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RECOVERY OF COPPER, CHROMIUM AND NICKEL FROM ELECTROPLATING
EFFLUENT BY ELECTROCHEMICAL TECHNIQUE

Miss Mali Hunsom

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for the Degree of Doctor of Philosophy in Chemical Technology

Department of Chemical Technology

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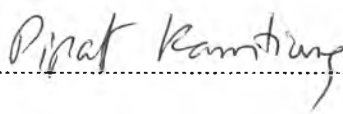
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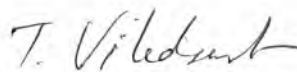
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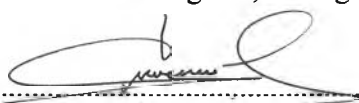
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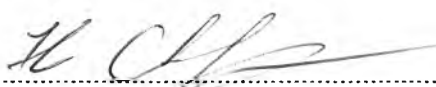
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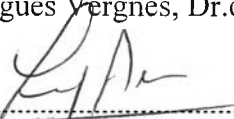
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มะลิ หุ่นสม : การนำทองแดง โครเมียม และนิกเกิลกลับคืนจากน้ำเสียโรงงานชุบโลหะด้วยเทคนิคเคมีไฟฟ้า (RECOVERY OF COPPER, CHROMIUM AND NICKEL FROM ELECTROPLATING EFFLUENT BY ELECTROCHEMICAL TECHNIQUE) อ.ที่ปรึกษา : ศ.ดร.สมศักดิ์ ดำรงค์เลิศ, อ.ที่ปรึกษาร่วม : ศ.ดร.Patrick Duverneuil, ผศ.ดร.เก็จวดี พงกษาทร, 257 หน้า, ISBN 974-03-0743-4

จุดประสงค์ของงานวิจัยนี้คือการประยุกต์ใช้เทคนิคทางเคมีไฟฟ้าเพื่อนำกลับของโลหะซึ่งประกอบด้วยทองแดง โครเมียมและนิกเกิลจากน้ำทิ้งจากโรงงานชุบโลหะ เนื่องจากเหตุผลทางสิ่งแวดล้อมและทางเศรษฐศาสตร์ โดยงานวิจัยนี้ได้แบ่งออกเป็น 3 ส่วนย่อย ส่วนแรกเป็นการนำกลับคืนโลหะทองแดงจากสารละลายสังเคราะห์ในเครื่องปฏิกรณ์แบบดั้งเดิมและแบบที่ได้มีการพัฒนาขึ้น ส่วนที่สองเป็นการนำกลับโลหะโครเมียมและนิกเกิลจากสารละลายสังเคราะห์ในเครื่องปฏิกรณ์ดั้งเดิมแบบมีเยื่อเลือกผ่าน ส่วนสุดท้ายเป็นการนำกลับของโลหะผสมของทองแดง โครเมียม และนิกเกิลจากสารละลายสังเคราะห์และน้ำเสียจากโรงงานชุบโลหะในเครื่องปฏิกรณ์ดั้งเดิมแบบมีเยื่อเลือกผ่าน จากผลการทดลองพบว่าโลหะแต่ละชนิดมีภาวะที่ดีที่สุดของการนำกลับเฉพาะตัว ซึ่งทำให้สามารถนำกลับโลหะทองแดง โครเมียมและนิกเกิลจากสารละลายผสมได้ ภาวะที่ดีที่สุดของการนำกลับทองแดง โครเมียมและนิกเกิลคือที่ความหนาแน่นกระแสไฟฟ้า 10, 90, 90 แอมแปร์ต่อตารางเมตร ตามลำดับ

โครเมียมที่มีเลขออกซิเดชันบวก 6 มีผลต่อการนำกลับของทองแดง ในขณะที่โครเมียมที่มีเลขออกซิเดชันบวก 3 ไม่มีผล

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REACTOR

MALI HUNSOM : RECOVERY OF COPPER, CHROMIUM AND NICKEL FROM ELECTROPLATING EFFLUENT BY ELECTROCHEMICAL TECHNIQUE. THESIS ADVISOR : PROFESSOR SOMSAK DAMRONGLERD, Dr.Ing., THESIS CO-ADVISOR : PROFESSOR PATRICK DUVERNEUIL, Dr.de l'INPT., ASSISTANT PROFESSOR KEJVALEE PRUKSATHORN, Dr.de l'INPT. 257 pp. ISBN 974-03-0743-4

The major purpose of this current work is to apply electrochemical techniques to recover heavy metals (such as copper, chromium and nickel) from electroplating effluent due to environmental and economic reasons. This work is divided into three sections. The first one is to recover copper from synthetic solution by using a classical reactor without membrane and by using a modified reactor, (Pulsed Porous Percolated Electrode, 3PE). The second section is to carry out a classical membrane reactor to recover chromium and nickel from a synthetic solution. The last one is to recover metals from a synthetic solution and a mixture of electroplating effluents. The results show that each metal has its own optimum recovery conditions. Then copper, chromium and nickel in the mixture can be recovered. The optimum current density to recover copper is 10 A/m^2 whereas those of chromium and nickel are 90 A/m^2 .

Chromium in hexavalent form (Cr^{6+}) affects copper recovery, whereas trivalent chromium (Cr^{3+}) does not.

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CONTENTS

	Page
ABSTRACT (in Thai).....	iv
ABSTRACT (in English).....	v
ACKNOWLEDGEMENTS.....	vi
CONTENTS.....	vii
LIST OF TABLES.....	xiii
LIST OF FIGURES.....	xiv
LIST OF ABBREVIATIONS.....	xix
CHAPTER	
I. GENERAL INTRODUCTION.....	25
II. THEORY.....	28
1. Electrochemistry.....	28
1.1 Oxidation - reduction processes.....	28
1.2 Nernst equation.....	30
1.3 Electrode potentials.....	31
1.4 Standard electrode potential (E^0).....	31
1.5 Equilibrium constants from standard electrode potentials.....	32
1.6 Potentials of real cells.....	33
1.6.1 Liquid - junction potential.....	33
1.6.2 Ohmic potential; iR drop.....	33
1.6.3 Polarization effects.....	34
1.7 Electrochemical thermodynamic.....	35
1.8 Electrode polarization.....	37
1.9 Current - overpotential equation.....	40
1.9.1 No mass transfer effects.....	42
1.9.2 Linear characteristic at small η	42

	Page
1.9.3 Tafel behavior at large η	42
1.9.4 Tafel plots.....	43
1.10 Double - layer region.....	44
1.11 Mass transport in electrochemical system.....	45
1.12 Faraday's laws.....	49
2. Depollution processes.....	51
2.1 Chemical precipitation process.....	51
2.1.1 Metal hydroxide precipitation.....	51
2.1.2 Metal sulfide precipitation.....	51
2.2 Sorptive flotation process.....	53
2.3 Electrodialysis process.....	54
2.4 Biological process.....	55
2.5 Reverse osmosis process.....	57
2.6 Ion exchange process.....	58
2.7 Adsorption process.....	59
3. Recovery of metal by electrochemical technique.....	60
3.1 Electrochemical process in classical reactor without membrane.....	60
3.2 Electrochemical process in classical reactor with membrane.....	61
3.3 Electrochemical process in Pulsed Porous Percolated Electrode (3PE reactor).....	64
3.3.1 Types of 3PE reactor.....	68
3.3.1.1 3PE in axial field configuration.....	68
3.3.1.2 3PE in radial field configuration.....	68
4 .Chemical engineering approach for electrochemical recovery of metals.....	70
4.1 Mass balance on electrochemical reactor.....	70
4.1.1 Equations of mass conservation.....	70
4.1.1.1 Balance of component i	70
4.1.1.2 Total balance.....	71
4.1.1.3 Balance of electrical charge.....	72
4.1.2 Material balance around ideal electrochemical reactor.....	73

	Page
4.1.3 Material balance around batch reactor.....	73
4.1.4 Material balance around continuous stirrer tank reactor, CSTR.....	76
4.1.5. Material balance around plug flow reactor, PFR.....	78
4.2 Dimensionless numbers.....	80
5. State of pollutant activities in Thailand.....	82
5.1 Electroplating process.....	83
5.2 Conventional methods for treatment electroplating effluents.....	86
6. Literature review.....	88
III. METHODOLOGY.....	91
1. Experimental set up of polarization curve.....	91
1.1 Potentiostat technique.....	91
1.2 Microbalance technique.....	92
2. Electrolysis of heavy metal.....	93
2.1 Description of experimental apparatus.....	93
2.1.1. Classical reactor without membrane or electrodeposition reactor.....	93
2.1.2. Classical reactor with membrane or electroprecipitation reactor.....	95
2.1.3 3PE reactor.....	96
2.2 Chemical substances.....	98
2.3 Description of solutions.....	98
2.4 Description of operating conditions.....	99
3. Polarization curves of heavy metals solutions.....	101
3.1 Potentiostat technique.....	101
3.1.1 Polarization curve of solvents.....	102
3.1.2 Polarization curve of synthetic copper solutions.....	103

	Page
3.1.3 Polarization curve of synthetic chromium solutions.....	104
3.1.4 Polarization curve of synthetic nickel solutions.....	106
3.1.5 Polarization curve of synthetic zinc solutions.....	108
3.1.6 Polarization of synthetic mixed solution of copper, chromium, nickel and zinc.....	109
3.2 Microbalance technique.....	110

IV. METAL RECOVERY BY ELECTRODEPOSITION TECHNIQUE...115

1. Copper recovery.....	115
1.1 Copper recovery in classical reactor without membrane.....	115
1.1.1 Influence of current density.....	115
1.1.2 Influence of electrolyte flow rate.....	120
1.1.2.1 Experimental results.....	120
1.1.2.1.1 Low copper concentration.....	120
1.1.2.1.2 High copper concentration.....	122
1.1.2.2 Reactor modelling.....	122
1.1.2.2.1 Low copper concentration.....	123
1.1.2.2.2 High copper concentration.....	128
1.1.3 Influence of initial concentration.....	130
1.1.4 Compare the results with literature.....	132
1.1.5 Provable experiments.....	134
1.2 Copper recovery in 3PE reactor.....	136
1.2.1 Effect of current intensity.....	136
1.2.2 Effect of air pulse frequency.....	139
1.2.3 Effect of electrode type.....	140
1.2.4 Effect of electrolyte flow rate.....	142
1.2.5 Mass transfer coefficient.....	143
1.2.6 Comparison with other works.....	144
2. Recovery of zinc by electrodeposition technique.....	146
3. Conclusion.....	148

V. METAL RECOVERY BY ELECTRO PRECIPITATION

TECHNIQUE.....	150
1. Chromium recovery.....	150
1.1 Influence of current density.....	150
1.2 Model for chromium recovery.....	156
1.2.1 The basic model.....	157
1.2.2 Non - constant pH precipitation model.....	159
1.2.3 Non - constant pH precipitation with loss flux of hydroxide ion model.....	164
1.3 Influence of initial pH and initial concentration.....	171
2. Nickel Recovery.....	174
2.1 Influence of current density.....	174
2.2 Model for nickel recovery.....	180
2.2.1 The basic model.....	181
2.2.2 Non - constant pH precipitation model.....	183
2.2.3 Non - constant pH precipitation with loss flux of hydroxide ion model.....	188
2.3 Influence of initial pH and initial concentration.....	196
3. Conclusion.....	198

VI. RECOVERY OF MIXED METALS BY ELECTROCHEMICAL

TECHNIQUE.....	200
1. Recovery of mixed metals in synthetic solution.....	200
1.1 Results of mixed metals solution of chromium, nickel and zinc.....	200
1.2 Results of mixed metals solution of copper, chromium, nickel and zinc.....	201
2. Recovery of mixed metals from electroplating effluent.....	203
2.1 Results of mixed metals solution from Plant I and Plant II.....	203

	Page
3. Effect of parameters on copper recovery	206
3.1 Effect of cyanide compound	206
3.2 Effect of brightener	207
3.3 Effect of nickel and chromium in the system	209
3.4 Effect of hexavalent chromium concentration	212
4. Cost analysis of mixed metals recovery from electroplating industry	214
5. Conclusion	216
GENERAL CONCLUSION	218
REFERENCES	221
APPENDICES	230
APPENDIX A	231
APPENDIX B	243
APPENDIX C	251
APPENDIX D	252
APPENDIX E	253
BIOGRAPHY	257

LIST OF TABLES

TABLE	Page
II.1: Zone of metal precipitation.....	52
II.2: Advantages and disadvantages of chemical precipitations.....	52
II.3: Classification of ion exchangers.....	59
II.4: Acceptable value of electroplating effluent.....	82
II.5: Characteristics of electroplating effluents in Thailand.....	85
III.1: Characteristics of graphite particles used in 3PE reactor.....	98
III.2: Characteristics of solutions in experimental studies.....	99
III.3: Operating conditions for metal recovery in a reactor without membrane.....	100
III.4: Operating conditions for metal recovery in a membrane reactor.....	101
IV.1: Mass transfer coefficient of solutions S1 and S3.....	132
IV.2: Comparison between literature and experimental dimensionless number.....	133
IV.3: Chemical and physical property of solution used for provable experiment.....	134
IV.4: Results of provable experiments.....	135
V.1: Material balance of proton in chromium precipitation process.....	164
V.2: Material balance of proton in nickel precipitation process.....	188
VI.1: Characteristics of effluent solution from Plant I and Plant II.....	203
VI.2: Summation characteristics of synthetic solution, Plant I and Plant II solutions.....	206
VI.3: Results of cyanide test by Prussian Blue Test method.....	207
VI.4: Composition of brightener.....	208
VI.5: Results of hexavalent chromium test.....	211
VI.6: Cost analysis of metal recovery from Plant I and Plant II solutions.....	215
VI.7: Comparison of operating costs of this work and conventional methods.....	215

LIST OF FIGURES

FIGURE	Page
II.1: Current - voltage curve for an electrolytic cell.....	34
II.2: Current potential curves for ideal polarizable (a) and non polarizable electrodes (b).....	38
II.3: The cell potential and its various components.....	39
II.4: Current overpotential curves for the system $O + ne^- \rightarrow R$	41
II.5: Tafel plot for anodic and cathodic branches of the $i - \eta$ curve.....	43
II.6: Proposed model of the electrode - solution, double - layer region.....	44
II.7: Potential profile across double - layer region.....	44
II.8: The relationships between charge, mass and heat transport.....	45
II.9: Nernst diffusion layer model.....	47
II.10: Pathway of a general electrode reaction.....	49
II.11: Overall scheme for sorptive flotation.....	54
II.12: Schematic diagram of electrodialysis membrane stack.....	55
II.13: Flow sheet of the biological method.....	56
II.14: Possible metal recovery flow sheet of pressure - driven membrane.....	57
II.15: Electrochemical process with cathodic reduction.....	60
II.16: Electrochemical process with soluble electrode.....	61
II.17: Evolution of exchange process with cationic membrane.....	63
II.18: Evolution of exchange process with anionic membrane.....	63
II.19: The periodic destabilization of the granular cathode bed.....	65
II.20: Behavior of particles in 3PE reactor.....	65
II.21: Schematic diagram of 3PE reactor.....	69
II.22: Representation of batch reactor.....	74
II.23: Global disposal of apparatus.....	74
II.24: Continuous stirrer tank reactor.....	77
II.25: Plug flow reactor.....	79
II.26: Definition for calculation of hydraulic diameter in parallel plan electrodes.....	81
II.27: Typical electroplating processes.....	83
II.28: Operation mode of an electroplating unit.....	84

	Page
III.1: Schematic diagram of apparatus for current density - potential studies	92
III.2: Scheme of the microbalance set up	93
III.3: Schematic view of classical reactor without membrane	94
III.4: Schematic presentation of electrodeposition reactor	95
III.5: Schematic view of classical reactor with membrane	96
III.6: Schematic presentation of 3PE reactor	97
III.7: Polarization curve of solutions SOL 1 and SOL 2	102
III.8: Polarization curve of solution S1	103
III.9: Polarization curve of solution S2	104
III.10: Polarization curve of solution S4	105
III.11: Polarization curve of solution S5	106
III.12: Polarization curve of solution S8	107
III.13: Polarization curve of solution S9	107
III.14: Polarization curve of solution S12	108
III.15: Comparison between polarization curve of solutions SOL 1 and S12	109
III.16: Polarization curve of solution S14	110
III.17: Polarization curve of nickel solution (0.25 g/l, pH = 1)	111
III.18: Thickness layer and frequency divided by time of nickel deposition versus potential (0.25 g/l, pH = 1)	111
III.19: Polarization curve of zinc solution (0.25 g/l, pH = 1)	112
III.20: Thickness layer and frequency divided by time of zinc deposition versus potential (0.25 g/l, pH = 1)	113
IV.1: Copper recovery percentage versus time (solution S1)	116
IV.2: Current efficiency versus current density (solution S1)	116
IV.3: Copper recovery percentage versus time (solution S2)	117
IV.4: Current efficiency versus current density (solution S2)	117
IV.5: Concentration evolution versus time of solutions S1 and S2 at 10 A/m ² and 0.42 l/min	118
IV.6: Copper recovery percentage versus time (solution S3)	119
IV.7: Current efficiency versus current density (solution S3)	119
IV.8: Concentration evolution of copper at different flow rates (solution S1)	121
IV.9: Concentration evolution of copper at different flow rates (solution S2)	121
IV.10: Concentration evolution of copper at different flow rates (solution S3)	122

	Page
IV.11: Model and experimental concentrations versus time (solution S1).....	124
IV.12: Mass transfer coefficient versus flow rates and Reynolds number (solution S1).....	124
IV.13: Model and experimental concentrations versus time (solution S2).....	126
IV.14: Mass transfer coefficient versus flow rates and Reynolds number (solution S2).....	127
IV.15: Model and experimental concentration versus time (solution S3).....	129
IV.16: Concentration evolution versus time at current density = 10 A/m ² , flow rate = 3 l/min (solutions S1 and S3).....	131
IV.17: Concentration evolution versus time at concentration lower than 1 g/l (solutions S1 and S3).....	131
IV.18: Comparison of Sherwood number and Reynolds number.....	132
IV.19: Polarization curves of provable experiments.....	135
IV.20: Comparison between experimental and provable results.....	136
IV.21: Copper recovery percentage versus electrolysis time.....	137
IV.22: Current efficiency versus current density at various percentages of copper recovery.....	138
IV.23: Operating cost versus current intensity at 99 % recovery.....	138
IV.24: Copper recovery percentage versus electrolysis time at various pulse frequency.....	139
IV.25: Polarization curve of copper solution with graphite and copper cathode.....	141
IV.26: Concentration evolution and copper recovery percentage versus time for the both cathodes (graphite and copper).....	142
IV.27: Copper recovery percentage versus electrolysis time at different electrolyte flow rates.....	143
IV.28: Mass transfer coefficient versus electrolyte flow rates.....	144
IV.29: Comparison of our mass transfer coefficient with Panizza et al.....	145
IV.30: Comparison of our mass transfer coefficient with Olive et al and Kalabelas et al.....	145
IV.31: Zinc recovery percentage versus time (solition S12).....	146
IV.32: Current efficiency versus current density (solution S12).....	147
IV.33: Operating cost versus current density (solution S12).....	148
V.1: Chromium recovery percentage versus time (solution S4).....	151

	Page
V.2: Chromium recovery percentage versus time (solution S5).....	151
V.3: Chromium recovery percentage and pH versus time (solution S4).....	153
V.4: Chromium recovery percentage and pH versus time (solution S5).....	154
V.5: Operating cost versus current density (solution S4).....	155
V.6: Operating cost versus current density (solution S5).....	155
V.7: Comparison between pH_{exp} and pH_{m1} evolution versus time (solution S4).....	158
V.8: Comparison between pH_{exp} and pH_{m1} evolution versus time (solution S5).....	159
V.9: Precipitation data of chromium solution.....	160
V.10: Comparison between pH_{exp} and pH_{m2} evolution versus time (solution S4).....	162
V.11: Comparison between pH_{exp} and pH_{m2} evolution versus time (solution S5).....	163
V.12: Comparison between pH_{exp} and pH_{m3} evolution versus time (solution S4).....	166
V.13: Plots of pH_{m1} , pH_{m2} , pH_{m3} and pH_{exp} evolution versus time (solution S4).....	167
V.14: Plots of C_{m1} , C_{m2} , C_{m3} and C_{exp} evolution versus time (solution S4).....	168
V.15: Plots of pH_{m1} , pH_{m2} , pH_{m3} and pH_{exp} evolution versus time (solution S5).....	169
V.16: Plots of C_{m1} , C_{m2} , C_{m3} and C_{exp} evolution versus time (solution S5).....	170
V.17: Plots of pH_{m1} , pH_{m2} , pH_{m3} and pH_{exp} evolution versus time at 203 A/m^2 (solutions S6 and S7).....	171
V.18: Effect of initial pH on chromium recovery at 203 A/m^2 (solutions S4 and S5).....	172
V.19: Chromium recovery percentage versus time at 203 A/m^2 (solutions S4 and S6).....	173
V.20: Chromium recovery percentage versus time at 203 A/m^2 (solutions S5 and S7).....	173
V.21: Nickel recovery percentage versus time (solution S8).....	175
V.22: Nickel recovery percentage versus time (solution S9).....	175
V.23: Nickel recovery percentage and pH versus time (solution S8).....	177
V.24: Nickel recovery percentage and pH versus time (solution S9).....	178
V.25: Operating cost versus current density (solution S8).....	179
V.26: Operating cost versus current density (solution S9).....	179
V.27: Comparison between pH_{exp} and pH_{m1} evolution versus time (solution S8).....	182
V.28: Comparison between pH_{exp} and pH_{m1} evolution versus time (solution S9).....	183
V.29: Precipitation data of nickel solution.....	184
V.30: Comparison between pH_{exp} and pH_{m2} evolution versus time (solution S8).....	186

	Page
V.31: Comparison between pH_{exp} and $\text{pH}_{\text{m}2}$ evolution versus time (solution S9).....	187
V.32: Comparison between pH_{exp} and $\text{pH}_{\text{m}3}$ evolution versus time (solution S 8)....	190
V.33: Plots of $\text{pH}_{\text{m}1}$, $\text{pH}_{\text{m}2}$, $\text{pH}_{\text{m}3}$ and pH_{exp} evolution versus time (solution S8).....	191
V.34: Plots of $\text{pH}_{\text{m}1}$, $\text{pH}_{\text{m}2}$, $\text{pH}_{\text{m}3}$ and pH_{exp} evolution versus time (solution S9).....	192
V.35: Plots of $C_{\text{m}1}$, $C_{\text{m}2}$, $C_{\text{m}3}$ and C_{exp} evolution versus time (solution S8).....	193
V.36: Plots of $C_{\text{m}1}$, $C_{\text{m}2}$, $C_{\text{m}3}$ and C_{exp} evolution versus time (solution S9).....	194
V.37: Nickel recovery percentage and pH versus time (solution S10).....	195
V.38: Nickel recovery percentage and pH versus time (solution S11).....	195
V.39: Plots of $\text{pH}_{\text{m}1}$, $\text{pH}_{\text{m}2}$, $\text{pH}_{\text{m}3}$ and pH_{exp} evolution versus time at 203 A/m^2 (solutions S10 and S11).....	196
V.40: Effect of initial pH on nickel recovery versus time at 203 A/m^2	197
V.41: Effect of initial concentration on nickel recovery versus time at 203 A/m^2	197
VI.1: Metal recovery percentage and pH evolution versus time (solution S13).....	201
VI.2: Metal recovery percentage and pH evolution versus time (solution S14).....	202
VI.3: Metal recovery percentage and pH evolution versus time (solution S15).....	204
VI.4: Metal recovery percentage and pH evolution versus time (solution S16).....	205
VI.5: Copper recovery percentage versus time in a presence of brightener.....	208
VI.6: Copper recovery percentage versus time (solution S16).....	209
VI.7: Copper recovery percentage versus time in a presence of several chromium concentrations (solution S16).....	212
VI.8: Current efficiency and time versus initial hexavalent chromium concentration (solution S16).....	213

LIST OF ABBREVIATIONS

A	area of membrane (m^2)
A_e	active area (m^2)
A_R	cross - sectional area of reactor (m^2)
a	pulse amplitude (m)
a, b, c, d, s	(a) number of moles (mol) (b) stoichiometric constant
a_e'	specific area of electrode (m^2/m^3)
C_{AE}, C_1	inlet concentration of species A (mol/m^3)
C_{AS}, C_2	outlet concentration of species A (mol/m^3)
C_{av}	average concentration (mol/m^3)
C_{exp}	experimental concentration
C_i	concentration of species i (mol/m^3)
C_i^*	bulk concentration of species i (mol/m^3)
$C_{i(x)}$	concentration of species i at distance x (mol/m^3)
$C_{i,(0,t)}$	concentration of species i at the electrode surface at time t (mol/m^3)
C_S, C_α	bulk concentration (mol/m^3)
C_0	(a) surface concentration (mol/m^3) (b) initial concentration (mol/m^3)
C_T	total concentration (mol/m^3)
C_t	concentration at time t (mol/m^3)
C_1	first level of model concentration (mol/m^3)
C^*	transition concentration (mol/m^3)
D_i	diffusion coefficient of species i (m^2/s)
d_h	hydraulic diameter (m)
d_{hS}	hydraulic diameter of smooth electrode (m)
d_{hR}	hydraulic diameter of rough electrode (m)
d_p	particle diameter (m)
E	potential of an electrode versus reference (V)
E_A, E_B	electrode potential of the half - cell (V)
E_a	anodic potential (V)
E_{ap}	applied potential (V)

E_c	cathodic potential (V)
E_{cell}	cell potential (V)
E_{eq}	equilibrium potential (V)
$E_{0,1}$	electrode potential of oxidation species (V)
$E_{0,2}$	electrode potential of oxidation species(V)
E^0	standard potential of an electrode or couple (V)
$E^{0'}$	formal potential of an electrode (V)
E_0	electrode potential (V)
e	electronic charge (C)
F	the Faraday constant (96500 C)
f	(a) $\frac{F}{RT}$ (b) pulse frequency (Hz) (c) diameter of hole (m) (d) dimension of square hole
G	Gibbs free energy change in a chemical process (kJ/mol)
G_1	free energy of half - reaction of oxidation (kJ/mol)
G_2	free energy of half - reaction of reduction (kJ/mol)
G_i	free energy of half - reaction of species i (kJ/mol)
g	gravity force (m/s ²)
H	height (m)
h	gap inter - electrode (m)
h_c	critical height bed (m)
h_f	final height of bed (m)
h_0	initial height of bed (m)
i	current (A)
i_a	anodic component current (A)
i_c	cathodic component current (A)
i_l	limiting current (A)
i_0	(a) exchange current (A) (b) intensity of incident radiation emitted by the light source (A)
iR	Ohmic drop (V)
i_t	intensity of transmitted radiation (amount not absorbed) (A)
j	current density (A/m ²)

j_d	Chilton - Colburn factor
j_l	limiting current density (A/m^2)
k	constant
k_{eq}	rate constant at equilibrium (depends on order)
k_L	mass transfer coefficient (m/s)
k_{sp}	solubility constant
k_W	water solubility
k^0	standard heterogeneous rate constant (m/s)
L	(a) length of electrode (m) (b) path length (m)
L_R	length of reactor (m)
l	width of electrode (m)
M_W	molecular weight (g/mol)
m	mass of substance (g)
N_{H^+}	loss flux of proton (mol/m^2s)
N_i	flux of component i (mol/m^2s)
$N_{i,conv}$	convection flux of species i (mol/m^2s)
$N_{i,diff}$	diffusion flux of species i (mol/m^2s)
$N_{i,m}$	migration flux of species i (mol/m^2s)
N_T	total flux (mol/m^2s)
n	(a) number of electrons involved in an electrode reaction (C) (b) number of holes (holes)
$n_{H^+consumed}$	proton consumption (mol)
n_{H^+diff}	proton difference (mol)
$n_{H^+difint}$	proton difference in time interval (mol)
n_{H^+exp}	proton measured during experiment (mol)
$n_{H^+theory}$	theory proton (mol)
O	oxidized form of active species
p	pressure (atm)
pH_{exp}	experimental pH
pH_i	initial pH
pH_{m1}, C_{m1}	pH and concentration developed by the first model
pH_{m2}, C_{m2}	pH and concentration developed by the second model
pH_{m3}, C_{m3}	pH and concentration developed by the third model

pH_{sol}	pH of solution
Q	flow rate (m^3/s , l/min)
q	excess charge (C)
R	(a) reduced form of active species (b) resistant (Ω) (c) gas constant (J/mol K) (d) recovery percentage (%)
R_C	recovery cost (Baht/ m^3)
R_{ct}	charge transfer resistance (Ω)
Re	Reynolds number
R_i	production rate of species i
R_W	recovery weight (kg/m^3)
S	(a) standard deviation (b) cross section area of bed (m^2)
Sc	Schmidt number
Sh	Sherwood number
S^0	standard entropy (kJ/mol K)
T	temperature (K)
t	(a) electrolysis time (s) (b) thickness (m)
t_{diff}	time difference (s)
t_l	latent time (s)
t_2	precipitation time (s)
t^*	transition period (s)
U	average velocity (m)
U_i	velocity of species i (m)
U_{mf}	minimum particle velocity (m/s)
U_p^+	upward final particle velocity (m/s)
U_p^-	downward final particle velocity (m/s)
$U(t)$	velocity at time t (m/s)
U_0	(a) reversible cell voltage (V) (b) liquid velocity (m/s)
U_2^+	upward final liquid velocity (m/s)
U_2^-	downward final liquid velocity (m/s)

V	(a) volume (m^3) (b) applied voltage (V)
V_R	volume of reactor (m^3)
V_S	volume of storage tank (m^3)
W_i	initial metal weight (g)
W_S	sludge weight (kg/m^3)
W_t	metal weight at time t (g)
x	(a) distance, often from a planar electrode (m) (b) fraction of conversion
x_1	distance of the inner Helmholtz plane from the electrode surface (m)
x_2	distance of the outer Helmholtz plane from the electrode surface (m)
α	(a) transfer coefficient (b) slope ($\text{mol}/\text{m}^3\text{s}$)
γ	rate of heterogeneous reaction
δ	diffusion layer (m)
ε_1	voidage of fixed bed
ε_2	voidage after fluidization
η	overpotential (V)
η_{ct}	charge transfer overpotential (V)
η_{mt}	mass transfer overpotential (V)
η_{rxn}	reaction overpotential (V)
μ	liquid viscosity ($\text{kg}/\text{m s}$)
μ_i	mobility of species i (m^2/Vs)
ν	kinematics velocity (m^2/s)
ξ	fraction of periodic destabilization
ρ	liquid density (m^3/kg)
ρ_p	particle density (m^3/kg)
τ	period of pulsating motion (s)
τ_T	residence time in plug flow reactor (s)
ϕ	(a) electrostatic potential (V) (b) Faraday current efficiency
ϕ^M	electrostatic potential of metal layer (V)

ϕ^S	electrostatic potential of bulk solution (V)
ϕ_1	potential at the inner Helmholtz plane (V)
ϕ_2	potential at the outer Helmholtz plane with (V)