REACTIVE CIBACRON BLUE DYE WASTEWATER TREATMENT USING COMBINED TECHNOLOGY OF THERMOLYSIS AND INORGANIC-ORGANIC HYBRID POLYMER COAGULATION-FLOCCULATION

by

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

MARCH 2016

ACKNOWLEDGEMENT

First of all, I would like to extend my deepest gratitude to my main supervisor, Professor Dr. Teng Tjoon Tow for his professional advice, guidance and suggestions throughout the course of my study. His never-ending encouragement and support has enabled me to complete this research and developed a greater understanding of the research field.

I would also like to thank my co-supervisors, Professor Dr. Norhashimah Morad and Dr. Mohd Rafatullah who have shared their advice and guidance to further improve my work and assist in the completion of my study.

Great appreciation goes to all the lab assistants who have provided technical support in the usage of the instruments during the course of my research. In addition, I would like to acknowledge USM graduate assistant scheme and USM fellowship scheme for the financial support.

A big thank you to all my dear friends who have given me unending encouragement, advice and companionship throughout this journey. The valuable friendships will be treasured.

Last but not least, my most sincere appreciation goes to my family members. Your support and love have been a continuous motivation for me.

Claire Su Xin-Hui

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LIST OF ABBREVIATIONS AND SYMBOLS

Al	Aluminium
$Al(OH)_3$-PAM	Aluminium hydroxide-polyacrylamide
Al_2SO_4	Aluminium sulphate
BOD	Biochemical oxygen demand
$CaCl_2$-PAM	Calcium chloride-polyacrylamide
Cl^-	Chloride ion
COD	Chemical oxygen demand
Cu^{2+}	Copper ion
CuO	Copper oxide
CuO/CeO_2	Copper oxide/Cerium dioxide
$CuSO_4$	Copper sulphate
$FeCl_3$	Ferric chloride
$FeCl_3$-PDMDAAC	Ferric chloride-polydimethyldiallylammonium chloride
$FeSO_4$	Ferrous sulphate
FT-IR	Fourier transform infrared
H_2O	Water
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulphuric acid
HCl	Hydrochloric acid
KBr	Potassium bromide
MC	Magnesium chloride
MCPEO	Magnesiumc chloride-polyethylene oxide
$Mg(OH)_2$	Magnesium hydroxide
$Mg(OH)_2$-PAM	Magnesium chloride-polyacrylamide

Mg^{2+}	Magnesium ion
$MgCl_2$	Magnesium chloride
$MgCl_2$-PAM	Magnesium chloride-polyacrylamide
$MgCl_2$-PEO	Magnesium chloride-polyethylene oxide
$MgCl_2$-PSA	Magnesium chloride-polysilicic acid
NaOH	Sodium hydroxide
OH^-	Hydroxide ions
PACl	Polyaluminium chloride
PACl-PDMDAAC	Polyaluminium chloride-polydimethyldiallylammonium chloride
PAFS	Polyaluminium ferric sulphate
PAM	Polyacrylamide
PDDA	Polydiallyldimethyl ammonium chloride
PDMDAAC	Polydimethyldiallylammonium chloride
PEO	Polyethylene oxide
PFS	Polyferric sulphate
PMSC	Poly-magnesium-silicate-chloride
PSA	Polysilicic acid
RCB	Reactive cibacron blue F3GA
rpm	Revolutions per minute
SBR	Sequential batch reactor
Ti/SnO_2-Sb	Titanium/Tin oxide-antimony
TiO_2	Titanium dioxide
TOC	Total organic carbon
TSS	Total suspended solids

UV-Vis	UV-visible
ZnO	Zinc oxide
-C=C-	Ethenyl
-CHO	Aldehyde
-C-H-	Carbon-hydrogen
-C=O-	Carbonyl
-C-N-	Carbon-nitrogen
-OH	Hydroxyl
$-NH_2$	Amino
-N=N-	Azo
$-NO_2$	Nitro
A	Calibration constant of viscometer
C_f	Final concentration of colour and COD of supernatant
C_i	Initial concentration of colour and COD of supernatant
η	Dynamic viscosity
ρ	Solution density
t	Flow time

RAWATAN AIR SISA PEWARNA REAKTIF CIBACRON BIRU MENGGUNAKAN TEKNOLOGI GABUNGAN TERMOLISIS DAN PENGENTALAN-PEMBERBUKUAN POLIMER HIBRID TAK ORGANIK-ORGANIK

ABSTRAK

Air sisa pewarna reaktif, cibacron biru F3GA (RCB), dirawat menggunakan teknologi gabungan hibrid termolisis dan pengentalan-pemberbukuan menggunakan polimer hibrid magnesium klorida-poliethylene oksida ($MgCl_2$-PEO). Apabila air sisa pewarna sintetik dirawat menggunakan termolisis-pemangkin sahaja, 63.78% pemecatan warna dan 56.33% penurunan COD telah dicapai. Pemangkin yang digunakan ialah kuprum sulfat ($CuSO_4$). Kecekapan maksimum bagi proses termolisis dicapai pada pH 2, dos pemangkin 5000 mg/L, suhu pemanasan 95°C dan tempoh pemanasan 120 minit. Polimer hibrid $MgCl_2$-PEO disediakan dan dicirikan. Kemudian, ia diaplikasikan dalam pengolahan RCB menggunakan teknik pengentalan-pemberbukuan. Polimer hibrid disediakan dalam pelbagai nisbah $MgCl_2$ kepada PEO melalui pengadunan fizikal. Kelikatan larutan akueus polimer hibrid menunjukkan tren menurun apabila komposisi $MgCl_2$ meningkat. Walau bagaimanapun, kekonduksian larutan akueus hibrid polimer menunjukkan tren meningkat. Bagi aplikasi pengolahan air sisa RCB, didapati bahawa nisbah 90% $MgCl_2$: 10% PEO menunjukkan prestasi tertinggi, dengan rekod 98.58% pemecatan warna dan 91.09% penurunan COD pada pH 11 dan dos pengental 1500 mg/L. Perbandingan antara prestasi $MgCl_2$ dengan polimer hibrid $MgCl_2$-PEO menunjukkan bahawa polimer hibrid $MgCl_2$-PEO adalah lebih efisien. Dos polimer hibrid yang diperlukan adalah lebih rendah, iaitu 1500 mg/L, berbanding 2000 mg/L $MgCl_2$, tetapi ia masih mampu menunjukkan prestasi yang tinggi. Nilai kajian potensi zeta berubah dari -25.78 mV ke 24.97 mV dan ini menunjukkan bahawa peneutralan caj merupakan

mekanisme bagi pengentalan-pemberbukuan RCB menggunakan polimer hibrid $MgCl_2$-PEO. Kedua-dua proses termolisis dan pengentalan-pemberbukuan digabungkan untuk mencapai peratus pemecatan warna and penurunan COD yang lebih tinggi. Bagi proses gabungan, air sisa yang telah dirawat menggunakan termolisis dibiarkan sehingga suhu air sisa mencapai suhu bilik, dan seterusnya dirawat menggunakan pengentalan-pemberbukuan. Bagi proses hibrid pula, air sisa RCB dirawat menggunakan termolisis dan pengental ditambah dalam air sisa yang masih bersuhu 95°C. Dalam proses gabungan, hanya 1250 mg/L $MgCl_2$ dan 1000 mg/L polimer hibrid $MgCl_2$-PEO diperlukan untuk mencapai kecekapan maksimum, berbanding dengan dos pengental yang diperlukan dalam proses pengentalan-pemberkukuan sahaja. Bagi kedua-dua pengental, pH yang paling sesuai ialah pH 6. Apabila kondisi-kondisi ini digunakan, 98.43% pemecatan warna dan 85.93% penurunan COD dicapai dengan menggunakan pengental $MgCl_2$, manakala 99.13% pemecatan warna dan 91.85% penurunan COD dicapai dengan menggunakan polimer hibrid $MgCl_2$-PEO. Bagi proses hibrid pula, pemecatan warna dan penurunan COD maksimum yang dicapai ialah 99.21% dan 91.11%, masing-masing dengan penggunaan $MgCl_2$, manakala 99.69% pemecatan warna dan 93.33% penurunan COD dicapai dengan penggunaan polimer hibrid $MgCl_2$-PEO. Dos pengental yang diperlukan dalam proses hibrid dikurangkan lagi, di mana hanya 750 mg/L pengental bagi kedua-dua pengental diperlukan untuk mencapai kecekapan maksimum. Dari segi isipadu enapcemar yang dihasilkan, proses hibrid menggunakan polimer hibrid menghasilkan isipadu enapcemar yang paling rendah. Kecekapan proses hibrid menggunakan polimer hibrid juga telah diaplikasikan atas air sisa industri tekstil. Dengan menggukan 750 mg/L polimer hibrid pada pH 6, 99.01% pemecatan warna dan 90.86% penurunan COD telah dicapai.

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ABSTRACT

A reactive dye, cibacron blue F3GA (RCB), was subjected to a combined and hybrid technology of thermolysis and coagulation-flocculation using the magnesium chloride-polyethylene oxide ($MgCl_2$-PEO) hybrid polymer. When the synthetic dye wastewater was subjected to catalytic thermolysis alone, maximum colour removal and COD reduction achieved were 63.78% and 56.33%, respectively. The catalyst used was copper sulphate ($CuSO_4$). Maximum efficiency of thermolysis was found to be at pH 2, catalyst mass loading of 5000 mg/L, heating temperature of 95°C and heating time 120 minutes. The $MgCl_2$-PEO hybrid polymer was prepared and characterised. It was then applied in the coagulation-flocculation of RCB. Various ratios of $MgCl_2$ to PEO were prepared through physical blending. The viscosities of the hybrid polymer showed a descending trend as the composition of $MgCl_2$ increased. However, the conductivities of the hybrid polymer aqueous solutions showed an ascending trend. For the application in RCB dye wastewater treatment, 90% $MgCl_2$:10% PEO ratio showed the best performance, recording 98.58% colour removal and 91.09% COD reduction at pH 11 and coagulant dosage of 1500 mg/L. The comparison between the efficiency of $MgCl_2$ coagulant and $MgCl_2$-PEO hybrid polymer showed that the hybrid polymer was more efficient. It required a lower coagulant dosage, which was 1500 mg/L, compared to 2000 mg/L $MgCl_2$, while producing greater colour removal efficiency. The zeta potential measurements obtained ranged from -25.78 mV to 24.97 mV, which showed that charge neutralisation was the dominant mechanism for the flocculation of RCB dyes using $MgCl_2$-PEO hybrid polymer. To further enhance the percentage of colour removal and COD reduction, thermolysis and coagulation-flocculation were combined. For the combined process, the wastewater was subjected to thermolysis and the wastewater allowed to cool to room temperature, then treated with coagulation-flocculation. For the hybrid process, the RCB dye wastewater was treated with thermolysis and coagulant was added to the wastewater while at 95°C. In the combined process, only 1250 mg/L of $MgCl_2$ and 1000 mg/L of $MgCl_2$-PEO hybrid polymer were necessary to achieve maximum efficiency, compared to when coagulation-flocculation was carried out on its own. The optimum pH for both coagulants were pH 6. Under these conditions, 98.43% colour removal and 85.93% COD reduction were achieved when $MgCl_2$ was used, while 99.13% colour removal and 91.85% COD reduction were achieved when $MgCl_2$-PEO hybrid polymer was used. When RCB synthetic dye wastewater was subjected to the hybrid process, the maximum colour removal and COD reduction for $MgCl_2$ were 99.21% colour removal and 91.11% COD reduction, while for $MgCl_2$-PEO hybrid polymer, the 99.69% colour removal and 93.33% COD reduction were achieved. In the hybrid process, the required coagulant dosages were further reduced, where only 750 mg/L of both coagulants were required to achieve maximum efficiency. In terms of sludge production, the use of the hybrid polymer in the hybrid process produced the lowest volume of sludge. The efficiency of the hybrid process using the hybrid polymer for the treatment of industrial textile wastewater was also evaluated. By using 750 mg/L of hybrid polymer at pH 6, 99.01% colour removal and 90.86% COD reduction was achieved.

CHAPTER ONE

INTRODUCTION

1.1 General Introduction

The efforts to curb environmental problems have become more significant, and one of the major environmental problems is the discharge of wastewaters sourced from either domestic use or industrial use. Water and wastewater treatments are carried out to remove the undesirable impurities and pollutants from the product water and to meet regulatory requirements regarding discharge of wastewater (Dükkancı and Gündüz, 2006). With the extensive development activities and ever-growing industrial sector, more wastewaters of various compositions are being produced. These wastewaters have to be treated before being discharged into water bodies.

Wastewaters are generated in large volumes from domestic and industrial sources, such as the textile, printing, food, cosmetics, electronic, chemical and pharmaceutical industries, which contain a wide range of contaminants that pose a threat to human life and the environment. Some of the commonly found contaminants in these wastewaters are colour, heavy metals, nitrogen, phenols, organics, and suspended solids (Gupta et al., 2009). The largest contributor of coloured wastewaters is the textile industry, which contributes two thirds of the total production of dye wastewater (Robinson et al., 2001).

The rapidly growing textile industry aims to utilize dyes with high degree of colour fixation and depth in the dyeing process to meet the demands of the consumers. This encourages the colour technologists and chemists to continuously improve the available dyes and at the same time develop new dyes that are durable and fast, with high resistance to washing, light and heat (Singh and Arora, 2011). In the textile industry, many chemical reagents of diversified compositions are used, such as inorganics, organics and polymers (Hai et al., 2007). The presence of these chemical reagents in addition to the dyes in textile industry wastewaters cause high total organic carbon (TOC), chemical oxygen demand (COD), biochemical oxygen demand (BOD), suspended solids, colour and salinity in the effluent (Kuberan et al., 2011; Verma et al., 2012b).

Discharge of dye wastewater into water bodies, even at very low concentrations, causes waters to be aesthetically displeasing and at the same time deems the water hazardous to aquatic and human life. Dye wastewater typically contains chemicals which are toxic, carcinogenic, mutagenic and teratogenic to organisms exposed to these wastewaters. Exposure to dye wastewater may cause acute or chronic effects on humans, depending on the duration of exposure and dye concentration. Colour in wastewaters hampers the penetration of light and this, in turn, obstructs the photosynthetic activity of aquatic life in the water bodies (Sharma et al., 2009). Therefore, it is of utmost importance to remove dyes from wastewaters before discharge into water bodies.

1.2 Laws and Regulations of Textile Industry Wastewater

The textile industry utilizes a large volume of water and wide array of chemical reagents during the wet processing operations. In these operations, improper dye uptake and the degree of fixation on the fibres of the material determine the amount of dye discharged in the wastewater (Singh and Arora, 2011).

Textile wastewater has been an environmental concern since the harmful effects of dye effluents have been made known. In the efforts of environmental administrators to control and prevent further deterioration of the environment caused by the textile industry, permissible limits of various parameters of concern were established by environmental administrators. The Environmental Quality (Industrial Effluent) Regulations 2009 was enforced in Malaysia, where industrial effluents are to comply with the Fifth Schedule upon discharge (Environmental Quality Act and Regulation, 2010). A total of 30 parameter limits were listed and divided into effluent of Standard A and B (Table A1 in Appendix). Standard A represents the effluent discharged into any inland waters with the catchment areas, while Standard B represents the effluent discharged into any other inland waters (Environmental Quality Act and Regulation, 2010). Based on the specific trade or industry, permissible limits for the discharge of effluent containing COD are listed in the Seventh Schedule (Table A2 in Appendix).

1.3 Wastewater Treatment Methods

To date, there have been many wastewater treatment methods studied and developed, whether physical, chemical or biological in nature. Each of these treatments has its own advantages and drawbacks. Physical treatment processes serve to separate undissolved chemicals and particulate matter present in the wastewater (Singh and Arora, 2011). Examples of physical treatment methods commonly used are adsorption, sedimentation, screening, filtration, floatation and skimming (Fitzpatrick and Gregory, 2003). However, the physical treatment methods are highly dependent on the particle size and face the problem of sludge generation and its disposal (Robinson et al., 2001).

Chemical treatment processes remove water-soluble and water-insoluble dyes from wastewater through sorption or chemical bonding (Pak and Chang, 1999). Commonly used chemical treatments are coagulation-flocculation, Fentons reagent, ozonation and photocatalysis. These methods have shown promising results but they incur high operation costs and generate a large amount of sludge.

Biological treatments are deemed as the cost-effective method for the treatment of dye wastewater. Microorganisms, in aerobic or anaerobic conditions, are used to degrade the dye molecules. However, dyes were designed to be stable and resistant to biodegradation to prolong the lifespan of the dye (Singh and Arora, 2011). Anaerobic degradation of dyes may produce toxic, carcinogenic and mutagenic products (Shah, 2014a).

1.3.1 Thermolysis

Thermolysis is a treatment methods where heat is used to decompose a substance, usually of complex nature, into other substances of lower molecular weights and simpler chemical structures. Thermolysis can be conducted under two conditions, either with the presence of a catalyst, or without the presence of a catalyst (Kumar et al., 2007).

The presence of catalysts during thermolysis speeds up the process. Thermolysis is a two-step process, where the first step is the fast step while the second step is slower than the first. These two steps are parallel but complementary to each other (Chaudhari et al., 2010; Chaudhari et al., 2012).

Through the process of thermolysis, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) of the wastewater can be reduced. At the same time, the products of thermolysis show good formation of settleable solid residue and filtration characteristics of the slurry (Mohana et al., 2009). Factors such as the solution pH, temperature and atmospheric pressure are those that control the formation of the solid residue.

1.3.2 Coagulation-flocculation Process

1.3.2(a) Conventional Coagulation-flocculation Process

Coagulation-flocculation process is a technique widely used for the treatment of dye wastewaters, particularly wastewaters containing dissolvable dyes, such as reactive dyes, sulphured dyes and reductive dyes (Gao et al., 2007). This process destabilizes particles that are dispersed in water. High-molecular weight polymers are usually used as flocculants, which function to agglomerate the non-settleable and slow settling colloidal solids (Lee et al., 2010). These large floc aggregates can then be removed from the wastewater through physical treatments, such as clarification and filtration. However, this process has some disadvantages in that high chemical dosages are usually required, large volumes of sludge are produced and the cost of sludge disposal is high (Gao et al., 2007).

1.3.2(b) Coagulation-Flocculation Using Hybrid Polymers

To overcome the drawbacks of the conventional coagulation-flocculation process, various flocculants have been developed such as inorganic flocculants, organic flocculants and composite as well as hybrid polymer flocculants. Hybrid polymer flocculants are made up of inorganic coagulants and organic water soluble polymers (Lee et al., 2011a; Lee et al., 2011b). Some examples of hybrid polymer flocculants are $MgCl_2$-PAM (Lee et al., 2014), $Al(OH)_3$-PAM (Sun et al., 2008) and $FeCl_3$-PDMDAAC (Wang et al., 2008).

The purpose of synthesizing hybrid polymer flocculants is to increase the molecular size and to enhance the aggregating power of the flocculants (Gao et al., 2005). According to Wang et al. (2008), the use of hybrid polymer flocculants enhances the aggregating power of flocculants by increasing the ratio of effective component and positive electric charge of the flocculants. The increase in molecular size and enhancement of aggregating power of the flocculants make the hybrid polymers a more effective flocculant compared to the traditional inorganic flocculants.

In the conventional coagulation-flocculation method, the coagulant and flocculant are added separately into the wastewater. With the use of hybrid flocculants, the coagulation and flocculation processes are combined into one process. This would be able to reduce operation time and is favourable to the industries that produce a large volume of wastewater discharge (Lee et al., 2011b).

1.4 Combined and Hybrid Treatment Methods for Dye Wastewaters

Due to the complex structure and recalcitrance of dye molecules to a wide array of wastewater treatment methods, it is not satisfactory that dye wastewaters are treated with a single treatment method. Each single treatment method has its own disadvantages. According to Loh et al. (2012), wastewaters containing compounds of complex nature, such as dyes and heavy metals, require a combination of treatment as a single treatment is not sufficient to meet regulatory requirements. By using combined treatments, the disadvantages of a single treatment can be subjugated, resulting in treatment processes that are more efficient in the removal of complex contaminants from wastewaters. Currently, with ever more stringent regulations on industrial wastewater discharge being implemented, a single treatment method is not realistic. Therefore, a combination of treatment methods have been proposed for more technically and economically practical alternatives (Hai et al., 2007). A combined process is a process where two or more treatment methods are carried out sequentially.

A hybrid process is a process where two or more treatment methods are fused into one process. It would be cost-saving and time-saving as it only requires one reactor to carry out the multiple processes which have been integrated into one process. In addition to the development of hybrid processes, hybrid materials have also gained reasonable attention recently, where materials are modified to function in multiple ways to enhance the treatment process.

1.5 Problem Statements

Reactive dyes are popular in the textile industry as they produce a bright and complete colour range, excellent wet and light fastness and simple application (Camp and Sturrock, 1990). They are widely used on cellulosic fibres. Reactive dyes in wastewater cause high alkalinity, high concentration of organic materials and strong colour. Their poor biodegradability, relatively low molecular weight, high solubility and low affinity for absorbents deem them unsuitable for conventional, single-step treatment methods (Arslan et al., 2000).

Dyes in wastewater have very complex structures and are difficult to treat. In the textile industry, wastewater contains not only dye, but also other pollutants. The complexity of the wastewater deems a single treatment process inadequate for the treatment of dye wastewaters. Through the combination of treatment processes, the disadvantages of individual treatment processes can be overcome, and at the same time achieve better treated wastewater quality (Lin and Lin, 1993). Therefore, a combined and hybrid treatment of thermolysis and hybrid polymer coagulation-flocculation which degrades the dye molecule into simpler molecules, then destabilizes these molecules is a promising enhancement in wastewater treatment.

Thermolysis has proven to be effective in breaking down the complex dye molecules into simpler molecules of lower molecular weight. However, the extent of dye degradation during thermolysis has never been studied. By studying the extent of dye degradation, the degradation of compounds, such as benzene and triazine, which may form hazardous, resilient molecules upon reacting among themselves after the treatment can be identified.

Coagulation-flocculation is widely used in the industries for the treatment of dye wastewaters. However, the flocculation process is highly complex due to the wide array of polymeric flocculants available and the optimization of this process in the industry is carried out under an experimental basis (Wong et al., 2006). The superior performance of hybrid polymers as flocculants has gained increasing attention. The inorganic coagulant, magnesium chloride ($MgCl_2$), is not as widely used in the industries compared to alum and polyaluminium chloride (PACl) but has shown good ability to remove impurities and pollutants in wastewater (Tan et al., 2000). A well-known polymer used as the organic component of a hybrid polymer flocculant is polyacrylamide (PAM). Its use has been reported by many researchers (Ariffin et al., 2012; Gao et al., 2012; Lee et al., 2014). A less extensively used polymer is polyethylene oxide (PEO). It is a non-ionic polymer which is water soluble and has high molecular weight (Mpofu et al., 2004). These properties of PEO make it a suitable polymer to be used as a flocculant.

Combined treatment of thermolysis and coagulation-flocculation for dye wastewater has been carried out by Kumar et al. (2008a) and Loh et al. (2012). Through the combination of these two processes, a noticeable enhancement in percentage of colour removal and COD reduction were achieved. Combined processes require the use of individual reactors for each treatment process. As for hybrid processes, the multiple treatments are carried out simultaneously, which signifies that only one vessel would be required to carry out the process. This indirectly leads to the reduction in operation time and cost.

The efficiency of the hybridisation of thermolysis and coagulation-flocculation using $MgCl_2$-PEO hybrid polymer is compared to that of the combined process in terms of colour removal and COD reduction. This would open up a new class of dye wastewater treatment that could potentially be adopted by the industries to enhance the efficiency of their treatment processes while saving cost.

1.6 Objectives

The objectives of the present study are:

a. To formulate and prepare $MgCl_2$-PEO hybrid polymers

b. To determine the characteristics of the hybrid polymer formed.

c. To determine the effects of different parameters on the efficiency of thermolysis and coagulation-flocculation as individual processes and when combined and hybridised in terms of colour removal and COD reduction.

1.7 Scope of the Study

The present study can be divided into three sections, namely, (i) thermolysis of synthetic dye wastewater, (ii) preparation, characterization and application of $MgCl_2$-PEO hybrid polymer as flocculant in coagulation-flocculation of synthetic dye wastewater, (iii) comparison between combined and hybrid processes of thermolysis and coagulation-flocculation on synthetic dye wastewater and industrial textile wastewater.

In the first section of the study, four factors known to affect the performance of thermolysis were studied. The factors studied were pH of the synthetic dye wastewater, catalyst dosage, treatment time and treatment temperature. To understand the mechanism of dye degradation during thermolysis, the kinetics of the thermal degradation of the synthetic dye were studied.

For the second section of the study, the $MgCl_2$-PEO hybrid polymers were prepared in different ratios (90% $MgCl_2$: 10% PEO, 70% $MgCl_2$: 30% PEO, 50% $MgCl_2$: 50% PEO, 30% $MgCl_2$: 70% PEO and 10% $MgCl_2$: 90% PEO) using physical blending and the characteristics of the hybrid polymers were studied in terms of conductivity, density, viscosity and chemical structure. Then, the hybrid polymers were used in the coagulation-flocculation of synthetic dye wastewater. In addition, the flocculation mechanisms were studied through zeta potential analysis.

In the third section, the efficiency of the combined and hybrid processes of thermolysis and coagulation-flocculation were studied and their efficiencies compared, in terms of percentage of colour removal, percentage of COD reduction and volume of sludge generated. The combined and hybrid processes were applied to both the synthetic dye wastewater and also industrial textile wastewater.

CHAPTER TWO

LITERATURE REVIEW

2.1 Characteristics of Dyes

Dyes are organic compounds of synthetic origin that imparts colour upon binding with a material (Velmurugan et al., 2011). Dye molecules consists of two main constituents, namely, chromophores and auxochromes. The auxochromes are attached to the chromophores and are responsible for intensifying the colour of the dye. Examples of chromophores are azo (-N=N-), carbonyl (-C=O-), and nitro ($-NO_2$) groups, while examples of auxochromes are hydroxyl (-OH), aldehyde (-CHO) and amino ($-NH_2$) groups (Raghavacharya, 1997). The absorption of light at various wavelengths by the chromophores and auxochromes determines the colour given out by the dyes (Kiernan, 2001). Hitherto, there are more than 9000 types of dyes incorporated in the colour index (Garg et al., 2003). The classification of dyes are based on their chromophore structures, such as acidic, basic, disperse, reactive, azo, diazo and anthraquinone dyes. According to Kiernan (2001), the colours, properties and uses of a dye are determined by the specific chemical structures of the dyes.

Among these dyes, reactive and disperse dyes are the two classes of dyes most widely used in the textile industry for dyeing cotton and polyester (Chen et al., 2010). Both reactive and disperse dyes pose a problem to the environment as they have high stability and are resistant to biodegradation (Somasiri et al., 2006). The classification and description of several dyes are shown in Table 2.1. The most problematic dyes among these that are resistant to conventional treatment systems are the brightly coloured, water-soluble reactive and acid dyes (Willmott et al., 1998).

Table 2.1 Classification of dyes

Class	Description	References
Cationic - Basic	Positively charged coloured ions; soluble in water	Kiernan (2001)
Anionic - Acidic - Direct - Reactive	Negatively charged coloured ions; hydrolyse easily; low fixation on material; brightly coloured; not susceptible to biological treatment	(Kuo, 1992); Wong et al. (2007)
Non-ionic - Disperse	Do not ionise in aqueous medium; low solubility in water; can be effectively removed by coagulation-flocculation	Robinson et al. (2001); Hou et al. (2014)
Azo	Contains azo group; very stable large molecule; resistant to degradation; may produce carcinogenic and toxic intermediates during degradation	Kiernan (2001); Singh and Arora (2011); Lau et al. (2014)
Anthraquinone	Contains anthraquinone fused aromatic ring structure; resistant to most degradation methods	Kiernan (2001); Robinson et al. (2001)

2.2 Treatment Technologies for Dye Wastewater

The treatment of dye wastewater does not only focus on diminution of dye concentration in the water but also other ecological parameters, such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), total organic carbon (TOC) and suspended solids. According to Slokar and Le Marechal (1998), when the -C=C- bonds, -N=N- bonds, and heterocyclic and aromatic rings in the organic dye molecules are broken, the absorption of light by the associated molecules shift from the visible to the ultraviolet or infrared region of the electromagnetic spectrum and hence the colour is removed from wastewater.

To date, many treatment technologies have been studied for the treatment of dye wastewaters and can be divided into three main categories, namely, physical, chemical and biological treatment methods. Examples of simple individual treatments that have been widely studied are shown in Table 2.2. However, due to the complexity of dye wastewaters, a single treatment method is not sufficient for the effluent to meet permissible limits.

Table 2.2 Simple individual treatments for dye wastewater

Treatment	**Application**	**References**
Coagulation-flocculation	Reactive cibacron blue F3GA and terasil yellow W-4G were treated using polyaluminium chloride-poly(3-acrylamido-isopropanol chloride) (PACl-PAMIPCI), resulting in 95% and 96% colour removal, respectively	Yeap et al. (2014)
Adsorption	Neem sawdust was used as an adsorbent for the removal of malachite green dye, resulting in 84% colour removal and adsorption capacity of 4.354 mg/g.	Khattri and Singh (2009)
Photocatalytic degradation	Zinc oxide/reduced graphene oxide hybrid photocatalyst was fabricated and used for the photocatalytic degradation of methylene blue, methylene orange and rhodamine 6G, achieving about 99% colour removal for all three dyes.	Fan et al. (2015)

Membrane filtration	Nanofiltration and ultrafiltration were applied to industrial wastewater, where nanofiltration resulted in 100% colour removal and 92% COD reduction.	Hairom et al. (2015)
Liquid-liquid extraction	Cibacron red FN-R was removed from aqueous solution through liquid-liquid extraction, using tetrabutyl ammonium bromide as an extractant. When dichloromethane was used as the diluent, 99.2% of dye was extracted.	Muthuraman et al. (2012)

2.2.1 Combined Processes for Treatment of Dye Wastewater

Combined treatment processes are a combination of two or more treatment methods which are carried out sequentially. Combined processes for the treatment of dye wastewater have been suggested to improve the efficiency of the treatment methods. At the same time, the drawbacks of each individual treatment may be overcome by the following treatment. For wastewaters which contain complex compounds such as dyes and heavy metals, a combination of treatments is more suitable (Loh et al., 2012). According to Hai et al. (2007), a combination of treatment methods is more realistic in the current world due to the increasingly stringent regulations with regards to dye wastewater discharge. They provide a more technically and economically practical alternative.

Many researchers have studied various combinations of processes to enhance the treatment process. Combinations between physical, chemical and biological processes have been studied, such as chemical and physical, physical and chemical, chemical and chemical, chemical and biological and biological and biological combinations. The advantages of these combinations are listed in Table 2.3.

Table 2.3 Advantages of combined processes

Classification	Combined Process	Application	Advantages	References
Chemical + Physical	Coagulation/flocculation and nanofiltration	Multiple dye waste (acid, basic and reactive dyes) of 1000 ppm was treated with 400 ppm PACl/ 200 ppm PDDA. Coagulation/flocculation removed ~ 90% of dyes and ~100% dyes were rejected by nanofiltration.	- Low generation of sludge - Lower dosage of coagulants required - Effective for the removal of anionic and cationic dyes - Decrease in membrane fouling - Increase in permeate flux	Liang et al. (2014)
	Coagulation and adsorption	A combination of $FeCl_3$-sugarcane bagasse fly ash was used to treat wastewater from a dye-producing factory and managed to achieve 83% colour removal, 96% TSS removal, and 54% COD reduction.	- Lower dosage of coagulant required - Lower dosage of adsorbent required - Effective for the treatment of industrial wastewater	(Shah et al., 2013)
	Electro-catalytic oxidation and nanofiltration	Acid Red 73 was subjected to electro-catalytic oxidation using Ti/SnO_2-Sb electrodes followed by nanofiltration. The electrode showed 96.9% dye rejection.	- Electro-catalytic oxidation is able to degrade and oxidize dyes - Membrane permeation flux increase	Zhang et al. (2014)

Physical + Chemical	Membrane filtration and electrolysis	Disperse dye wastewater of 10 ppm was treated using membrane filtration followed by electrolysis and achieved 75-85% colour removal and 57% COD reduction after 30 min retention time.	- Organic matter were successfully oxidized and degraded - Short operation times	Shin et al. (2014)
	Adsorption and coagulation	Reactive dyes were treated using a combination of adsorption and coagulation. Adsorbent used was bentonite while PACl was used as coagulant and this system achieved 99.92% colour removal with 2.5 mL PACl and 0.001 g bentonite.	- Sedimentation time is short - Lower coagulant and adsorbent dosage required	Yang et al. (2007)
	Adsorption and AOP	- Procion yellow H-EXL was subjected to adsorption over TiO_2 followed by photocatalytic degradation. Colour removal increased from 46.4% after adsorption to 100% after photocatalytic oxidation. - Real textile wastewater was adsorbed onto TiO_2 nanotubes, followed by sonocatalytic degradation, achieving 79.9 % colour removal, 59.4% COD reduction and 49.8% TOC removal.	- Able to mineralize azo dyes - Shorter operation time	Barakat (2011); Pang and Abdullah (2013)

Chemical + Chemical	Thermolysis and coagulation-flocculation	Malachite green was subjected to thermolysis, followed by coagulation with $MgCl_2$. When coagulation was carried out after thermolysis, coagulant dosage was reduced 6 times and achieved 98.78% colour removal and 91.26% COD reduction.	- Lower coagulant dosage required - Able to degrade dyes - Less sludge generated	Loh et al. (2012)
	Coagulation-flocculation and Fenton's oxidation	Simulated textile wastewater was subjected to coagulation with $FeSO_4$ and then followed by Fenton's oxidation, achieving 98% colour removal and 50% COD reduction.	- Degradation of organics was fast - Lower coagulant dosage and chemicals for Fenton's oxidation was required - Less sludge produced	Yadav et al. (2013)
Chemical + Biological	Fenton's oxidation and SBR	Industrial cotton dyeing wastewater was treated by a combination of Fenton's oxidation and SBR and achieved 63% COD reduction and 96.5% colour removal.	- Dosage of chemicals for Fenton's oxidation was reduced	Rodrigues et al. (2014)
Biological + Biological	Anaerobic and microaerophilic-aerobic degradation	Reactive black was subjected to anaerobic degradation followed by microaerophilc-aerobic degradation, achieving 95% colour removal and 50% TOC reduction.	-Anaerobic degradation mineralizes azo dyes - Aerobic degradation oxidizes aromatic amines into non-toxic metabolites	Shah (2014b)

2.2.2 Hybrid Processes for Treatment of Dye Wastewater

The success of the combined processes have brought about the research on hybrid processes. Hybrid processes are different from combined processes as the multi-staged treatment processes are integrated into one process, compared to the combined processes which are carried out individually and sequentially. In the hybrid process, the individual treatment criteria are adjusted to integrate the treatments together. The integration of multiple processes into one process in one vessel would deem the hybrid process cost-saving (capital and operations), time-saving and is easier to operate.

Although the term "hybrid process" is relatively new, many researchers have actually developed several hybrid processes but classified them as combined processes. A classification of hybrid processes that have been researched and their advantages are shown in Table 2.4.

2.3 Thermolysis

Thermolysis is commonly used as a pre-treatment of wastewaters, where inorganic or organic substances present in the wastewater are decomposed by heat, producing insoluble precipitates (Kumar et al., 2009; Verma et al., 2011). It has been applied to composite textile mill effluent (Kumar et al., 2013), alcohol distillery wastewater and biodigester effluent (Prajapati et al., 2015), pulp and paper mill wastewater (Garg et al., 2005), sugar industry wastewater (Sahu and Chaudhari, 2014), and petrochemical wastewater (Verma et al., 2011).

Thermolysis is a dual mechanism process where the large molecules present in the wastewater undergo chemical and thermal breakdown first, followed by

Table 2.4 Advantages of hybrid processes

Classification	Hybrid Process	Application	Advantages	References
Chemical-chemical	Microwave enhanced catalytic oxidation	Methyl orange was subjected to synergistic microwave irradiation over CuO/CeO_2 catalyst in presence of H_2O_2 and degraded 85.2% of dye.	- Able to degrade azo dyes - Shorter reaction time required	Xu et al. (2014)
	Sonophotocatalysis	Direct blue 71 was subjected to low ultrasonic irradiation and ultraviolet lamps with ZnO nanoparticles catalyst, achieving 100% colour removal.	- Able to completely remove the toxicity generated during storage or toxicity from the formation of intermediate compounds - Low-cost	Ertugay and Acar (2014)
	Sono-electrocoagulation	Rhodamine 6G was treated using ultrasound irradiation and electro-generated coagulant, resulting in 95% colour removal.	- Lower electric charge is required - Effective at pH range of 6-8	Raschitor et al. (2014)
Chemical-physical	Photocatalytic membrane bioreactors (PMR)	Acid Red 1 was subjected to photocatalytic degradation in a reactor containing submerged microfiltration module, resulting in 92% COD reduction and 84% TOC removal.	- Restrict penetration of large molecules - Able to degrade recalcitrant organic pollutants - Energy saving - Require smaller reactor	Kertesz et al. (2014)

Chemical-biological	Submerged membrane bioreactor (MBR)	Industrial textile wastewater was treated using submerged membrane bioreactor and achieved COD reduction of 100%.	- Retains microbial communities that aid in the degradation of pollutants in the wastewater - No solids and pathogens present in the effluent	Friha et al. (2015)
	MBR with powdered activated carbon	Remazol Yellow Gold RNL was treated using a submerged membrane bioreactor with powdered activated carbon in its interior and resulted in 94% colour removal and COD removal.	- Controls toxicity - Minimizes membrane fouling	Baeta et al. (2013)
Physical-biological	SBR and adsorption	Direct Blue 85 was treated using simultaneous sequential biological reactor (SBR) and adsorption. The low-cost adsorbent of waste sludge from an electroplating industry was added to the beginning of the reaction stage of SBR. This system achieved 77% TOC removal and 79% colour removal.	- Reaction equilibrium was achieved after a shorter period of time - Sludge settling time is shorter	Santos and Boaventura (2015)
Biological-biological	Anoxic-aerobic SBR	Azo dyes were subjected to anoxic-aerobic operated SBR in a single bioreactor and achieved 100% bio-decolourization and >80% COD reduction.	- High COD reduction even at short reaction period - Benzene-based aromatic amines were easily degradable - No co-substrate required	Al-Amrani et al. (2014)

conversion into settleable insoluble particles at moderate temperature (70 - 150°C) and autogenous pressure (1 atm) (Prajapati et al., 2015). These moderate operating conditions of thermolysis deem the process advantageous compared to the advanced oxidation processes such as wet air oxidation which require high temperature and pressure. The decomposition of large inorganic or organic substances result in the reduction of BOD and COD and removal of colour from wastewater (Sahu et al., 2014).

Metal salts are typically used as catalysts during thermolysis to hasten the thermal degradation of large substances. With the addition of catalysts, the organics in the wastewater could either undergo polymerization with the metal salts or decomposition into smaller organic molecules (Sahu et al., 2014). Examples of catalysts that have been studied are copper sulphate ($CuSO_4$), copper oxide (CuO), zinc oxide (ZnO) and ferric chloride ($FeCl_3$) (Table A3 in Appendix A).

Copper-based catalysts have been applied on a various number of wastewaters and are proven to be more effective compared to the other catalysts. In particular, $CuSO_4$ has been used as a catalyst for the thermolysis of cotton textile mill wastewater (Kumar et al., 2008a), sugar industry wastewater (Sahu and Chaudhari, 2014), petrochemical wastewater (Verma et al., 2011) and rice grain-based biodigester effluent of an alcohol distillery plant (Prajapati et al., 2015). In the works of Kumar et al. (2013), reactive red 74 was subjected to catalytic thermolysis using $CuSO_4$ catalyst and achieved 67.59% colour removal and 91.67% COD reduction. A comparison between $CuSO_4$, $FeSO_4$, $FeCl_3$, CuO, ZnO and PACl showed that $CuSO_4$ was superior as a catalyst in the treatment of cotton textile mill wastewater compared to the other catalysts, giving 92.85% colour removal (Kumar et al., 2008a).

The catalytic thermolysis process can be represented by a simple chemical equation (Eq. 2.1):

$$\text{Organics} \xrightarrow{+\text{ catalyst}+\text{ H}_2\text{O}+\text{heat}} \text{Precipitate} + \text{Lower molecular weight organics} \qquad (2.1)$$

2.3.1 Factors Affecting Performance of Thermolysis

The performance of thermolysis is affected by several factors namely, solution pH, catalyst mass loading, heating time and heating temperature. The effects of these factors have to be studied to obtain the optimum performance of this process.

2.3.1(a) Solution pH

During thermolysis, various chemical reactions take place which are responsible for the thermal degradation of the large complex substances present in the wastewater. In order for these chemical reactions to take place, the initial pH of the wastewater has to be adjusted, depending on the characteristics of the wastewater and the catalyst used. After the reactions have taken place, the final pH of the solution could change due to the formation of new substances and release of dissociated ions (Sahu et al., 2014).

Researchers have found that thermolysis is most efficient either under highly acidic ($pH < 2$) or highly alkaline ($pH > 9$) conditions, depending on the catalyst used (Chaudhari et al., 2010). For example, when $CuSO_4$ catalyst was used, the highest COD reduction was observed at pH 4 (49%) and any further increase in pH decreased the efficiency of the process while the use of CuO catalyst was most efficient at pH 10 (60.3%) (Sahu and Chaudhari, 2014). The efficiency of the process was highly dependent on the reaction between the functional groups present in the wastewater with the functional groups of the catalysts at specific pH values.

Kumar et al. (2008a) observed a slight decrease in the final pH of the solutions with various catalysts ($CuSO_4$, CuO, $FeSO_4$, $FeCl_3$ and ZnO). This drop in pH was associated to the dissociation of anions which lead to the formation of acids like H_2SO_4 or HCl, in addition to the formation of carboxylic acids as a result from the degradation of large hydrocarbons.

2.3.1(b) Catalyst Mass Loading

The role of a catalyst is to accelerate the chemical reaction between reactants and products to achieve equilibrium (Sahu et al., 2014). At this equilibrium, the catalyst mass loading is considered to be the optimum. An increase in the load of catalyst after equilibrium is achieved would not result in an increase in the production of reaction products.

In the work of Kumar et al. (2013), the addition of $CuSO_4$ catalyst from 1 g/L to 4 g/L showed an increase in both COD reduction and colour removal. At 4 g/L of $CuSO_4$, the number of active Cu^{2+} present in the solution was adequate for 92% COD reduction and 65% colour removal. Further addition of $CuSO_4$ did not increase the COD reduction but instead resulted in the decline of performance. The overloading of a catalyst could result in the formation of complexes that compete for hydroxide ions (OH^-) and this causes the decrease in reaction rate. The decrease in OH^- concentration would limit the removal of dye (Kumar et al., 2013).

Similar trends were also observed by Sahu and Chaudhari (2014) and Prajapati et al. (2015) where the efficiency of thermolysis increased when the CuO catalyst dose was increased and after the optimum COD reduction and colour removal were achieved, further increase in catalyst loading resulted in no significant increase in performance if not a decrease.

2.3.1(c) Heating Time

The heating time for thermolysis refers to the time at which the wastewater has been heated at the desired temperature. During this period of heating, the activation of the catalyst increases up to a certain extent and after that, the deactivation of catalyst takes place. In the catalytic thermolysis of biodigester effluent of an alcohol distillery plant carried out by Prajapati et al. (2015), it was found that the increase of treatment time from 3 hours to 9 hours brought about and increment in COD reduction from 73% to 80.4%. Similarly, the colour removal increased from 57% at 3 hours to 72% at 9 hours. After 9 hours, the COD reduction and colour removal efficiency did not increase further.

The pre-heating period of the wastewater from room temperature to the desired temperature also contributes to COD reduction and colour removal from the wastewater. As in the work of Sahu and Chaudhari (2014), during the pre-heating period of the sugar industry wastewater from 0°C to 75°C, 40% COD reduction and 50% colour removal were achieved. Heating of the wastewater at 75°C for 9 hours increased the COD reduction and colour removal to 74% and 80%, respectively, after which no significant increment was observed. Over time, the amount of reactants and catalyst decreased.