

**REMOVAL OF HEAVY METAL IONS FROM AQUEOUS  
SOLUTIONS BY POLYMER-ENHANCED ULTRAFILTRATION**

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## ABSTRACT

The effects of pH, polymer concentration and metal ions feed concentration for four selected heavy metals, Zn(II), Pb(II), Cr(III) and Cr(VI), were investigated in this work; these metals were tested through a Polymer Enhanced Ultrafiltration (PEUF) system. Two conventional water-soluble polymers were selected, namely polyethylene glycol (PEG) and polyethyleneimine (PEI), and an unmodified starch as a biopolymer is proposed as an alternative binding reagent for four selected metal ions used for heavy metals' removal from wastewater.

Speciation profiles of Zn(II), Pb(II), Cr(III) and Cr(VI) species were obtained using available software to identify the soluble complexes of Zn(II), Pb(II), Cr(III), Cr(VI) ions and hydroxides ions (OH<sup>-</sup>) present in various charged ions, either as anions or cations, at a certain pH range. Potentiometric titration studies were carried out at first to investigate the potential interactions between the selected polymer and metal ions for complexation.

Investigation through experimental works was done using ultrafiltration systems obtained by a laboratory ultrafiltration bench scale equipped with 10 kDa polysulfone hollow fiber membrane. The main operating parameter, namely the effects of pH, polymer composition and metal ions concentrations, were significantly affected by the retention coefficient and permeate flux conducted at constant pressure and flowrate.

Unmodified starch and PEG as binding polymers performed complexation interactions due to non-ionic attraction of metal ions to the polymer on the molecular

surface with a high possibility of chemical occurrence. However, these selected metal ions are mainly complexes by polymer functional groups whenever there is interaction with PEI polymer.

For study of single metal ions solutions, Zn(II) ions retentions approaching over 90% were obtained at pH 7 for each tested polymer. This behavior was similar to Pb(II), Cr(III) and Cr(VI) for which the retentions were obtained at a lower acidic pH and increased at a neutral pH of 7. Different behavior was found by Cr(VI) ions where a high retention was only achieved at an acidic pH region with PEI. Polymer concentration and metal ions concentration are found to have a significant effect on retentions.

For mixed metal ions solutions, the behavior of metal ions retentions was similar to single metal ions solutions for investigation on the effects of pH. Retention values were high at pH 7 for Zn(II) and Cr(III) ions corresponding to higher binding interactions with unmodified starch. Pb(II) ions obtained high retentions when tested with PEG whenever carried out in mixed metal ions solutions. High Cr(VI) ion retention was found with PEI in single and mixed metal ions solutions in a neutral pH range. The retention of these metal ions by starch in this study is found to be influenced by the granule structure that generally behaved in a non-ionic manner.

No significant effects on permeate flux were obtained when tested at different pH ranges, polymer concentrations and metal ions feed either by single or a mixture of metal ions solutions. The Canizares Model was employed as the theoretical model to

predict permeate flux and metal ions retention on the study of heavy metal ions removal.

## ABSTRAK

Pengkajian berkenaan kesan pH, kepekatan polimer dan kepekatan permulaan bagi ions logam bagi empat logam berat yang dipilih seperti Zn(II), Pb(II), Cr(III) dan Cr(VI) yang dijalankan dalam kerja ini telah diuji menggunakan sistem Ultrapenurasan Ditingkatkan dengan Polymer. Dua polimer perlekatan konvensional berasaskan air dipilih untuk ujikaji iaitu polyethylene glycol (PEG) dan polyethyleneimine (PEI), dan kanji tak diubah biopolimer yang dicadangkan sebagai alternative pelekatan reagent bagi empat ion logam yang dipilih untuk menyingkirkan logam berat daripada sisa air.

Profil spesies ions Zn(II), Pb(II), Cr(III) dan Cr(VI) telah dilakarkan menggunakan perisian yang ada untuk mengenalpasti larutan kompleks Zn(II), Pb(II), Cr(III) dan Cr(VI) ions dan juga ions hidroksida ( $\text{OH}^-$ ) yang hadir dalam pelbagai cas ions, sama ada anion atau kation pada pH tertentu. Pengajian tentang titrat potentiometri dijalankan pada permulaannya untuk mengkaji potensi interaksi di antara ions logam dan polimer untuk menjadi kompleks.

Penyiasatan melalui kerja eksperimen dilakukan melalui sistem ultrapenurasan oleh alat berskala makmal ultrapenurasan bersaiz 10 kDa membran fiber geronggang. Parameter operasi utama iaitu kesan pH, komposisi polimer dan kepekatan permulaan logam ion memberi kesan nyata kepada pekali penolakan dan fluks tertapis pada tekanan dan kadar aliran yang tetap.

Kanji tak diubah berserta PEG, sebagai polimer perlekatan menunjukkan interaksi kompleks kemungkinan berlaku berpandukan interaksi bukan ionik pada permukaan

molekul dan juga berkemungkinan berlaku secara kimia. Walaubagaimanapun, utamanya, logam ion yang dipilih dikomplekskan oleh kumpulan berfungsi polimer apabila berinteraksi dengan polimer PEI.

Bagi kajian tentang ion larutan tunggal, penyingkiran Zn(II) ion mencapai lebih 90% pada pH 7 untuk setiap polimer yang dikaji. Ion Pb(II), Cr(III) dan Cr(VI) menunjukkan perlakuan yang sama di mana penyingkiran pada permulaannya rendah pada pH berasid dan meningkat pada pH neutral 7. Perlakuan berbeza ditunjukkan oleh Cr(VI) dengan PEI di mana penyingkiran yang tinggi hanya dicapai pada julat pH berasid. Bagi kedua-dua iaitu kesan ke atas kepekatan polimer dan kepekatan permulaan ion logam, ia menunjukkan kesan nyata terhadap penyingkiran.

Untuk larutan campuran, penyingkiran ion logam yang ditunjukkan sama dengan perlakuannya dengan larutan tunggal dari aspek kesan terhadap pH. Penyingkiran ion Zn(II) dan Cr(III) yang tinggi didapati menunjukkan iaitu interaksi perlekatan yang tinggi dengan kanji tak diubah. Ion Pb(II) mencapai penyingkiran yang tinggi apabila diuji dengan PEG apabila dijalankan pada larutan campuran. Penyingkiran Cr(VI) ion didapati dikaji dengan PEI pada julat pH neutral secara larutan tunggal ataupun larutan campuran serentak. Penyingkiran oleh semua ion logam yang digunakan di dalam kajian ini menunjukkan ianya dipengaruhi oleh struktur granul yang tidak bersifat ionik.

Tiada kesan nyata pada fluk diperolehi apabila dikaji pada perbezaan julat pH, kepekatan polimer dan kepekatan permulaan ion logam sama ada melalui larutan tunggal ataupun campuran serentak. Model Canizares yang digunakan sebagai Model

teori bagi menjangka fluks tertapis dan penyingkiran logam ion bagi pengkajian terhadap penyingkiran ion logam berat.

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<b>TABLE OF CONTENTS</b>		<b>PAGE</b>
<b>ORIGINAL LITERARY WORK DECLARATION</b>		ii
<b>ABSTRACT</b>		iii
<b>ABSTRAK</b>		vi
<b>ACKNOWLEDGEMENTS</b>		ix
<b>TABLE OF CONTENTS</b>		x
<b>LIST OF FIGURES</b>		xvi
<b>LIST OF TABLES</b>		xxv
<b>LIST OF SYMBOLS AND ABBREVIATIONS</b>		xxvi
<b>CHAPTER 1:</b>	<b>INTRODUCTION</b>	<b>1</b>
1.1	Background of research	1
1.2	Problem statement	4
1.3	Objectives	6
1.4	Scope of study	7
1.5	Thesis Outline	8
<b>CHAPTER 2:</b>	<b>LITERATURE REVIEW</b>	<b>10</b>
2.1	Heavy Metals and the Environment	10
2.1.1	Definitions	10
2.1.2	Uses of Heavy Metals	11
2.1.3	Heavy Metal Toxicity	12
2.1.4	Discharge standards	14
2.1.5	Typical Malaysian Wastewater Containing Heavy Metals	17
2.2	Membrane Processes as Emerging Technologies for Heavy Metal Removal	23
2.2.1	Dead-end filtration	26
2.2.2	Cross-flow filtration	26

2.3	Polymer Enhanced Ultrafiltration (PEUF) Process for Heavy Metal Removal	27
2.3.1	Complex binding	27
2.3.2	Adsorption of metal ions onto polymers	30
2.3.3	Polymer reagents for metal ions' adsorption	33
2.3.4	Binding conditions	35
2.3.4.1	Binding Degree	35
2.3.4.2	pH Value	36
2.3.4.3	Selectivity of polymer on binding behavior of metal ions in aqueous solutions by employed ultrafiltration process	37
2.3.5	Ligand Composition	39
2.3.6	Synergism	39
2.4	Studies of Polymer Types Used in PEUF Process	40
2.4.1	Overview	40
2.4.2	Details of Unmodified Starch	42
	a. Sources for starch	43
	b. Structural unit	43
	c. Molecular structure	45
	d. Functionality	49
2.4.3	Details of Polyethylene Glycol (PEG)	50
	a. Molecular structure	51
2.4.4	Details of Polyethyleneimine (PEI)	52
	a. Molecular structure	52
2.5	Previous work on the applications of heavy metal ions removal by Polymer Enhanced Ultrafiltration (PEUF) : Limitation and Gaps	54
2.6	Canizares Models applied as theoretical Model to predict concentration of permeate, retentate and volume of metal ions in comparison with experimental data	85
2.7	Summary highlighting gaps addressed in research	88

<b>CHAPTER 3:</b>	<b>EXPERIMENTAL SETUP AND METHODOLOGY</b>	<b>90</b>
3.1	Flowchart	90
3.2	Literature Review	91
3.3	Studied the equipment handling (Titration process and Speciation Studies)	91
3.3.1	Titration process	91
3.3.2	Speciation studies	94
3.4	Selection of heavy metals and polymers	96
3.5	Basic study on Design of Experiments (DOE) using software of Minitab 16 Software	96
3.6	Polymer Enhanced-Ultrafiltration Studies	96
3.6.1	Materials	96
3.6.2	Experimental Setup	99
3.6.3	UF Experimental Procedures	99
3.7	Design of Experiments (DOE) to determine the effect of the major operating parameter on metal ion retention and flux	102
3.8	Experimental works	107
3.8.1	First phase of experimental works (single metal ion solutions)	107
3.8.2	Second phase experimental works (mixtures metal ion solutions)	108
3.8.3	Complexation–ultrafiltration procedure	110
3.9	Data analysis	112
3.10	The similarities and differences in using single and metal ions solution	112
3.11	Fitting the existing available Model (Canizares Model) and regression coefficient by ANOVA	113
3.11.1	Fitting Canizares Model	113
3.11.2	ANOVA application for regression coefficient analyses	113
<b>CHAPTER 4:</b>	<b>RESULTS AND DISCUSSION</b>	<b>115</b>
4.1	Introduction	115
4.2	Single Metal Ion Solutions	115
4.2.1	Speciation studies	115
4.2.1.1	Speciation profile of Zinc (II)	116
4.2.1.2	Speciation profile of Lead (II)	117
4.2.1.3	Speciation profile of Chromium (III)	118

4.2.1.4	Speciation profile of Chromium (VI)	119
4.2.2	Potentiometric Titrations Study	120
4.2.2.1	Potentiometric titration study on Zinc (II)	121
4.2.2.2	Potentiometric titration study on Lead (II)	124
4.2.2.3	Potentiometric titration study on Chromium(III)	128
4.2.2.4	Potentiometric titration study on Chromium (VI)	133
4.3	<b>Polymer Enhanced Ultrafiltration of Single Metal Ion Solutions</b>	140
4.3.1	Effect of pH on metal ions retention by unmodified starch	140
4.3.2	Effect of pH on retention of metal ions by PEG	145
4.3.3	Effect of pH on retention of metal ions by PEI	148
4.4	Effect of polymer concentration on retention	151
4.4.1	Effect of unmodified starch concentration	151
4.4.2	Effect of PEG concentration	153
4.4.3	Effect of PEI concentration	155
4.5	The effect of metal ion concentration on retention	159
4.5.1	The effect of metal ion feed concentration by unmodified starch	159
4.5.2	The effect of metal ion feed concentration by PEG	161
4.5.3	The effect of metal ion feed concentration by PEI	163
4.6	Effect of pH on PEUF flux	164
4.6.1	Effect of pH on PEUF flux using unmodified starch	165
4.6.2	Effect of pH on PEUF flux using PEG	168
4.6.3	Effect of pH on PEUF flux using PEI	169
4.7	Effect of polymer concentration on PEUF flux	171
4.7.1	Effect of unmodified starch on PEUF flux	171
4.7.2	Effect of PEG on PEUF flux	173
4.7.3	Effect of PEI on PEUF flux	175
4.8	The effect of metal ion concentration on PEUF flux	176
4.8.1	The effect of unmodified starch on PEUF flux	176
4.8.2	The effect of PEG on PEUF flux	179
4.8.3	The effect of PEI on PEUF flux	181

4.9	Canizares's Model employed as theoretical model on selected heavy metal ions removal through PEUF system Removal through PEUF system	182
4.9.1	Introduction	182
4.9.2	Model for metal ions removal via PEUF system	183
4.10	The ANOVA analyses of regression of experimental data and Canizares theoretical model	192
4.11	<b>Polymer Enhanced Ultrafiltration of Mixed Metal Ion Solutions</b>	198
4.11.1	Effect of pH on retention using unmodified starch	198
4.11.2	Effect of pH on retention using PEG	204
4.11.3	Effect of pH on retention using PEI	206
4.12	The effect of polymer concentration on retention	209
4.12.1	The effect of unmodified starch concentration	209
4.12.2	The effect of PEG concentration	211
4.12.3	The effect of PEI concentration	212
4.13	Effect of metal ion feed concentration on retention	214
4.13.1	Effect of metal ion feed concentration by unmodified starch	214
4.13.2	Effect of metal ion feed concentration by PEG	215
4.13.3	Effect of metal ion feed concentration by PEI	218
4.14	Effect of pH on flux	222
4.14.1	Effect of pH by unmodified starch, PEG and PEI	222
4.15	Effect of polymer concentration on flux	225
4.15.1	Effect of unmodified starch, PEG and PEI concentration	225
4.16	Effect of metal ion feed concentration on PEUF flux	228
4.16.1	Effect of unmodified starch, PEG and PEI on PEUF flux	228
4.17	Model for metal ions removal via PEUF system	230
4.18	The ANOVA analyses of regression of experimental data and Canizares theoretical model	235
4.19	Overall conclusions for ANOVA Regression Coefficient Coefficient Analyses of Retention Coefficient for	240

Single and Mixed System Solutions via PEUF Fitting  
Canizares Models

<b>CHAPTER 5:</b>	<b>CONCLUSIONS AND RECOMMENDATIONS</b>	<b>243</b>
5.1	Conclusions	243
5.2	Recommendations for future work	246
	<b>REFERENCES</b>	<b>248</b>
	<b>APPENDICES</b>	<b>272</b>
APPENDIX A	Calibration Curves for Selected Metal Ions Standard Using ICP(-OES)	272
APPENDIX B	Calculation Data for Theoretical Analyses using Canizares Models Single and Mixed Metal Ion Solutions	374
APPENDIX C	Regression Coefficient ( $R^2$ ) of Theoretical and Experimental Data Fitting Canizares Models Using ANOVA	304
APPENDIX D	List of Publications and Papers Presented	377

<b>LIST OF FIGURES</b>		<b>PAGE</b>
Figure 2.1	Malaysia River Water Quality Trend (2005-2011)	19
Figure 2.2	Tangential flow of membrane separation process for cross flow type	24
Figure 2.3	Dead-end and cross-flow filtration processes	27
Figure 2.4	Amylose Structure	43
Figure 2.5	Amylopectin Branched Structure	44
Figure 2.6	Detailed structure of starch granule	45
Figure 2.7	Amylopectin structure	47
Figure 2.8	Schematic features of different amylopectin structures	48
Figure 2.9	PEG polymer structure	51
Figure 2.10	PEI polymer structure	53
Figure 3.1	Flow diagram of research methodology	90
Figure 3.2	The example of selection on selected metal ions conditions to develop speciation studies using Visual Minteq Version 3.0	94
Figure 3.3	The example of metal ions species presents in unit log K in Visual Minteq Version 3.0	95
Figure 3.4	Schematic diagram of laboratory-scale ultrafiltration system. (1) – power supply and digital meter of flowrate, pressure in and out , (2) - magnetic stirrer and 250 ml of feed solutions, (3) – peristaltic pump, (4) – pressure in, (5) – hollow fibre filtration cell, (6) - electronic balance and permeate solutions, (7) – pressure out, (8) - personal computer.	99
Figure 3.5	Example of experimental parameters after design with Minitab 16 before starting the research work.	104

Figure 3.6	Optimization plots of unmodified starch and Zn(II) showing the major effects at each tested parameter range.	105
Figure 3.7	The selected range of operating parameters for Zn(II) bound with unmodified starch effects on retention.	106
Figure 3.8	Response optimization using unmodified starch polymer and Zn(II) achieved about 97% in this experimental works indicate highly accurate results.	106
Figure 4.1	Speciation profile of Zn(II) in aqueous solutions	116
Figure 4.2	Speciation profile of Pb(II) in aqueous solutions	117
Figure 4.3	Speciation profile of Cr(III) in aqueous solutions	118
Figure 4.4	Speciation profile of Cr(VI) in aqueous solutions	119
Figure 4.5	Acid-base titration with NaOH of unmodified starch 0.05% (w/v) in the presence of Zn (II)	121
Figure 4.6	Acid-base titration with HCl of unmodified starch 0.05% (w/v) in the presence of Zn(II)	122
Figure 4.7	Acid-based titration with NaOH of PEG 1.0% (v/v) in the presence of Zn(II)	123
Figure 4.8	Acid-base titration with HCl of PEI 0.01% (v/v) in the presence of Zn(II)	124
Figure 4.9	Acid-base titration with NaOH of unmodified starch 0.05% (w/v) in the presence of Pb(II)	125
Figure 4.10	Acid-base titration with HCl of unmodified starch 0.05% (w/v) in the presence of Pb(II)	126
Figure 4.11	Acid-base titration with NaOH of PEG 1.0% (v/v) in the presence of Pb(II)	127
Figure 4.12	Acid-base titration with HCl of PEI 0.01% (v/v) in the presence of Pb(II)	128

Figure 4.13	Acid-base titration with NaOH of unmodified starch 0.05% (w/v) in the presence of Cr(III)	130
Figure 4.14	Acid-base titration with HCl of unmodified starch 0.05% (w/v) in the presence of Cr(III)	130
Figure 4.15	Acid-base titration with NaOH of PEG 1.0% (v/v) in the presence of Cr(III)	131
Figure 4.16	Acid-base titration with HCl of PEI 0.01% (v/v) in the presence of Cr(III)	132
Figure 4.17	Acid-base titration with NaOH of unmodified starch 0.05% (w/v) in the presence of Cr(VI)	133
Figure 4.18	Acid-base titration with HCl of unmodified starch 0.05% (w/v) in the presence of Cr(VI)	134
Figure 4.19	Acid-base titration with NaOH of PEG 1.0% (v/v) in the presence of Cr(VI)	136
Figure 4.20	Acid-base titration with HCl of PEI 0.01% (v/v) in the presence of Cr(VI)	137
Figure 4.21	The effect of pH on retention using 0.05% (w/v; g/ml) unmodified starch (TMP= 1.5 bar, flowrate= 115 ml/min, metal ion concentration= 10 mg/L)	140
Figure 4.22	Effect of pH on retention when using 1.0% (v/v; ml/ml) PEG (TMP= 1.5 bar, flowrate=115 ml/min, metal ion concentration = 10 mg/L)	145
Figure 4.23	The effect of pH on retention using 0.01% (v/v;ml/ml) PEI (TMP= 1.5 bar, flowrate= 115 ml/min)	148
Figure 4.24	Effect of unmodified starch concentration on selected metal ions (Zn(II), Pb(II), Cr(III), and Cr(VI)) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)	151
Figure 4.25	Effect of PEG concentration on selected metal ions (Zn(II), Pb(II), Cr(III), and Cr(VI)) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)	153

Figure 4.26	Effect of PEI concentration on selected metal ions (Zn(II), Pb(II), Cr(III), and Cr(VI)) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)	155
Figure 4.27	The effect of metal ion concentration on selected metal ions (Zn(II), Pb(II), Cr(III), and Cr(VI)) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7, unmodified starch concentration= 0.05 (w/v %), g/ml)	159
Figure 4.28	The effect of metal ion concentration on selected metal ions (Zn(II), Pb(II), Cr(III), and Cr(VI)) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7, PEG concentration= 1.0% (v/v %), ml/ml).	161
Figure 4.29	The effect of metal ion concentration on selected metal ions (Zn(II), Pb(II), Cr(III), and Cr(VI)) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7, PEI concentration= 0.01% (v/v %), ml/ml)	163
Figure 4.30	Permeate water flux, on selected metal ions (Zn(II), Pb(II), Cr(III), and Cr(VI)) using 0.05 (w/v %), g/ml unmodified starch and 10 mg/l of metal ions concentrations at different pH values	165
Figure 4.31	Permeate water flux, on selected metal ions (Zn(II), Pb(II), Cr(III) and Cr(VI)) using 1.0 (v/v %), ml/ml PEG and 10 mg/l of metal ions concentrations at different pH values	158
Figure 4.32	Permeate water flux on selected metal ions (Zn(II), Pb(II), Cr(III) and Cr(VI)) using 0.01 (v/v %), ml/ml PEI and 10 mg/l of metal ions concentrations at different pH values	169
Figure 4.33	The effect of unmodified starch concentrations on selected metal ions (Zn(II), Pb(II), Cr(III) and Cr(VI)) flux (TMP=1.5 bar, flowrate=115 ml/min, pH=7, metal ions concentrations= 10mg/l)	171
Figure 4.34	The effect of PEG concentrations on the selected metal ions of (Zn(II), Pb(II), Cr(III) and Cr(VI)) flux (TMP=1.5 bar, flowrate=115 ml/min, pH=7, metal ion concentrations = 10 mg/l), flowrate=115 cm/min, pH=7)	173
Figure 4.35	Effect of PEI concentration on the selected metal ions	175

	(Zn(II), Pb(II), Cr(III) and Cr(VI)) flux (TMP=1.5 bar, flowrate=115 ml/min, pH=7, metal ions concentrations= 10 mg/l)	
Figure 4.36	The effect of metal ion concentration on selected metal ions (Zn(II), Pb(II), Cr(III) and Cr(VI)) flux (TMP=1.5 bar, flowrate=115 ml/min, pH=7, unmodified starch = 0.05% (w/v; g/ml), metal ions concentrations = 10 mg/l)	177
Figure 4.37	The effect of metal ion feed concentration on selected metal ions (Zn(II), Pb(II), Cr(III) and Cr(VI)) flux (TMP=1.5 bar, flowrate=115 ml/min, pH=7, PEG= 1.0% (v/v; ml/ml), metal ions concentrations = 10 mg/l)	179
Figure 4.38	The effect of metal ion feed concentration on selected metal ions (Zn(II), Pb(II), Cr(III) and Cr(VI)) flux (TMP=1.5 bar, flowrate=115 ml/min, pH=7, PEG= 1.0% (v/v; ml/ml), metal ions concentrations = 10 mg/l)	181
Figure 4.39	Schematic diagram of Canizares's Model employed in this research as theoretical model of PEUF system. This would show the F: feed tank included [M] and [L] in the reactor, UF: UF system, P: permeate stream included [M <sub>p</sub> ] and [L <sub>p</sub> ], R: retentate solutions included [M <sub>R</sub> ] and [L <sub>R</sub> ], B: Electronic balance, P <sub>p</sub> : Peristaltic pump, M: pressure meter, D: Damper.	183
Figure 4.40	Regression coefficient (R <sup>2</sup> ) of the effect of pH on 10 mg/l concentration of selected metal ions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions using 0.05% (w/v; g/ml) of unmodified starch (TMP=1.5 bar, flowrate=115 ml/min)	192
Figure 4.41	Regression coefficient (R <sup>2</sup> ) of the effect of pH on 10 mg/l concentration of selected metal ions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions using 1.0% (v/v; ml/ml) of PEG (TMP=1.5 bar, flowrate=115 ml/min)	193
Figure 4.42	Regression coefficient (R <sup>2</sup> ) of the effect of pH on 10 mg/l concentration of selected metal ions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions using 0.01% (v/v; ml/ml) of PEI (TMP=1.5 bar, flowrate=115 ml/min)	193

Figure 4.43	Regression coefficient ( $R^2$ ) of the effect of unmodified starch concentration on 10 mg/l concentrations of selected metal ions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)	194
Figure 4.44	Regression coefficient ( $R^2$ ) of the effect of PEG concentration on 10 mg/l concentrations selected metal ions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)	195
Figure 4.45	Regression coefficient ( $R^2$ ) of the effect of PEI concentration on 10 mg/l concentrations selected metal ions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)	195
Figure 4.46	Regression coefficient ( $R^2$ ) of the effect of metal ion feed concentration of single solutions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions ( TMP=1.5 bar, flowrate=115 ml/min, pH=7, unmodified starch concentration= 0.05 % (w/v; g/ml))	196
Figure 4.47	Regression coefficient ( $R^2$ ) of the effect of metal ion feed concentration of single solutions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7, PEG concentration= 1.0% (v/v; ml/ml))	196
Figure 4.48	Regression coefficient ( $R^2$ ) of the effect of metal ion feed concentration of single solutions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7, PEI concentration= 0.01% (v/v; ml/ml))	197
Figure 4.49	Effect of pH on 10 mg/l concentration of each metal ions ( Zn(II), Pb(II), Cr(III) and Cr(VI)) retentions in mixed metal ions solutions using 0.05% (w/v; g/ml) unmodified starch , TMP=1.5 bar, flowrate =115 ml/min)	198
Figure 4.50	Effect of pH on 10 mg/l concentration of each metal ions ( Zn(II), Pb(II), Cr(III) and Cr(VI)) retentions in mixed metal ions solutions using 1.0% (v/v; ml/ml) of PEG, TMP=1.5 bar, flowrate=115 ml/min)	204
Figure 4.51	Effect of pH on 10 mg/l concentration of each metal ions	206

( Zn(II), Pb(II), Cr(III) and Cr(VI)) retentions in mixed metal ions solutions using 0.01% (v/v; ml/ml) of PEI, TMP=1.5 bar, flowrate=115 ml/min)

Figure 4.52	The effect of unmodified starch concentration on 10 mg/l concentration of each metal ions ( Zn(II), Pb(II), Cr(III) and Cr(VI)) retentions in mixed metal ions solutions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)	209
Figure 4.53	The effect of PEG concentrations on 10 mg/l concentration of each metal ions ( Zn(II), Pb(II), Cr(III) and Cr(VI)) retentions in mixed metal ions solutions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)	211
Figure 4.54	The effect of PEI concentration on 10 mg/l concentration of each metal ions ( Zn(II), Pb(II), Cr(III) and Cr(VI)) retentions in mixed metal ions solutions (TMP=1.5 bar, flowrate=115 cm/min, pH=7)	212
Figure 4.55	The effect of metal ion feed concentrations for mixed metal ion solutions on Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7, unmodified starch = 0.05% (w/v; g/ml))	214
Figure 4.56	The effect of metal ion feed concentrations of mixed metal ion solutions on Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7, PEG = 1.0% (v/v; ml/ml))	215
Figure 4.57	The effect of metal ion feed concentration of mixed metal ion solutions on Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7, PEI= 0.01% (v/v; ml/ml))	218
Figure 4.58	The effect of permeate water flux, on mixed metal ions solutions on Zn(II), Pb(II), Cr(III) and Cr(VI) and 10 mg/l of each metal ions concentrations at different pH value ( TMP= 1.5 bar, flowrate= 115 ml/min)	222
Figure 4.59	The effect of polymer concentration on mixed metal ion solutions on Zn(II), Pb(II), Cr(III) and Cr(VI)) flux (TMP=1.5 bar, flowrate=115 ml/min, pH=7, each metal ions concentrations= 10 mg/L)	225
Figure 4.60	The effect of metal ions feed concentration of mixed	228

metal ion solutions on Zn(II), Pb(II), Cr(III) and Cr(VI) flux (TMP=1.5 bar, flowrate =115 ml/min, pH=7, unmodified starch = 0.05% (w/v; g/ml), PEG= 1.0% (v/v; ml/ml), PEI= 0.01% (v/v; ml/ml))

Figure 4.61	Regression coefficient ( $R^2$ ) of the effect of pH on 10 mg/l of each concentration of mixed metal ion solutions using ANOVA to analyze (Zn(II), Pb(II), Cr(III) and Cr(VI)) retentions using 0.05% (w/v; g/ml) of unmodified starch (TMP=1.5 bar, flowrate=115 ml/min)	235
Figure 4.62	Regression coefficient ( $R^2$ ) of the effect of pH on 10 mg/l of each concentration of mixed metal ion solutions using ANOVA to analyze (Zn(II), Pb(II), Cr(III) and Cr(VI)) retentions using 1.0% (v/v; ml/ml) of PEG (TMP=1.5 bar, flowrate=115 ml/min)	236
Figure 4.63	Regression coefficient ( $R^2$ ) of the effect of pH on 10 mg/l of each concentration of mixed metal ion solutions using ANOVA to analyze (Zn(II), Pb(II), Cr(III) and Cr(VI)) retentions using 0.01% (v/v; ml/ml) of PEI (TMP=1.5 bar, flowrate=115 ml/min)	236
Figure 4.64	Regression coefficient ( $R^2$ ) of the effect of unmodified starch concentration on mixed metal ion solutions using ANOVA to analyze 10 mg/l of each Zn(II), Pb(II), Cr(III) and Cr(VI) concentrations on retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)	237
Figure 4.65	Regression coefficient ( $R^2$ ) of the effect of PEG concentration on mixed metal ion solutions using ANOVA to analyze 10 mg/l of each Zn(II), Pb(II), Cr(III) and Cr(VI) concentrations on retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)	238
Figure 4.66	Regression coefficient ( $R^2$ ) of the effect of PEI concentration on mixed metal ion solutions using ANOVA to analyze 10 mg/l of each Zn(II), Pb(II), Cr(III) and Cr(VI) concentrations on retentions (TMP=1.5 bar, flowrate=115 ml/min, pH=7)	238
Figure 4.67	Regression coefficient ( $R^2$ ) of the effect of metal ion feed concentration of mixed metal ion solutions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (p=1.5 bar, flowrate=115 ml/min, pH=7, unmodified starch = 0.05% (w/v; g/ml))	239

Figure 4.68	Regression coefficient ( $R^2$ ) of the effect of metal ion feed concentration of mixed metal ion solutions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (p=1.5 bar, flowrate=115 ml/min, pH=7, PEG concentration = 1.0 % (v/v; ml/ml))	239
Figure 4.69	Regression coefficient ( $R^2$ ) of the effect of metal ion feed concentration of mixed metal ion solutions using ANOVA to analyze Zn(II), Pb(II), Cr(III) and Cr(VI) retentions (p=1.5 bar, flowrate=115 ml/min, pH=7, PEI concentration = 0.01 % (v/v; ml/ml))	240

	<b>LIST OF TABLES</b>	<b>PAGE</b>
Table 2.1	Acceptable Conditions for Discharge of Industrial Effluent for Mixed Effluent of Standards A and B Extracted from Environmental Quality (Industrial Effluents) Regulations 2009 [Paragraph 11(1) (a)]	16
Table 2.2	Quantity of Scheduled Waste Generated by Category, 2011	20
Table 2.3	National Water Quality Standards for Malaysia	21
Table 2.4	Important Parameter of National Water Quality Standards for Malaysia	22
Table 2.5	Criteria in selection of polymer reagent in separation process	33
Table 2.6	Previous work on the applications of heavy metal ion removal in single metal ion solutions	54
Table 2.7	Previous work on the applications of heavy metal ion removal in mixed metal ion solutions	69
Table 3.1	The scope of work (chemicals and polymers) used in this research work	98
Table 3.2	The scope of experimental work for major parameters tested	102
Table 4.1	pH complexation range of four selected ions with unmodified starch, PEG, PEI as polymer	138
Table 4.2	The permeate and retentate parameters and retention coefficients for aqueous solutions containing Zn(II), Pb(II), Cr(III) and Cr(VI) ions in mixed metal ion solutions (pH = 7, transmembrane pressure = 1.5bar, t = 2 hours, flowrate = 115 ml/min)	221

## LIST OF SYMBOLS AND ABBREVIATIONS

### Symbols

%	Percentage
<	Less than
>	More than
$\Delta t$	Net increment in time, min or hour
®	Prestal
°C	Degrees Centigrade
°F	Degrees Fahrenheit
C	Carbon units
CaCl <sub>2</sub>	Calcium (II) chloride
CaCO <sub>3</sub>	Calcium (II) carbonate
C <sub>e</sub>	Final concentration of liquid, mg/L
C <sub>o</sub>	Initial concentration of the liquid, mg/L
Cr (III)	Chromium (III)
Cr (VI)	Chromium (VI)
CuSO <sub>4</sub>	Copper (II) sulfate
H <sub>2</sub> SO <sub>4</sub>	Sulphuric acid
I <sub>2</sub>	Iodine
J <sub>w</sub>	permeate water flux
K	Kelvin
K <sub>A</sub>	Acid dissociation constant
K <sub>ads</sub>	Measure of affinity of adsorbate for adsorbent (Langmuir Isotherm)
K <sub>Ha</sub>	Apparent dissociation constant
K <sub>i,n</sub>	Effective stability constants of complexes
KOH	Potassium hydroxide
M	Molar, mol/liter
Me	Metal
mM	Milimolar, mmol/liter
mg/l	Miligram/liter
mm	Milimeter
MW	Molecular weight, g/mol
n	Freundlich intensity parameter
Na <sub>2</sub> CO <sub>3</sub>	Sodium carbonate

Na <sub>2</sub> SO <sub>4</sub>	Sodium sulfate
NaNO <sub>3</sub>	Sodium nitrate
NaOCl	Sodium hypochlorite
NaOH	Sodium hydroxide
NH <sub>3</sub> -N	Ammonical nitrogen
nm	Nanometer, 10 <sup>-9</sup>
Pb (II)	Lead
Pc	Concentrate pressure, bars
Pf	Feed pressure, bars
pKa	Cologarithm of the apparent dissociation constant of polymer
pK <sub>w</sub>	Negative log of the water ion product , K <sub>w</sub>
Q	Flowrate, cm <sup>3</sup> /min or L/h
rpm	Revolutions per minute
SS	Suspended solids
T	Temperature, °C
Zn (II)	Zinc
α <sub>a</sub>	Dissociation degree
ΔPd	Difference between the feed and concentrate pressures
μm	Micrometer, 10 <sup>-6</sup>

### Subscripts

AAS	Atomic Adsorption Spectrometer
ADMI	American Dye Manufactures Institute
BOD	Biological Oxygen Demand
CMC	Carboxymethyl cellulose
DADMAC	Diallyldimethylammonium Chloride
DOE	Department of Environment
EDTA	Ethylenediaminetetraacetic acid
EQA	Environmental Quality Act
ICP-AES	Inductively Coupled Plasma-Atomic Emission
IR spectroscopy	Infrared spectroscopy
LPR	Liquid Phase Polymer-based Retention
MBR	Membrane Bioreactor
mPEG	Methoxypoly(ethylene glycol)
OSHA	Occupational Safety and Health Administration
PAA	Poly(acrylic acid)
PAAS	Polyacrylic acid sodium
PAM-Na	Poly(acrylic acid–maleic anhydride) sodium salt

PEG	Polyethylene Glycol
PEI	Polyethyleneimine
PEO	Polyethylene oxide
PEPEI	Partially ethoxylated polyethylenimine
PEUF	Polymer Enhanced Ultrafiltration
POE	Polyoxyethylene
PVDF	Polymer of vinylidene fluoride
TMP	Transmembrane Pressure
WHO	World Health Organization
WQI	Overall Water Quality Index

### Membrane notations

A	Filtration area, cm <sup>2</sup>
[L]	Free ligand concentration or polymer concentration
[L] <sub>free</sub>	Concentration of dissociated polyelectrolyte
[L] <sub>R,0</sub>	Initial polymer concentration in reactor
[L] <sub>R,t+1</sub>	Polymer concentration in reactor at time t + 1
[L] <sub>T</sub>	Total ligand concentration
[M]	Metal concentration
[M] <sub>0</sub>	Initial metal retention for polymer regeneration process concentration
[M] <sub>F</sub>	Metal concentration in feed stream
[M] <sub>P</sub>	Metal concentration in permeate stream
[M] <sub>R,0</sub>	Initial metal retention process concentration in reactor
[M] <sub>R,t+1</sub>	Metal and polymer concentration at time t + 1
C <sub>A</sub>	Analytical concentration of polyelectrolyte
C <sub>f</sub>	Solute concentration in feed stream
C <sub>p</sub>	Solute concentration in permeate stream
CP	Concentration polarization
DOE	Design of Experiments (using computer software)
F	Permeate flux, cm <sup>3</sup> /cm <sup>2</sup> .min
HL	Represents the polymer used in modelling equations
K	Kilo ( x 10 <sup>3</sup> )
kDa	Kilo Dalton
MF	Microfiltration
Mi	Metal ions
MWCO	Molecular Weight Cut-Off membrane, kDa
n	Empirical constant taking into account the intramolecular electrostatic forces of the

polyelectrolyte ( value higher than 1 and usually near 2 )

NF	Nanofiltration
NMWL	Nominal molecular weight limit
Qf	Feed flow rate
Qp	Permeate stream flow rate
R	Retention coefficient or recovery, %
R <sub>0</sub>	Membrane–metal interaction coefficient
RM	Metal retention coefficient in polymer regeneration process, %
R <sub>M</sub>	Metal retention coefficient
R <sub>M,0</sub>	Initial metal retention coefficient
RO	Reverse Osmosis
SR	Solutes retention, %
UF	Ultrafiltration
V	Volume, cm <sup>3</sup> or m <sup>3</sup>
V <sub>P</sub>	Permeate volume, cm <sup>3</sup> or m <sup>3</sup>
V <sub>R</sub>	Retentate volume, cm <sup>3</sup> or m <sup>3</sup>

### **Greek symbols**

ρ	Density, ft <sup>2</sup> /ft <sup>3</sup> or m <sup>2</sup> /m <sup>3</sup>
p	Pressure, psi or kg/m <sup>2</sup> or bar
φ	phi
ψ	psi torsions