commonly is one of the major environmental concern and the most important problems of the modern world (Verma et al. 2012). The wastewater are highly coloured and the disposal of these wastes into receiving waters causes damage to the environment. These colour compounds are aesthetically displeasing and inhibit the sunlight blockage penetration into the stream thus affecting aquatic ecosystem. Dye absorbs and reflects sunlight entering water so that it can interfere with the growth of bacteria and hinder photosynthesis in aquatic plants (Ramesh 2013).

Methylene blue is an important basic dye that has various harmful effects such as increased heart rate, shock, vomiting, heinz body formation, profuse sweating, mental confusion and tissue necrosis in humans (Saber-Samandari & Heydaripour

2015). Besides that, it can causes eye burns and if inhaled, it can cause rapid problems in breathing (Netai Muchanyereyi et al. 2014). Some dyes are toxic to some microorganisms so that it may cause direct destruction or inhibition of their catalytic abilities (Venkateswaran et al. 2015). Furthermore, dyes are usually composed of complex aromatic molecular structure which makes them carcinogenic and mutagenic, inert and no biodegradable when discharged into the environment (Khouni et al. 2011). Hence, the removal of such coloured agents from aqueous effluents is of significant environmental, technical and commercial importance. (Venkateswaran et al., 2015).

2.5 Dye Waste Treatment Studies

2.5.1 Adsorption and Degradation

Several techniques have been used to treat coloured effluents that are discharged from industries. There are photocatalytic degradation (Kumar et al. 2013), microbiological decomposition (Ali 2012), electrochemical oxidation (Kruthika et al. 2013), membrane filtration (Li et al. 2017), and adsorption degradation methods (Saratale et al. 2011). Among these methods, adsorption is the one that have been successfully employed for effective removal of dyes due to its high potential of removing different types of colouring materials from wastewater (Anisuzzaman et al. 2015). Besides that, due to its efficiency, low cost, easy operation, simple design, less energy intensiveness and non-toxicity, this method was the most widely used (Saber-Samandari & Heydaripour 2015)).

Activated carbon has been found to be an effective technology for decolourization of wastewater in adsorption process. It is widely used as absorbent due to its ability to adsorb the organic pollutant from wastewater. However, due to the relatively high cost for a large-scale use of activated carbon and the difficulty in the