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PREPARATION, CHARACTERIZATION AND APPLICATION OF HYBRID POLYMER IN DYE WASTEWATER TREATMENT

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UNIVERSITI SAINS MALAYSIA
2014

PREPARATION, CHARACTERIZATION AND APPLICATION OF HYBRID POLYMER IN DYE WASTEWATER TREATMENT

by

YEAP KIEW LEE

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

September 2014

ACKNOWLEDGEMENTS

I would like to show my greatest appreciation and gratitude to my supervisor, Professor Dr. Teng Tjoon Tow, for his professional advice, helpful suggestions, encouragement, unfailing assistance and guidance throughout the completion of this study. Without his continuous support, this project would not have been completed.

I would like to thank my co-supervisors, Associate Professor Dr. Norhashimah Morad and Associate Professor Dr. Poh Beng Teik, who have guided and inspired me with their helpful knowledge. I am heartily thankful to Associate Professor Dr. Abbas F.M. Alkarkhi who has offered advice and insight throughout my work on statistical part. Their willingness to supervise me, improve my study a lot.

I am grateful to Penfabric Sdn. Bhd. for supplying textile wastewater sample for the study. Also, I feel thankful to the support of Dr. Lim Jit Kang from the School of Chemical Engineering for the use of Zetasizer equipment for zeta potential measurement.

Next, I would like to extend appreciation to all the laboratory assistants especially to Mdm. Teh Siew Hong, Mr. Ravi Vinayagamuerty, Mdm. Noraida Bukhari and Mr. Shamsul Zoolkiffli for their cooperation and helpfulness toward the success of this study.

I am indebted to my dearest friends, Ang Chai Tew, Lee Khai Ern, Ho Yeek Chia, Low Ling Wei, Tang Soke Kwan, Lim Han Khim, Chou Kian Weng, Tan Kah Aik, Lim Yee Ling, Chang Pei Xi, Li Zhimin, Claire Su Xin Hui and Chai Chuan Chun who always assist me when I am facing difficulty in my study. Besides, I wish to thank Universiti Sains Malaysia for financial support in the form of postgraduate fellowship and research grant (RU-PRGS).

Last but not least, thanks go out to my family members for being supportive and their unconditional love which makes my study possible.

Yeap Kiew Lee
2014

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NOMENCLATURES

PART 1

c	Concentration of polymer
e	Electronic charge
i	Ionic strength
k	Number of variable
$k*$	Constant
n	Avogadro’s number
η	Viscosity
η_i	Viscosity of the polymer
η_o	Viscosity of the water
η_{sp}	Specific viscosity
$\eta_{\mathrm{sp}}/\mathrm{c}$	Reduced viscosity
$[\eta]$	Intrinsic viscosity
ρ	Density of the solution
t	Measured flow time
w_{p}	Organic content

PART 2

A	Calibration constant of the viscometer
B	Basicity
β_0	Offset term
β_i	Linear effect
β_{ii}	Squared effect

β_{ij}	Interaction effect
C_f	Final values of color point (Pt-Co) and COD of supernatant (mg/L)
C_i	Initial values of color point (Pt-Co) and COD of supernatant (mg/L)
C_0	Number of center point
ε	Error
□□	Electrical permittivity of the solvent
$1/K$	Double layer thickness
M_w	Molecular weight
N	Number of experimental point
θ	Surface coverage
R^2	Determination coefficient
R^2adj	Adjusted determination coefficient
T	Absolute temperature
W	Overall stability ratio
W_f	Weight of filter paper with sludge
W_i	Weight of filter paper
X	Factor
Y	Response
□	Zeta potential

PART 3

$Al(OH)_3$	Aluminium hydroxide

$AlCl_3$	Aluminium chloride
$FeCl_3$	Ferric chloride
$Fe(OH)_3$	Ferric hydroxide
$FeSO_4$	Ferric sulphate
$MgCl_2$	Magnesium chloride
$Mg(OH)_2$	Magnesium hydroxide
$NaHSO_3$	Sodium bisulphite
$(NH_4)_2S_2O_8$	Ammonium persulphate
$TiCl_4$	Titanium tetrachloride

PART 4

AM	Acrylamide
ANOVA	Analysis of variance
AS-Ee	Aluminium sulphate-Enteromorpha extract
BBD	Box behnken design
BOD	Biochemical oxygen demand
CAC_1	First critical associating concentration
CAC_2	Second critical associating concentration
CBF-PACl	Compound bioflocculant- polyaluminium chloride
CCD	Central Composite Design
CMC-PAM	Carboxymethyl chitosan-graft-polyacrylamide
COD	Chemical oxygen demand
CSAX	Crosslinked starch-graft-polyacrylamide-co-sodium xanthate
DO	Dissolved oxygen

DTY	Disperse terasil yellow W-4G
Ep	Enteromorpha polysaccharides
EPI	Epichlorohydrin
EDS	Energy-dispersive x-ray spectroscopy
FCCD	Face-centered central composite design
FT-IR	Fourier transform infrared spectroscopy
HPMC-PAM	Hydroxypropyl methyl cellulose-grafted-polyacrylamide
IEP	Iso-electric point
IPC	Inorganic polymeric coagulant
k-cgn-HMAAm	k-carrageenan-graft-N-(hydroxymethyl) acrylamide
KGM-PAM-SX	Konjac glucomannan-graft-polyacrylamide-co-sodium xanthate
OPC	Organic polymeric coagulant
ORP	Oxidation reduction potential
PAA	Poly(acrylic acid)
P(AA-AM)	Poly(acrylamide-co-acrylic acid)
P(AM-AA-AMPS)	Poly(acrylamide-co-acrylic acid-2-acrylamido-2-methyl-1-propanesulfonic acid)
PACl	Polyaluminium chloride
PACl-CBF	Polyaluminium chloride-compound bioflocculant
PACl-chitosan	Polyaluminium chloride-chitosan
PACl-EPI-DMA	Polyaluminium chloride-epichlorohydrin dimethylamine
PACl-PAMIPCl	Polyaluminium chloride-poly(3-acrylamido-isopropanol chloride)

PACl-PDMDAACl	Polyaluminium chloride- polydiallydimethylammonium chloride
PACS	Polyaluminium chloro-sulphate
PAFCl	Polyaluminium-ferric chloride
PAFS	Polyaluminium-ferric-sulphate
PAFSiCl	Polyaluminium-ferric-silicate-chloride
PAS	Polyaluminium-sulphate
PASiCl	Polyaluminium-silicate-chloride
PAM	Polyacrylamide
PAMIPCl	Poly(3-acrylamido-isopropanol chloride)
PDA	Photometric dispersion analyzer
PDMDAACl	Polydiallydimethylammonium chloride
PDMDAACl-PAM	Polydiallydimethylammonium chloride-polyacrylamide
$(PEG)_x LiClO_4$	Poly(ethylene) glycol-lithium perchlorate salt
PEO	Poly(ethylene oxide)
PFACl-PDMDAACl	Polyferric aluminium chloride-polydimethyldiallylammonium chloride
PFASiS	Polyferric-aluminium-silicate-sulphate
PFCl	Polyferric chloride
PFCl-EPI-DMA	Polyferric chloride-epichlorohydrin-dimethylamine
PFCl-PDMDAACl	Polyferric chloride- polydimethyldiallylammonium chloride
PFCl-LA	Polyferric chloride lignin-acrylamide polymer
PFMS	Polyferric-magnesium-sulphate
PFSiS	Polyferric-silicate-sulphate

PFS	Polyferric sulphate
PFS-PAM	Polyferric sulphate-polyacrylamide
Pt-Co	Platinum-Cobalt scale
PZSS	Polyzinc-silicate-sulphate
RCB	Reactive cibacron blue F3GA
RSM	Response surface methodology
SCPAMPAA	3-chloro-2-hydroxypropyl trimethylammonium chloride modified starch-graft-poly(acrylamide-co-acrylic acid)
SEM	Scanning electron microscopy
TEM	Transmission electron microscope
TDS	Total dissolved solid
TOC	Total organic carbon

PENYEDIAAN, PENCIRIAN DAN PENGGUNAAN POLIMER HIBRID DALAM RAWATAN AIR SISA PEWARNA

ABSTRAK

Polimer hibrid organik-bukan organik, polyaluminium klorida-poli (3-acrylamido-isopropanol klorida) (PACl-PAMIPCl) disediakan, dicirikan dan digunakan untuk pengolahan air sisa pewarna Reaktif Cibacron Biru F3GA (RCB), Dispersi Terasil Kuning W-4G (DTY) dan industri tekstil. Copolimer PAMIPCl telah disediakan dengan mengubah nisbah molar epichlorohydrin (EPI) dengan acrylamide (AM). Hasil maksimum PAMIPCl adalah 98.12% dengan kelikatan tertinggi 23.65 cP apabila nisbah molar EPI kepada AM mencapai 4% : 96%. Polimer hibrid PACl-PAMIPCl telah disediakan melalui pengadunan fizikal PAMIPCl dengan PACl. Pengimbasan mikroskop elektron (SEM) telah dijalankan berasingan untuk menjelaskan mikrostruktur polimer hibrid dalam bentuk akueus dan pepejal. 90% PACl : 10% PAMIPCl merupakan nisbah terbaik dalam pengolahan air sisa pewarna simulasi: 95.00 dan 100.00% pemecatan warna untuk pewarna RCB dan DTY masing-masing. Kajian potensi zeta menunjukkan bahawa peneutralan caj dan penjerapan-penyambung berlaku dalam mekanisme pemberbukuan untuk pengolahan pewarna RCB dan DTY masing-masing. Morfologi permukaan enapcemar dibentuk dengan menggunakan polimer hibrid PACl-PAMIPCl bagi air sisa pewarna RCB dan DTY didapati lebih padat secara relatif, agregat dan licin daripada menggunakan PACl. Kaedah gerak balas permukaan (RSM) digunakan untuk menyiasat faktor bebas yang menjejas penyingkiran warna dan penurunan COD dalam air sisa pewarna RCB dan DTY.

Faktor bebas seperti kepekatan awal pewarna, pH awal, dos, kelajuan pengadukan dan masa pengadukan telah dikaji melalui reka bentuk faktorial pecahan 2^{5-1} dan reka bentuk komposit berpusat pendekatan muka (FCCD). Semua faktor bebas didapati signifikan dalam mempengaruhi penyingkiran warna dan penurunan COD. Model tertib kedua berpadanan dengan tindak balas bagi data eksperimen. Keadaan operasi optimum untuk merawat air sisa pewarna RCB telah ditunjukkan seperti berikut: 170 mg/L kepekatan awal pewarna, pH 6.07, 30.00 mg/L polimer hibrid, 100 rpm kelajuan pergolakan dan 15 min masa pergolakan. Ramalan optimum penyingkiran warna dan penurunan COD adalah sebanyak 98.85 dan 66.00% masing-masing. Keadaan operasi optimum untuk merawat air sisa pewarna DTY ditunjukkan seperti berikut: 300 mg/L kepekatan awal pewarna, pH 4.00, 30.00 mg/L polimer hibrid, 300 rpm kelajuan pergolakan dan 3 min pergolakan masa. Ramalan optimum penyingkiran warna dan pengurangan COD adalah sebanyak 100.00 dan 85.47%, masing-masing. Akhirnya, air sisa industri tekstil mencapai penyingkiran warna sebanyak 83.43% dan penurunan COD setinggi 79.17% dengan syarat optimum 24.60 mg/L polimer hibrid, pH 6.88, 300 rpm kelajuan pergolakan dan 14 min masa pergolakan.

PREPARATION, CHARACTERIZATION AND APPLICATION OF HYBRID POLYMER IN DYE WASTEWATER TREATMENT

ABSTRACT

Inorganic-organic hybrid polymers, polyaluminium chloride-poly(3-acrylamido-isopropanol chloride) (PACl-PAMIPCl) were prepared, characterized and applied for Reactive Cibacron Blue F3GA (RCB), Disperse Terasil Yellow W-4G (DTY) and industrial textile wastewaters treatment. The PAMIPCl copolymers were prepared by varying the molar ratio of epichlorohydrin (EPI) to acrylamide (AM). The maximum yield of PAMIPCl was 98.12% with the highest viscosity of 23.65 cP when EPI to AM molar ratio attained 4% : 96%. PACl-PAMIPCl hybrid polymers were prepared with PAMIPCl and PACl through physical blending. Scanning electron microscopy (SEM) was performed to clarify the microstructure of the hybrid polymer in aqueous and solid forms, correspondingly. 90% PACl : 10% PAMIPCl was the best ratios in treating synthetic dye wastewaters: 95.00 and 100.00% of color removal for RCB and DTY dyes, respectively. Zeta potential study concluded that charge neutralization and adsorption-bridging dominated in the flocculation mechanism of RCB and DTY dye, respectively. The surface morphology of dried sludge formed using PACl-PAMIPCl hybrid polymer for RCB and DTY dye wastewaters were relatively compact, well aggregated and smooth compared to that of PACl. Response surface methodology (RSM) was applied to investigate the independent factors which affecting color removal and COD reduction of RCB and DTY dye wastewaters. The independent factors such as initial dye concentration, initial pH, dosage, agitation speed and agitation time were studied through 2^{5-1} fractional factorial design and face-centered central composite design (FCCD). All the independent factors were found to be statistically significant in affecting color removal and COD reduction. The second-order model adequately represented the experimental data of responses. The optimum operating conditions to treat RCB dye wastewater are shown as follows: initial dye concentration of 170 mg/L, initial pH of 6.07, dosage of 30.00 mg/L, agitation speed of 100 rpm and agitation time of 15 min. The predicted optimum color removal and COD reduction are 98.85 and 66.00%, respectively. The optimum operating conditions to treat DTY dye wastewater are shown as follows: initial dye concentration of 300 mg/L, initial pH of 4.00, dosage of 30.00 mg/L, agitation speed of 300 rpm and agitation time of 3 min. The predicted optimum color removal and COD reduction are 100.00 and 85.47%, respectively. Finally, industrial textile wastewater attained 83.43% of color removal and 79.17% of COD reduction with optimum conditions of 24.60 mg/L hybrid polymer, pH 6.88, 300 rpm of agitation speed and 14 min of agitation time.

CHAPTER 1

INTRODUCTION

1.1 Overview of Textile Industry

Textile industry is one of the chemically intensive industries which demands large amounts of water during manufacturing stages. The worldwide annual production of dyes is approximately 7×10^5 tons (Athalathil et al., 2014). In Malaysia, textile industry is one of the fastest growing industries and highly contributes to the economic growth (Pang and Abdullah, 2013). According to the Malaysia Investment Performance Report (2012), the textile industry emerged as the country's 12th largest export earner contributing approximately RM 9.5 billion (1.4%) to the country's total exports of manufactured goods.

However, this industry requires high water consumption (approximately 100 to 200 L of water to process 1 kg of textile) and subsequently generates high discharge rate as aqueous effluent with high load of complex chemical substances (Department of Environment, 2000; Lotito et al., 2012). Wastewater generated from different manufacturing unitary operations includes preparation, dyeing, soaping, softening, finishing, etc. Effluent from textile industry contains different types of dyes and persistent organics which is generally characterized by high alkalinity, turbidity, temperature, chemical oxygen demand (COD), biochemical oxygen demand (BOD), suspended solid and high intense color (Kim et al., 2004; Gao et al., 2007; Verma et al., 2012).

The direct discharge of this toxic colorants effluent into environment affects its ecological status as some of the dyes are carcinogenic and create a potential health hazard to the aquatic biosphere (Wang et al., 2011b; Moghaddam et al., 2011;

Zahrim and Hilal, 2013). Among the commercial textile dyes, reactive and disperse dyes are of great environmental concern due to their widespread use in dyeing cotton and polyester (Chen et al., 2010). Reactive dyes have been considered as the most problematic compound in textile wastewater due to their high water solubility as well as high stability and persistence in nature (García Montaῆo, 2007). Non-ionic disperse dyes have extremely low water solubility and complex chemical structure that are resistant to typical aerobic degradation (Somasiri et al., 2006).

As environmental issue has become global concern, industrial effluent must be treated before discharged into environment. According to the Environmental Quality Act 1974 which was gazetted in the year of 2009 – Environmental Quality (Industrial Effluent) Regulation 2009, the discharge of industrial effluent or mixed effluent must comply with the Fifth Schedule (Environmental Quality Act 1974 (Act 127), Regulations, Rules & Orders, 2012). There are a total of 30 parameters as stated in the Fifth Schedule (Table A1.1 in Appendix). Acceptable conditions for the discharge of industrial effluent containing COD for specific trade or industry sectors have been stated in the Seventh Schedule (Table A1.2 in Appendix).

As stated in the Fifth Schedule (Table A1.1 in Appendix), the discharge limits of industrial effluent or mixed effluent of color in standard A and B are 100 and 200 ADMI, respectively. The ADMI (American Dye Manufacturers' Institute) weighted ordinate method was applied to measure colored waters and wastewaters with color characteristics using platinum-cobalt (Pt-Co) unit (Allen et al., 1973). For textile industry, the discharge limits of COD in standard A and B are 80 and 250 mg/L, respectively (Table A1.2 in Appendix). Standard A shows the limits that must be complied for effluent to be discharged into any inland waters within the catchment areas while Standard B lists the limits for effluent to be discharged into any other inland waters. The regulation is related to the prevention, abatement, control of pollution and enhancement of the environment.

1.2 Wastewater Treatment Methods

In common, wastewater treatment methods can be classified into three categories: physical, chemical and biological. However, there is no single economically and technically viable method in dye wastewater treatment technologies. Usually, two or more treatment methods have to be combined in order to attain a more efficient treatment (Robinson et al., 2001; Apollo et al., 2014; Cui et al., 2014; Guieysse and Norvill, 2014). The removal efficiency of each method is limited based on the specific dye chemical structure. This is the driving force for researchers to constantly develop for new materials as well as processes to be applied in physical, chemical and biological wastewater treatments (Jairton et al., 2014).

Physical treatment involves processes where no gross chemical or biological changes are carried out and only physical phenomena such as particle separation processes are implemented to improve the wastewater. The processes that are included in physical treatments are sedimentation (clarification), screening, membrane filtration, flotation and skimming, degasification, equalization and the most commonly applied adsorption (Fitzpatrick and Gregory, 2003; Konsowa et al., 2010). Adsoption method is excellent in a wide variety of dye removal but the limitations of this process are difficulties in adsorbent regeneration, excessive maintenance costs and pre-treatment of wastewater to reduce the amount of suspended solid before it can be fed into the adsorption column to avoid clogging and blockage (Barredo-Damas et al., 2006; Hai et al., 2007).

Chemical treatment processes such as coagulation, flocculation, chlorination, oxidation (ozonation, electro-chemical oxidation, photocatalysis, sonolysis), neutralization and ion exchange involve a series of chemical reactions to enhance the water quality. Plenty of physic-chemical methods operated in pre-treatment, post treatment as well as main treatment have been studied by various researchers to attain a better wastewater treatment. The main drawback of these processes is high sludge generation (Azbar et al., 2004; Ciabatti et al., 2010). However, the sludge production can be minimized by optimizing the operation parameters and selection of appropriate coagulant and flocculant. Therefore, coagulation is still regarded as a promising technology in wastewater treatment due to its high color removal efficiency and cost effectiveness (Huang et al., 2009; Verma et al., 2012).

Biological treatment uses bacteria and other microorganisms to decompose organic contaminants in wastewater into harmless or volatile compounds. Biological treatment processes can be classified into aerobic (presence of oxygen) and anaerobic (absence of oxygen) methods. According to Gavrilescu and Macoveanu (1999), conventional aerobic process based on aerobic activated sludge process can have high color removal efficiency and high operational flexibility. Nevertheless, the huge energy consumed and high sludge production, which requires handling, treatment and disposal increase the operation cost drastically (Sun et al., 2012b). The conventional anaerobic treatment processes are feasible and cost effective but they are time consuming and do not always provide satisfactory results, especially when applied to industrial wastewater, since many of the containing organic pollutants are toxic or resistant to biodegradation process (Oller et al., 2011; Kushwaha et al., 2011; Pariente et al., 2013).

1.3 Hybrid Polymers in Coagulation-flocculation

Coagulation is a charge neutralization process on colloidal particles and maintains the particles in suspension. The electrostatic repulsion force between destabilized colloidal particles prevents colliding particles from aggregation. Flocculation is a process of bridging the microscopic particles and slow-settling colloidal particles into larger agglomerates in the presence of flocculant usually used after coagulation (Teng et al., 2014).

Coagulation-flocculation is a commonly used in wastewater treatment due to its high efficiency and cost effectiveness. Practical application has shown that coagulation-flocculation minimizes the pollution load by optimizing the process parameters and selection of suitable coagulant and flocculant (Ahmad et al., 2007; Verma et al., 2012). Thus, treatment plant should be designed with higher energy efficiency at a smaller footprint and built at lower investment costs with the smaller load.

Various materials have been applied as coagulants. Among them are inorganic metal salts with high cationic charges, such as aluminium sulphate (alum) ferric sulphate ($FeSO_4$) and ferric chloride ($FeCl_3$) (Huang et al., 2014a). Polyelectrolytes of inorganic-based flocculant, organic-based flocculant as well as bioflocculant of various structures have been developed to assist the formation of larger flocs with the purpose of improving the rate of sedimentation. Industry faces increasing pressure to reduce pollutant discharge, water usage, and energy consumption. The continuous raise of market demands for effective materials in wastewater treatment has lead to development of hybrid polymers.

Recently, the use of hybrid polymers in wastewater treatment has grown rapidly as hybrid polymers are reported to be more efficient compared to conventional inorganic coagulants due to the synergism effect of two components in one material (Lee et al., 2012a; 2012b; Liu et al., 2013; Yang et al., 2013; Dawood and Li, 2014; Verma et al., 2014). The molecular weight (M_w) and size of inorganic polymeric coagulant (IPC) is lower compared to those of organic polymeric coagulant (OPC) (Moussas and Zouboulis, 2008). Thus, the aggregating capacity of IPC remains lower. By introducing high M_w water soluble polymer such as polyacrylamide (PAM) into inorganic coagulants for preparing the hybrid polymers, the bridging capacity of the polymers will be enhanced.

1.4 Problem Statements

At present, the coagulation-flocculation process in the industry is still reliant, to a very large extent, on experimental stage due to the extremely complex nature of the process and the numerous types of polyelectrolytes available (Razali et al., 2011). Hybrid polymers which composed of two or more different types of polymeric matrix have recently received increasing attention due to their superior performance in wastewater treatments compared to that of conventional organic or inorganic-based flocculants (Moussas and Zoubolulis, 2009).

PAM-based hybrid flocculants with PAM combining with a wide variety of inorganic coagulants have been reported by many researchers. For examples: alum (El-Gohary and Tawfik, 2009), polyaluminium chloride (PACl) (Sanghi et al., 2006; Tun et al., 2007), magnesium chloride ($MgCl_2$) (Lee et al., 2012c), magnesium hydroxide ($Mg(OH)_2$) (Lee et al., 2012d), aluminium hydroxide ($Al(OH)_3$) (Ani and Li et al., 2012), $FeCl_3$ (Lee et al., 2011c), etc. Besides, EPI-based hybrid flocculants have been widely applied in water and wastewater treatment processes. In spite of operating in wider effective pH range, EPI-based hybrid flocculants are easy to handle and work effectively in lower dosage. This has directly led to reduction of operating cost (Joo et al., 2003; Gao et al., 2011). Examples of EPI-based hybrid flocculants are polyaluminium chloride-epichlorohydrin dimethylamine (PACl-EPI-DMA) (Yue et al., 2008; Wang et al., 2009; Wang et al., 2011), polyferric chloride-epichlorohydrin-dimethylamine (PFCl-EPI-DMA) (Chen et al., 2010; Gao et al., 2011), etc.

Therefore, a hybrid copolymer of poly(3-acrylamido-isopropanol chloride) (PAMIPCl)-based flocculant combined of PAM and epichlorohydrin (EPI) may look promising in enhancement of wastewater treatment. Subsequently, in my continuing pursuit for polymeric structures with the improved properties, new types of inorganic-organic hybrid polymers, polyaluminium chloride-poly(3-acrylamido-isopropanol chloride) (PACl-PAMIPCl) were synthesized to boost the aggregating power of flocculant. PACl was selected to compose with PAMIPCl copolymer as pre-hydrolyzed metallic salts have been proven to be more effective than the hydrolyzing metallic salts such as alum, $FeCl_3$ and $FeSO_4$ (Verma et al., 2012; Lee et al., 2012b).

Characteristics of the copolymers and hybrid polymers were studied to predict the performance in wastewater treatment in both synthetic and industrial wastewaters. Among the commercial textile dyes, reactive and disperse dyes are chosen to determine the color removal and COD reduction efficiencies of PACl-

PAMIPCl hybrid polymer as these dyes have widespread applications and caused great environmental concern. The present research also enhances our understanding of hybrid polymer on the flocculation performance and gives better choices for flocculant in industrial application such as textile industry which discharges large volume of wastewater.

1.5 Objectives

The objectives of the present study include:

a. To prepare and characterize the chemical, physical and morphological properties of PAMIPCl copolymers and PACl-PAMIPCl inorganic-organic hybrid polymers.

b. To determine the flocculation mechanisms of PACl-PAMIPCl inorganic-organic hybrid polymers in treating synthetic dyes.

c. To determine the effects of operating parameters (initial concentration of dye, initial pH, dosage of PACl-PAMIPCl hybrid polymer, agitation speed and agitation time) in order to optimize the coagulation-flocculation activity of PACl-PAMIPCl inorganic-organic hybrid polymers in treating synthetic dyes and industrial textile wastewater.

1.6 Scope of the Study

This present work can be divided into three stages. The first and second stages involve the synthesis and characterization of PAMIPCl copolymers and PACl-PAMIPCl hybrid polymers, respectively. Ammonium persulphate $(NH_4)_2S_2O_8$ and sodium bisulphite ($NaHSO_3$) were used to initiate the redox polymerization of

PAMIPCl copolymers at 65°C by varying the molar ratio of EPI to acrylamide (AM). The physicochemical properties of PAMIPCl copolymers were studied in terms of chemical structure, conductivity, intrinsic viscosity and viscosity. PAMIPCl of the highest viscosity was prepared when EPI to AM molar ratio attains 4% : 96%. This may be due to intra and intermolecular associations. PACl-PAMIPCl hybrid polymers were then prepared with PAMIPCl and PACl through physical blending. PACl-PAMIPCl hybrid polymers were characterized in terms of chemical, physical and morphological. In the third stage, the PACl-PAMIPCl hybrid polymers were applied in treating synthetic dye wastewaters and industrial textile wastewater. Their efficiency as flocculants was determined through color removal and COD reduction in synthetic dyes and industrial textile wastewater. After coagulation-flocculation treatment using PACl-PAMIPCl hybrid polymer, discharge of both synthetic and industrial textile wastewaters shall be complied with the Environmental Quality Act 1974 of Fifth Schedule for color concentration (not more than 200 Pt-Co) and Seventh Schedule for COD concentration (not more than 250 mg/L). The flocculation mechanisms were studied through zeta potential (ζ) analyses.

CHAPTER 2

LITERATURE REVIEW

2.1 Textile Dye

Dyes are used in the coloration of wide variety of materials, including papers, leathers, plastics as well as textile products. These dyes are aromatic compounds associated with a side chain required for resonance and therefore to impart color. Characterization of dyes is based on their chemical structure, functional group and application. They are composed of the acceptor of electrons called chromophore and the donor of electrons responsible for dyeing capacity, called auxochrome (Christie, 2001; Zee, 2002). The chromophore configurations are represented by azo (–N=N–), methane (–CH=), ethenyl (–C=C–), ethylene (=C=C=), carbonyl (–C=O), carbon-nitrogen (=C=NH; –CH=N–), carbon-nitrogen (=C=NH; –CH=N–), carbon-sulphur (=C=S; ≡CS–S–C≡), imino (–C=N–), thiocarbonyl (–CH=S), nitroso (–N=O), nitro (–NO_2;-NO–OH), nitrozo (–N=O; =N–OH) and chinoid groups. Common auxochrome is ionizable groups, including amino, (–NH_2), carboxyl (–COOH), sulphonyl (–SO_3H) and hydroxyl (–OH) (Suteu et al, 2011; Zaharia and Suteu, 2012).The intensity of color depends upon the number of the groups. Compounds of benzene naphthaline or antracene containing chromophore radicals are called chromogens (Verma et al., 2012).

2.1.1 Textile Fibre

According to Christie (2001), textile fibres can be generally categorized as follows:

2.1.1.1 Natural fibre

Before 1856, the natural textile dyes were mainly used in textile processing. The natural fibres are extracted from three main sources. There are plant (production of cellulosic fibre), animal (production of protein fibre) and rock (mineral fibre). Compared to synthetic fibre, natural fibre could only produce a shorter length of fibre (staple yarn). The dimensional structure of natural fibre would be in hairiness surface due to their origin (Welham, 2000). Natural fibre requires a long time to restock the production although it is renewable sources. To ensure natural fibre can compete well with synthetic fibre in terms of availability, countries such as China, Australia, Sudan and Greece have their own farms or fields in order to meet the local and world demands (Maxwell, 2003).

2.1.1.2 Synthetic / Man-made fibre

The first synthetic dye was mauve‘dye (aniline),a brilliant fuchsia color discovered in 1856 synthesized by W.H. Perkin (UK), and subsequently some azo dyes were synthesized by diazotization reaction discovered in 1958 by P. Gries (Germany) (Welham, 2000). Unlike natural fibre, synthetic fibre is produced in a filament yarn based on the end-use. The dimensional appearance of synthetic fibre can be varied according to the demand usage. There are two basic types of synthetic fibre that have been widely used by the textile industry: a) natural polymer-based and b) synthetic-based (Collier and Tortora, 2001).

a) Natural polymer-based fibre or regenerated fibre is manufactured fibre that is derived from natural cellulosic sources (wood pulp or cotton linters). New forms of fibre will be produced after the compositions of cellulosic go through some polymerization processes. Examples of natural polymer-based fibres include viscose rayon, acetate and lyocell.

b) Synthetic-based fibre refers to a fibre that has been made totally by using chemical substances. Examples of synthetic-based fibres include polyester, polyamide (nylon), olefin, elastomeric and acrylic fibres.

2.1.2 Classification of Dye

The textile dyes are mainly classified based on their application characteristics. They can belong to the class of acid, basic, direct, disperse, mordant, reactive, sulphur, pigment or vat (Verma et al., 2012). 65 to 75% of textile dyes can be classified through chemical structure, namely azo and anthraquinone. Azo dye, characterized by reactive groups that form covalent bonds with –OH, –NH, or –SH groups in fibre (cotton, wool, silk, nylon) is the most commonly used for yellow, orange and red colors. Anthraquinone dye represents the second most significant class of textile dyes and has a wide range of colors in almost the whole visible spectrum, especially for violet, blue and green colors (Fontenot et al., 2003).

Considering only the general structure, the textile dyes can be categorized into anionic, non-ionic or cationic dyes. The anionic dyes are mostly composed of acid, direct and reactive dyes (Robinson et al., 2001). The major non-ionic dye is the disperse dye and the major cationic dye is the azo basic. The most problematic dyes are those which are composed of benzidine and aromatic components that are highly carcinogenic and toxic to the biotic. For instances, naturally reactive dye is non-toxic; however, under anaerobic conditions, they may break down into aromatic amine (Zee and Villaverde, 2005; Zaharia and Suteu, 2012). The interactions between dye molecules and the fibre are usually performed in aqueous media, which involve many different types of chemical forces, such as ionic bond, covalent bond, hydrogen bond, electrostatic attraction, intermolecular force and Van der Waals force (Jairton et al., 2014). The characteristics and types of pollutant of different textile dyes are summarized in Table 2.1.

2.2 Treatment of Dye Wastewater

Treatment of textile industry wastewater remains a great challenge due to its wide coverage of pH, COD, dissolved solids and variety of synthetic dyestuff. The textile wastewater exhibits range of pH from 2 to 14, COD from 50 to 18,000 mg/L and total dissolved solid (TDS) from 50 to 6000 mg/L. This wide variation in the characteristics of textile wastewater is due to large numbers of chemical constituents used in the textile industry during textile processing (Verma et al., 2012). A complete set of treatment for dye wastewater usually requires a number of steps and a combination of several treatment methods and purification before the maximal efficiency/purity can be obtained. This is because each method has its own advantages and disadvantages (Sher et al., 2013).

In general, wastewater treatment can be divided into four stages: preliminary primary (physical), primary (physical), secondary (biological) and tertiary or advanced (chemical) treatment (Gupta and Suhas, 2009). First, incoming raw wastewater is passed through a series of screens, where the ranges of suspended solids and BOD are reduced from 50 to 65% and 30 to 40%, respectively. Subsequently, wastewater is pumped into secondary (biological) treatment, followed by disinfection before discharge. When the standard of the effluent discharged from the secondary treatment is unacceptable, tertiary or advanced wastewater treatment

Table 2.1: Characteristics of dyes used in textile industry (Kirk, 1993; Christie, 2001; Lau and Ismail, 2009; Low, 2011).

Class	**Characteristic**	**Dye-fibre interaction**	**Method of application**	**Fibre**	**Pollutant**
Acid	– Anionic, water soluble – Poor to excellent color fastness and from dull tones to brilliant shade – Used in most synthetic food color	Electrostatic attraction, hydrogen bond	Applied in the dye bath ranges from neutral to acidic at near boiling temperature	Wool, nylon, silk, leather	Color, organic acid, unfixed dye
Basic	– Cationic, water soluble – Excellent color fastness on acrylic; poor fastness on natural fibre – Bright dye, used in the coloration of paper, dried flower	Electrostatic attraction	Applied in the dye bath ranges from acidic by adding acetic acid to help the uptake of the dye onto the fibre	Acrylic, cotton, silk, nylon	Color, organic acid, unfixed dye
Direct	– Anionic, water soluble – Applied directly to cellulosics without mordant – Excellent color fastness – Used as pH indicators and as biological stains	Intermolecular forces	Applied in the dye bath ranges from neutral to slightly alkaline at near boiling temperature	Cotton, rayon, leather, nylon	Color, salt, unfixed dye, cationic fusing agent, surfactant; defoamer, leveling and retarding agent, finish, diluent
Disperse	– Non-ionic, low water soluble – The smallest dye molecules – Belong mainly to diphenylamine, azo and anthraquinone – The only dyes effective for polyester, heating in a temperature of 103ºC which requires elevated pressure	Hydrophobic-solid state mechanism	Applied by high temperature pressure or lower temperature carrier	Polyester, nylon, acetate, acrylic	Color, organic acid, carrier, leveling agent, phosphates, defoamer, lubricant, dispersant, diluent

Table 2.1 (continued)

Mordant	– Cationic or anionic, water soluble – Requires a mordant (a chemical that aids attachment of a dyestuff to fibre by bonding to both fibre and dye) – Often pale in color	Ionic bond	Applied in conjunction with chelating chromium salts	Wool, leather	Mordant (particularly in heavy metal categories) will cause hazardous to health
Reactive	– Anionic, water soluble – The largest dye class – Excellent color fastness – High resistance against degradation – Bright in color	Covalent bond	Dye (reactive site) attaches to the fibre (functional group) under influence of heat and pH (alkaline)	Cotton, wool, silk, nylon	Color, salt, alkali, unfixed dye, surfactant, defoamer, finish, diluent
Sulphur	– Colloidal, water insoluble – Excellent color fastness but sensitive to bleach – Made by reacting sulfur with organic compounds – Dull in color but inexpensive	Covalent bond	Aromatic substrate vatted with sodium sulphide and re-oxidized to the fibre	Cotton, rayon	Color, alkali, oxidizing agent, reducing agent, unfixed dye
Vat	– Colloidal, water insoluble – The oldest dyes, chemically complex – Common vat dye is indigo, the blue of blue jeans – Excellent color fastness and have good resistance to chlorine bleach	Impregnation, oxidation	Solubilized by reducing with sodium hydrosulphite, then exhausted on fibre and reoxidized	Cotton, rayon, wool	Color, alkali, oxidizing agent, reducing agent

must be employed. Nowadays, varies types of fundamental primary and secondary treatments are used in sewage treatment plants for treating large quantities of sewage (Botkin and Keller, 2005). The relative advantages and disadvantages of the selected treatment processes are summarized in Table 2.2.

2.3 Coagulation-flocculation

The most practised technology; coagulation-flocculation is widely applied on industrial wastewater treatment. Typical applications are the removal of colloids particles, natural organic matter, metal ions, color and odour. Coagulation-flocculation has been employed for the treatment of wastewaters from tannery, yeast wastewater, textile, petroleum refinery, dye house, aquaculture, municipal, landfill leachates, pulping, olive mill and others (Sher et al., 2013; Papaphilippou and Yiannapas, 2013).

The suspended materials and colloidal particles in water or wastewater mostly originate from the dissolution of minerals, domestic and industrial waste discharges. The materials or particles have to be removed, as they cause deterioration of water quality by reducing the clarity, causing turbidity and infection. Particles with the size 1.0 and 0.1mm may be known as coarse sand and fine sand; respectively. Particles smaller than 0.00001 mm can be referred to as colloid (Bratby, 2006). With decrease of the particle size, the time required for settling increases, from minutes to several years for certain solution ingredients.

To remove the tiny particles in wastewater, all the small particles should be aggregated, then larger particles are formed which assist settling and finally separation or filtration (Tzoupanos and Zouboulis, 2008). In nature, colloidal particles normally carry charges on their surfaces, leading to stabilization of the

Table 2.2: Advantages and disadvantages of different methods of dye removal from textile wastewater.

No.	Treatment	Method description	Advantages	Disadvantages	References
	PHYSICAL				
1	Adsorption 1.1 Activated carbon	Dye removal based on solid support	– Cheap absorbent – Biodegradable and non-toxic nature	– Different adsorbent will have different adsorption behaviour; therefore need more effort in modifying to improve their adsorption capabilities – Cost intensive regeneration process	Lin et al., 2008
	1.2 Cationic polymer/bentonite		– High adsorption capacity of wide variety of dyes	– Separation inconvenience/ regeneration difficulty – Costly for disposal of used absorbent	Li et al., 2010
	1.3 Ni@SiO_2core-shell nanoparticle		– The magnetic adsorbent is cost effective and easy to prepare – The used absorbent is easy-separation and recovery	– Restrained adsorption capacity at certain type of dyes	Jiang et al., 2014
2	Ion-exchange	Ion exchange resin	– Easy for regeneration	– Not applicable for wide range of dyes – High operating cost	Hai et al., 2007
			– Development of mathematical models to predict membrane performance and assist to accomplish the engineering tasks easier – Shorten the process time due to absence of diffusive paths	– Not applicable for all type of dyes	Labanda et al., 2009; Labanda et al., 2011

Table 2.2 (continued)

3	Membrane filtration 3.1 Combinations of ultrafiltration, loose & tight nanofiltration and reverse osmosis	Physical separation	– Effective in removal of dye as well as for recycling of specific contaminants in textile effluents	– For industry application, the reusability of the water recycled to the process may degrade the quality of dyeing – High operating cost	Vergili et al., 2012
	3.2 Hollow fiber nanofiltration		– Excellent color removal for cationic dye – Higher packing density, no requirement of feed and infuse spacers, lower in maintenance cost	– Production of high dissolved solids makes discharge of treated effluents into surface water almost impossible	Zheng et al., 2013b
4	UV irradiation	Ionizing radiation	– Effective removal of the pollutant	– Increase of toxicity due to the accumulation of toxic transformation products – High energy consumption	Santiago-Morales et al., 2013
			– Excellent color removal for acid dye at low dye initial concentration – Environmental friendly – Cost effective	– Work at very limited pH range – Color removal decrease with the increasing of dye initial concentration	Muthirulan et al., 2014
	CHEMICAL				
5	Chemical coagulation and flocculation 5.1 PACl/ Sludge of PACl	Addition of coagulants and flocculants	– The use of PACl sludge reduce the chemical sludge – High color removal efficiency for acid dye	– Work at limited pH range	Moghaddam et al., 2011
	5.2 PACl		– Economical treatment method – High color removal efficiency for reactive dye	– Large amount of chemical sludge	Taheri et al., 2013

Table 2.2 (continued)

	5.3 Aluminium chloride ($AlCl_3$)/ Alum + Enteromorpha polysaccharides (Ep)		– High color removal efficiency for reactive dye – Environmental friendly – Cost effective – Operate well at wide pH range	– May not effective in removing other type of dyestuffs	Zhao et al., 2014b
6	Electro-coagulation	Treatment based on anode and cathode	– Excellent color removal for textile dye – Simple operation design – Shorter retention time – Lower sludge amount	– High remaining toxicity level – Low in mineralization	Palácio et al., 2009; Pi et al., 2014
				– High cost – Less electrode reliability	Phalakornkule et al., 2010
7	Fenton reagent 7.1 Photo-fenton	Oxidation using zero-valent iron (Fe^0-H_2O_2) + UV-C irradiation	– Higher mineralization extents in reactive dye – Cost effective	– Treatment efficiency depends mainly of effluent characteristics – Sludge generation and its handling	Grčić et al., 2012
	7.2 Electro-fenton	Oxidation using H_2O_2-Fe (II)	– More effective capacity to degrade refractory organic materials with less sludge production – Chemical cost-effective with the potentials of on-line monitoring of oxidation reduction potential (ORP) and dissolved oxygen (DO) as both ORP and DO are key parameters in the E-Fenton	– Dynamically regulating the E-Fenton process is difficult and complicated	Yu et al., 2013

Table 2.2 (continued)

8	Ozonation	Oxidation using ozone-oxygen mixture	– Excellent color removal for reactive dye even at lower ozone feed concentration – Does not increase the volume of wastewater and sludge – Require little space, and it is easily installed on a site	– Low in mineralization (Removal rate of total organic carbon (TOC) is low, 17%) – High operating cost – Occurrence of reaction complexity during ozonation as pH of wastewater decrease after the treatment. Thus, evaluating of the toxicity is needed	Tehrani-Bagha et al., 2010
				– High operating cost – Short half-life (20 min)	Tabrizi et al., 2011
9	Sonolysis 9.1 NanoTiO$_2$ and H$_2$O$_2$ work as catalyst	Destruction of chemical bond by using free radical through ultrasonic wave	– Appropriate tool for degradation of azo dyes as it leads to non-toxic end products	– Efficiency of color removal decrease with the increase of initial dye concentration – High operating cost	Abbasi and Asl, 2008
	Sonolysis		– No extra sludge production	– High operating cost – High energy consumption	Srinivasan et al., 2011
	BIOLOGICAL				
10	Aerobic 10.1 Biological reactor	Treatment based on microbiological degradation	– Environmental friendly – High color removal and COD reduction for textile dyes	– Slow process – Narrow operating range	Khelifi et al., 2008
	10.2 Oxidation reactor		– Complete mineralization ensured for azo dye	– Unclear on design and operation parameters essential for scale-up of oxidation reactor (cathode size effect & hydraulic retention time effect on reductive by-products of azo dye in post-aerobic system)	Cui et al., 2014

Table 2.2 (continued)					
11	Anaerobic		– Energy generation potential	– Low color removal and COD reduction in anthraquinone dye – Long hydraulic retention times in order to achieve significant elimination of the biorecalcitrant components – Narrow operating range	Wijetunga et al., 2008; Oller et al., 2011
			– Low cost and convenient operation		Huang et al., 2013a

suspension. The charge structure surrounding the particle is called the electrical double layer, which can be divided into stern and Gouy-Chapman layers. To facilitate the particle of a stable dispersion to flocculate, sufficient kinetic energy should be provided to the particle for overcoming the potential energy barrier. In coagulation phase destabilization is stimulated either by the reduction of repulsive forces between particles or by the enmeshment in precipitates. For insoluble particles, such as minerals, inter-particle repulsion is typically caused by electrical double layer interaction.

The surface potential (electrical potential difference between the particle surface and the bulk solution) of colloidal particles will be affected by the addition of some chemicals, either adsorption to the particle surface or by double layer compression, facilitating the separation of particles by filtration. Chemicals that bind at the surface of the particles may be due to multivalent cations and anions, ionic surfactants and, H^+ and OH^- ions bonding (Hogg, 2005; Harif et al., 2012). The agglomerates formed by coagulation are smaller in size and loosely bound, whereas the flocs formed by flocculation are of larger size and strongly bound (Tripathy and Ranjan De, 2006).

2.3.1 Mechanism of Coagulation-flocculation

Coagulation-flocculation is a complex physiochemical process which generally involves several different types of mechanism. Although the destabilization process in neutral polymeric flocculant may occur by an increase in Van der Waals attraction, this is regarded as being less critical compared to charge neutralization (double layer compression), electrostatic patch and bridging flocculation (adsorption of flocculant onto the particle surface) mechanisms

(Tripathy and Ranjan De, 2006). According to Lu et al. (2005), flocs formed by bridging are entirely different from those formed by charge-patch neutralization. These mechanisms will be further discussed at a later stage.

2.3.1.1 Charge Neutralization

Charge neutralization by double layer compression is dominated in wastewater process when flocculation is effective through an increase in solution ionic strength. The expression of the Debye-Huckel length, which was derived from the Gouy-Chapman model of the electric double layer, is stated as

$$K = \left(\frac{4 \times 10^{-3} e^{2} ni}{E k_{B}^{*} T}\right)^{1/2} \tag{2.1}$$

where, e is the electronic charge, n represents the Avogadro’s number, i is the ionic strength, □□is the electrical permittivity of the solvent, $k*_B$ is the Boltzman constant, and T is the absolute temperature. The double layer thickness is assumed to be $1/K$. Therefore, increasing ionic strength decreases the thickness of the double layer. This compression allows the approach of the colloidal particles to predominate over electrostatic repulsive forces (Tripathy and Ranjan De, 2006).

It is frequently found that the most effective polyelectrolytes are those with opposite sign of charge (such as aluminium or iron salt) to the suspension particles. The charge is neutralised by adsorption of cationic polyelectrolyte onto the particle surface. In such cases there is a strong adsorption affinity and neutralization of cationic polymers onto the negatively charged particle surface and consequently reduction of double layer repulsion, allowing aggregation to take place. Addition of excessive cationic polyelectrolytes causes restabilization of particle charge due to overload of polyelectrolytes adsorption onto particle surface. This raises the importance of the cationic polymer’s role on charge effects in the destabilization and restabilization of negative colloids.

In fact, occurrence of charge neutralization is studied by comparison of □ measurement within the entire flocculation process. Theoretically, when optimum dosage occurs at the point close to zero in □ , the flocculation process is assumed to be dominated by charge neutralization mechanism (Barany and Szepesszentgyorgyi, 2004; Zhao et al., 2014a). However, practically, the value of □ tends to become negative at optimum flocculation with an increase in M_w of the polyelectrolytes. This is because increasing M_w of polyelectrolytes favours bridging mechanism. The charge density and M_w of polymers are critical in determining optimum flocculation performances. With high M_w polyelectrolytes, bridging mechanism remains a possibility, but the rather flat adsorbed configuration would be a limiting factor (Gregory and Barany, 2011).

When charge neutralization becomes the dominant mechanism, flocs formed are stronger and is more readily to reform when broken by high shear rates compared to flocs formed through bridging mechanism (Lu et al., 2005). Polyelectrolytes characteristics that favour charge neutralization are substantial doses of a high charge density and low M_w polymer. Thus high charge density cationic polyelectrolytes are effective in removing organic materials in wastewater treatment. When the polymeric flocculants dose is low, electrostatic patch mechanism dominates (Bolto, 2006).

2.3.1.2 Electrostatic Patch

The electrostatic patch mechanism proposed by Gregory (1973) usually includes flocculation process characterized by cationic polymeric flocculants (high