

**PREPARATION, CHARACTERIZATION AND APPLICATION OF
MAGNESIUM SALT-POLYACRYLAMIDE HYBRID MATERIALS IN DYE
WASTEWATER TREATMENT**

by

LEE KHAI ERN

**Thesis submitted in fulfillment of the
requirements for the degree of
Doctor of Philosophy**

2012

ACKNOWLEDGEMENTS

First of all, I would like to convey my gratitude to my supervisor, Associate Professor Dr. Norhashimah Morad, for her unlimited ideas, advice and encouragement. I would like to thank my co-supervisors Professor Dr. Teng Tjoon Tow and Associate Professor Dr. Poh Beng Teik, who guided and inspired me with their ideas. Without their continuous support, this project would not have been completed.

I am grateful to Penfabric Sdn. Bhd. for supplying textile wastewater sample for the experiments. Besides that, I would like to thank the laboratory staff, Mdm. Teh Siew Hong, Mr. Sadali Othman, Mr. Mohd. Fadzli Ghazali, Mr. Mazlan Mohamed, Mr. Ravi Vinayagamuerty, Mdm. Noraida Bukhari and Mr. Shamsul Zoolkiffli for their help throughout my study. I would like to extend my sincere appreciation to my friend and colleagues, Dr. Imran Khan, Dr. Aamir Bhat, Dr. Md. Bazlul Mobin Siddique, Dr. Reem Al-Rawi, Mr. Tan Kah Aik, Ms. Lim Yee Ling, Ms. Low Ling Wei, Mr. Lim Han Khim, Ms. Tang Soke Kwan, Mdm. Ang Chai Tew, Mr. Chou Kian Weng, Mr. Loh Kit Mun, Ms. Li Zhimin and Ms. Yeap Kiew Lee. Thank you for your kindness and helpfulness throughout my research. I am also thankful to the financial assistance from USM Research University grant 1001/PTEKIND/314049 and USM Fellowship.

Last but not least, I would like to convey my special credit to my parents Mr. Lee Jin Kong and Mdm. Kung Poe Tin for their love, support and encouragement. For the unmentioned name and my fellow friends, thank you for your support.

Lee Khai Ern

2012

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	xii
LIST OF FIGURES	xviii
LIST OF PLATES	xxviii
LIST OF SYMBOLS	xxx
LIST OF ABBREVIATION	xxxiii
ABSTRAK	xxxvi
ABSTRACT	xxxix
CHAPTER ONE : INTRODUCTION	
1.1 Textile industry	1
1.2 Overview of hybrid materials in wastewater treatment	2
1.3 Dye wastewater treatment through coagulation-flocculation process	2
1.4 Problem statements	3
1.5 Objectives	4
1.6 Scope of the study	5
1.7 Organization of thesis	6

CHAPTER TWO : LITERATURE REVIEW

2.1	Classification of hybrid materials	8
2.1.1	Structurally-hybridized materials (composites)	8
2.1.2	Chemically-bond-hybridized materials	9
2.1.3	Functionally-hybridized materials	9
2.2	Terminology of hybrid materials	10
2.3	Combinations of hybrid materials	12
2.3.1	Inorganic-inorganic hybrid materials	16
2.3.2	Inorganic-organic hybrid materials	17
2.3.3	Inorganic-natural polymer hybrid materials	20
2.3.4	Inorganic-biopolymer hybrid materials	21
2.3.5	Organic-organic hybrid materials	22
2.3.6	Organic-natural polymer hybrid materials	22
2.4	Preparation of hybrid materials	23
2.4.1	Hydroxylation-prepolymerization	23
2.4.2	Physical blending (at ambient temperature)	27
2.4.3	Physical blending (at elevated temperature)	28
2.4.4	Copolymerization (redox polymerization)	28
2.4.5	Chemical grafting / crosslinking	29
2.5	Properties of hybrid materials	30
2.5.1	Chemical properties	31
2.5.1.1	Chemical structure	31
2.5.1.2	Chemical species distribution	33

2.5.2 Physical properties	35
2.5.2.1 Molecular weight/intrinsic viscosity	35
2.5.2.2 Conductivity	37
2.5.2.3 Zeta potential	37
2.5.3 Thermal properties	39
2.5.4 Morphological properties	41
2.5.5 Structural properties	42
2.6 Application of hybrid material in wastewater treatment	42
2.6.1 Effect of operating parameters	43
2.6.1.1 pH	44
2.6.1.2 Dosage	45
2.6.1.3 Stirring speed and time	46
2.6.1.4 Temperature	48
2.6.2 Kinetics and mechanism	49

CHAPTER THREE : MATERIALS AND METHODS

3.1 Materials and chemicals	54
3.2 Equipments and instruments	54
3.3 Overview of methodology	55
3.4 Redox polymerization of polyacrylamide	58
3.4.1 Experimental design for redox polymerization of polyacrylamide	59

3.4.1.1	Screening of factors in redox polymerization of polyacrylamide	59
3.4.1.2	Optimization of redox polymerization of polyacrylamide	60
3.4.1.3	Statistical analysis	61
3.4.2	Kinetics studies	62
3.4.2.1	Classical kinetics model	62
3.4.2.2	Kinetics model using experimental design	63
3.4.3	Thermodynamic of redox polymerization of polyacrylamide	63
3.5	Preparation of magnesium salt-polyacrylamide hybrid materials	64
3.6	Characterization of polyacrylamide and magnesium salt-polyacrylamide hybrid materials	65
3.6.1	Chemical properties analysis	65
3.6.1.1	Fourier Transform Infrared Spectroscopy	65
3.6.2	Physical properties analysis	66
3.6.2.1	Gel Permeation Chromatography (GPC)	66
3.6.2.2	Solution conductivity	66
3.6.2.3	Solution viscosity	66
3.6.3	Rheological properties analysis	67
3.6.3.1	Rheological properties measurements	67
3.6.4	Thermal properties analysis	68

3.6.4.1	Differential Scanning Calorimetry	68
3.6.4.2	Thermal Gravimetric Analysis	68
3.6.5	Morphological properties analysis	69
3.6.5.1	Transmission Electron Microscopy (TEM)	69
3.6.5.2	Scanning Electron Microscopy-Energy Dispersive X-ray spectroscopy (SEM-EDX)	70
3.7	Application of magnesium salt-polyacrylamide hybrid materials in synthetic dye wastewater treatment	70
3.7.1	Experimental design for application of magnesium salt- hybrid materials in synthetic dye wastewater treatment	71
3.7.1.1	Screening of factors	71
3.7.1.2	Optimization of synthetic dye wastewater treatment	73
3.7.2	Experimental design for application of hybrid materials in textile industrial wastewater treatment	73
3.7.2.1	Screening of factors	73
3.7.2.2	Optimization of textile industrial wastewater treatment	74
3.7.3	Statistical analysis	74
 CHAPTER FOUR : RESULTS AND DISCUSSION		
4.1	Redox polymerization of polyacrylamide	75

4.1.1	Classical kinetics and thermodynamic of redox polymerization of polyacrylamide	79
4.1.2	In situ rheological properties	84
4.1.2.1	In situ viscosity	84
4.1.2.2	Steady state flow	86
4.1.2.3	Oscillatory frequency sweep	88
4.1.3	Experimental design for redox polymerization of polyacrylamide	90
4.1.3.1	Screening of factors in redox polymerization of polyacrylamide	90
4.1.3.2	Optimization of redox polymerization of polyacrylamide	96
4.1.4	Kinetics model using experimental design	103
4.1.5	Validation and comparison of classical kinetics model and experimental designed kinetics model	104
4.1.6	Characterization of optimized polyacrylamide	106
4.1.6.1	Fourier transform infrared spectra analysis	106
4.1.6.2	Molecular weight distribution	108
4.1.6.3	Transmission electron microscopy (TEM)	109
4.2	Preparation of magnesium salt-polyacrylamide hybrid materials	110
4.3	Characterization of magnesium salt-polyacrylamide hybrid materials	111

4.3.1	Chemical properties	111
4.3.1.1	Fourier transform infrared spectroscopy	111
4.3.2	Physical properties	114
4.3.2.1	Solution conductivity	114
4.3.2.2	Intrinsic viscosity	116
4.3.2.3	Solution viscosity	118
4.3.3	Rheological properties	120
4.3.3.1	Linear viscoelastic region (LVR)	120
4.3.3.2	Steady state flow	122
4.3.3.3	Oscillatory frequency sweep	124
4.3.4	Thermal properties	126
4.3.4.1	Differential scanning calorimetric (DSC) analysis	126
4.3.4.2	Thermal gravimetric analysis (TGA)	129
4.3.4.3	Thermal decomposition kinetics	133
4.3.5	Morphological properties	139
4.3.5.1	Transmission electron microscopy (TEM)	140
4.3.5.2	Scanning electron microscopy (SEM)	142
4.3.5.3	Energy-dispersive X-ray spectroscopy (EDX)	144
4.4	Application of magnesium salt-polyacrylamide hybrid materials in dye wastewater treatment	147
4.4.1	Dye wastewater sample characteristics	147

4.4.2	Effect of composition in magnesium salt- polyacrylamide hybrid materials in dye removal	148
4.4.3	Kinetics of dye removal	151
4.4.4	Mechanism of dye removal using magnesium salt- polyacrylamide hybrid materials	155
4.4.4.1	Variation of conductivity and pH	155
4.4.4.2	Chemical structure of sludge	158
4.4.4.3	Comparison of sludge formation	162
4.4.4.4	Microstructure of flocs in aqueous phase	164
4.4.4.5	Surface morphology of sludge	168
4.4.5	Screening of variables for dye wastewater treatment	171
4.4.5.1	Magnesium chloride-polyacrylamide (MCPAM) hybrid materials	171
4.4.5.2	Magnesium hydroxide-polyacrylamide (MHPAM) hybrid materials	179
4.4.6	Optimization of variables for dye wastewater treatment	186
4.4.6.1	MCPAM hybrid materials	187
4.4.6.2	MHPAM hybrid materials	199
4.5	Application of magnesium salt-polyacrylamide hybrid materials in textile industrial wastewater treatment	211
4.5.1	Textile industrial wastewater sample characteristics	211
4.5.2	Screening of variables for dye wastewater treatment	212
4.5.3	Optimization of variables for dye wastewater treatment	220

4.6	Comparison of MCPAM hybrid material with other inorganic-organic hybrid materials in treating dye wastewater	232
	CHAPTER FIVE: CONCLUSION	234
	CHAPTER SIX: RECOMMENDATION FOR FUTURE RESEARCH	239
	REFERENCES	240
	APPENDICES	255
	LIST OF PUBLICATIONS AND SEMINARS	288

LIST OF TABLES

		Page
2.1	Classifications of hybrid materials for wastewater treatment.	11
3.1	Materials and chemicals used.	52
3.2	Equipment and instruments used.	53
3.3	Levels of factors used in 2^4 full factorial design for redox polymerization of polyacrylamide.	57
3.4	Levels of factors used in central composite design for redox polymerization of polyacrylamide.	58
3.5	Levels of factors used in 2^{5-1} fractional factorial design for dye wastewater treatment using MCPAM hybrid material.	69
3.6	Levels of factors used in 2^{5-1} fractional factorial design for dye wastewater treatment using MHPAM hybrid material.	70
3.7	Levels of factors used in central composite design for dye wastewater treatment using MCPAM hybrid material.	70
3.8	Levels of factors used in central composite design for dye wastewater treatment using MHPAM hybrid material.	71
3.9	Levels of factors used in 2^4 full factorial design for textile industrial wastewater treatment using MCPAM hybrid material.	71

3.10	Levels of factors used in central composite design for textile industrial wastewater treatment using MCPAM hybrid material.	72
4.1	Polymerization conversion (%) as a function of time at different acrylamide feed concentrations.	76
4.2	Rate constants and activation energies for acrylamide redox polymerization at different temperatures.	77
4.3	Characteristics relaxation time τ , for different acrylamide feed concentrations.	86
4.4	2^4 full factorial design for redox polymerization of polyacrylamide.	88
4.5	ANOVA table for the conversion (%) of polyacrylamide redox polymerization using factorial design – reduced model.	93
4.6	Central composite design for redox polymerization of polyacrylamide.	95
4.7	Estimated regression coefficients for conversion (%) of polyacrylamide redox polymerization using data in coded units	97
4.8	ANOVA table for polyacrylamide redox polymerization using central composite design – reduced model.	98
4.9	Optimal operating conditions to obtain the highest conversion of polyacrylamide redox polymerization	101

4.10	Observed FT-IR wavenumbers and their corresponding functional group and assignments for acrylamide and polyacrylamide.	106
4.11	Molecular weight distribution of polyacrylamide.	107
4.12	Observed FT-IR wavenumbers and their corresponding functional group and assignments for MCPAM and MHPAM hybrid materials.	111
4.13	Glass transition temperature and heat capacity of the magnesium salt-polyacrylamide hybrid materials.	125
4.14	Activation energy of thermal decomposition of MCPAM hybrid materials.	136
4.15	Activation energy of thermal decomposition of MHPAM hybrid materials.	136
4.16	Characteristics of Cibacron Red FN-R.	145
4.17	Kinetics rate constants with pseudo-first order and pseudo-second order models for dye removal using MCPAM at different initial dye concentrations.	150
4.18	Kinetics rate constants with pseudo-first order and pseudo-second order models for dye removal using MHPAM at different initial dye concentrations.	150
4.19	Comparison of sludge production between MCPAM hybrid material and magnesium chloride.	161

4.20	Comparison of sludge production between MHPAM hybrid material and magnesium hydroxide.	161
4.21	2^{5-1} fractional factorial design matrix for dye wastewater treatment using MCPAM hybrid material.	168
4.22	ANOVA analysis for colour removal (%) using MCPAM hybrid material.	174
4.23	ANOVA analysis for COD reduction (%) using MCPAM hybrid material – reduced model.	175
4.24	2^{5-1} fractional factorial design matrix for dye wastewater treatment using MHPAM hybrid material.	176
4.25	ANOVA analysis for colour removal (%) using MHPAM hybrid material – reduced model.	182
4.26	ANOVA analysis for COD reduction (%) using MHPAM hybrid material – reduced model.	182
4.27	Central composite design matrix for dye wastewater treatment using MCPAM hybrid material.	184
4.28	Estimated regression coefficients for colour removal (%) using MCPAM hybrid material.	186
4.29	Estimated regression coefficients for COD reduction (%) using MCPAM hybrid material.	187
4.30	ANOVA analysis for colour removal (%) using MCPAM hybrid material – reduced model.	188

4.31	ANOVA analysis for COD reduction (%) using MCPAM hybrid material – reduced model.	188
4.32	Optimal conditions and model validation using MCPAM hybrid material.	194
4.33	Central composite design matrix for dye wastewater treatment using MHPAM hybrid material.	196
4.34	Estimated regression coefficients for colour removal (%) using MHPAM hybrid material.	198
4.35	Estimated regression coefficients for COD reduction (%) using MHPAM hybrid material.	199
4.36	ANOVA analysis for colour removal (%) using MHPAM hybrid material – reduced model.	200
4.37	ANOVA analysis for COD reduction (%) using MHPAM hybrid material – reduced model.	200
4.38	Optimal conditions and model validation using MHPAM hybrid material.	206
4.39	Characteristics of textile industrial wastewater.	208
4.40	2 ⁴ full factorial design for textile industrial wastewater treatment using MCPAM hybrid material.	209
4.41	ANOVA analysis for colour removal (%) of textile industrial wastewater using MCPAM hybrid material – reduced model.	215

4.42	ANOVA analysis for COD reduction (%) of textile industrial wastewater using MCPAM hybrid material – reduced model.	216
4.43	Central composite design matrix for textile industrial wastewater treatment using MCPAM hybrid material.	217
4.44	Estimated regression coefficients for colour removal (%) of textile industrial wastewater using MCPAM hybrid material.	219
4.45	Estimated regression coefficients for COD reduction (%) of textile industrial wastewater using MCPAM hybrid material.	220
4.46	ANOVA analysis for colour removal (%) using MCPAM hybrid material – reduced model.	221
4.47	ANOVA analysis for COD reduction (%) using MCPAM hybrid material – reduced model.	221
4.48	Optimal conditions and model validation using MCPAM hybrid material.	227
4.49	Comparison of MCPAM hybrid material with other inorganic-organic hybrid materials in treating dye wastewater.	229
A1	Summary of the applications of hybrid materials in the wastewater treatment using coagulation/flocculation processes.	255

LIST OF FIGURES

		Page
2.1	Hierarchy of classifications for hybrid materials used in coagulation-flocculation.	10
2.2	Chemical structure of polyacrylamide (PAM).	18
2.3	Chemical structure of polydimethyldiallyl ammonium chloride (PDMDAAC).	18
2.4	Chemical structure of chitosan.	19
2.5	Master curve for typical ratio distribution as a function of coagulation/flocculation.	51
3.1	Flow chart of the overall methodology of the study.	55
4.1	Polyacrylamide conversion (%) versus sodium bisulfite concentration.	73
4.2	Polyacrylamide conversion (%) versus polymerization time (min).	75
4.3	Arrhenius plot ($\ln k$ versus $1/T$).	77
4.4	Eyring plot ($\ln (k/T)$ versus $1/T$).	78
4.5	\ln Rate versus \ln [acrylamide] to determine the reaction order for the acrylamide concentration.	79
4.6	\ln Rate versus \ln [ammonium persulphate] to determine the reaction order for the ammonium persulphate concentration.	80

4.7	In Rate versus In [sodium bisulfite] to determine the reaction order for the sodium bisulfite concentration.	81
4.8	In situ viscosities over redox polymerization time at shear rate of 10.72s^{-1} .	83
4.9	Shear viscosity versus shear rate (different acrylamide feed concentrations, polymerized at 50°C).	84
4.10	Shear stress versus stress rate (different acrylamide feed concentrations, polymerized at 50°C).	85
4.11	Oscillatory frequency sweep (different acrylamide feed concentrations, polymerized at 50°C).	86
4.12	Complex viscosities (different acrylamide feed concentrations, polymerized at 50°C).	87
4.13	Normal probability plot of standardized effect of the conversion (%) of polyacrylamide redox polymerization.	89
4.14	Main effects plots (temperature, concentrations of acrylamide, ammonium persulphate and sodium bisulfite) for the conversion of polyacrylamide redox polymerization.	91
4.15	Interaction plots (temperature, concentrations of acrylamide, ammonium persulphate and sodium bisulfite) for the conversion of polyacrylamide redox polymerization.	93

4.16	Comparison of predicted conversion (%) and experimental conversion (%) of polyacrylamide redox polymerization.	99
4.17	Normal probability plot of the conversion of polyacrylamide redox polymerization.	100
4.18	Contour plots for the conversion of polyacrylamide redox polymerization.	101
4.19	Experimental rate versus predicted rate of polyacrylamide redox polymerization using classical kinetics model.	103
4.20	Experimental rate versus predicted rate of polyacrylamide redox polymerization of kinetics model using experimental design.	104
4.21	FT-IR spectra for acrylamide and polyacrylamide.	105
4.22	Molecular weight distribution of polyacrylamide.	107
4.23	FTIR spectra of MCPAM hybrid materials.	111
4.24	FTIR spectra of MHPAM hybrid materials.	112
4.25	Conductivity of MCPAM hybrid materials in aqueous solution.	113
4.26	Conductivity of MHPAM hybrid materials in aqueous solution.	113
4.27	Solution viscosities of MCPAM and MHPAM hybrid materials at different ratio of magnesium salts.	115
4.28	Reduced viscosities of MCPAM hybrid materials at different concentrations.	117

4.29	Reduced viscosities of MHPAM hybrid materials at different concentrations.	117
4.30	Linear viscoelastic regions of MCPAM hybrid materials.	119
4.31	Linear viscoelastic regions of MHPAM hybrid materials.	119
4.32	Effect of shear on the aqueous solutions of MCPAM hybrid materials.	121
4.33	Effect of shear on the aqueous solutions of MHPAM hybrid materials.	121
4.34	Oscillatory frequency sweep of MCPAM hybrid materials.	123
4.35	Oscillatory frequency sweep of MHPAM hybrid materials.	123
4.36	DSC curves of MCPAM at different ratios of magnesium chloride to polyacrylamide.	125
4.37	DSC curves of MHPAM at different ratios of magnesium hydroxide to polyacrylamide.	126
4.38	Thermal gravimetric curves of MCPAM hybrid materials at different ratios of magnesium chloride to polyacrylamide.	127
4.39	Thermal gravimetric curves of MHPAM hybrid materials at different ratios of magnesium hydroxide to polyacrylamide.	127
4.40	Differential thermal gravimetric curves of MCPAM hybrid materials at different ratios of magnesium chloride to polyacrylamide.	129

4.41	Differential thermal gravimetric curves of MHPAM hybrid materials at different ratios of magnesium hydroxide to polyacrylamide.	130
4.42	Thermal gravimetric curves of MCPAM hybrid materials at different rate of heating (10, 20 and 40°C/min).	132
4.43	Thermal gravimetric curves of MHPAM hybrid materials at different rate of heating (10, 20 and 40°C/min).	133
4.44	Logarithmic rate of heating versus inverse absolute temperature of MCPAM hybrid materials using Flynn and Wall's model.	134
4.45	Logarithmic rate of heating versus inverse absolute temperature of MHPAM hybrid materials using Flynn and Wall's model.	135
4.46	Energy-Dispersive X-ray spectroscopy graph of polyacrylamide.	142
4.47	Energy-Dispersive X-ray spectroscopy graph of MCPAM hybrid material (50%MgCl ₂ :50%PAM).	143
4.48	Energy-Dispersive X-ray spectroscopy graph of MHPAM hybrid material (50%Mg(OH) ₂ :50%PAM).	143
4.49	Effect of different ratios of MCPAM hybrid material in removing reactive dye from wastewater at different pH.	146
4.50	Effect of different ratios of MHPAM hybrid material in removing reactive dye from wastewater at different pH.	148

4.51	Pseudo-second order plot of dye removal using MCPAM hybrid material.	151
4.52	Pseudo-second order plot of dye removal using MHPAM hybrid material.	151
4.53	Variation of conductivity and pH using different dosage of MCPAM hybrid material.	154
4.54	Variation of conductivity and pH using different dosage of MHPAM hybrid material.	155
4.55	Chemical structure of sludge formed using $MgCl_2$ and MCPAM.	156
4.56	Schematic diagram of dye wastewater treatment mechanism with MCPAM hybrid material. (a) The introduction of MCPAM hybrid material into the high pH dye wastewater; (b) The formation of Dye- $Mg(OH)_2$ -PAM sludge complex.	157
4.57	Chemical structure of sludge formed using $Mg(OH)_2$ and MHPAM.	158
4.58	Schematic diagram of dye wastewater treatment mechanism with MHPAM hybrid material. (a) The introduction of MHPAM hybrid material into the high pH dye wastewater; (b) The formation of Dye- $Mg(OH)_2$ -PAM sludge complex.	159

4.59	Normal probability plot of standardized effect for colour removal (%) using MCPAM hybrid material.	169
4.60	Normal probability of standardized effect for COD reduction (%) using MCPAM hybrid material.	170
4.61	Main effects plot on colour removal (%) using MCPAM hybrid material.	171
4.62	Main effects plot on COD reduction (%) using MCPAM hybrid material.	172
4.63	Interaction effects plot on colour removal (%) using MCPAM hybrid material.	173
4.64	Main effects plot on COD reduction (%) using MCPAM hybrid material.	173
4.65	Normal probability plot of standardized effect for colour removal (%) using MHPAM hybrid material.	177
4.66	Normal probability of standardized effect for COD reduction (%) using MHPAM hybrid material.	178
4.67	Main effects plot on colour removal (%) using MHPAM hybrid material.	179
4.68	Main effects plot on COD reduction (%) using MHPAM hybrid material.	179
4.69	Interaction effects plot on colour removal (%) using MHPAM hybrid material.	180

4.70	Main effects plot on COD reduction (%) using MHPAM hybrid material.	181
4.71	Plot of predicted vs experimental colour removal (%) using MCPAM hybrid material.	189
4.72	Plot of predicted vs experimental COD reduction (%) using MCPAM hybrid material.	190
4.73	Normal probability plot of the residuals for colour removal (%) using MCPAM hybrid material.	191
4.74	Normal probability plot of the residuals for COD reduction (%) using MCPAM hybrid material.	191
4.75	Two-dimensional response contour plots of colour removal (%) using MCPAM hybrid material.	193
4.76	Two-dimensional response contour plots of COD reduction (%) using MCPAM hybrid material.	193
4.77	Plot of predicted vs experimental colour removal (%) using MHPAM hybrid material.	201
4.78	Plot of predicted vs experimental COD reduction (%) using MHPAM hybrid material.	202
4.79	Normal probability plot of the residuals for colour removal (%) using MHPAM hybrid material.	203
4.80	Normal probability plot of the residuals for COD reduction (%) using MHPAM hybrid material.	203

4.81	Two-dimensional response contour plots of colour removal (%) using MHPAM hybrid material.	204
4.82	Two-dimensional response contour plots of COD reduction (%) using MHPAM hybrid material.	205
4.83	Normal probability plot of standardized effect for colour removal (%) of textile industrial wastewater using MCPAM hybrid material.	210
4.84	Normal probability plot of standardized effect for COD reduction (%) of textile industrial wastewater using MCPAM hybrid material.	211
4.85	Main effects plot on colour removal (%) of textile industrial wastewater using MCPAM hybrid material.	212
4.86	Main effects plot on COD reduction (%) of textile industrial wastewater using MCPAM hybrid material.	213
4.87	Interaction effects plot on colour removal (%) of textile industrial wastewater using MCPAM hybrid material.	214
4.88	Interaction effects plot on COD reduction (%) of textile industrial wastewater using MCPAM hybrid material.	214
4.89	Plot of predicted vs experimental colour removal (%) of textile industrial wastewater using MCPAM hybrid material.	222

4.90	Plot of predicted vs experimental COD reduction (%) of textile industrial wastewater using MCPAM hybrid material.	223
4.91	Normal probability plot of the residuals for colour removal (%).	224
4.92	Normal probability plot of the residuals for COD reduction (%).	224
4.93	Two-dimensional response contour plots of colour removal (%) of textile industrial wastewater using MCPAM hybrid material.	225
4.94	Two-dimensional response contour plots of COD reduction (%) of textile industrial wastewater using MCPAM hybrid material.	226
A1	Calibration curve of measured density of water versus density of water at temperature of 15 to 40°C.	252
A2	Calibration curve of measured viscosity of water versus viscosity of water at temperature of 15 to 40°C.	252
A3	Absorbance of Cibacron Red FN-R ($\lambda_{\max} = 540 \text{ nm}$).	253
A4	Absorbance of Cibacron Red FN-R versus concentration.	253
A5	Colour point of Cibacron Red FN-R versus concentration.	254
A6	Chemical oxygen demand of Cibacron Red FN-R versus concentration.	254

LIST OF PLATES

	Page	
4.1	Transmission Electron Microscopy (TEM) image of polyacrylamide solution under magnification power 52,000x.	108
4.2	Transmission Electron Microscopy (TEM) image of MCPAM hybrid material in aqueous solution.	138
4.3	Transmission Electron Microscopy (TEM) images of MHPAM hybrid material in aqueous solution.	138
4.4	Scanning Electron Microscopy (SEM) image of polyacrylamide.	140
4.5	Scanning Electron Microscopy (SEM) image of MCPAM hybrid material.	140
4.6	Scanning Electron Microscopy (SEM) image of MHPAM hybrid material.	141
4.7	Flocs formed using $MgCl_2$.	162
4.8	Flocs formed using MCPAM hybrid material.	163
4.9	Flocs formed using $Mg(OH)_2$.	163
4.10	Flocs formed using MHPAM hybrid material.	164
4.11	Surface morphology of sludge using $MgCl_2$.	165
4.12	Surface morphology of sludge using MCPAM hybrid material.	165
4.13	Surface morphology of sludge using $Mg(OH)_2$.	166

4.14	Surface morphology of sludge using MHPAM hybrid material.	166
4.15	Comparison of dye wastewater before and after treatment using MCPAM hybrid material.	195
4.16	Comparison of dye wastewater before and after treatment using MHPAM hybrid material.	206
4.17	Comparison of textile industrial wastewater before and after treatment using MCPAM hybrid material.	227

LIST OF SYMBOLS

$\text{Al}_2(\text{SO}_4)_3$	aluminium sulphate
FeCl_3	ferric chloride
$\text{Al}(\text{OH})_3$	aluminium hydroxide
CaCl_2	calcium chloride
MgCl_2	magnesium chloride
$\text{Mg}(\text{OH})_2$	magnesium hydroxide
FeSO_4	ferric sulphate
Na_2SiO_3	sodium silicate
AlCl_3	aluminium chloride
k	rate constant
R	gas constant
T	temperature
h	Planck's constant
t	time
A	calibration constant of the viscometer
T_g	glass transition temperature
C_p	heat capacity
M	molarity
K	Kelvin
G'	storage modulus
G''	loss modulus
G_c	crossing point of G' and G''

PtCo	Platinum-Cobalt Scale
k_B	Boltzmann's constant
ΔG^\ddagger	Gibbs energy of activation
ΔH^\ddagger	enthalpy of activation
ΔS^\ddagger	entropy of activation
$^\circ\text{C}$	degree Celcius
g/mL	gram per mililiter
μm	micrometer
μL	microliter
mL/min	mililiter per minute
g cm^{-3}	gram per cubic centimeter
$^\circ\text{C}/\text{min}$	degree celcius per minute
mL/min	mililiter per minute
mg/L	milligram per liter
g/mol	gram per mol
%	percent
α	axial point
β_0	offset term
β_i	linear effect
β_{ii}	squared effect
β_{ij}	interaction effect
x_i	coded variables
ε	error

η	viscosity
ρ	density
τ_r	relaxation time
ω_c	angular frequency of the crossing point of G' and G''
η^*	complex viscosity
ω	angular frequency
$[\eta]$	intrinsic viscosity

LIST OF ABBREVIATION

AA	acrylic acid
AFPSi	aluminium ferric polysilicate
AM	acrylamide
ANOVA	Analysis of Variance
CCD	Central Composite Design
COD	Chemical Oxygen Demand
CMC	carboxymethyl cellulose
CMS	carboxymethylstarch
CTAB	cetyl trimethyl ammonium bromide
CTS	chitosan
DLVO	Derjaguin-Landau-Verwey-Overbeek theory
DMA	dimethylamine
DSC	Differential Scanning Calorimetry
DTG	Differential Thermal Gravimetric
Ea	activation energy
EPI	epichlorohydrin
EDX	Energy-Dispersive X-ray
FT-IR	Fourier Transform Infrared Spectroscopy
GPC	Gel Permeation Chromatography
IPC	inorganic polymeric coagulant
MBFGA1	microbial flocculant GA1
MCPAM	magnesium chloride-polyacrylamide

MHPAM	magnesium hydroxide-polyacrylamide
MMT	montmorillonite
PAC	polyaluminium chloride
PACS	polyaluminium-chloride-sulfate
PACSAM	PAC-starch-graft-acrylamide
PAFC	polyaluminium-ferric-chloride
PAFSiC	polyaluminium-ferric-silicate-chloride
PAM	polyacrylamide
PASiC	polyaluminium-silicate-chloride
PDMDAAC	polydimethyldiallylammonium chloride
PFASiS	poly-ferric-aluminium-silicate-sulfate
PFC	polyferric chloride
PFMS	poly-ferric-magnesium-sulfate
PFSiS	polyferric-silicate-sulfate
PFSiC	polyferric-silicate-chloride
PGS	palygorskite
PMAS	poly-magnesium-aluminium-sulfate
PPFS	polymeric phosphate ferric sulfate
PFS	polyferric sulphate
PSiAF	polysilicate aluminium ferric
PSiF	polysilicic-ferric
PSiFA	polysilicate-ferro-aluminium-sulfate
PZSiS	poly-zinc-silicate-sulfate

RSM	Response Surface Methodology
RH	rate of heating
SAG	sodium alginate
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TGA	Thermal Gravimetric Analysis
XRD	X-Ray Diffraction

PENYEDIAAN, PENCIRIAN DAN PENGGUNAAN BAHAN HIBRID GARAM MAGNESIUM-POLIAKRILAMIDA DALAM RAWATAN AIR SISA PEWARNA

ABSTRAK

Bahan hibrid garam magnesium-poliakrilamida disediakan, dicirikan dan digunakan untuk rawatan air sisa pewarna. Poliakrilamida disediakan melalui pempolimeran redoks daripada akrilamida. Aspek asas pempolimeran poliakrilamida redoks telah dikaji melalui penyiasatan mekanisme, kinetik, termodinamik dan sifat reologi in situ sepanjang proses pempolimeran redoks. Pempolimeran redoks poliakrilamida dioptimumkan melalui reka bentuk eksperimen. Ciri fisikokimia poliakrilamida yang sudah dioptimumkan dikaji dari segi struktur kimia, taburan jisim molekul serta kelikatan dalam larutan akuas. Hasil pempolimeran poliakrilamida optimum redoks adalah 96.89% dengan jisim molekul 1.66×10^6 Da. Bahan hibrid garam magnesium-poliakrilamida telah disediakan melalui pengadunan fizikal magnesium klorida dan magnesium hidroksida dengan poliakrilamida dalam larutan akuas untuk membentuk bahan hibrid MCPAM dan MHPAM, masing-masing. Ciri-ciri bahan hibrid MCPAM dan MHPAM telah dikaji dari segi kimia, fizikal, sifat reologi, terma dan morfologi. Ciri-ciri bahan hibrid berubah dengan komponen serta komposisi dalam bahan hibrid. Bahan hibrid MCPAM dan MHPAM merupakan sejenis campuran daripada percampuran fizikal dan tiada ikatan kimia baru yang terbentuk di antara garam magnesium dan poliakrilamida. Bahan-bahan hibrid MCPAM dalam larutan akueus mempunyai keberaliran yang lebih tinggi berbanding dengan bahan-bahan hibrid MHPAM tetapi kelikatan menunjukkan tingkah laku yang songsang berbanding dengan keberaliran. Bahan hibrid MHPAM mempunyai kestabilan terma yang lebih baik di

mana tenaga pengaktifan yang diperlukan untuk menguraikan bahan hibrid MHPAM adalah lebih tinggi daripada bahan hibrid MCPAM. Transmisi Mikroskopi Elektron (TEM) dan Pengimbasan Mikroskopi Elektron (SEM) telah dijalankan untuk menjelaskan mikrostruktur dalam bentuk akuas dan pepejal, masing-masing. Mikrostrukturnya berubah dengan komponen dalam bahan hibrid. Bahan hibrid MCPAM dan MHPAM telah digunakan dalam merawat air sisa pewarna reaktif (Cibacron Red FN-R). Bahan hibrid MCPAM dan MHPAM dengan nisbah 90% MgCl₂:10% PAM dan 90% Mg(OH)₂:10% PAM, masing-masing, didapati merupakan nisbah terbaik dalam menyingkirkan pewarna dari air sisa tekstil. Bahan-bahan hibrid tersebut mampu untuk menyingkirkan 98% pewarna dari air sisa tekstil. Rawatan air sisa pewarna reaktif yang menggunakan bahan MCPAM dan MHPAM hibrid telah didapati sesuai bagi model kinetik pseudo kedua. Enapcemar terbentuk daripada kedua-dua bahan hibrid MCPAM dan MHPAM mempunyai struktur kimia yang hampir sama yang mana enapcemar adalah terdiri daripada kompleks Pewarna-Mg(OH)₂-PAM. Isipadu enapcemar terenap dan indeks isipadu enapcemar (SVI) berkurangan dengan ketara dengan menggunakan bahan hibrid MCPAM dan MHPAM berbanding dengan MgCl₂ dan Mg(OH)₂. Flocc yang dibentuk menggunakan bahan hibrid MCPAM dan MHPAM telah didapati lebih padat dan bersaiz lebih besar daripada menggunakan MgCl₂ dan Mg(OH)₂ masing-masing. Kesan faktor-faktor yang mempengaruhi penyingkiran warna (%) dan pengurangan COD (%) daripada air sisa pewarna reaktif menggunakan bahan hibrid MCPAM dan MHPAM disiasat melalui reka bentuk 2⁵⁻¹ faktorial pecahan. Semua faktor bebas seperti kepekatan pewarna, pH, dos, kelajuan pengadukan dan masa pengadukan telah diambil kira untuk menentukan kesan mereka ke atas penyingkiran warna (%) dan pengurangan COD (%). Reka bentuk 2⁵⁻¹ faktorial pecahan telah

ditambah ke dalam rekabentuk komposit pusat untuk mengoptimumkan prestasi penyingkiran warna (%) dan pengurangan COD (%). Model regresi kuadratik bagi penyingkiran warna (%) dan pengurangan COD (%) menggunakan bahan hibrid MCPAM dan MHPAM sebagai fungsi faktor yang penting telah diggunakan. Bahan hibrid MCPAM telah dipilih untuk merawat air sisa industri tekstil kerana kesesuaian bahan hibrid MCPAM untuk merawat air sisa industri tekstil dalam pH yang tinggi. Bahan hibrid MCPAM dapat menyingkirkan warna sebanyak 82.83%.

**PREPARATION, CHARACTERIZATION AND APPLICATION OF
MAGNESIUM SALT-POLYACRYLAMIDE HYBRID MATERIALS IN DYE
WASTEWATER TREATMENT**

ABSTRACT

Magnesium salt-polyacrylamide hybrid materials were prepared, characterized and applied for reactive dye wastewater treatment. Polyacrylamide was prepared from acrylamide monomer through redox polymerization. The fundamental aspects of polyacrylamide redox polymerization were studied through investigation of mechanism, kinetics, thermodynamics and in situ rheological properties of the redox polymerization process. The redox polymerization of polyacrylamide was optimized through design of experiment. The physicochemical properties of the polyacrylamide were investigated in terms of chemical structure, molecular weight distribution as well as viscosity in aqueous solution. The yield of the optimal redox polymerization of polyacrylamide was 96.89% with molecular weight of 1.66×10^6 Da. Magnesium salt-polyacrylamide hybrid materials were prepared through physical blending of magnesium chloride and magnesium hydroxide with polyacrylamide in aqueous solution to form magnesium chloride-polyacrylamide (MCPAM) and magnesium hydroxide-polyacrylamide (MHPAM) hybrid materials, respectively. The characteristics of MCPAM and MHPAM hybrid materials were investigated in terms of chemical, physical, rheological, thermal and morphological properties. The characteristics vary with the components as well as the compositions. MCPAM and MHPAM hybrid materials are physical mixtures and no new chemical bonding was formed between magnesium salts and polyacrylamide. MCPAM hybrid materials in aqueous solution have higher conductivities compared to

that of MHPAM hybrid materials but the viscosity shows a reverse behaviour. MHPAM hybrid materials have better thermal stability where the activation energies needed to decompose MHPAM hybrid materials are higher than that of MCPAM hybrid materials. Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) were carried out to elucidate the microstructure in aqueous and solid form, respectively. The microstructure varies with the component in hybrid materials. MCPAM and MHPAM hybrid materials were applied in treating reactive dye (Cibacron Red FN-R) wastewater. MCPAM and MHPAM hybrid materials with the ratios of 90% MgCl₂:10% PAM and 90% Mg(OH)₂:10% PAM, respectively, were found to be the best ratios in removing of reactive dye from the wastewater. They were able to remove 98% of reactive dye from the wastewater. The reactive dye removal percentage using MCPAM and MHPAM hybrid materials was found to fit pseudo-second order kinetics model. Both sludge formed using MCPAM and MHPAM hybrid materials have an almost similar chemical structure where the sludge were constituted of Dye-Mg(OH)₂-PAM complex. The settled sludge volume and sludge volume index are reported to be lower using MCPAM and MHPAM hybrid materials compared to that of MgCl₂ and Mg(OH)₂. The flocs formed using MCPAM and MHPAM hybrid materials were found to be relatively compact and larger in size compared to that of MgCl₂ and Mg(OH)₂. The factors affecting colour removal (%) and COD reduction (%) of reactive dye wastewater using MCPAM and MHPAM hybrid materials were investigated through 2⁵⁻¹ fractional factorial design. All independent factors such as dye concentration, pH, dosage, agitation speed and agitation time were taken into account to determine their effects. 2⁵⁻¹ fractional factorial design was augmented into central composite design to optimize the performance of colour removal (%) and COD reduction (%). Quadratic regression

models for colour removal (%) and COD reduction (%) using MCPAM and MHPAM hybrid material as a function of significant factors were applied. MCPAM hybrid material was selected to treat textile industrial wastewater in view of its suitability in treating high pH textile industrial wastewater. MCPAM hybrid material is able to remove 82.83% of colour.

CHAPTER 1

INTRODUCTION

1.1 Textile industry

Textile industry is one of the industries that pose a high demand on water supply and produce large amounts of wastewater. One of the common dyestuffs, reactive azo dye, has been extensively used to colour cellulosic and cotton-based fabric in textile industry. It constitutes 60 – 70 % of all produced dyestuffs. The degree of dye fixation on fabric is never complete during the dyeing process, results in producing coloured effluents (García-Montaño et al., 2008). The wastewater from textile dyeing and printing industries is often characterized by high pH, alkalinity and temperature, contains high concentration of organic matter, non-biodegradable matter, toxic substances, detergents and soaps, oil and grease, sulfide and suspended/dissolved solids (Gao et al., 2007a). The discharged textile effluent not only poses aesthetic problems when the coloured effluents reach the natural water currents, but also absorb sunlight, thus impeding the photosynthesis activity of aquatic plants and seriously threatening the whole ecosystem (Nuñez et al., 2007). This highly polluted wastewater is also highly toxic to the organisms and causes skin irritation, cancer, and mutation of aquatic organic organisms and human. (Noppakundilokrat et al., 2010). In line with Environmental Quality Act 1974 which was gazette in year 2009 - Environmental Quality (Industrial Effluent) Regulations 2009, industrial effluent from textile industry needs to be treated before being discharged into environment. The regulations focus on prohibition of discharging hazardous substances from textile industries into Malaysia waters in contravention to acceptable conditions as specified by the Act (Halimoon and Goh, 2010).

1.2 Overview of hybrid materials in wastewater treatment

Various materials have been developed in recent years for wastewater treatment. Among them are inorganic-based coagulants, organic-based flocculants as well as hybrid materials (Moussas and Zouboulis, 2009). Though many materials have been developed and used in removing pollutants from wastewater, there is still a need to improve their performance (Moussas and Zouboulis, 2008). The increasing needs for efficient and effective materials in wastewater treatment have initiated the development of hybrid materials for wastewater treatment. Hybrid materials thus have emerged as new materials of tremendous potential in treating wastewater due to their better performance compared to that of conventional inorganic-based coagulants and organic-based flocculants (Wang et al., 2006).

Hybrid materials refer to materials obtained from the addition of effective components into the original material to enhance the aggregating power. It is logical to introduce functional chemical groups or components into the hybrid which can strengthen the aggregating power (Tzoupanos and Zouboulis, 2011). Due to the synergetic effect of hybrid components in one material, hybrid materials hence pose a superior performance than that of individual components (Tang and Shi, 2002; Yang et al., 2004).

1.3 Dye wastewater treatment through coagulation-flocculation process

Conventional solid-liquid separation through coagulation-flocculation is an important unit operation in dye wastewater treatment (Gao et al., 2003a). Coagulation of dissolved and colloidal substances in wastewater is essentially understood in light of Derjaguin-Landau-Verwey-Overbeek theory (DLVO theory) whereby coagulation is referred to overcoming the interparticle repulsive energy

barrier by simply increasing in ionic strength and destabilizes colloids by neutralizing the forces that keep them apart. Coagulation can be induced by introducing aluminium and iron based substance (Addai-Mensah and Prestidge, 2005). Flocculation is the action of polymers to form bridges between flocs and bind the particles into large clumps. Bridging occurs when the polymer chains adsorb on different particles and help particles to form bigger flocs (Somasundaran et al., 2005; Natalia and Olli, 2006). Coagulation-flocculation process has been proven to be an effective method in treating dye wastewater (Tan et al., 2000). It is applied as a treatment process to decolourize dye wastewater and reduce the total load of pollutants with the help of hybrid materials (Gao et al., 2003a; Gao et al., 2008).

1.4 Problem statements

In this study, polyacrylamide is selected to be the polymeric matrix due its high water soluble and high molecular weight which is desirable for wastewater treatment (Daughton, 1998). Though the application of polyacrylamide has been studied in previous literature (Wong et al., 2006), the synthesis of polyacrylamide is still the interest for current study. Redox polymerization was used to synthesize polyacrylamide. The effect of reducing agent in affecting the redox polymerization is able to give insight of polyacrylamide synthesis (Sarac, 1999). The in situ rheological property change of polyacrylamide is particularly novel and it is able to depict the conformation change of acrylamide in solution during redox polymerization (Feng et al., 2005). Hybrid materials have been recognized to be able to give better treatment performance (Wang et al., 2009). Hybrid materials are products which are composed of two or more different types of components in one polymeric matrix. They have been receiving increased attention in recent years due

to their unique properties and superior performance compared to that of conventional inorganic coagulants and organic polymeric flocculants (Moussas and Zouboulis, 2009). Magnesium salt-polyacrylamide hybrid materials were prepared using magnesium salts (magnesium chloride and magnesium hydroxide) with polyacrylamide in this study. Combination of magnesium salts and polyacrylamide in hybrid matrixes produces a series of inorganic-organic hybrid materials. Magnesium salts are selected due to its less toxicity to the environment compared to aluminium and iron salts. Magnesium salts are chosen to be the components in hybrid materials due to Mg^{2+} has a relatively higher ionic potential ($3.08 \text{ e}/\text{\AA}$) compared to other cation ($Ca^{2+} = 2.02 \text{ e}/\text{\AA}$). Thus, it is expected to have stronger effect in coagulation (Gao et al., 2007; Ozkan and Yekeler, 2004). Magnesium salt-polyacrylamide hybrid materials were characterized in terms of chemical, physical, rheological, thermal as well as morphological in view of these properties are yet to be investigated by other researchers (Moussas and Zouboulis, 2009; Yang et al., 2004). With the characteristics obtained, it is able to predict the performance of wastewater treatment. For industries that discharge large volume of wastewater, such as textile industry, effective materials in treating their wastewater are required (Gao et al., 2003a). The application and the effect of properties of hybrid materials in treating dye wastewater are also the interests of this study. The effect of operating parameters on treatment efficiency was also studied. Hybrid materials that are applied in treating dye wastewater will have better efficiency than that of their individual component (Gao et al., 2003a).

1.5 Objectives

The specific objectives of the present study are:

1. To synthesize and determine the kinetics, mechanism and the optimized conditions of redox polymerization of polyacrylamide.
2. To develop a method of preparation of magnesium salt-polyacrylamide hybrid materials using magnesium salts and polyacrylamide and to characterize their chemical, physical, rheological, thermal as well as morphological properties.
3. To determine the effects of operating parameters, as well as to optimize the performance of magnesium salt-polyacrylamide hybrid materials, in treating dye wastewater.

1.6 Scope of study

There are three focus areas in this research. The first focus area is the synthesis of polyacrylamide where polyacrylamide is synthesized through redox polymerization. The kinetics, thermodynamic as well as the mechanism of the redox polymerization is investigated. Magnesium salts-polyacrylamide hybrid materials are prepared using magnesium chloride and magnesium hydroxide with polyacrylamide. The second focus area is the characterization of magnesium salt-polyacrylamide hybrid materials. The characteristics of the magnesium salt-polyacrylamide hybrids in terms of chemical, physical, rheological, thermal as well as morphological properties are systematically studied. In the third focus area, magnesium salt-polyacrylamide hybrids are applied in treating reactive azo dye synthetic wastewater as well as the textile industrial wastewater.

1.7 Organization of thesis

This thesis is divided into six chapters. In Chapter one, a general description on the textile wastewater as well as the environmental problem arises from textile industry are highlighted. A general overview of the hybrid materials in wastewater treatment is mentioned. The problem statement, significance of study, objectives and scope of study are also covered in this chapter.

Chapter two reviews the classifications and preparation methods for hybrid materials. A particular emphasis is given to the characterization and application of hybrid materials in wastewater treatment. The properties of hybrid materials are reviewed in terms of chemical, physical, thermal, morphological as well as structural properties. Effect of operating parameters, such as pH, dosage, stirring speed, stirring time as well as operating temperature during the application of hybrid material in wastewater treatment is also reported in this chapter.

Chapter three covers the materials and methods employed in this study. Detailed descriptions concerning the preparation, characterizations as well as the application of hybrid materials in wastewater treatment are given in this chapter.

Chapter four presents the results and discussion of the three main studies. First, polyacrylamide is synthesized and used for the preparation of magnesium salt-polyacrylamide hybrid materials. Second, characteristics of magnesium salt-polyacrylamide hybrid materials are discussed. Third, magnesium salt-polyacrylamide hybrid materials are applied in treating dye wastewater. Experimental design is used in screening and optimizing the performance of magnesium salt-polyacrylamide hybrid materials in treating dye wastewater.

Chapter five outlines the conclusions obtained from the study whereas chapter six provides the recommendations and suggestions for the future research in this area of research.

CHAPTER 2

LITERATURE REVIEW

2.1 Classifications of hybrid materials

A number of terminologies have been used to address hybrid materials used for wastewater treatment, e.g. composite coagulant (Gao et al., 2003a), composite flocculant (Gao et al., 2005a), composite polymer (Liu et al., 2011), hybrid coagulant (Zhao et al., 2009b), hybrid flocculant (Dong et al., 2009), hybrid polymer so on and so forth. A standardized terminology system is yet to be established. Researchers tend to use the terms “hybrid” and “composite” interchangeably regardless of the macroscopic and microscopic properties of the materials. The same is observed with the terms “coagulant” and “flocculant”. These would create confusion in classifying hybrid materials. In this study, “hybrid materials” is used as a general term to address hybrid materials to avoid confusion. Three primary groups of hybrid materials have been proposed (Nanko, 2009):

- (i) Structurally-hybridized materials (composites)
- (ii) Chemically-bond-hybridized materials
- (iii) Functionally-hybridized materials

2.1.1 Structurally-hybridized materials (composites)

Structurally-hybridized materials, also known as composites are referred to the hybridization of macroscopic structure where the combination of materials takes place. This is usually practised in preparing inorganic-organic hybrid materials which are physical mixtures in which contain no new chemical species) such as polyferric chloride-polydimethyldiallylammonium chloride (PFC-PDMDAAC hybrid material)

(Gao et al., 2008; Moussas and Zouboulis, 2009). The performance of the materials in wastewater treatment can be enhanced with the synergetic properties of component materials.

2.1.2 Chemically-bond-hybridized materials

There are some hybrid materials with excellent properties and performance in treating wastewater due to some particular chemical-bonds at the interface between the component materials. Such a material is produced under hybridization through chemical-bonding where a new chemical group is introduced into the composition of materials to produce a new hybrid material complex (Nanko, 2009). Inorganic polymeric coagulant, for instance, polyaluminium chloride (PAC) performs better than inorganic coagulants but the performance of PAC is lower than organic polymeric flocculants, e.g. PDADMAC in the process of coagulation-flocculation. The lower molecular weight of inorganic polymeric coagulant than that of organic polymeric flocculant has resulted in lower aggregating capacity of inorganic polymeric coagulant. As such, a new chemical group such as polysilicic acid is introduced into the composition of coagulants to form Al-polysilicate chemically-bond hybrid material complex to increase the molecular weight (Gao et al., 2002a).

2.1.3 Functionally-hybridized materials

Functionally-hybridized materials are referred to the combination of two or more functions that results in new or superior functions to be created. As mentioned earlier, inorganic coagulants and inorganic polymeric coagulants pose lower aggregating capacity than that of organic polymeric flocculants. To achieve the objective of producing functionally-hybridized materials, inorganic coagulants or

inorganic polymeric coagulants are selected to hybridize with organic polymeric flocculants to perform coagulation-flocculation simultaneously. It is a new material that requires only one unit operation instead of the conventional two stages of process, coagulation-flocculation. The three primary groups can be clearly identified with their respective preparation methods which are discussed in the latter section.

2.2 Terminology of hybrid materials

The term “composite” has been extensively used and it serves a quite similar definition at macroscopic level with the term of “hybrid” (Nanko, 2009). However, from the aspect of terminology, a “composite” can be considered as a “hybrid” but not the other way round; composite is a subset of hybrid. To address these materials in general, the term “hybrid materials” would be more appropriate to be used throughout the research in view of its suitability to address all combinations of hybridizing materials (Nanko, 2009). A hierarchy of classifications for hybrid materials used in coagulation-flocculation is proposed in Figure 2.1 which is modified based on the idea of Nanko (2009). To further elaborate the classifications of hybrid materials, the hybrid materials that are used for wastewater treatment can be classified into four secondary groups after the three primary groups in which they can be composed with each other to form new hybrid materials:

- (i) Inorganic
- (ii) Organic
- (iii) Natural polymer
- (iv) Biopolymer

The hierarchy of classifications of hybrid materials as shown in Figure 2.1 is modified based the idea of Nanko (2009) on the combinations that have been

reported in recent literatures (Nanko, 2009). The hybrid materials which have been developed are indicated with black lines, e.g. inorganic-inorganic hybrid, inorganic-organic hybrid, inorganic-natural polymer hybrid, inorganic-biopolymer hybrid, organic-organic hybrid, organic-natural polymer hybrid and natural polymer-natural polymer hybrid. For those which are indicated in grey lines are the potential hybrid materials to be developed, e.g. organic-biopolymer hybrid, natural polymer-biopolymer hybrid and biopolymer-biopolymer hybrid. Inorganic-organic hybrid materials are the focus of this research in view of its characteristics and performance are yet to be fully explored.

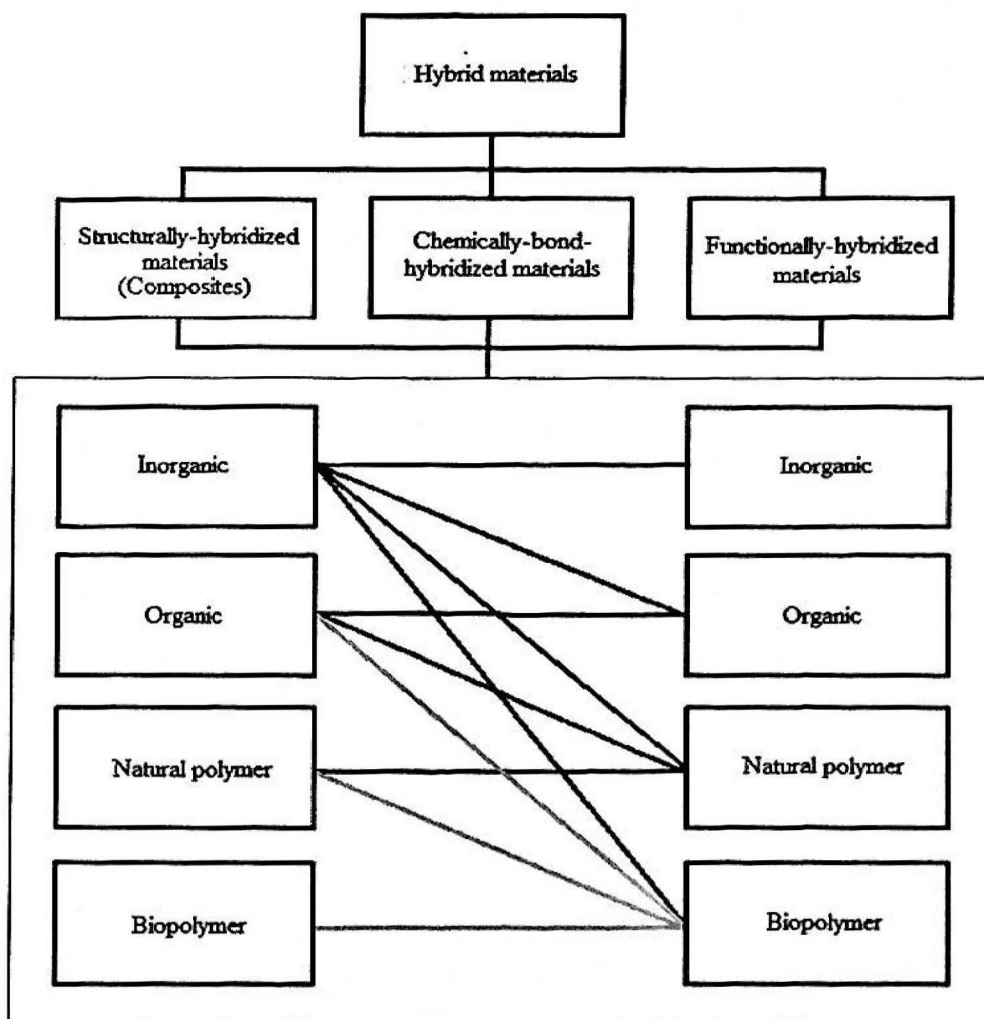


Figure 2.1 Hierarchy of classifications for hybrid materials used in coagulation-flocculation (Nanko, 2009).

2.3 Combinations of hybrid materials

The components for hybrid materials are available commercially or they can be obtained through different preparation routes. Among the most important requirements for technological applications of these hybrid materials are water soluble and high aggregating power to molecules, colloids as well as particles of pollutants (Bolto, 1995). The selection of components for hybrid materials is based on the characteristics of wastewater. Table 2.1 summarizes the types of hybrid materials used for wastewater treatment based on secondary group classifications. Inorganic-inorganic hybrid and inorganic-organic hybrid are the most developed combinations among hybrid materials currently used in wastewater treatment.

Table 2.1 Classifications of hybrid materials for wastewater treatment.

Type of hybrid materials	Hybrid materials	Reference
Inorganic-inorganic hybrid	PACS (Polyaluminium-chloride-sulfate)	(Gao and Yue, 2005b)
	PASiC (Polyaluminium-silicate-chloride)	(Gao et al., 2002a, Gao et al., 2002b, Gao et al., 2003b, Song et al., 2003, Zhang et al., 2004, Cheng et al., 2008, Tzoupanos et al., 2008, Tzoupanos et al., 2009, Zouboulis and Tzoupanos, 2009, Xu et al., 2010, Gao et al., 2007b)
	PFSiS (Polyferric-silicate-sulfate)	(Wu and Zhang, 2004, Moussas and Zouboulis, 2008, Zouboulis and Moussas, 2008)
	PFSiC (Polyferric-silicate-chloride)	(Zhang et al., 2007)

	PSiF (Polysilicic-ferric)	(Fu et al., 2009)
	PSiF (Polysilicate-ferric)	(Xu et al., 2009)
	PAFC (Polyaluminium-ferric-chloride)	(Gao et al., 2003a, Zhang et al., 2004, Yang et al., 2007b, Lan et al., 2009a, Lan et al., 2009b)
	PAFSiC (Polyaluminium-ferric-silicate-chloride)	(Gao et al., 2006, Cheng et al., 2008)
	PSiFA (Polysilicate-ferro-aluminium-sulfate)	(Qiu et al., 2009)
	PSiAF (Polysilicate aluminium ferric)	(Zhang et al., 2010a)
	PFASiS (Poly-ferric-aluminium-silicate-sulfate)	(Sun et al., 2011b)
	PMAS (Poly-magnesium-aluminium-sulfate)	(Sang et al., 2008, Liu et al., 2011)
	PFMS (Poly-ferric-magnesium-sulfate)	(Liu et al., 2009, Wei et al., 2010)
	PZSiS (Poly-zinc-silicate-sulfate)	(Zeng and Park, 2009)
	PPFS (Polymeric phosphate ferric sulfate)	(Zheng et al., 2011)
	PFS-Na-Bentonite	(Wang et al., 2010b)
	PFC-magnetic nanoparticles	(Jiang et al., 2010a)
	Clinoptilolite- $\text{Al}_2(\text{SO}_4)_3$	(Ostapenko et al., 2000)
	Oxotitanium sulfate- $\text{Al}_2(\text{SO}_4)_3$	(Chernoberezhskii et al., 2002)
	FeCl_3 -PAC (Ferric chloride-polyaluminium chloride)	(Yang et al., 2010)
	Iron-aluminium polymer hybrid	(Fan et al., 2003)
Inorganic-organic hybrid	$\text{Al}(\text{OH})_3$ -PAM (Aluminium hydroxide-polyacrylamide)	(Qian et al., 2004, Yang et al., 2004, Zheng et al., 2007, Sun et al., 2008)
	$\text{Al}(\text{OH})_3$ -P(AM-co-AA)	(Noppakundilokrat et al., 2010)
	PAC-PAM (Polyaluminium chloride-polyacrylamide)	(Huang et al., 1994, Tzoupanos and Zouboulis, 2011)
	PFS-PAM (Polyferric chloride-polyacrylamide)	(Moussas and Zouboulis, 2009, Jiang et al., 2010b)
	PAFC-CPAM (Polyaluminium ferric	(Ma et al., 2011)

chloride-cationic polyacrylamide)	
AFPSi-PAM+-CTAB	(Wang et al., 2011a)
Al ₂ (SO ₄) ₃ -PDMDAAC (Aluminium sulfate-polydimethyldiallylammonium chloride)	(Li et al., 2008b, Zhang et al., 2009, Zhao et al., 2009c, Li et al., 2010, Zhao et al., 2010a, Zhang et al., 2011)
FeCl ₃ -PDMDAAC (Ferric chloride-polydimethyldiallylammonium chloride)	(Wang et al., 2008)
FeSO ₄ -PDMDAAC (Ferric sulfate-polydimethyldiallylammonium chloride)	(Li et al., 2008a)
PFS-FeSO ₄ -PDMDAAC (Polyferric sulfate-ferric sulfate- polydimethyldiallylammonium chloride)	(Li et al., 2008a)
PAC-PDMDAAC (Polyaluminium chloride-polydimethyldiallylammonium chloride)	(Gao et al., 2005a, Lu et al., 2007, Li et al., 2008c, Zhang et al., 2008, Chu et al., 2010, Tzoupanos and Zouboulis, 2010, Wang et al., 2010a, Zhang et al., 2010b, Zhang et al., 2010c, Zhao et al., 2010b, Xiang et al., 2011)
PFS-PDMDAAC (Polyferric sulfate-polydimethyldiallylammonium chloride)	(Liu and Gong, 2005, Huang et al., 2011)
PFC-PDMDAAC (Polyferric chloride-polydimethyldiallylammonium chloride)	(Gao et al., 2007a, Gao et al., 2008, Wang et al., 2008, Wei et al., 2009a, Wei et al., 2009b, Wei et al., 2009c, Wang et al., 2011b, Wang et al., 2011c, Wang et al., 2006)
PFAC-PDMDAAC (Polyferricaluminium chloride-polydimethyldiallylammonium chloride)	(Sun et al., 2011a)
SiO ₂ -CSSAD	(Zou et al., 2011)
PAC-starch-graft-acrylamide (PACSAM)	(Yang and Jiang, 2008)
P(AM-DMC-MPMS)-PFS	(Shang and Zheng, 2009)

	PAC-EPI-DMA-PM (Polyaluminum chloride-epichlorohydrindimethylamine Polyamine)	(Wang et al., 2009)
	PFC-EPI-DMA (Polyferric chloride-epichlorohydrin-dimethylamine)	(Gao et al., 2011)
	PFCNS	(Zheng and Shu, 2001)
	MMT-PAM (Montmorillonite-polyacrylamide)	(Dong et al., 2009)
	Palygorskite-polyacrylamide (PGS-PAM)	(Qian et al., 2004)
Inorganic-natural polymer hybrid	Al ₂ (SO ₄) ₃ -CTS (Aluminium sulfate-chitosan)	(Yao et al., 2004)
	PAC-CTS (Polyaluminium chloride-chitosan)	(Huang et al., 2008b)
	PSiAF-CTS (Polysilicatealuminiumferric-chitosan)	(Wu et al., 2010)
	CTS-PAC-Na ₂ SiO ₃ (Chitosan-Polyaluminium chloride-sodium silicate)	(Zeng et al., 2008)
	Rectorite-amylose	(Zeng et al., 2005)
	Red mud-hydrochloric pickle liquor of bauxite	(Zhao et al., 2011)
Inorganic-biopolymer hybrid	Pullulan-PAC (Pullulan-polyaluminium chloride)	(Yang et al., 2007a)
	MBFGA1-PAC (Microbial flocculant GA1-polyaluminium chloride)	(Huang et al., 2008a, Yang et al., 2009)
	MBF(<i>Aspergillus niger</i>)-zeolite	(Cao et al., 2010)
Organic-Organic hybrid	poly(acrylamide-co-acrylic acid)	(Liu et al., 2000)
Organic-natural polymer hybrid	SAG-g-PAM (Sodium alginate grafted polyacrylamide)	(Tripathy et al., 2001)
	Chitosan-g-N,N-dimethylacrylamide	(Tripathy et al., 2010)
	PAM-g-CMS (Polyacrylamide grafted carboxymethylstarch)	(Sen et al., 2009)
	CMC-starch hybrid (Carboxymethyl cellulose and starch)	(Hebeish et al., 2010)
	starch-g-PAM	(Mishra et al., 2011)
	chitosan-g-N-vinyl formamide	(Mishra et al., 2008)
	starch-g-PAM-co-sodium xanthate	(Chang et al., 2008)
Natural polymer-natural polymer hybrid	Cationic starch-chitosan crosslinking copolymer	(You et al., 2009)

2.3.1 Inorganic-inorganic hybrid materials

For inorganic-inorganic hybrid group, hybrid materials are developed on the basis of Inorganic Polymeric Coagulants in which they are usually called as IPCs (Moussas and Zouboulis, 2009, Zouboulis and Moussas, 2008, Moussas and Zouboulis, 2008, Tzoupanos and Zouboulis, 2011). IPCs are referred to pre-hydrolyzed coagulants such as polyaluminium chloride (PAC), polyferric chloride (PFC), and polyferric sulphate (PFS), which are prepared by partially neutralization of inorganic salts e.g. AlCl_3 , FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$ in the control of basicity. Wang et al. (2008) and Zhang et al.(2004) have described the detailed preparation method for polymeric species of iron and aluminium, respectively.

During hydrolysis, several polymerization reactions occur and result in the formation of various polymeric species of aluminium and iron (Gao and Yue, 2005b; Moussas and Zouboulis, 2008; Moussas and Zouboulis, 2009; Tzoupanos and Zouboulis, 2011). Due to the existence of effective polymeric coagulating species, IPCs were proven to be more effective than conventional inorganic coagulating salts in coagulation (Gao et al., 2007a). This is because IPCs are more resistant to the influence of temperature and pH of the wastewater to be treated (Moussas and Zouboulis, 2009). However, regardless of the fact that IPCs perform significantly better compared to conventional aluminium-based or iron-based inorganic coagulating salt, e.g. AlCl_3 , $\text{Al}_2(\text{SO}_4)_3$, FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$, the treatment performance of IPCs are still much lower compared to that of organic polymeric flocculants (Moussas and Zouboulis, 2008). This is attributed to the molecular weight and size of IPCs that are still much lower than that of organic polymeric flocculants resulting in a lower aggregating capacity.

Several authors suggested that such a disadvantage can be compensated by the addition of silicate group into the composition of IPCs. Therefore, chemically-bonding hybridized materials that consist of IPCs and silicate group, such as aluminium-silicate (Gao et al., 2002a; Gao et al., 2002b; Gao et al., 2003b; Song et al., 2003; Zhang et al., 2004; Cheng et al., 2008; Tzoupanos et al., 2008; Tzoupanos et al., 2009; Zouboulis and Tzoupanos, 2009; Xu et al., 2010) or iron-silicate (Wu and Zhang, 2004; Moussas and Zouboulis, 2008; Zouboulis and Moussas, 2008; Zhang et al., 2007; Fu et al., 2009; Xu et al., 2009) hybrid material complexes have been developed. There are also a few reports on the combination of aluminium, iron and silicate groups in one hybrid material complex for coagulation-flocculation purposes. Such attempt is to gather as many as effective components into one hybrid material complex in which the aim is to form a bigger molecular structure as well as to enhance the aggregating capacity (Fan et al., 2003; Zhang et al., 2004; Gao et al., 2003a; Yang et al., 2007b; Lan et al., 2009a; 2009b; Cheng et al., 2008; Gao et al., 2006; Qiu et al., 2009; Zhang et al., 2010a; Sun et al., 2011b). Some researchers attempted to introduce other new effective chemical groups such as magnesium (Sang et al., 2008; Liu et al., 2011; Liu et al., 2009; Wei et al., 2010), zinc (Zeng and Park, 2009), phosphate (Zheng et al., 2011), sodium-bentonite (Wang et al., 2010b), magnetic nanoparticles (Jiang et al., 2010a) into the composition of IPCs to enhance the performance of inorganic-inorganic hybrid materials.

2.3.2 Inorganic-organic hybrid materials

The application of inorganic salts poses a limitation in coagulation where the coagulation capacity is lower than that of IPCs and organic flocculants if they were applied individually. To overcome this limitation, organic polymeric flocculants such

as polyacrylamide (PAM) and polydimethyldiallylammonium chloride (PDMDAAC) are introduced to prepare inorganic-organic hybrid materials in which are the most developed combination among the hybrid materials for coagulation-flocculation purposes. PAM and PDMDAAC share the common characteristics of relatively high molecular weight and high solubility in water.

PAM as shown in Figure 2.2 is a high molecular weight water soluble polymer of amenable to diverse chemical modifications. Inorganic coagulants and IPCs such as $\text{Al}(\text{OH})_3$ (Qian et al., 2004a; Yang et al., 2004; Zheng et al., 2007; Sun et al., 2008), PAC (Huang et al., 1994; Tzoupanos and Zouboulis, 2011), PFS (Moussas and Zouboulis, 2009; Jiang et al., 2010b), PAFC (Ma et al., 2011) and PAFSi (Wang et al., 2011a) have been used to compose with PAM to form inorganic-organic hybrid materials. With the addition of PAM in the composition of inorganic-organic hybrid materials, the bridging mechanism hence can be enhanced, which in turn improves the aggregating capacity (Tzoupanos and Zouboulis, 2011).

PDMDAAC as shown in Figure 2.3 is characterized with its cationic nature and high charge density and water solubility. The presence of allyl monomers in the molecular chain causes PDMDAAC to form a high molecular weight polymer during polymerization (Tian et al., 2006; Yu et al., 2006). PDMDAAC is not only effective in removing the pollutants from wastewater but it is also able to reduce the formation of CHCl_3 during wastewater treatment. Therefore, PDMDAAC has been selected to compose with various inorganic substances such as $\text{Al}_2(\text{SO}_4)_3$ (Li et al., 2008b; Zhang et al., 2009; Zhao et al., 2009c; Li et al., 2010; Zhao et al., 2010a; Zhang et al., 2011), FeCl_3 (Wang et al., 2008), FeSO_4 (Li et al., 2008a), PFS- FeSO_4 (Li et al., 2008a), PAC (Gao et al., 2005a; Lu et al., 2007; Li et al., 2008c; Zhang et al., 2008; Chu et al., 2010; Tzoupanos and Zouboulis, 2010; Wang et al., 2010a; Zhang et al.,

2010b; 2010c; Zhao et al., 2010b; Xiang et al., 2011), PFS (Liu and Gong, 2005; Huang et al., 2011), PFC (Gao et al., 2007a; 2008; Wang et al., 2008; Wei et al., 2009a; 2009b; 2009c; Wang et al., 2006; 2011b; 2011c) and PFAC (Sun et al., 2011a) to improve the wastewater treatment efficiency as well as to reduce the dosage of inorganic substance (Gao et al., 2007a).

In spite of increasing studies of PAM and PDMDAAC based inorganic-organic hybrid materials for coagulation-flocculation purposes, there are still tremendous species of water soluble polymers that can be adopted to prepare hybrid materials. Among them are polyamines, polyimines, polyvinylpyridines, polyacrylic acid, polyvinyl sulfonic acid, polystyrene sulfonic acid, polyethylene oxide and so forth (Tripathy and Ranjan De, 2006). In anticipation of versatile inorganic and organic possible hybrids that are yet to be explored, inorganic-organic hybrid materials pose a tremendous potential area to be studied. With a good selection of inorganic and organic components for the hybrid material; it is possible to improve the efficiency of wastewater treatment.

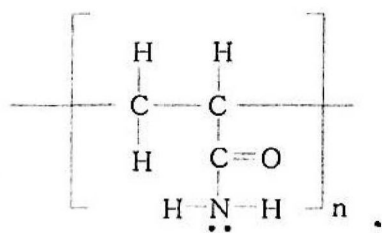


Figure 2.2 Chemical structure of polyacrylamide (PAM).

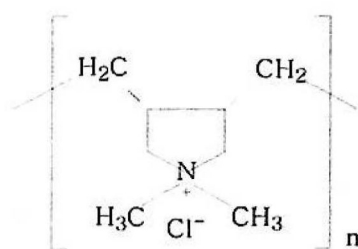


Figure 2.3 Chemical structure of polydimethyldiallyl ammonium chloride (PDMDAAC).

2.3.3 Inorganic-natural polymer hybrid materials

Considering the increasing demand over the environmental friendly materials to be applied in wastewater treatment, researchers have discovered the feasibility of several new natural polymeric materials to be composed in hybrid materials for coagulation-flocculation process. Chitosan-based hybrid materials have received diverse modifications, where several inorganic additives such as $Al_2(SO_4)_3$ (Yao et al., 2004), PAC (Huang et al., 2008b), PSAF (Wu et al., 2010), PAC-sodium silicate (Zeng et al., 2008) have been introduced to enhance the performance in wastewater treatment. Chitosan is a kind of amino-polysaccharide produced by deacetylation of chitin. It is a polymer of D-glucosamine with an NH_2 group in place of the OH group on carbon-2-of D-glucose as shown in Figure 2.4. It contains cationic charge and commonly used to remove negatively charged suspended particles in aqueous medium (Divakaran and Sivasankara Pillai, 2001; Pinotti et al., 2001; Roussy et al., 2005; Guibal and Roussy, 2007). Apart from chitosan, other naturally derived substances based on polysaccharides skeleton such as starch, guar gum, xanthan gum, sodium carboxymethyl cellulose (Tripathy and Ranjan De, 2006), pectin (Yokoi et al., 2002) and amylopectin (Rath and Singh, 1998) could be composed with inorganic substances to produce a series of new inorganic-natural polymer hybrid materials.

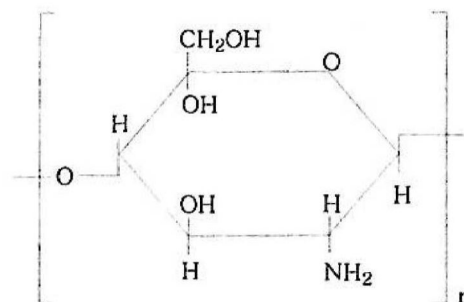


Figure 2.4 Chemical structure of chitosan.

2.3.4 Inorganic-biopolymer hybrid materials

There is another environmental-friendly hybrid material consisting of biopolymer and inorganic substance where the biopolymer is associated with inorganic coagulant to form new hybrid materials (Huang et al., 2008a, Yang et al., 2009). MBFGA1 and Pullulan are associated with PAC to form hybrid materials. MBFGA1 represents microbial flocculant GA1 which is a flocculant-producing strain identified as *Paenibacillus polymyxa* by 16S rDNA sequence in which the strain was screened from the soil (Yang et al., 2009). Pullulan is an extracellular water-soluble microbial polysaccharide by strains of *Aureobasidium pullulans*. With merits like innocuity, edibility, bio-degradability and non-polluting agent, it becomes an excellent flocculant in wastewater treatment (Yang et al., 2007a). However, biopolymers often pose limitation in flocculation performance and cultivation cost. Therefore, screening of new strains producing biopolymer with high flocculation performance and optimizing the culture condition for a higher yield has become the focus in recent years. Composing biopolymer with an inorganic substance becomes another option to reduce the dosage of biopolymer as well as to improve flocculating activity. Apart from that, biopolymer hybrids reduce the risk brought by synthetic chemical substance with reduced dosage (Huang et al., 2008a; Yang et al., 2009). There are not many reports on the development of inorganic-biopolymer hybrid materials. This indicates that it is still a tremendous potential area to be explored where more work on the isolation and screening of effective strains that can produce biopolymer should be carried out.

2.3.5 Organic-organic hybrid materials

Hybrid materials that consist of two different organic groups can be considered as a new group of hybrid material. To date, “hybrid material” is not commonly used to address this group of materials but the terms such as copolymer, grafted-polymer and chemically-modified polymer are used to represent the organic-organic hybrid. For instance, poly(acrylamide-co-acrylic acid) (Liu et al., 2000), in which it is a new group of organic monomer is introduced into the organic polymeric chain to form organic-organic hybrid materials. Although the terms copolymer, grafted-polymer as well as chemically-modified polymer have been used for decades, it is still considered as organic-organic hybrid materials where they pose a distinguished characteristics from the homopolymer after they have been hybridized.

2.3.6 Organic-natural polymer hybrid materials

There are other organic-based hybrid materials available in the literature in which other constituents are incorporated, e.g. natural polymer. The chemical combination of organic synthetic polymer with natural polymer produces organic-natural polymer hybrid materials with desirable properties of both components. These organic-natural polymers can be synthesized by grafting certain proportion of organic group into the main chain of natural polymer, e.g. SAG-g-PAM hybrid (Tripathy et al., 2001), chitosan-g-N,N-dimethylacrylamide (Tripathy et al., 2010), PAM-g-CMS (Sen et al., 2009), CMC-starch hybrid (Hebeish et al., 2010), starch-g-PAM (Mishra et al., 2011), chitosan-g-N-vinyl formamide (Mishra et al., 2008) and starch-g-PAM-co-sodium xanthate (Chang et al., 2008). Natural polymers can also hybridize one another, for instance, cationic starch-chitosan crosslinking copolymer (You et al., 2009).

2.4 Preparation of hybrid materials – an overview

There are various routes to prepare hybrid materials. The methods of preparation vary with the type of hybrid materials. To date, there is no literature has reviewed the preparation methods of hybrid materials. Generally, there are five main preparation methods, namely, hydroxylation-prepolymerization, physical blending (at ambient temperature), elevated temperature blending, copolymerization (redox polymerization) and chemical grafting/crosslinking. For structurally-hybridized materials, methods such as physical blending and elevated temperature blending, are usually used where two different natures of materials are combined into one matrix. Hydroxylation-prepolymerization, copolymerization and grafting/crosslinking are extensively used to prepare chemically-bond-hybridized materials where a new chemical group is introduced into the composition of the materials. The products which are mixed coagulant and flocculant, regardless of the nature of the materials, in one hybrid material complex are considered as functionally-hybridized materials that are able to induce coagulation-flocculation functions simultaneously. Such materials can be prepared using any one of the mentioned methods. An overview of the hybrid material preparation methods based on the current literature is discussed in the following sections.

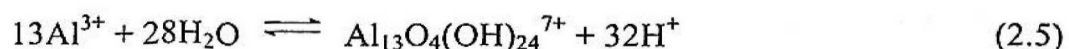
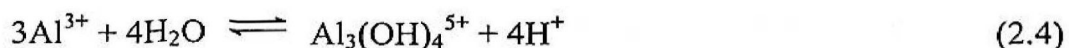
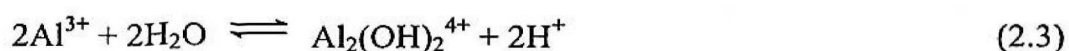
2.4.1 Hydroxylation-prepolymerization

This method is applicable to prepare inorganic-inorganic hybrid material which is one of the chemically-hybridized materials. It is commonly used to prepare polymeric aluminium and iron based hybrid materials. Zhang et al. (2004) and Tzoupanos et al. (2009) reported the formation of various aluminium species in aqueous solution. Aluminium appears as six-coordinated Al^{3+} ion at pH lower than 3.

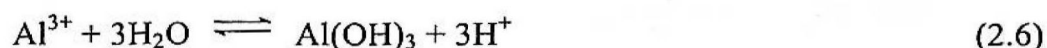
As the pH increases beyond 3, aluminium ion is hydrolyzed by OH⁻ ion and forms various species. At low concentration of OH⁻ where the ratio of OH/Al is below 0.5 and the concentration of total Al species of 10⁻² to 10⁻⁵ M, monomeric Al is formed:



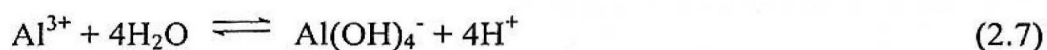
However, with the increase of OH⁻ concentration where the ratio of OH/Al is between 0.5 and 2.46, polymerization of aluminium occurs and various polymeric Al species, e.g. Al₂(OH)₂⁴⁺, Al₃(OH)₄⁵⁺, Al₁₃O₄(OH)₂₄⁷⁺ (A₁₃) are formed:



As hydrolysis and polymerization proceed, the solution of polymeric hydroxide complexes reaches a metastable state among different aluminium species and hydroxide precipitates. As the ratio of OH/Al increases over 2.5 and the concentration of total Al species is higher than 10⁻² M, polymeric species precipitate as Al(OH)₃:



While in alkaline solutions, Al(OH)₃ may convert to Al(OH)₄⁻:



As the concentration of OH⁻ ion increases in the Al solution, the hydroxylation of Al species leads to partially neutralization of Al solution and, under aging, reactions (2.1) to (2.7) may take place to certain extent that lead to the formation various of Al species. Al₁₃ is regarded as the most stable and efficient species for coagulation due to its high positive charge and molecular weight compared to other species in a partially neutralized aluminium solution. In the application of conventional