STUDY OF BI-FUNCTIONALIZED LATERITE SOIL IN TREATING DYE WASTEWATER THROUGH COAGULATION-FLOCCULATION AND DEGRADATION

By

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Thesis submitted in fulfillment of the requirements for the degree of Master of Science

May 2015

ACKNOWLEDGEMENTS

During my research project, I have come to contact with many people who had rendered their help to assist me for the completion of research. Due to their support, advices and encouragement, this had ensured progression of my research project run smoothly.

Firstly, I would like to express my sincere gratitude and appreciation to my main project supervisor, Professor Teng Tjoon Tow for his guidance, support and encouragement throughout my master research and thesis preparation. I am very grateful to my co-supervisors, Professor Madya Norhashimah and Dr. Mohd Rafatullah for their guidance and advices. Additionally, I also wish to express my grateful gratitude and appreciation to Mr. Wong Yee Shian and Dr. Ong Soon An who had provided useful views and tips throughout my research. Without their continuous support and interest, this thesis would not have been completed.

Last but not least, I would like to express a sense of gratitude and love to my friends and my beloved family for their manual support, strength, help and everything throughout the project completion.

LAU YEN YIE

JULY 2014

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LIST OF SYMBOLS

Ag_2SO_4	Silver sulphate
Ag_3PO_4	Silver phosphate
$Al(OH)_3$	Aluminum hydroxide
$Al(OH)_4^-$	Hydroxylaluminate
Al_2O_3	Aluminum trioxide
Al_2SO_4	Aluminum sulphate
$(Al_2SO_4)_3.(18H_2O)$	Alum
Cd^{2+}	Cadmium ion
$(CH)_n$	Hydrocarbon
$(CH_3)_2NC_6H_4NH_2$	N,N-dimethyl-p-phenylenediamine
$C_6H_5N(CH_3)_2$	N,N-dimethylaniline
C_6H_6	Benzene
$C_6H_6NO_3S$	p-amino-benzenesulfonic acid
$C_6H_6SO_3$	Benzenesulfonic acid
C_6H_8Si	Phenylsilane
$C_{10}H_8N_2$	Naphthalenediazonium

$C_{10}H_7Si$	Naphthalenylsilane
$C_{10}H_8N_2O$	Hydroxynaphthalenediazonium
Fe^{2+}	Iron (II)
Fe^{3+}	Iron (III)
Fe_2O_3	Ferric trioxide
Fe_3O_4	Ferrosoferric oxide
$Fe(OH)_4^-$	Hydroxylferric
$FeCl_3$	Ferric chloride
H_2O_2	Hydrogen peroxide
HN=NH	Diazene
HS^-	Sulfanide ion
H_2SO_4	Sulphuric acid
$Mg(OH)_2$	Magnesium hydroxide
$MgCl_2$	Magnesium chloride
$PA\text{-}NH_4$	Poly(ammonium acrylate)
R_2SiO_3	Siloxane molecule
SiO_2	Silica dioxide

$TiCl_4$	Titanium tetrachloride
W_1	Initial weight of filter disc (mg)
W_2	Weight of filter disc + dried residue (mg)
β-CD-AA-DMC	β-cyclodextrin-acrylic acid-[2-(Acryloyloxy)ethyl]trimethyl ammonium chloride copolymer
–C=C-	Ethenyl
-C=O-	Carbonyl
-C=N-	Imino
-CH=S	Thio-Carbonyl
-N=N-	Azo
-N=O	Nitroso
$-NO_2$	Nitro
$–NH_2$	Amino
-COOH	Carboxylic
$-SO_3H$	Sulphonated

LIST OF ABBREVIATIONS

ABS	Aqueous biphasic system
ACCs	Activated carbon cloths
AOP	Advanced oxidation process
CNT	Carbon nanotube
CTAB	Cethyltrimethyle-ammoniumbromide
COD	Chemical oxygen demand
EfOMs	Effluent organic matter
FT-IR	Fourier transforms infrared spectroscopy
HCl	Hydrochloric acid
KOH	Potassium hydroxide
L-DAF	Lignin-base dimethylamine-acetone-formaldehyde
MEUF	Micellar enhanced ultrafiltration
MMT	Montmorillonite
NaOH	Sodium hydroxide
nZVI	Nanoscale zero valent iron
PAA	Poly(acrylic acid)

PAC	Poly(amidoamine-co-acrylic acid)
PACl	Polyaluminum chloride
PACl-PAMIPCl	Polyaluminum chloride-poly(3-acrylamido-isopropanol chloride)
PAFS	Polymeric aluminum ferric sulphate
PDDA	Polydiallyldimethyl ammonium chloride
PEI	Polyethyleneimine
PES	Polyethersulfone
PEUF	Polyelectrolyte-enhanced ultrafiltration
PFC-DAM-ECH	Polyferric chloride-poly-epichlorohydrin-dimethylamine
PFCl	Polyferric chloride
PSSA	Poly(styrenesulfonic acid)
PVA	Poly(vinyl alcohol)
PVDF	Polyvinylidene fluoride
PVP	Poly(N-vinyl-2-pyrrolidone)
PZC	Point of zero charge
rpm	Revolution per minute

SDS	Sodium dodecylsulfate
SBR	Sequential batch reactor
SVI	Sludge volume index
TFC	Thin film composite
TGA	Thermogravimetric analysis
TMC	Trimesoyl chloride
UV-Vis	UV-Visible
XRF	X-Ray Fluorescenece

LIST OF PUBLICATION

Journal paper

Lau, Y.Y., Wong, Y.S., Teng, T.T., Morad, N., Rafatullah, M., and Ong, S.A. (2014) Coagulation-flocculation of azo dye Acid Orange 7 with green refined laterite soil, Chem. Eng. J., 246; 383-390.

Lau, Y.Y., Wong, Y.S., Teng, T.T., Morad, N., Rafatullah, M., and Ong, S.A. (2015) Degradation of cationic and anionic dyes in coagulation-flocculation process using bi-functionalized silica hybrid with aluminium-ferric as auxiliary agent, Royal Society Chem. Adv., 5; 34206-34215

PENGGUNAAN TANAH MERAH SEBAGAI PENGENTAL DAN PENGUMPAL SEMULAJADI UNTUK RAWATAN AIR SISA BERWARNA DAN DEGRADASI

ABSTRAK

Mulanya, prarawatan perlu dijalankan ke atas tanah merah mentah yang dikumpul dari Bukit Merah Perlis, Malaysia sebelum digunakan sebagai pengental dan pengumpal. Tanah merah mangandungi 36.30 % silika, 27.10 % aluminum dan 26.86 % besi. Pengaktifan silika adalah pada pH 2 di mana silika berupaya untuk membelahkan struktur molekul pewarna melaluipenggantian, pemampatan electrik dan cas peneutralan. Di samping itu, aluminium dan besi bertindak sebagai ajen pembantu dalam proses pengentalan dan pengumpalan. Tanah merah mampu menyahwarnakan: asid jingga 7 dengan 99.50 % pada dos 14000 mg/L; metilena biru dengan 99.61 % pada dos 2500 mg/L; metil jingga dengan 99.11 % pada dos 9000 mg/L, sibakron brillian kuning 3G-P dengan 99.46 % pada dos 8000 mg/L dan reaktif merah 120 dengan 99.53 % pada dos 6000 mg/L. Projek ini telah memberi inspirasi tentang penggunaan sumber semulajadi bagi proses degradasi pewarna. Pewarna bercas positif (metilena biru), bercas negatif (metil jingga) dan azo (asid jingga 7) digunakan untuk mengkaji laluan degradasi serta mengenal pasti hasil pengantara dan sampingan. Tindak balas yang terlibat dalam degradasi pewarna seperti pembelahan molekul, desulfurisasi, serangan silica, diazin reaksi dan pempolimeran. Oleh yang demikian, penggunaan tanah merah sebagai pengental dan pengumpal menjanjikan penghasilan produk yang tidak berbahaya dengan mendegradasikan molekul-molekul complex. Produk-produk yang terhasil adalah n-metildisiloxan dan n-metilldisilathian. Selain itu, kajian ini juga mendapati penemuan baru mengenai kesan R'-Tosil ke atas degradasi dengan munggunakan tanah merah sebagai pengental dan pengumpal. Asid jingga 7,

sibakron brillian kuning 3G-P dan reaktif merah 120 dipilih kerana masing-masing mengandungi satu, tiga dan enam R'-Tosil. R'-Tosil ini berupaya mempercepatkan proses pengentalan dan pengumpalan melalui ikatan dan tindak balas silika. Tambahan pula, tanah merah memberi prestasi yang menakjubkan dalam proses pempolimeran. Ciri-ciri pempolimeran yang ditunjukkan oleh tanah merah seperti masa dan halaju pengenapan yang cepat serta indeks isipadu enapcemar (SVI) yang rendah. Indeks isipadu enapcemar bagi asid jingga 7 adalah 21.7 mL/g, metilena biru adalah 28.04 mL/g, metil jingga adalah 29.45 mL/g, sibakron brillian kuning 3G-P adalah 20.29 mL/g dan reaktif merah 120 adalah 18.69 mL/g. Pempolimeran ini disokong oleh pembentukan struktur organisilikon polimer (n-metildisiloxan dan n-metilldisilathian). Tanah merah sebagai pengental semulajadi dibandingkan dengan pengental kimia yang sering digunakan di industri iaitu aluminum sulfat atau dikenali sebagai alum. Tahap penyahwarnaan, penggunaan semula enapcemar, SVI, impak ke atas persekitaran alam dan kesihatan manusia telah dbandingkan di antara kedua-dua pengental ini. Tanah merah mampu menyahwarnakan pewarna secara kseluruhan tanpa destabalization berbanding dengan aluminium sulfat. Tambahan pula, aluminium sulfat hanya boleh mengitar guna semula sekali sahaja sebelum ia merosoykan kualiti air disebabkan pelepasan resapan. Sebaliknya, tanah merah mampu mengitar guna semula sebanyak tujuh kali tanpa menyebabkan pelepasean resapan berlaku. Enapcemar yang dihasilkan daripada aluminium sulfat dalam kuantiti yang banyak berbanding dengan tanah merah. Secara keseluruhan, tanah merah memberikan prestasi yang lebih baik. Air sisa berwarna dari Kilang Master Wan Batik dikumpul untuk membuat penilaian ke atas applikasi tanah merah terhadap air sisa yang sebenar. Tanah merah mampu menyahwarna air sisa sebanyak 99.57 % dan mengurangkan COD sebanyak 99.10 %.

DEGRADATION

ABSTRACT

Raw laterite soil collected from Bukit Merah, Perlis, Malaysia went through decolorization pre-treatment before being used as coagulant-flocculant. This key material is dominated by silica component (36.30 %), followed by aluminum (27.10 %) and ferric (26.86 %). Silica was activated at the acidic region (pH 2) which allowed the silica to cleave the dye molecular structure through substituition, electrical double layer compression and charge neutralization. Meanwhile, aluminium and ferric act as auxiliary agents in the coagulation-flocculation process. Laterite soil was able to remove: acid orange 7 with 99.50 % at dosage of 14000 mg/L; methylene blue with 99.61 % at dosage of 2500 mg/L; methyl orange with 99.11 % at dosage of 9000 mg/L, cibacron brilliant yellow 3G-P with 99.46 % at dosage of 8000 mg/L and reactive red 120 with 99.53 % at dosage of 6000 mg/L. This project has provided a new insight into an effective dye degradation using a new class of natural coagulant-flocculant-natural resources. The novelty of this study is mainly focus on degradation pathways of several dyes, such as cationic dye (methylene blue), anionic dye (methyl orange) and azo dye (acid orange 7). In order to poses a complete dye pathway, degradation intermediates and by-products during and after the coagulation-flocculation process are determined. A linkage of reaction such as cleavage on weaker bond, desulfonation, silication, diazene reduction and polymerization took place to degrade the dye molecules. Degradation of dye using this natural material has promising zero hazardous compounds formed since it able to degrade the complex dye molecular structure into a simplest hydrocarbon form. The final products formed are n-methyldisiloxane and n-methyldisilathiane. During the study, there is a discovery on the effects of R'-Tosyl number(s) which acts as the initiator of dye degradation during the coagulation-flocculant process using laterite soil. Thus, acid orange 7, cibacron brilliant yellow 3G-P and reactive red 120 which contained one, three and six R'-Tosyl(s), respectively have been selected for this study. R'-Tosyl was able to enhance the performance of coagulation-flocculation process by laterite soil through substitution on the silica bonding. Furthermore, laterite soil coagulant-flocculant shows polymerization effects with good settling times, fast settling velocities of flocs and low sludge volume index (SVI). SVI for acid orange 7 was 21.7 mL/g, methylene blue was 28.04 mL/g, methyl orange was 29.45 mL/g, cibacron brilliant yellow 3G-P was 20.29 mL/g and reactive red 120 was 18.69 mL/g. SVI for all the dyes are less than 50 mL/g which is laid in the best range of SVI test. This is supported by the formation of organosilicon polymer structure (n-methyldisilathiane and n-methyldisiloxane). Lastly, a comparison on natural coagulant-flocculant (laterite soil) and mostly industrial utilized chemical based coagulant (alum) is studied. Laterite soil was able to completely remove the dye without destabalization in comparison with aluminium sulphate. In term of recyclability, aluminum sulphate sludge can only perform one time before it deteriorates the water quality due to back-diffusion mechanism. In contrast, the laterite soil sludge can perform up to seven times of reuse without causing back-diffusion in the system. Voluminous of sludge was yielded by aluminium sulphate in comparison with laterite soil. Overall, natural coagulant-flocculant of laterite soil shows the best performance. Industrial batik dye wastewater from Master Wan Batik Industry is collected for the evaluation of exact laterite soil application. Laterite soil was able to reduce the color of textile dye wastewater up to 99.57 % and 99.10 % of COD.

CHAPTER ONE

INTRODUCTION

In this modern and fast-paced world, developing countries primarily rely on large scale industrialization to boost their economy. Simultaneously, significant quantities of pollutants or contaminants generation are unavoidable and it has critically increased. Indirectly, potential inflow of these contaminants into the earth's surface environment is escalating. The magnitude of the problem has been mooted many years ago and undeniably that, this scenario had depleted our environment. Countries which menace with the contamination bring a great concern and this issue ought to be addressed before it snowballs into a greater problem.

1.1 Dye

Dye is extensively used to impart colours on materials or fibres. Atoms make up a dye that responsible for dye colour are known as chromophores; whereas electrons withdrawing or donating substituents that responsible to intensify the colour of chromophores are known as auxochromes (Christie, 2001). Chromophores are coloured, but they are not dyes since they do not have the affinity to unite with tissue/fibre. Thus, integration of chromophores and auxochromes groups makes up a dye that potentially imparts colour on materials. Chromosphores consist of –C=C- (ethenyl), -C=O- (carbonyl), -C=N- (imino), -CH=S (thio-carbonyl), -N=N- (azo), -N=O (nitroso), $-NO_2$ (nitro); Auxochromes are $-NH_2$ (amino), -COOH (carboxylic), $-SO_3H$ (sulphonated), and –OH (hydroxyl) (Verma et al., 2012).

Azo dyes are widely used in coloring industries. The annual global market of azo dyes is estimated to be around 1 million tonnes. Structurally dissimilar azo dye is found to be more than about 10,000 types (Moosvi et al., 2007). One of these is the sulphonated reactive azo dye, which contains a chromophoric azo group whereby nitrogen atoms are linked to sp^2-hybridized carbon atoms of the aromatic ring (Pathak et al., 2014). Nowadays, the structures of dyes are altered to enhance the dye properties. Several technologies have been applied to improve delivery of dyes to fabrics, resistance to fade, and control intensity of dyes. These properties make dyes resist to degradation, thus contributing to environmental pollution (Kabra et al., 2013).

1.1.1 Types of industry utilizing dye in manufacturing process

Many industries such as textile, paper, leather, plastics, cosmetics, food, printing and pharmaceutical industries all over the world apply dyes for their coloration processes, but by far the major industry utilizing dye is textile manufacturing industry. There are about 0.3 million tonnes of different dyestuffs used annually for textile dyeing operations (Pathak et al., 2014). Acid, basic, direct, sulphur, reactive and metal complex dyes are the common types of dye used in textile industries. In Malaysia, textile industry consists of four major sub-sectors: primary textile, made-up garments, made-up textiles, and clothing accessories. Small scale factories primarily rely on batik type products.

Different industries utilize different types of dye since each dye has its their own chemical structure and application. Laser printing industry employs cyanide dyes which have two nitrogen containing heterocyclic groups connected with a conjugated methine bridge. These types of dye have unique electron delocalization property causing them to be highly fluorescent and exhibiting span from the visible to infrared region wavelength scan (Levitz et al., 2014). Wool industries utilize mordant dyes that introduce color on the wool fibres. Mordant dyes such as mordant black 8, mordant black 17, mordant red 73 and mordant orange 1 have been used in wool industries due to fast adsorption on dye fibres (Shen et al., 2014).

1.1.2 Dyeing process

Dyeing process is the concept of binding dye molecules covalently to fibre molecules. Fig. 1.1 presents the dyeing processes in textile mill industries. The beginning step in textile dyeing process is pre-treatment of raw textile material through de-sizing, scouring, bleaching and mercerizing processes. De-sizing process is to remove the sizing ingredients on the fabric which may hinder the subsequent processes. Sizing ingredient such as starch may hinder the penetration of dye into the fibre. Scouring process is performed to remove impurities such as wax, fatty acids and oils. Whereas bleaching process functions to decolorize the yarn since natural color matter of yarn imparts a creamy appearance to the fabric.

Subsequently, the bleached fabric was sent for mercerization. This process is to impart luster on the fabric which potentially increases the fabric strength and enhance the dye uptake for the following dyeing process. Desired color is imparted to the fabric in the dyeing process. Dye particles are in contact with the surface of fibre, thereafter a thin layer is formed on the surface, and ultimately diffusion of dye molecules takes place. Two techniques of dyeing are prevalently conducted: batch technique and continuous technique. For batch technique, the textile and liquid as dilution for preferential intensity are combined in a vessel, and then fabrics is passed through the

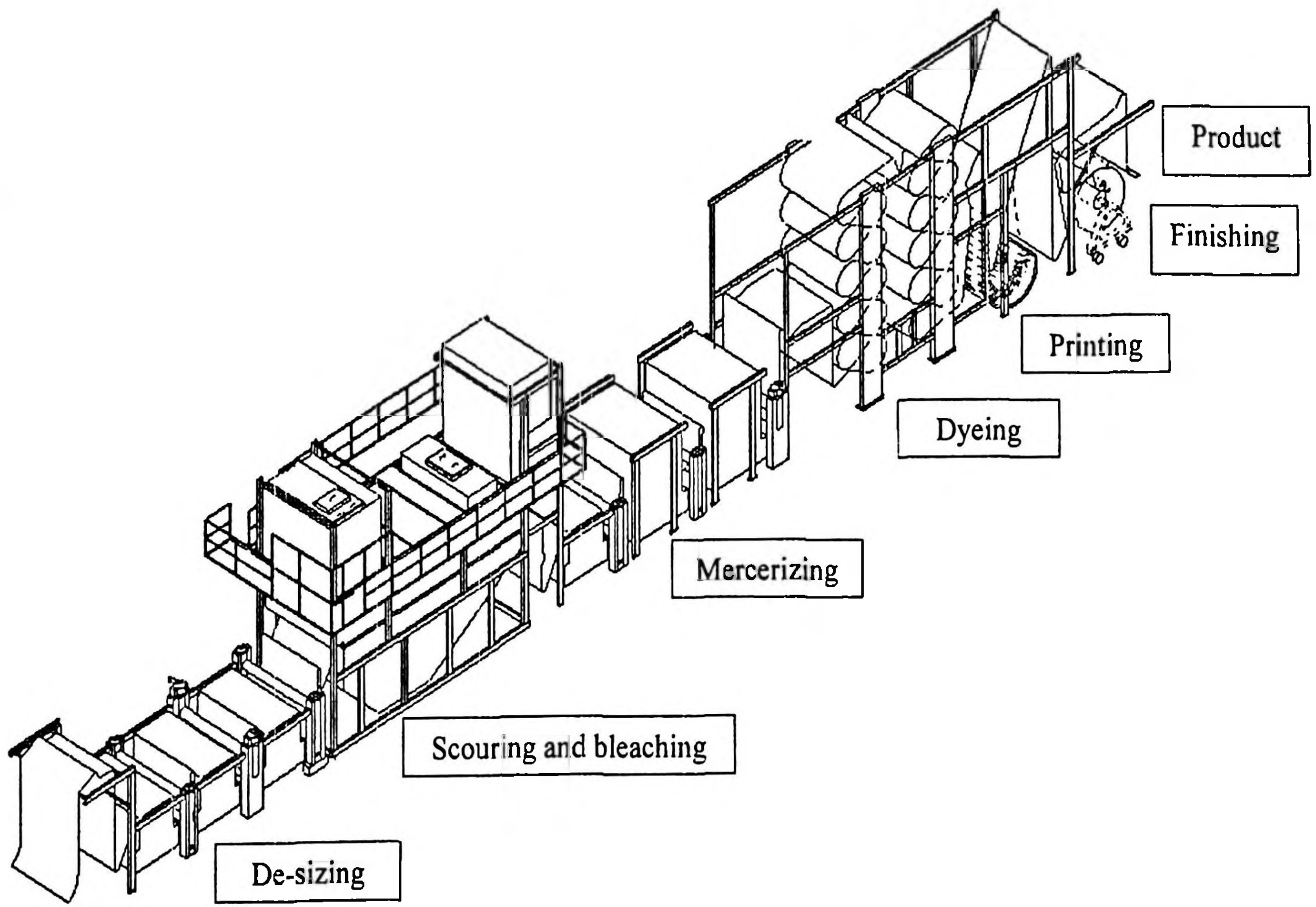

Fig. 1.1 Dyeing process in textile mill industry

vessel for coloration. In the continuous technique, dye is initially dissolved in liquid. The prepared dye liquid is then applied to the textile. Application of dyes depends on on the dye structure and characterization. Direct dyes are particularly applied on cotton; reactive dyes are usually applied on cellulose typed textile. After dyeing process, the fabric is subjected to printing process whereby desired colored graphic images are produced on the specific areas of the fabric for designation purpose. Pigment, wet and discharged printings are commonly practised in textile industry. Eventually, the fabric reaches finishing process. In this stage, the fabric is converted into useable products. The fabric is led through drying machine to remove moisture, and is dimensioned into required sizes and undergoes calendaring step to make the fabric stiff. These stiffed fabrics are softened at the last stage and high quality fabric products are produced (Babu et al., 2007; Verma et al., 2012).

1.1.3 Dye wastewater effluent characteristics

When dyes are used in the dyeing process, a small portion of dyes does not adhere to the stuff owing to the incomplete exhaustion of dyes onto textile fibres (Pereira et al., 2014). Subsequently, various pollutants such as remaining dyes, organic compounds and surfactants could be found in textile effluents (Tan et al., 2000). Textile industry uses high molecular weight and complex structures of dyes, cleaved products of these dyes show very low biodegradability (Kim et al., 2004; Gao et al., 2007). Incompletely degraded products would create toxicological and ecotoxicological issues due to their toxic, non-biodegradable and mutagenic nature. For example, benzene can imperil the nervous and vascular systems of human being; phenol can affect aquatic system by hindering marine plants and organisms growth (Li et al., 2014a).

Apart from dyes, various types of suspended and dissolved compounds can be found in textile effluent. Textile effluents are very complicated due to the addition of chemicals including dyes, carriers, biocides, bearing agents, complexion agents, ionic and non-ionic surfactants, sizing agents during washing, scouring, mercerizing, dyeing and finishing processes. Thus, it is undeniable that textile plants produce highly toxic wastewater (Selcuk, 2005). The effluents contain acids, alkalis, salts, surfactants or metal ions. Chloride, sulphate, carbonate and nitrate are the most common ions present in textile effluents (Szygula et al., 2008; Khandegar and Saroha, 2013).

The potential adverse impact of dyes on the environment is global nowadays due to their potential mutagenicity, carcinogenicity and intense coloration. Moreover, dyes may significantly affect the photosynthetic activity of aquatic life due to reduced light penetration (Ghodake et al., 2009). Therefore, all pollutants contained in the wastewater must be treated appropriately before discharged into receiving water body. Only the treated wastewater conforming to the new regulations regarding to industrial effluent cited as the Environmental Quality (Industrial Effluent) Regulations 2009 is allowed to discharge into water stream. Appendix A presents the acceptable conditions for industrial effluent of standard A and B (EQA, 1974).

Until now, several treatment systems have been applied in industries for dye wastewater treatment. Among them are nanofiltration, adsorption, reverse osmosis, coagulation-flocculation, ozonation, advanced oxidation process (AOP), Fenton reaction, photocatalytic process and sequential batch reactor (SBR), Aerobic and anaerobic processes. Coagulation-flocculation process is the most commonly utilized dye waste treatment method in industry (Tan et al., 2000).

1.2 Problem Statement

Industries are confronted with the problem pertaining to the increase of wastewater that ought to be treated. Modification of the under-designed treatment plant and replacement of new sustainable treatment system are thought to involve high cost. Thus, physicochemical treatment process particularly coagulation-flocculation is preferred as the alternative means and cost effective way to cope with the problem. Owing to the dosage of coagulant-flocculant utilized that can vary depend on the treatment necessity.

Coagulation-flocculation is a physicochemical treatment process that has shown high performance in treating dye wastewater (Tan et al., 2000; Verma et al., 2012).Various inorganic coagulants such as aluminum, ferric, magnesium salts and lime had been applied alone to treat dye wastewater. However, the sludge produced from inorganic coagulants is voluminous and toxic (Hao et al., 2000). Flaten (2001) reported that aluminum is a neurotoxicant product that contributes to Alzheimer's disease. Therefore, development of new coagulants based on green chemistry processes is increasingly of interest in coagulation-flocculation process due to environment and public health concern. Advancement of green processes using natural coagulant-flocculant has drawn great interest in recent years. Various natural coagulants had been identified from animal and plant origins such as chitosan (Renault et al., 2009), M.oleifera, tannin and cactus (Yin, 2010) and okra extracted from okra seeds pod tips, plant stalk and root (Al-Samawi and Shokralla, 1996). Scientific results showed that requirement of alum could be reduced 50 – 90 % upon replacement of okra as primary coagulant and coagulant aid. A new material, laterite soil which is naturally available on the earth is selected as natural coagulant-flocculant since it contains elements of coagulation-flocculation functions. Laterite soil is not underlying in animal and plants origin. Therefore a new class of natural coagulant is established which can be named as natural resources.

Azo dyes which are responsible for color richness and widely used in textile industry and have posed a major pollution problem to environment due to color visibility and toxicity. The azo dye molecules could not be broken down under sunlight or radiant energy due to their high photolytic stable characteristic, thus critically affecting the aquatic system. In degradation, azo dyes cleavages potentially generate aromatic amines. Some aromatic amines are considered carcinogenic since it can accumulate in the food chain and imperil human health and ecosystem (Sirtori et al., 2012). A few methods have been proven to be effective for dye degradation, such as photocatalytic process (Niyomkarn et al., 2014), sonalysis (Jamalludin and Abdullah, 2014) and biological process (Tan et al., 2014). It is necessary to develop pathway of dye degradation to understand and ensure that the degradation intermediates and byproducts yielded are safe to discharge into water streams. To date, the pathway on the degradation of dyes in coagulation process is yet to be explored. Therefore, dye degradation in coagulation-flocculation process using laterite soil is established in this study. Degradation pathway can assist in ensuring zero potential hazards of intermediates and products formed.

1.3 Objectives

The objectives for the present research project are:

- To distinguish the laterite soil's components behaviour under various pH range.
- To determine the degradation pathways and initiator of azo, cationic and anionic dyes using laterite soil as natural coagulant-flocculant.
- To determine presence of polymerization phenomena.
- To compare effectiveness between chemical and natural coagulants.

1.4 Scope of Research

In the present work, laterite soil as a natural coagulant-flocculant was used in treating dyeing bath effluent. Preliminary study on the laterite soil's components behaviour under various pH ranges was carried out. It was intended to understand the roles of silica, aluminum and iron as well as coagulation-flocculation mechanisms involved. Degradation pathway of acid orange 7, methylene blue and methyl orange dyes using naturally prepared laterite soil was determined. Dyes degradation under various dosages of laterite soil coagulant-flocculant was performed. UV-Vis spectra and FT-IR analysis were used to identify the degradation products in the treatment process and to establish a pathway of degradation. An initiator to ensure degradation of dyes was determined. The results provided comparison of effectiveness of laterite soil as natural coagulant with chemical-based coagulants in terms of color removal trends, reusability of sludge, sludge volume index (SVI), effects on environment and human health and industrial dye wastewater treatment.

1.5 Organization of Thesis

This thesis consists of five chapters. Chapter one (introduction) briefly discusses about the categories of dyes extensively used in industry, types of industries applying dyes, textile mill dyeing processes and the characteristics of dye wastewater. It also covers the problems confronted with the steps of technology developments. Therefore, this research is carried out to overcome the stated problems. The objectives and scope of this research are stated.

Chapter two (literature review) focuses on a review of present practices for textile wastewater treatment, advantages and limitations of the treatment technologies. Moreover, intermediates and by-products during and after treatment processes are covered. Specific topics related to coagulation-flocculation such as mechanisms, types of coagulant-flocculant, factors affecting thos process are discussed. Characterization of laterite soil is included in the last section.

Chapter three (methodology) presents the materials and equipment utilized in the present work. The detailed description regarding experimental procedures and the means of samples analysis are described.

Chapter four (results and discussion) illustrates and discusses the results of the laboratory studies conducted and detailed evaluation concerning to the result analysis.

Chapter five (conclusion and recommendations) provides a final conclusive resolution based on the results obtained towards the objectives of this study. Recommendation section suggests ideas for further studies in the related field.

CHAPTER TWO

LITERATURE REVIEW

2.1 Treatment of Dye Wastewater

2.1.1 Present practices for textile wastewater treatment

Textile wastewater is considered to be recalcitrant, photo catalytic stable and non-biodegradable. It ought to be treated before discharged into water bodies. Recently, two treatment systems are applied to treat dye wastewater: single and multistage treatment systems. Single stage treatment system comprises of physical, chemical or biological treatment. Multistage treatment system is the combination or hybridization of physical and/or chemical and/or biological treatment.

Single stage physical treatment system or known as membrane process such as physisorption, microfiltration, ultrafiltration, nanofiltration and reverse osmosis is commonly applied in treating dye wastewater. Physisorption or physical adsorption allows the accumulation of substances (adsorbate) on the interface bonded by weak Van der Waals forces and thus it is reversible (Yagub et al., 2014). Filtration (Zheng et al., 2013) refers to a solid liquid separation process using specific size range of semipermeable membrane or filter medium driven by pressure. Microfiltration allows the suspended matter removal; ultrafiltration removes particles and macromolecules; nanofiltration permits separation of low molecular weight compounds and divalent salts; reverse osmosis is mainly used for removal of mineral salts and chemicals (Koseoglu-Imer, 2013).

Single stage chemical treatment includes coagulation-flocculation, advanced oxidation process (AOP), ozonation, Fenton reagents, sonolysis and photocatalytic process. Chemical coagulation-flocculation process is the application of coagulant (metal salts) to destabilize dye molecules and flocculant tends to bridge the destabalized particles into larger agglomerates for easy separation. Advanced oxidation process (AOP) is the application of oxygen based radicals generated in-situ by water and oxygen to degrade dye (Hisaindee et al., 2013). Ozonation utilizes ozone which is a powerful and promising oxidizing agent that can effectively break down chromophores and complex aromatic rings of dyes (Tehrani-Bagha et al., 2010). Fenton process is a technology with powerful oxidant which can convert organic matter into water, carbon dioxide and inorganic compounds. The oxidant is hydroxyl radical generated by Fenton reaction of H_2O_2 with Fe^{2+} and Fe^{3+} salts (Ertugay and Acar, 2013). Surface of metal-oxide semiconductor photocatalyst promotes photocatalytic process whereby the UV light causes the transfer of electrons in valence band to conduction band. Subsequently, degradation and mineralization of dangerous organic pollutants take place (Khan et al., 2014).

Sequential batch reactor (SBR), aerobic and anaerobic processes are the examples of single stage biological treatment. SBR is a modified sludge process used to treat dye wastewater. Aerobic (presence of oxygen) and anaerobic (without oxygen) processes involve microorganisms to degrade dyes. Rate of dye degradation depends on the synergistic metabolic activities of microbial communities (Jain et al., 2012).

Table 2.1 lists some recent single stage treatment systems used in treating dye wastewater.

Table 2.1 Single stage treatment system for dye wastewater treatment

Treatment	Method	Concluding remarks	References
Biological	Aerobic	95.42 % degradation of Mordant black 17 by an aerobic microbial consortium consists of 5 different bacterial species.	Karunya et al., 2014
	Anaerobic	Anaerobic baffled reactor was able to remove 98 % of Reactive violet 5.	Ozdemir et al., 2013
	Sequential batch reactor (SBR)	Macrocomposite based sequencing batch biofilm reactor could decolorize azo dye Acid orange 7 within 3 hours and more than 80 % of COD was removed.	Lim et al., 2014
		Textile dye wastewater reached up to 71.3 % maximum decolorization and 79.4 % COD reduction by using SBR.	Sathian et al., 2014
Chemical	Chemical Coagulation-Flocculation	Polyaluminum chloride-poly(3-acrylamido-isopropanol chloride) (PACl-PAMIPCl) is an inorganic-organic hybrid polymer that used in flocculation. It could treat 95 % Reactive cibacron blue F3GA at pH 7.5 and 96 % Disperse terasil yellow W-4G at pH 3.0.	Yeap et al., 2014

	Aluminum sulphate (coagulant) and sodium alginate (enhancer) was able to remove 90% disperse & reactive yellow	Wu et al., 2012
Fenton process	(Nanoscale zero valent iron) nZVI-Fenton was able to remove 90 % color and 15 % COD from textile wastewater	Yu et al., 2014
	More than 95 % decolorization on phthalocyanine dye using Fe(II)/γ-Al_2O_3 as catalyst in Fenton process.	Cheng et al., 2014
	Methyl orange degradation rate after one hour could reach up to 97.8 % by using magnetic NdFeB-activated carbon Fenton catalyst.	Yang et al., 2014b
	Fenton process could treat 94 % of Direct blue 71 azo dye at optimum conditions: pH =3, Fe^{2+}= 3mg/L, H_2O_2 = 125 mg/L.	Ertugay and Acar, 2013
Ozonation	Ozonation could decolorize textile dye wastewater up to 90 % with six hours reaction period.	Wijannarong et al., 2013
	Ozonation could degrade Remazol red RB, Remazol Turquoise, Remazol Black RL and Remazol golden yellow RNL.	Tabrizi et al., 2011

	The performance of ozonation in the decolorization of Reactive blue 19 showed complete removal.	Tehrani-Bagha et al., 2010
Photocatalytic	99 % of decolorization and 47 % of mineralization of basic fuchin and basic red 9 were achieved under visible light irradiation for 10 min.	Wang et al., 2014
	Rhodamine B, Methylene blue and Congo Red could photo-degraded in photocatalytic process using Ag_3PO_4 nanorod under visible light irradiation.	Li et al., 2014b
	Solar photocatalysis using Ag@TiO_2 core shell structures nanoparticles could degrade Reactive blue 220.	Khanna and Shetty, 2014
Sonochemical	Sonolysis alone could only treat 24 % of Acid red 17. Once sonocatalyst was added, the removal reached up 100 %.	Khataee et al., 2014a
	Sonocatalytic was able to treat an organic dye (Basic blue 3) using TiO_2/Montmorillonite nanocomposite which was prepared by hydrothermal method.	Khataee et al., 2014b

		Aluminum powder irradiated by ultrasound could decolorize hydrophilic azo dye Orange G at pH 2.	Cai et al., 2014
Physical	Adsorption	Maize stem parenchymatous ground tissue was able to completely adsorbed cationic (Methylene blue) and anionic (Eriochrome black T) dyes with adsorption capacity of 160.84 and 167.01 mg/g, respectively.	Vucurovic et al., 2014
		Agricultural waste, rambutan (*Nephelium lappaceum)* peel activated by microwave –induced (potassium hydroxide) KOH acts as an activated carbon to treat acid yellow 17 dye. With adsorption capacity up to 215.05 mg/g.	Njoku et al., 2014
		Cetyltrimethylammonium bromide (CTAB) modified montmorillonite (MMT) nanomaterial was used to adsorb acid orange 7 at optimum pH of 6 with removal efficiency up to 94.08 %.	Klransan et al., 2014
	Microfiltration	Tubular carbon microfiltration could remove 80 % of textile wastewater color, 57 % of COD and 90 % of turbidity.	Tahri et al., 2013

	Thin film composite (TFC) membrane fabricated by mixed matrix nanoclay/chitosan on PVDF microfiltration could remove methylene blue and acid orange 7 dyes efficiently.	Daraei et al., 2013
Nanofiltration	Interfacial polymerization on the lumen side of hollow fiber support membranes is a new thin-film-composite (TFC) nanofiltration membranes used in treating Safranin O and Aniline blue dyes. Both dyes could be removed up to 90 % at a pH of 11.	Shao et al., 2013
	Interfacial polymerization with polyethyleneimine (PEI) and trimesoyl chloride (TMC) were used to prepare positively charged composite nanofiltration hollow fiber membrane. This nanofiltration membrane was able to treat Brilliant blue KN-R, Cationic red X-GTL, Acid red B, Rhodamine B and Gold yellow X-GL with 99.9 %, 99.8 %, 98.8 %, 97.5 % and 96.7 %, respectively.	Wei et al., 2014
	O-carboxymethyl chitosan/Fe_3O_4 PES nanofiltration membrane was fabricated to remove Direct red 16 azo dye.	Zinadini et al., 2014

	Nanofiltration could decolorize textile wastewater and reduce 99 % of COD.	Gozalvez-Zafrilla et al., 2008
Reverse osmosis	Reverse osmosis membrane fouling is able to remove reactive dye (anionic dye).	Srisukphun et al., 2009
Ultrafiltration	Ultrafiltration with a ceramic membrane was able to remove 70 % of Reactive black 5.	Alventosa-deLara et al., 2014
	Polyelectrolyte-enhanced ultrafiltration (PEUF) could remove 98 % of methylene blue. Polyelectrolytes used are anionic polyelectrolytes, poly(acrylic acid) (PAA) and poly(ammonium acrylate) ($PA\text{-}NH_4$).	Ben Fraj et al., 2014
	Micellar enhanced ultrafiltration (MEUF) by binary mixture of sodium dodecylsulfate (SDS) and polyoxyethylene octyl phenyl ether was able to remove 99.40 % of methylene blue and 98.06 % of Cadmium (Cd^{2-}).	Huang et al. 2014

Besides that, multistage or hybrid treatment processes have been developed in order to ensure complete mineralization of dye wastewater. Examples of multistage treatment system are physical-physical, physical-chemical, physical-biological, chemical-chemical, chemical-biological, biological-biological hybrid treatment.

Kertesz et al. (2014) attempted photocatalytic process hybrid with microfiltration to decolorize azo dye acid red 1. Photocatalytic process was able to remove the acid red 1 color. However, analysis showed that chemical oxygen demand and total organic carbon were still present in the solution. Therefore, microfiltration was introduced as the subsequent treatment for the removal of the organic carbon. In nanofiltration, fouling occurs due to strong attachment of dye molecules on the membrane. These main foulants (chromophore and auxochrome) ought to be removed before entering nanofiltration. Pretreatment process using coagulation with polymer is to aggregate the foulants, minimizing the membrane fouling occurrence (Zahrim et al., 2011). Combination of Fenton and coagulation process has reduced the acute and genotoxicity of dye effluent before discharged into water stream (Zhang et al., 2014a). Anaerobic process alone cannot mineralize dye molecule completely. Sequential integration of anaerobic/microaerophilic process followed by aerobic process was proposed by Khalid et al. (2010) to effectively mineralize dye-based compounds. De Souza et al. (2010) reported that the application of ozonation in treating dye wastewater led to the production of carcinogenic by-products. In order to overcome this problem, biological treatment with a biofilm after ozonation was installed. Fenton process alone took a long time to decolorize and degrade Reactive Blue 19. Therefore combined ultrasound with the Fenton process has been proposed by Siddique et al. (2014). After the combination, dye degradation rate has increased due to the acceleration of hydroxyl radical production.

Several examples of multistage treatment are listed and discussed in Table 2.2.

Table 2.2 Multistage treatment system for dye waste treatment

Hybrid Methods	Concluding remarks	References
	Physical-Physical Treatment Methods	
Micofiltration-Nanofiltration	Hybridization of microfiltration and nanofiltration could remove 100 % of color, 99.9 % of suspended matter and 73-85 % of COD for a dyeing-containing effluent.	Tahri et al., 2012
Adsorption-Ultrafiltration	Activated carbon cloths (ACCs) are used as adsorbent and a membrane filtration (3000 Da molecule weight cut-off) operated continuously were able to treat about 70 % of colored wastewater and > 98% of turbidity.	Metivier-Pignon et al., 2003

Physical-Chemical Treatment Methods		
Phtocatalytic-Microfiltration	Photocatalysis could remove Acid red 1 completely. Subsequently, microfiltration was used to remove the remaining organic compounds.	Kertesz et al., 2014
Coagulation-Flocculation-Nanofiltration	Polyaluminum chloride and polydiallyldimethyl ammonium chloride (PDDA) were chosen as the coagulant and flocculant. Hollow fiber membrane was selected as nanofiltration membrane.	Liang et al., 2014
Oxidation-Nanofiltration	Electro-catalytic oxidation was followed by nanofiltration to treat Acid red 73. The electrode used was Ti/SnO_2-Sb-CNT. Acid red 73 was decolorized up to 95.7 % and COD reduction up to 80.2 %.	Zhang et al., 2014b
Electrochemical advanced oxidation-Microfiltration	Electrochemical advanced oxidation- microfiltration hybrid system had successfully removed acid yellow 36 with 100 % COD reduction, 97.8 % turbidity and 99.6 % color.	Juang et al., 2013

Photocatalysis-Ultrafiltration	Photocatalysis/ultrafiltration hybrid process was used to degrade Reactive brilliant red X-3B azo dye. The photocatalyst used was titanium dioxide (TiO_2). The degradation process showed that acids production was the dominant factor affecting TiO_2 aggregate size.	Zhang et al., 2013
Coagulation-Nanofiltration	Pretreatment (coagulation) could minimize the problem of nanofiltration membrane fouling.	Zahrim et al., 2011
	Physical-Biological Treatment Methods	
Sequential biological-Aqueous biphasic system (ABS)	A thermophilic bacterium (*Anoxybacillus flavithermus*) isolated from a hot spring could decolorize almost 60 % of Reactive black 5 and Acid black 48. Subsequently, ABS was introduced and the removal could achieve up to 99 %.	Alvarez et al., 2013

	Chemical-Chemical Treatment Methods	
Fenton-Coagulation	Combination of both processes could effectively remove carcinogenic compounds.	Zhang et al., 2014a
Fenton-Ultrasound	Ultrasound accelerated the hydroxyl production in Fenton process, thus decoloration rate of Reactive blue 19 also increased.	Siddique et al., 2014
	Biological-Biological Treatment Methods	
Anaerobic/ Microaerophilic-Aerobic	Anaerobic/micoaerpohilic process could not mineralize dyes completely, combination with aerobic could effectively mineralize dyes.	Khalid et al., 2010
	Chemical-Biological Treatment Methods	
Ozonation-Biological	Carcinogenic by-products produced from ozonation were treated by biofilm.	De Souza et al., 2010

2.1.2 Advantages and limitations

Each of the treatment systems has its advantages and disadvantages. The relative advantages and limitations of the treatment methods are stated in Table 2.3.

Table 2.3 Advantages and limitations of various dye removal treatment methods

Treatment methods	Advantages	Disadvantages	References
Membrane processes	-High efficiency -Ease to operate -Small footprint -No addition of chemical is required	-Membrane fouling (Cake layer formation/Concentrated sludge produced) -Pore constriction and blockage -Concentration polarization	Zuriaga-Agusti et al., 2014;