

**SYNTHESIS OF COPOLYMER POLY(*N*-ISOPROPYLACRYLAMIDE-co-
ACRYLIC ACID) HYDROGELS AS ADSORBENT FOR COPPER (II) IONS
REMOVAL IN POLYMER-ENHANCED ULTRAFILTRATION (PEUF)**

By

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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	iv
LIST OF TABLES	ix
LIST OF FIGURES	x
LIST OF PLATES	xiii
LIST OF ABBREVIATIONS	xiv
LIST OF SYMBOLS	xvi
ABSTRAK	xvii
ABSTRACT	xix
CHAPTER 1 – INTRODUCTION	
1.1 Research Overview	1
1.1.1 Polymeric Hydrogels	2
1.1.2 Polymer-enhanced Ultrafiltration and Its Application in Heavy Metal Removal	4
1.1.3 Membrane Fouling	5
1.1.4 Copper	6
1.2 Problem Statement	7
1.3 Research Objectives	9
1.4 Scopes of Study	9
1.5 Organization of the Thesis	10

CHAPTER 2 – LITERATURE REVIEW

2.1	Hazards of Copper Containing Effluents	12
2.2	Water Quality Standards for Copper Containing Effluents	13
2.3	Methods for Heavy Metal Removal	17
2.3.1	Ion Exchange	17
2.3.2	Chemical Precipitation	19
2.3.3	Electrodialysis	21
2.3.4	Adsorption	23
2.3.4 (a)	Carbon Adsorbents	25
2.3.4 (b)	Mineral Adsorbents	27
2.3.4 (c)	Polymeric Adsorbents	28
2.3.5	Adsorption Isotherm Analyses	31
2.3.5 (a)	Langmuir Isotherm Model	32
2.3.5 (b)	Freundlich Isotherm Model	34
2.3.5 (c)	Dubinin-Radushkevich Isotherm Model	35
2.3.5 (d)	Temkin Isotherm Model	37
2.4	Applications of Polymeric Hydrogels in Heavy Metal Removal	37
2.5	Polymer-enhanced Ultrafiltration (PEUF)	44
2.5.1	Metal-polymer Complexation	45
2.5.2	Membrane Filtration	46

CHAPTER 3 – MATERIALS AND METHODS

3.1	Raw Materials and Chemicals	51
3.1.1	Raw Materials	51
3.1.2	Chemicals	51

3.2	Flowchart of the Overall Experimental Works	52
3.3	Synthesis and Characterization of Polymeric Hydrogels	54
3.3.1	Synthesis of Poly(<i>N</i> -isopropylacrylamide) (PNIPAM) Hydrogels	54
3.3.2	Synthesis of Poly(<i>N</i> -isopropylacrylamide-co-acrylic acid) (PNIPAM-co-AA) Hydrogels	55
3.3.3	Fourier-Transform Infrared Spectroscopy (FT-IR)	56
3.3.4	Dynamic Light Scattering (DLS)	56
3.3.5	Transmission Electron Microscopy (TEM)	56
3.3.6	Atomic Force Microscopy (AFM)	57
3.4	Adsorption Experiments	57
3.4.1	Adsorption Capacity Study	57
3.4.3	Adsorption Kinetics	58
3.4.4	Adsorption Thermodynamics	60
3.4.5	Desorption Study	61
3.5	Membrane Performance Evaluation based on PEUF Process	62
3.5.1	Experimental Setup	62

CHAPTER 4 – RESULTS AND DISCUSSION

4.1	Synthesis and Characterization of Cross-linked PNIPAM and PNIPAM-co-AA Hydrogels	66
4.1.1	FT-IR Spectra of Hydrogels	67
4.1.2	TEM Images on Hydrogel Size with Different AA Content	69
4.1.3	Thermoresponsive study of Hydrogels	70
4.2	Copper (II) Cation Adsorption	74

4.2.1	FT-IR Spectra of Hydrogels after Cu ²⁺ Adsorption	74
4.2.2	TEM Images of Hydrogels after Cu ²⁺ Adsorption	79
4.2.3	Thermo-responsive Study on Hydrogels after Cu ²⁺ Adsorption	81
4.2.4	Effect of AA Content on Cu ²⁺ Adsorption	86
4.2.5	Effect of Solution pH on Cu ²⁺ Adsorption	87
4.2.6	Effect of Initial Cu ²⁺ Concentration on Cu ²⁺ Adsorption	90
4.2.7	Effect of Temperature on Adsorption Capacity of Hydrogels	94
4.3	Adsorption Isotherm, Kinetic and Thermodynamic Studies	95
4.3.1	Adsorption Isotherm Analyses	95
4.3.2	Adsorption Kinetics	104
4.3.3	Adsorption Thermodynamics	102
4.3.4	Desorption Test under Effect of Temperature	106
4.4	Performance Evaluation of Polymer-enhanced Ultrafiltration (PEUF)	111
4.4.1	Effect of Temperature on Permeate Flux and Rejection	112
4.4.2	Effect of Feed Flow-rate on Permeate Flux and Rejection	123
4.4.3	Effect of Initial Cu ²⁺ Concentration on Permeate Flux and Rejection	126
4.4.4	Effect of Polymeric Hydrogel Concentration on Permeate Flux and Rejection	128

CHAPTER 5 – CONCLUSIONS AND RECOMMENDATIONS		
5.1	Conclusions	132
5.2	Recommendations	137
REFERENCES		138
APPENDICES		
APPENDIX A	Sample of Calculation for Cu ²⁺ Adsorption by Hydrogels	158
APPENDIX B	Sample of Calculation for PEUF Performance	160
LIST OF PUBLICATIONS		162

LIST OF TABLES

		Page
Table 2.1	WHO guideline limits of several examples of heavy metals (WHO, 2008).	14
Table 2.2	Maximum acceptance limits of several examples of heavy metals in National Standard for Drinking Water Quality prepared by Ministry of Health Malaysia (MOH, 2004)	15
Table 2.3	Acceptance limits of heavy metals of effluents of Standard A and B (Environmental Quality Regulations, 1979)	16
Table 3.1	List of chemicals and reagents used	52
Table 4.1	Isotherm parameters for Cu^{2+} adsorption on monoolymeric PNIPAM and co-polymeric PNIPAM-co-AA hydrogels of different AA contents (10, 30 and 50 mol% AA) at temperature of 303 K and pH 5	99
Table 4.2	Isotherm parameters for Cu^{2+} adsorption on P-30 hydrogels at different temperatures (pH 5)	99
Table 4.3	Thermodynamic data K_0 and ΔG (kJmol^{-1}) for adsorption of Cu^{2+}	103
Table 4.4	Kinetic parameters for Cu^{2+} adsorption onto P-30 hydrogels (pH 5) at different initial Cu^{2+} concentrations	105
Table 4.5	Surface paramaters from AFM analysis for CA membrane surface after PEUF processes at different temperatures	121
Table 4.6	Surface paramaters from AFM analysis for CA membrane surface after PEUF processes for different P-30 hydrogel concentrations	131

LIST OF FIGURES

		Page
Figure 3.1	Flowchart of the research works	53
Figure 3.2	Schematic diagram of the experimental setup of cross-flow PEUF process	65
Figure 4.1	FT-IR spectra of PNIPAM, P-10, P-30 and P-50 hydrogels	68
Figure 4.2	Chemical structure of the cross-linked PNIPAM-co-AA hydrogel	68
Figure 4.3	Temperature-induced hydrodynamic diameter, D_h change before Cu^{2+} adsorption for (a) PNIPAM, (b) P-10, (c) P-30 and (d) P-50 hydrogels	75
Figure 4.4	FT-IR spectras of PNIPAM, P-10, P-30 and P-50 hydrogels after Cu^{2+} adsorption	78
Figure 4.5	Temperature-induced hydrodynamic diameter, D_h change after Cu^{2+} adsorption for (a) PNIPAM, (b) P-10, (c) P-30 and (d) P-50 hydrogels	85
Figure 4.6	Effect of the AA content of hydrogels on the adsorption of Cu^{2+} ($C_0 = 50 \text{ mgL}^{-1}$, $V = 250 \text{ mL}$, $M = 0.125 \text{ g}$, $T = 303 \text{ K}$)	86
Figure 4.7	Effect of the solution pH on the adsorption of Cu^{2+} onto hydrogels of different AA contents ($C_0 = 50 \text{ mg L}^{-1}$, $V = 250 \text{ mL}$, $M = 0.125 \text{ g}$, $T = 303 \text{ K}$)	89
Figure 4.8	Effect of initial Cu^{2+} concentration on (a) Cu^{2+} adsorption percentage and (b) adsorption capacity, q_e for hydrogels of different AA contents (0.5 g L^{-1} hydrogel, at pH 5)	93
Figure 4.9	Effect of initial Cu^{2+} concentration on (a) Cu^{2+} adsorption percentage and (b) adsorption capacity, q_e at different pH (0.5 g L^{-1} P-30 hydrogels)	93
Figure 4.10	Plot of adsorption capacity, q_e of P-30 as a function of C_0 at different temperatures ($V = 250 \text{ mL}$, $M = 0.125 \text{ g}$, pH = 5)	94

Figure 4.11	Comparison of different isotherm models for Cu ²⁺ adsorption onto (a) PNIPAM, (b) P-10, (c) P-30 and (d) P-50 hydrogels ($V = 250$ mL, $M = 0.125$ g, $T = 303$ K, pH = 5)	100
Figure 4.12	Comparison of different isotherm models for Cu ²⁺ adsorption onto P-30 hydrogels at different temperatures ($V = 250$ mL, $M = 0.125$ g, pH = 5)	101
Figure 4.13	Plot of $\ln K_0$ versus $1/T$	103
Figure 4.14	Adsorption kinetics of Cu ²⁺ onto P-30 hydrogels at different initial Cu ²⁺ concentrations ($V = 250$ mL, $M = 0.125$ g, $T = 303$ K, pH = 5)	104
Figure 4.15	Temperature-swing Cu ²⁺ desorption from P-30 hydrogels at: (a) pH 5, (b) pH 4 and (c) pH 3 ($V = 250$ mL, $M = 0.125$ g)	110
Figure 4.16	Effect of temperature on permeate flux at pH 5 for different loading ratio, L (50 ppm Cu ²⁺ in feed; transmembrane pressure, $\Delta P = 1.5$ bar)	116
Figure 4.17	Effect of temperature on permeate flux for 50 ppm Cu ²⁺ in feed at different pH ($L = 0.1$; 50 ppm Cu ²⁺ in feed; transmembrane pressure = 1.5 bar)	116
Figure 4.18	Effect of temperature on Cu ²⁺ rejection percentage at pH 5 for different loading ratio, L . (50 ppm Cu ²⁺ in feed; transmembrane pressure, $\Delta P = 1.5$ bar)	119
Figure 4.19	Effect of temperature on Cu ²⁺ rejection for 50 ppm Cu ²⁺ in feed at different pH ($L = 0.1$; 50 ppm Cu ²⁺ in feed; transmembrane pressure, $\Delta P = 1.5$ bar)	119
Figure 4.20	AFM images of CA membrane surface after PEUF processes at: (a) 30 °C, (b) 35 °C, (c) 40 °C, (d) 45 °C and (d) 50 °C	122
Figure 4.21	Effect of feed flowrate on (a) permeate flux and (b) Cu ²⁺ rejection for different temperatures ($L = 0.1$; pH =5; transmembrane pressure, $\Delta P = 1.5$ bar)	125
Figure 4.22	Effect of initial Cu ²⁺ concentration on (a) permeate flux and (b) Cu ²⁺ rejection (0.5 g L ⁻¹ P-30 in feed; $T = 303$ K; pH =5; transmembrane pressure, $\Delta P = 1.5$ bar)	127

Figure 4.23	Effect of P-30 hydrogel concentrations on: (a) permeate flux and (b) Cu^{2+} rejection (50 ppm Cu^{2+} in feed; $T = 303$ K; $\text{pH} = 5$; transmembrane pressure, $\Delta P = 1.5$ bar)	130
Figure 4.24	AFM images of CA membrane surface after PEUF processes for different P-30 hydrogel concentrations: (a) 0.01 g L^{-1} , (b) 0.1 g L^{-1} , (c) 0.5 g L^{-1} and (d) 0.7 g L^{-1}	131

LIST OF PLATES

		Page
Plate 3.1	Set-up for the preparation of hydrogels with water-bath and magnetic hot plate stirrer	55
Plate 4.1	TEM images for: (a) PNIPAM, (b) P-10, (c) P-30 and (d) P-50 hydrogel particles. Scale bar 500 nm	71
Plate 4.2	From left to right: PNIPAM, P-10, P-30 and P-50 hydrogel solutions	71
Plate 4.3	TEM images for: (a) P-30 hydrogel particles and (b) Cu ²⁺ loaded P-30 hydrogel particles. Scale bar 500 nm	80
Plate 4.4	TEM images for P-30 hydrogel particles after Cu ²⁺ adsorption at: (a) pH 5, (b) pH 6, and (c) pH 7. Scale bar 200 nm.	80
Plate 4.5	From left to right: PNIPAM, P-10, P-30 and P-50 hydrogel solutions after Cu ²⁺ adsorption	84

LIST OF ABBREVIATIONS

AA	Acrylic acid
AC	Activated carbon
ACRH	Activated carbon from rice hulls
AMPS	2-acrylamido-2-methyl-1-propanesulfonic acid
APS	Ammonium persulfate
BSE	Bovine spongiform encephalopathy
CA	Cellulose acetate
CMC	Carboxyl methyl cellulose
CNT	Carbon nanotube
CO	Carbonyl group
COO	Carboxylate group
COOH	Carboxylic group
CP	Concentration polarization
Cu ²⁺	Copper (II) cation
Cu(OH) ⁺	Copper (I) monohydroxide
Cu(OH) ₂	Copper hydroxide
CuSO ₄ · 5H ₂ O	Copper (II) sulphate pentahydrate
DETA	Diethylenetriamine
Dh	Hydrodynamic diameter
DLS	Dynamic light scattering
ED	Electrodialysis
EDA	Ethylenediamine
EFB	Oil palm empty fruit bunch
EPA	Environmental protection agency
FT-IR	Fourier transform infrared spectroscopy
HCl	Hydrochloric acid
HEC-g-PAA	Hydroxyethyl cellulose-g-poly(acrylic acid)
IE	Ion-exchange
IPCS	International programme on chemical safety
MA	Malei anhydride
MBA	<i>N,N'</i> -methylene-bis-acrylamide

MCLGs	Maximum contaminant level goals
MOH	Ministry of health
MSWI	Municipal solid waste incinerator
MWCO	Molecular weight cut-off
NaOH	Sodium hydroxide
NIPAM	<i>N</i> -isopropylacrylamide
NF	Nanofiltration
NH	Amine group
NPN	Nipa palm nut
OH	Hydroxyl group
OPF	Oil palm fibre
OPS	Oil palm shell
PAA	Poly(acrylic acid)
PDADMAC	Poly(diallyldimethylammonium chloride)
PEI	Polyethyleneimine
PEPEI	Partially ethoxylated polyethylenimine
PES	Polyethersulfone
PEUF	Polymer-enhanced ultrafiltration
PPN	Palmyra palm nut
PVSA	Poly(vinyl sulfonic acid)
SiOH	Silanol
SiOSi	Siloxane
SO ₃ H	Sulfonic acid
TETA	Triethylenetetraamine
TS-SPE	Temperature-swing solid-phase extraction
VPT	Volume phase transition
VPTT	Volume phase transition temperature
WHO	World Health Organization

LIST OF SYMBOLS

ΔP	Transmembrane pressure gradient
ΔC	Concentration gradient
ΔE	Electrical potential gradient
ΔT	Temperature gradient
D_h	Hydrodynamic diameter
C_0	Initial concentration of copper (II) cations in solution
C_e	Equilibrium concentration in solution
C_{e0}	Initial equilibrium Cu^{2+} concentration at 25 °C (desorption)
C_{eT}	Equilibrium Cu^{2+} concentration at temperature T (desorption)
M	Dry mass of adsorbent
V	Total volume of solution
q_e	Equilibrium adsorption capacity
q_m	Maximum equilibrium capacity
q_t	Equilibrium adsorption capacity at time t
K_L	Langmuir constant
K_F	Freundlich constant
K_T	Temkin constant related to heat of adsorption
R	Rejection
J	Permeate Flux

**SINTESIS HIDROGEL KOPOLIMER POLI(*N*-ISOPROPILAKRILAMIDA-
ko-ASID AKRILIK) SEBAGAI PENJERAP ION KUPRUM (II) DALAM
PENURASAN ULTRA TERTINGKAT BERPOLIMER (PEUF)**

ABSTRAK

Dalam kajian ini, hidrogel bertautsilang poli(*N*-isopropilakriamid) (PNIPAM) yang bersifat monopolimer dan poli(*N*-isopropilakrilamid-ko-asid akrilik) (PNIPAM-ko-AA) yang bersifat ko-polimer dengan kandungan asid akrilik (AA) yang berbeza (10, 30 dan 50 mol%) telah berjaya disediakan melalui kaedah pemolimeran radikal bebas. Sifat-sifat fizikal hidrogel-hidrogel termasuk sifat terma-responsif sebelum dan selepas penjerapan Cu^{2+} telah dinilai dengan menggunakan spektroskopi inframerah terubah fourier (FT-IR), penyerakan cahaya dinamik (DLS) dan mikroskop elektron penghantaran (TEM). Penambahan kandungan AA telah menyebabkan peningkatan dalam saiz zarah-zarah yang ditunjukkan oleh keputusan DLS and imej-imej TEM. Kesan histerisis yang semakin menonjol juga diperhatikan daripada graf-graf perubahan diameter dinamik (D_h) dengan penambahan kandungan AA. Hidrogel-hidrogel yang mengandungi 30 mol% AA (P-30) mempunyai kapasiti penjerapan (q_e) yang optimum pada pH 5 tanpa pemendakan $\text{Cu}(\text{OH})_2$. Data-data penjerapan hidrogel P-30 didapati sepadan dengan model isoterma Langmuir yang berhubungan dengan penjerapan lapisan tunggal. Magnitud-magnitud E yang dikira daripada model isoterma Dubinin-Radushkevich (DR) menandakan peralihan mekanisme penjerapan daripada penjerapan fizikal bagi PNIPAM ke penjerapan secara kimia bercampurkan pertukaran ion dengan penambahan kandungan AA. Kapasiti penjerapan maksimum (q_m) untuk P-30 yang dikira daripada model Langmuir ialah $68.8705 \text{ mg g}^{-1}$ pada suhu 323 K. Suhu mempunyai kesan yang boleh

diabaikan terhadap nyah-penjerapan Cu^{2+} daripada hidrogel-hidrogel disebabkan daya penjerapan secara kimia yang kuat. Data-data kinetik hidrogel P-30 mematuhi model kinetik pseudo tertib kedua dan resapan intra-zarah. P-30 yang mempunyai keupayaan penjerapan yang optimum telah dipilih sebagai penjerap polimer dalam penurasan ultra tertingkat berpolimer (PEUF). Keputusan eksperimen menampilkan peningkatan fluks penelapan dengan suhu yang meningkat disebabkan oleh pembentukan gumbulan-gumbulan hidrogel di atas permukaan membran dan interaksi hidrofobik semakin mendominasi pada suhu operasi tertingkat. Pada nisbah muatan suapan (L) yang lebih tinggi, penolakan menurun dengan suhu. Pada L yang lebih rendah, penolakan adalah terbebas daripada pengaruh perubahan suhu kerana ketumpatan zarah-zarah hidrogel semakin menaik dan mempertingkatkan penjerapan serta kesan pengutuban kepekatan pada permukaan membran. Peningkatan dalam kepekatan awal Cu^{2+} telah mengakibatkan kejatuhan pada fluks penelapan dan penolakan. Kepekatan hidrogel pula mempunyai pengaruh yang menonjol untuk mempertingkatkan penolakan Cu^{2+} , tetapi kepekatan hidrogel yang meningkat juga dapat menjejaskan fluks penelapan. Pada kesimpulannya, penjerap hidrogel yang disintesis adalah terma-responsif dan sifat tersebut boleh diaplikasi untuk meringankan masalah kotoran membran dalam proses PEUF.

SYNTHESIS OF COPOLYMER POLY(*N*-ISOPROPYLACRYLAMIDE-co-ACRYLIC ACID) HYDROGELS AS ADSORBENT FOR COPPER (II) IONS REMOVAL IN POLYMER-ENHANCED ULTRAFILTRATION (PEUF).

ABSTRACT

In this study, monopolymeric poly(*N*-isopropylacrylamide) (PNIPAM) and copolymeric Poly(*N*-isopropylacrylamide-co-acrylic acid) (PNIPAM-co-AA) cross-linked hydrogels with different acrylic acid (AA) content (10, 30 and 50 mol %) were successfully prepared via free radical polymerization method. The physical properties of hydrogels including their thermo-responsiveness properties before and after Cu²⁺ adsorption were characterized by fourier transform infrared spectroscopy (FT-IR), dynamic light scattering (DLS) and transmission electron microscopy (TEM). The increasing AA content caused the increase in particle size as shown by DLS results and AFM images. More pronounced hysteresis effect was also observed on the graphs of hydrodynamic diameter (D_h) change with increasing AA content. Hydrogels with 30 mol % AA (P-30) was found to have the optimum adsorption capacity (q_e) at pH 5 without precipitation of Cu(OH)₂. Adsorption data of P-30 hydrogels were best fitted with Langmuir isotherm model corresponding to monolayer adsorption. The E magnitudes calculated from Dubinini-Radushkevich (D-R) isotherm model indicated the transition of adsorption mechanism from physisorption for PNIPAM to the mixed chemisorption and ion exchange with the increase in AA content. The maximum adsorption capacity (q_m) of P-30 calculated from Langmuir model is 68.8705 mg g⁻¹ at 323 K. Temperature had negligible effect on the desorption of Cu²⁺ from hydrogels due to the strong chemisorptions force. The kinetic data of P-30 hydrogels follows the pseudo-second-order kinetic model and

intra-particle diffusion. P-30 hydrogels with optimum adsorption performance was selected as the polymeric adsorbent in polymer-enhanced ultrafiltration (PEUF). The experimental results revealed that the permeate flux increased with increasing temperature due to the formation of hydrogel lumps on the membrane surface and hydrophobic interactions had gradually dominated at elevated operating temperature.. At higher loading ratio (L), the rejection is decreasing with temperature. At lower L , the rejection is getting independent of temperature change as the density of hydrogels is getting higher which helps enhancing both adsorption and concentration polarization effect on membrane surface. The increase in initial Cu^{2+} concentration has caused decline in both permeate flux and rejection. Hydrogel concentration had profound influence in enhancing Cu^{2+} rejection but increasing concentration of hydrogel could also impair the permeate flux. In conclusion, the synthesized hydrogel adsorbent is thermal responsive and this characteristic could be employed to mitigate the membrane fouling problem in PEUF process.

CHAPTER ONE:

INTRODUCTION

1.1 Research Overview

Polymeric materials such as hydrogels and micelles that contain metal-binding ligands (functional groups) are always applied as adsorbents or chelators for complexing metal ions in aqueous. The macromolecules of metal-polymer complexes formed are sufficiently large to be retained by UF membranes and to achieve higher permeate flux than that for RO and NF membranes due to larger pores. This integrated process for removing metal ions by combination of both adsorption and UF separation is manifested as polymer-enhanced ultrafiltration (PEUF) (Barakat and Schmidt, 2010, Cañizares *et al.*, 2005, Almutairi and Lovitt, 2012). The PEUF is a promising method for the selective removal of heavy metal from aqueous solutions. Nevertheless, PEUF is vulnerable to membrane fouling that leads to the permeate flux decline owing to the interactions of metal-polymer complex macromolecules with the membranes and concentration polarization on the membrane surfaces (Porter, 1990, Palencia *et al.*, 2009, Almutairi and Lovitt, 2012).

The membrane fouling could be reduced by using thermo-responsive polymeric hydrogels with tunable hydrophilicity as a function of temperature. The solute-membrane interactions can be avoided by reducing the hydrophilicity of the hydrogels at increasing temperature. This mechanism is expected to enhance the permeation flux and rejection of the metal ions simultaneously (Morris *et al.*, 1997, Yamashita *et al.*, 2003, Palencia *et al.*, 2009).

1.1.1 Polymeric Hydrogels

Polymeric hydrogels are a group of polymers or co-polymers with three-dimensional cross-linked structures that exhibit volume phase transition (VPT) in response to the change in external stimuli such as temperature, solution pH, electrical field and ionic strength. Hence, sometimes such hydrogels are termed as ‘smart’ or ‘intelligent’ gels corresponding to its swelling behaviour responsive under the effect of stimulus (Saunders and Vincent, 1999, Pelton, 2000, Ballauff and Lu, 2007).

The VPT process is characterized by the ability of these cross-linked hydrogel networks to absorb (swelling) and release (shrinking) water in aqueous solution. These cross-linked hydrogel networks consist of a polymer backbone (polymer chains) and a cross-linking agent that help maintain the elasticity and prevent the hydrogel from dissolving in water. The water-imbibing ability is contributed by the hydrophilic functional groups such as amide (-CONH₂), carboxylic (-COOH) and hydroxyl (-OH) present in the hydrogel structures. These functional groups also possess ion-recognition which provides most polymeric hydrogels with ion-chelating or ion-binding ability including heavy metal ions with multivalent charges (Wu and Zhou, 1997, Morris *et al.*, 1997, Fernandez-Nieves *et al.*, 2000, Shibayama *et al.*, 1999). The first batch of stimuli-responsive hydrogels was synthesized, characterized and reported by Pelton and Chibante (1986). The hydrogels they produced are thermo-responsive and homogeneous poly(*N*-isopropylacrylamide) (PNIPAM) which had been used in various applications in many areas such as biomedical engineering, drug delivery and wastewater treatments (Ma *et al.*, 2004, Ballauff and Lu, 2007, Gibas and Janik, 2010, Saha *et al.*, 2011)

These thermo-responsive hydrogels exhibit phase transition above their volume phase transition temperature (VPTT). Below the VPTT, the hydrogels are hydrophilic and water is absorbed to cause swelling due to the formation of hydrogen bonds between water molecules with the functional groups in the hydrogels. As temperature increases above VPTT, water is expelled from the hydrogel matrices as water-related hydrogen bonds are broken (Morris *et al.*, 1997, Saunders and Vincent, 1999, Pelton, 2000, Ballauff and Lu, 2007, Burmistrova *et al.*, 2011). The hydrogels could be synthesized by various free-radical polymerizations (FRP) that involve the generation of radicals to initiate the polymerization. Among all, the most widely used FRP technique for hydrogel synthesis is precipitation polymerization. The recipe of the polymerization is generally constituted by three integral components namely: monomers, cross-linking agents and initiators.

The properties of the hydrogels can also be adjusted by incorporation of co-monomers with functional groups into the hydrogel networks such as acids or alkalines. These functional co-monomers enable the increase in density of surface charges of the hydrogel particles for more stable dispersions. Meanwhile, the co-monomers also introduce the ion-recognition functionalities in the hydrogels to enhance the ion-binding ability including metal ions (Morris *et al.*, 1997, Sharaf *et al.*, 2009, Burmistrova *et al.*, 2011).

1.1.2 Polymer-enhanced Ultrafiltration and Its Application in Heavy Metal Removal

Heavy metal ions are usually di- or multivalent cations having molecular weights that are too low to be retained by the UF membranes with the pore-size range of 0.1 – 0.01 μm . In order to increase the effectiveness of the UF process on metal ion retention, it has to be integrated with the complexation of metal-polymer. The complexation refers to an adsorption process of metal ions by ligands which are ionic polymers with metal-binding functionalities. It is a pre-treatment in which the targeted metal ions in feed solutions are initially enhanced in size and molecular weight via adsorption by the polymeric adsorbents to form metal-polymer complexes for increasing both selectivity and metal rejection of the UF process. Hence, the overall combination process is known as polymer-enhanced ultrafiltration (PEUF) (Cheryan, 1986, Porter, 1990, Labanda *et al.*, 2009).

Since the concept of using ionic polymers to retain metal ions in UF was first proposed in 1960s, there had been plenty of studies on different polymers as metal ion adsorbents in PEUF. Among all attempted polymeric materials, water-soluble polyethylenimine (PEI) which contain high density of metal-chelating amine (-NH₂) and hydroxyl (-OH) groups has been the most common polymeric adsorbent for PEUF studies. Researchers such as Camarillo *et al.* (2012), Cañizares *et al.* (2002, 2008), Uludag *et al.* (1997), İslamoğlu and Yilmaz (2006), Labanda *et al.* (2009) and Almutairi *et al.* (2012) had extensively studied the feasibility of hydrophilic PEI and its derivatives as metal-chelating polymers in PEUF. Acidic polymers such as poly(vinyl sulfonic acid) (PVSA) and poly (acrylic acid) (PAA) containing sulfonyl hydroxide and carboxylic groups, respectively with high metal-chelating capacity

have also been utilized for enhancing molecular weights of metal ions in PEUF processes (Palencia *et al.*, 2009, Labanda *et al.*, 2009, Camarillo *et al.*, 2010).

There some advantages of using these hydrophilic polymers for metal ion adsorption include good adsorption kinetics which refers to high rate of adsorption and the maximum utilization of their adsorption capacity. Nevertheless, the major drawback behind PEUF is the high tendency of metal-polymer complex macromolecules to interact with the membranes that can lead to membrane fouling via the occurrence of concentration polarization (CP) onto active layer of UF membrane. This resulted in permeate flux decline in most of the PEUF studies (Muslehiddinoglu *et al.*, 1998, Rivas *et al.*, 2011, Palencia *et al.*, 2009, Llanos *et al.*, 2008, Almutairi and Lovitt, 2012).

1.1.3 Membrane Fouling

In general, the major drawback of most membrane filtration processes including UF is none other than membrane fouling. This membrane fouling is a mechanism affected by several factors such as feed composition, membrane materials and operating parameters. The mechanism of membrane fouling can basically be classified into two major regimes namely: irreversible and reversible fouling (Cheryan, 1986, Porter, 1990, Palencia *et al.*, 2009, Wang *et al.*, 2011).

The irreversible fouling is induced by the interactions of solutes with the membrane surface or within the membrane porous matrices. These solute-membrane interactions can in turn cause the reduction in membrane porosity and hydrophilicity as well as increase in membrane thickness and surface roughness. Pore-blocking is the most common type of irreversible fouling in which the solutes are captured

within membrane pores via adsorption among functionalities of membrane and solutes (Cheryan, 1986, Susanto and Ulbricht, 2009, Palencia *et al.*, 2009).

The reversible fouling refers to the accumulation of solutes on the membrane surfaces promoted by the solute-solute interactions. Since the interactions among solutes are pre-dominating in this fouling scenario, it is highly dependent on parameters including solute concentration, transmembrane pressure and pH. At high solutes concentration, the solute particles tend to agglomerate by electrostatic interactions and the solute concentration on the membrane surface rises to the gel precipitation point. Consequently, a gel cake layer is formed as a “secondary membrane” which increases the resistance to the hydraulic flow resulting in permeate flux decline. In most cases, the reversible fouling mechanism is also termed as concentration polarization (CP) (Porter, 1990, Susanto *et al.*, 2009, Palencia *et al.*, 2009, Wang *et al.*, 2011).

1.1.4 Copper

Copper is a type of heavy metals that are generally defined as elements having atomic weight within the range from 63.5 to 200.6 g mol⁻¹ with specific gravity > 5.0 (specific density > 5 g cm⁻³). Copper are usually discharged into the surface water bodies like rivers, lakes and ground water due to the rapid development in certain industrial activities such as metal plating, mining, refineries, textile, automobile, batteries manufacturing and so forth (Srivastava and Majumder, 2008, Al-Ghouti *et al.*, 2004, Hawari and Mulligan, 2006).

The common source of Cu²⁺ cations for adsorption study is a blue crystalline of copper (II) sulphate pentahydrate (CuSO₄ 5H₂O). This crystalline solid dissolves

in water to give aquo complex ion $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ instead of purely Cu^{2+} . These hexaaquocopper divalent complex cations bind with anionic chelator to form complexes. Hence, when the carboxyl group (COO^-) of AA moieties bind with the cation, one of the H_2O molecules coordinated with the Cu^{2+} is replaced to form chelator-copper cationic complex $[\text{COOCu}(\text{H}_2\text{O})_5]^+$. The coordination of the remaining H_2O molecules with complex nuclear, Cu^{2+} had contributed pronouncedly in the expansion of the copper-loaded hydrogel particle (Sham *et al.*, 1980).

1.2 Problem Statement

Poly(*N*-isopropylacrylamide) (PNIPAM) is a type of thermo-sensitive globular polymeric gel which exhibits thermo-reversible phase transition from solvated gel (swollen) to collapsed globule (shrunken) conformation at above its volume phase transition temperature (VPTT). It has been attracting extensive attention from many researchers due to its thermo-sensitive shrinking-swelling characteristic that is potential in the application of metal ion recognition in aqueous solutions. This is because the amine ($-\text{NH}_2$) and the carbonyl ($-\text{C}=\text{O}$) groups present in NIPAM moieties of PNIPAM contribute to the conformational change via formation of hydrogen bonds, and they could also act as ligands for binding metal ions in aqueous solutions. Nevertheless, the metal adsorption capacity of these pure monopolymeric PNIPAM hydrogels is limited by their fixed VPTT and the density of functional groups available for metal-binding (Tokuyama and Iwama, 2007, Ju *et al.*, 2009).

Hence, for more favourable adsorption, acidic co-monomer, acrylic acid (AA) is co-polymerized with NIPAM monomer to enhance the adsorption capability by

achieving the following improvements: a) introduce strong metal-binding functionalities on the polymer backbone of PNIPAM, b) increase the surface charge density of the hydrogel to improve particle dispersion (stability) as well as surface adsorption of metal ions, c) increase the VPTT of hydrogels for wider range of temperatures available for metal adsorption, d) impose dual-stimuli-responsiveness (temperature and pH) on hydrogels (Morris *et al.*, 1997, Saunders and Vincent, 1999, Yamashita *et al.*, 2003, Ju *et al.*, 2008, Burmistrova *et al.*, 2011). However, the incorporation of higher AA content into the hydrogel could increase the tendency for the agglomeration of hydrogels into colloids which impaired the adsorption efficiency. Furthermore, higher AA density could also induce formation of more hydrogen bonds. Thus, the detailed investigation on this impact is necessary to be carried out and AA content is optimized.

Membrane fouling is always the main deficiency that reduces the feasibility of PEUF in the application of heavy metal removal as it raises costs in energy consumption, membrane operation and maintenance. The utilization of the thermo-responsive PNIPAM and PNIPAM-co-AA hydrogels is expected to prevent serious pore-blocking. This is because their shrinking behaviour at high temperature causes water to be released and the inner interactions formed among functional groups within hydrogel networks could prevent the interactions between hydrogels and membrane. Nevertheless, at higher AA content and temperature, the agglomeration of hydrogel particles may lead to the concentration polarization (CP) on the membrane surface (Llanos *et al.*, 2008, Labanda *et al.*, 2009, Palencia *et al.*, 2009, Bade and Lee, 2011, Almutairi and Lovitt, 2012, Camarillo *et al.*, 2012). Hence, the effects of experimental parameters such as temperature, pH and hydrogel concentration are studied and optimized to avoid possible membrane fouling.

1.3 Research Objectives

The objectives of this study are outlined as followed:

- 1) To synthesize and characterize monopolymeric PNIPAM and co-polymeric PNIPAM-co-AA hydrogels with different AA content.
- 2) To evaluate the adsorption capability, mechanism and kinetic of hydrogels towards model copper ion.
- 3) To investigate the effect of thermo-responsiveness of hydrogels on the copper removal and membrane flux in PEUF system.
- 4) To determine the fouling phenomenon of thermo-responsive hydrogels on hydrophilic membrane under varied temperature.

1.4 Scopes of Study

Monopolymeric PNIPAM and co-polymeric PNIPAM-co-AA hydrogels with different AA contents (10, 30 and 50 mol %) were synthesized via free-radical polymerization technique. The presence of functional groups and thermo-responsive behaviour of the hydrogels were characterized by fourier transform infrared spectroscopy (FT-IR), dynamic light scattering (DLS) and transmission electron microscopy (TEM). Then, the copper adsorption abilities of the hydrogels were evaluated and the adsorption capacities of hydrogels were obtained under effects of different paramaters.

The adsorption isotherm analyses were also carried out to study the adsorption mechanism for all hydrogel samples at constant temperature by fitting the

adsorption data to different isotherm models. In addition, the adsorption kinetics and thermodynamic studies were performed to justify the rate of adsorption, adsorption mechanism as well as the temperature effect on adsorption efficiency of the hydrogels. The hydrogels with optimum adsorption performance was selected as adsorbent in the subsequent PEUF tests. The PEUF processes were carried out under effects of different experimental parameters including temperature, pH, initial Cu^{2+} concentration and hydrogel concentration to obtain the optimized experimental conditions.

1.5 Organization of the Thesis

There five chapters in this thesis that covers the introduction, literature review, materials and methods, results and discussion, while the conclusions and recommendations were the last chapter.

Chapter one outlined the utilization of polymeric hydrogels as metal adsorbents in PEUF process. Problem statement was highlighted based on the limitations of metal adsorption by hydrogels in PEUF and suggestions to mitigate the problems. It was followed by a list of objectives corresponding to the main purpose of this research project. The organization of the thesis presented the highlighted content of each chapter.

Chapter two presents a review of various research works reported in the literature of this research area. First, a review on various conventional techniques for the removal of copper cations from wastewater was discussed. Then, the different of commonly used copper adsorbent materials were reviewed. Subsequently, the synthesis of polymeric hydrogels and their application in heavy metal removal were

described and highlighted. At the end of this chapter, the polymer-enhanced ultrafiltration and their development was discussed.

Chapter three elaborated the experimental materials and methodology. The laboratory-scale procedure of hydrogel synthesis and characterization were discussed. Then, the adsorption studies, adsorption isotherm models, adsorption kinetic models and thermodynamics were described. The details information on experimental procedure and overview of the experimental work flow were summarized in a flowchart. The equipment used, the procedure of the adsorption tests were reported and the set-up for PEUF experiments was illustrated in a schematic diagram. The required equations for data analyses were also provided.

Chapter four presents all the experimental results that include the characterization, adsorption analyses and the membrane test sections. The characterization section consists of FT-IR spectra, hydrodynamic diameter change curves and the TEM images of hydrogels and their respective explanation. The adsorption section refers to the equilibrium adsorption tests, adsorption isotherm analyses, adsorption kinetic and thermodynamic analyses. Then, the membrane section contains the PEUF results under effects of various parameters and discussion on the performance.

Chapter five contains the conclusions and several recommendations for the future research. The conclusions of the research project were established according to the outlined objectives and the recommendations for the related research in the future were provided.

CHAPTER TWO:

LITERATURE REVIEW

2.1 Hazards of Copper Containing Effluents

Heavy metal are usually discharged into the surface water bodies like rivers, lakes and ground water due to the rapid development in certain industrial activities such as metal plating, mining, refineries, textile, automobile, batteries manufacturing and so forth (Srivastava and Majumder, 2008, Al-Ghouti *et al.*, 2004, Hawari *et al.*, 2006).

Heavy metals are toxic contaminants that tend to accumulate in bodies of living organisms especially humans. The dissolved heavy metal concentrations in the stream of industrial effluents exceeding the trace quantities are carcinogenic. They can cause adverse health effects to both humans and aquatic organisms in water bodies as a consequence of prolonged exposure through consuming heavy metal contaminated water often due to the food chain effect (Susana *et al.*, 2005, Theofanis *et al.*, 2001).

In aquatic environment, heavy metal is usually distributed as in the forms of: water-soluble ion species, colloids, suspended solids or sediments. Unlike organic pollutants, heavy metals are non-biodegradable owing to the facts that their rigid atomic and molecular structures of heavy metal species cannot be decomposed by microbes. Instead, they are usually accumulated in sediments by microorganisms or other compounds in water (Salomons and Stigliani, 1995).

There are numbers of heavy metals available in industrial applications including the following highly toxic examples: leads (Pb), zinc (Zn), cadmium (Cd), chromium (Cr), cobalt (Co), mercury (Hg) and arsenic (Ar). However, in this section, the hazards of targeted metal in our study, copper (Cu), is discussed in details. Copper is considered as an essential nutrient for both plants and animals due to its important functions in sustaining the enzymatic and metabolic processes in the bodies of organisms. Ironically, excessive level of copper uptake can result in detrimental effects to lives (Bremner, 1998).

Georgopoulos *et al.* (2001) had concluded that humans are primarily exposed to copper through the consumption of food and drinking water (about 20 – 25 % of copper intake is from drinking water). Some studies had also proven that high level of copper intake is related to certain neurological disorders. Llanos and Mercer (2002) associated copper toxicity indirectly to Alzheimer's diseases and several prion diseases including bovine spongiform encephalopathy (BSE) which is also commonly known as mad cow disease.

2.2 Water Quality Standards for Copper Containing Effluents

World Health Organization (WHO) had established guidelines for drinking water quality to ensure the public health and safety. Several examples of heavy metal contaminant guideline limits from the WHO Guidelines for Drinking Water Quality 2008 are summarized in Table 2.1:

Table 2.1: WHO guideline limits of several examples of heavy metals (WHO, 2008)

Heavy Metal	Guideline Value (mg L⁻¹)	Remarks
Arsenic	0.01	
Cadmium	0.003	
Chromium	0.05	For total chromium
Copper	2.0	From staining of laundry and sanitary ware may occur below guideline value
Lead	0.01	
Nickel	0.07	

According to WHO Drinking Water Guidelines, the copper content in our drinking water can be originated from a wide range of sources, but the corrosion of copper-made piping system is considered to be the primary source which can account for the copper concentrations in drinking water ranging from ≤ 0.005 to > 30 mg L⁻¹. The upper limit of the acceptable range for oral intake of copper in adults concluded in the International Programme on Chemical Safety (IPCS) held by WHO still remained uncertain, but IPCS suggested that it is probably in the range of 2 or 3 mg day⁻¹ in adults (IPCS, 1998, WHO, 2008). Drinking Water Standards and Health Advisories published by Environmental Protection Agency (EPA) of United States, provides another parameter as guideline values for the various contaminants in drinking water known as Maximum Contaminant Level Goals (MCLGs). The MCLGs of copper in tap water is suggested to be 1.3 mg L⁻¹ (EPA, 2012).

In Malaysia, the authorized guideline for drinking water standard should refer to the National Standard for Drinking Water Quality prepared by Engineering

Service Division, Ministry of Health Malaysia in 1983 and its revision in 2004. In this national guideline, heavy metals are categorized as inorganic parameters and their maximum acceptance levels in drinking water are shown in Table 2.2:

Table 2.2: Maximum acceptance limits of several examples of heavy metals in National Standard for Drinking Water Quality prepared by Ministry of Health Malaysia (MOH, 2004)

Metals	Maximum Acceptance Values (mg L⁻¹)
Iron	0.3
Aluminium	0.2
Mercury	0.001
Cadmium	0.003
Lead	0.01
Copper	1.0
Zinc	3.0

On top of that, another authorized standard guideline known as Malaysia Environmental Quality (Sewage and Industrial Effluent) Regulations had also been established in 1979 according to the Environmental Quality Act, 1974 which functions as a set of law to regulate the water quality of effluents from both public sewage and industrial water treatment plants. The regulations had been revised twice in 1999 and 2000. Two standards of parameter limits are applied for different discharging sources of effluent namely: Standard A and B. The effluents discharged upstream of the water catchment area should refer to Standard A, whereas the

effluents discharged downstream must fulfill Standard B. Both Standard A and B for heavy metals in the schedule are presented in Table 2.3:

Table 2.3: Acceptance limits of heavy metals of effluents of Standard A and B [Environmental Quality (Industrial Effluent) Regulations, 2009]

Metals	Standard A (mg L⁻¹)	Standard B (mg L⁻¹)
Mercury	0.005	0.05
Cadmium	0.01	0.02
Chromium (VI)	0.05	0.05
Chromium (III)	0.2	1.0
Arsenic	0.05	0.1
Lead	0.1	0.5
Copper	0.2	1.0
Zinc	2.0	2.0
Iron	1.0	5.0

2.3 Methods for Removal of Heavy Metals

Heavy metals could exist as arbitrary forms in aqueous solutions ranging from dissolved ions carrying charges to solid phase precipitates depending on solution pH, metal concentration and other variables. This means the chemical and physical properties of heavy metals in aqueous solution are changeable by varying the variables. Hence, an efficient separation process of heavy metals from aqueous solution should have certain characteristics includes high selectivity, high removal capacity and wide range of tolerance on the influential variables such as solution pH. Several techniques have been commonly employed to separate heavy metals from aqueous solutions including ion-exchange, chemical precipitation, electrodialysis and adsorption.

2.3.1 Ion Exchange

Ion exchange is a process involving an exchange of ions between an electrolyte solution (aqueous phase) and ions of identical charge being immobilized in an insoluble ion exchange material (usually refers to a solid matrix). As the functional groups of the solid materials are negatively charged, the exchange involves cations and vice versa. The process takes place through a stoichiometric reversible reaction, where equivalent amounts of ions of identical charges from an electrolyte solution are exchanged with exchangeable cations or anions carried by the functional groups of the ion-exchange materials (Helfferich, 1995, Inamuddin and Luqman, 2012, Nasef, 2008). Ion exchange method is widely used to remove heavy metal ions from wastewater due to its several important advantages such as: high

nadsorption capacity, fast kinetics and easily prepared ion-exchangers especially resins (Kang *et al.*, 2004).

Ion exchangers are materials containing functional groups on the fixed ionic sites, which exhibit ion-exchange properties by allowing the adsorption of oppositely charged ions into their framework structures through ionic bonds. They are sometimes, called polyions. As a result, the adsorption process by the ion-exchange materials is always dependent on several variables including concentration of free ions, solution pH and amount of ion-exchangers. Ion-exchangers are usually available in various types of solids depending on their physical forms, functional groups of their fixed ionic sites and the nature of the materials (Helfferich, 1995, Nasef, 2008).

However, there are some serious drawbacks arose from using this method including resin fouling caused by the organic contamination. The traces of organic particulate matters such as some microorganisms and other dissolved organic impurities present in the wastewaters could be irreversibly adsorbed onto the ion-exchangers. This could foul the resin structures and impair the ion-exchange capacity of resins which prevent the regeneration of resins. Apart from that, strong acids commonly applied for regenerating the used resins especially sulphuric acid, could easily induce formation of salt precipitates with mineral cations in the solution which clogs the resins and hinders ion-exchange processes. In addition, the formation of metal hydroxides precipitate at high pH ($> \text{pH } 5$) could also result in resin fouling via blocking the porous structures of resin beads (Reichenberg, 1953, Clearfield, 1988, Helfferich, 1995, Inamuddin and Lugman, 2012).

Veli and Pekey (2004) utilized two types of styrene-typed gel resins, Dowex HCR S/S and Dowex Marathon for adsorption of Cu^{2+} cations from aqueous solutions. Both resins contain high density of sulfonic group ($-\text{SO}_3\text{H}$) which is the strong cation-exchange functional group. The results obtained elucidated that the adsorption percentage increased with increasing pH, contact time, initial Cu^{2+} concentration and resin amount. However, Dowex Marathon has higher adsorption capacity than Dowex HCR S/S owing to the higher sulfonic group content in Dowex Marathon resins carrying more exchanger cations, Na^+ for Cu^{2+} .

Chandramohan and Marimuthu (2011) applied synthetic Amberlite as acidic ion-exchange resin for the adsorption of Cu^{2+} from aqueous solutions. Their results showed that the adsorption is directly related to the pH, contact time and dosage of resin. The experimental data was best fitted into the Redlich – Peterson isotherm model which is the combination model of both Langmuir and Freundlich models. This indicated both monolayer and multilayer adsorption had taken place on the surface of resin. The optimum pH was found to be pH 5 and the duration needed for achieving equilibrium was around 100 minutes.

2.3.2 Chemical Precipitation

Chemical precipitation is a simple and widely used process that involves oxidation or reduction of heavy metal ions by selective metal precipitants to convert the metal ions into insoluble metal species (metal salts) in aqueous solution such as insoluble metal hydroxides, sulfides, carbonate, phosphates and oxides. The precipitates can be easily removed from solution by filtration or sedimentation. Among these species, hydroxide precipitation is the most commonly adopted process

in industrial wastewater treatment owing to its simplicity in operation and low-cost basic precipitants with wide availability such as lime and sodium hydroxide (NaOH) (Peters *et al.*, 1985, Lewis, 2010, Fu and Wang, 2011).

The precipitation process of insoluble metal salts can be described by a two-step mechanism of crystallization: a) nucleation and b) crystal growth. At the nucleation stage, the metal salt molecules start to agglomerate into clusters to form stable crystalline nuclei. These nuclei could grow further into larger crystals until the formation of precipitates. The supersaturated concentration of the metal salt acts as the driving force along the precipitation process. Hence, the precipitation is determined by the solubility of metal salt in aqueous solution which is also a strong function of metal salt concentration and pH (Peter *et al.*, 1985, Patterson, 1988, Gregory and Duan, 2001, Blais *et al.*, 2008). Simplicity is the main factor contributes to the feasibility of precipitation in the treatment of effluent containing heavy metals. However, the process also has certain disadvantages that could impair the metal removal efficiency. For instance, the precipitation can be hindered by some metal-chelating impurities present in the wastewaters that have high affinity towards metal ions. Moreover, the precipitation of solid metal salts generates large quantity of sludge that causes disposal problem. In addition, certain metal precipitants are harmful especially sulphide precipitating agent such as hydrogen sulphide (H₂S) exists as toxic gas at low pH (< pH 3) and therefore the sulphide precipitation is usually performed under neutral condition (Lewis, 2010, Fu and Wang, 2011).

Mirbagheri and Hosseini (2005) used Ca(OH)₂ and NaOH as precipitating agents for the removal of hydroxide species of Cu²⁺ and Cr⁶⁺ cations from petrochemical wastewater. First, they used ferrous sulphate for the reduction of Cr⁶⁺ to Cr³⁺, then it was followed by the addition of Ca(OH)₂. Their experimental results

showed that maximum precipitation of Cr^{3+} cations occurred at pH 8.7 and the concentration of Cr^{3+} was successfully reduced from 30 to 0.01 mg L^{-1} . Then, the maximum copper precipitation took place at about pH 12 for both Ca(OH)_2 and NaOH . The concentration of Cu^{2+} was reduced from 48.51 to 0.694 mg L^{-1} .

Nevertheless, the use of Ca(OH)_2 in the strongly acidic effluents containing sulphates could lead to the formation of $\text{CaSO}_4 \cdot \text{H}_2\text{O}$, a secondary sludge which raises the cost of treatment and disposal. Hence, in most of the studies, NaOH and NH_4OH are always the preferable precipitating agents to be used as they produce no insoluble sludge (Jüttner *et al.*, 2000).

2.3.3 Electrodialysis

Electrodialysis (ED) is a form of membrane process used for the separation of ions through a semi-permeable charged membrane from one solution to another driven by electrical field. Two basic types of membranes are used as to achieve the ion-separation purposes: a) negatively charged cation-exchange and b) positively charged anion-exchange membranes. ED was known to be the earliest industrial application of ion-exchange membranes in large-scale that had been widely applied for the desalination of brackish water and recovery of useful substances from industrial effluents (Baker *et al.*, 1991, Wang *et al.*, 2011, Fu and Wang, 2011, Baker, 2012).

An ED system usually refers to a chamber which consists of cation and anion exchange membranes that are arranged alternately to establish a multi-cell pair structure in between cathode and anode. Each cell is formed by a pair of cation and anion exchange membranes. As electrical current is applied across the membranes, it

acts as driving force to move cations in the solution toward the cathode, while anions move toward the anode. The cations can permeate the cation-exchange membrane, but are retained by the anion-exchange membrane in the adjacent cell and vice versa. As a result, ion-concentrated and ion-depleted cells emerge in an alternating pattern where concentrated effluent released from the former and desalinated (dilute) effluent released from the latter (Nunes and Peinemann, 2006, Drioli and Giorno, 2009, Baker, 2012).

The application of ED system for the removal of heavy metal ions from industrial wastewater is not rare to be seen in many literatures. It is especially used for treating the effluents contaminated with high metal concentrations that are above ppm-scale. Perdesen *et al.* (2003) had used electro-dialytic treatment for the removal of Cd^{2+} , Pb^{2+} , Zn^{2+} and Cu^{2+} cations from fly ashes. They had tested the method on 3 different fly ashes: two were obtained from municipal solid waste incinerator (MSWI) and the remaining one was wood combustion fly ash. The results revealed that 8% of Pb^{2+} and 73 % of Zn^{2+} were removed from one of the MWSI fly ash samples.

However, for another MWSI sample, only 2.5 % Pb^{2+} and 24 % Zn^{2+} were extracted by ED method. They suggested that the obvious differences in removal percentages between two samples were due to variations in pH leading to different extent of metal speciation occurred in two samples. About 70 % of Cd^{2+} was removed from each of the three samples. The laboratory-scale ED cell they used consists of three compartments, but they did not specify the type of IE membranes in the cell.

Membrane fouling is the most common limitation arose from the operation of ED. The ion-exchange membranes are easily fouled via concentration polarization

(CP) due to accumulation of ions on the boundary layers of membranes in the ion-concentrated cells. The extent of CP is affected by variables include the density of electrical current, permeability of membrane, osmotic pressure across the membranes and solubility of the ions. Furthermore, the deposition of ions with low solubility on the membrane surfaces could also reduce the membrane selectivity which results in adverse effect on the ion separation efficiency (Baker *et al.*, 1991, Nunes and Peinemann, 2006).

2.3.4 Adsorption

Adsorption is always regarded as the most promising and efficient technique for removing trace levels of heavy metal ions from effluents. The adsorption is a mass transfer process in which a substance (heavy metals exist in the form of ions in aqueous solutions) is transferred from a liquid or gaseous mobile phase onto or into a solid through physical or chemical adsorbate – adsorbent interactions (Zhao *et al.*, 2011, Gregg and Sing, 1982).

The nature of adsorption is separated into 2 categories: a) physical adsorption (physisorption) and b) chemical adsorption (chemisorption). For physical adsorption, the adsorption of adsorbate onto the adsorbent surface through relatively weak Van der Waals forces. On the other hand, chemisorption involves the sharing and exchange of electrons between the adsorbate and the adsorbent surface which leads to a chemical reaction. There are several ways to distinguish these 2 types of adsorptions; one of the common differences between physisorption and chemisorption is in the magnitudes of the heat of adsorption, ΔH . In the regime of physisorption, ΔH is usually not more than 20 kJ mol^{-1} , while in chemisorption, ΔH

is usually within 40 to 400 kJ mol⁻¹ (Bansal and Goyal, 2005). Hence, the chemical properties and physical properties of adsorbents are crucial to be evaluated for the viable adsorption of metal ions.

Duong (1998) described that the heart of an adsorption process is usually a porous solid medium in most of the cases. This is because porous solids have high surface area and pore volume in which high adsorption capacity can be achieved. An adsorption process is characterized by 3 mechanisms: a) steric, b) equilibrium and c) kinetic mechanisms. In steric mechanism, an adsorption is altered by the dimension of pores of porous adsorbent. Only small adsorbate molecules are trapped in the pores and large molecules are prevented from entering the pores. For equilibrium mechanism, it is based on the adsorbent ability to trap different species of adsorbates in which the adsorbate – adsorbent interactions are taken into account for the capture of adsorbate species. In kinetic mechanism, rates of diffusion of different adsorbate species into the pores are determined.

The adsorption of heavy metals is usually a type of liquid phase adsorption which is influenced by factors such as pH, type of adsorbent, adsorbate concentration as well as temperature (Rouquerol *et al.*, 1999, Gregg and Sing, 1982). There are numerous materials have been used as sorbents for the adsorption of heavy metal ions. The researchers attempted to classify the adsorbent materials into 3 major categories namely; a) Carbon adsorbents, b) mineral adsorbents and c) polymeric adsorbents. Carbon adsorbents refers to activated carbons and carbon nanotubes; mineral adsorbents embrace silica gel, metal oxides, zeolites, and clay materials; while polymeric sorbents include both natural and synthetic polymers (Babel and Kurniawan, 2003, Asouhidou *et al.*, 2004).