UNIVERSITI PUTRA MALAYSIA

REMEDIATION OF CRUDE OIL CONTAMINATED KAOLIN BY ADSORPTION USING SOLID-LIQUID TWO-PHASE PARTITIONING

MAZYAR PEYDA

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By

MAZYAR PEYDA

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the Degree of Doctor of Philosophy

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Chairman: Professor Fakhrul-Razi Ahmadun, PhD

Faculty: Engineering

Soil contamination by crude oil is a major environmental and health hazard. The main goal of this research was to investigate the applicability of using a solid-liquid two-phase partitioning bioreactor (TPPB) to remediate crude oil contaminated kaolin. To achieve this objective, sorption studies were carried out on kaolin contaminated by crude oil using commercial thermoplastic polyurethane (Desmopan®) and 2-propanol as a mobilizing agent followed by bio-regeneration of crude oil loaded polymer beads in the TPPB. The equilibrium sorption capacity (q_e) as well as the kinetic behaviour of the thermoplastic polyurethane (TPU) was determined as a function of the crude oil dilution with 2-propanol. The polymeric sorbent exhibited the highest q_e value when immersed in a 50% diluted crude oil.

The sorption experimental data correlated well with different kinetic models. The Elovich kinetic model correlated accurately with the diluted crude oil experimental data; while the pseudo-first order and pseudo-second order kinetic models could also

predict the sorption of *n*-alkanes (C_{14}-C_{36}) and polycyclic aromatic hydrocarbons (PAHs) into the polymeric sorbent, respectively.

Parameters of the power law model showed that the mechanism of transport for both diluted and undiluted-crude oil into the TPU was Fickian. The sorption kinetics of the PAHs and the short-chain *n*-alkanes (C_{14}-C_{18}) were also shown to be a direct function of their octanol/water partitioning coefficient. In contrast, the sorption rates of the long chain *n*-alkanes (C_{20}-C_{36}) were inversely associated with their molecular volumes. Finally, intraparticle diffusion analysis indicated that the 2-propanol present in crude oil had reduced both the external and the internal mass transfer resistances within the internal structure of the TPU.

A central composite design (CCD) under response surface methodology (RSM) was employed for experimental design in kaolin remediation study and analysis of the results. The influences of independent variables on the total petroleum hydrocarbon (TPH) reduction efficiency were determined using a statistically significant quadratic model. Remediation was more efficient when the ratio of the mobilizing agent to the kaolin was equal to 3.00 mL g^{-1}. The results exhibited that the interaction between the extraction phase ratio and the initial concentration of crude oil in kaolin had significantly influenced the TPH removal.

Bio-regeneration of crude oil loaded TPU was optimized in a solid-liquid TPPB by applying a RSM based D-optimal design. The bacterial strains in the consortium were identified as *Brevibacillus brevis*, *Gordonia* sp., *Ochrobactrum anthropic*, *Cellulosimicrobium terreum*, and *Bacillus* sp through analysis of the 16S rRNA gene. Optimum combinations of key factors with a statistically significant cubic model were used to maximize biodegradation in the TPPB. The validity of the model was successfully verified by the agreement between the model-predicted results and the

experimental results. The bio-regeneration studies in a 5L reactor showed a significant reduction (72.07±0.63%) of low molecular weight (2-3 ring) PAHs and *n*-alkanes (97.75±0.26%) present in the crude oil loaded solid polymers. Regeneration and reusability of the crude oil loaded TPU were also confirmed by subjecting the sorbent to successive sorption-regeneration cycles in the TPPB. These findings show that solid polymer extraction followed by bio-regeneration of sorbents in a TPPB is applicable to treat crude oil contaminated kaolin.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

RAWATAN KAOLIN YANG TERCEMAR OLEH MINYAK MENTAH MENGGUNAKAN PENYERAPAN SOLID-LIQUID DALAM PEMBAHAGIAN DUA FASA

Oleh

MAZYAR PEYDA

Disember 2012

Pengerusi : Profesor Fakhrul-Razi Ahmadun, PhD

Fakulti : Kejuruteraan

Pencemaran tanah olehminyak mentah merupakan isu besar kerana berkaitan dengan alam sekitar dan resikio kesihatan. Matlamat utama kajian ini adalah untuk mengkaji kemungkinan penggunaan pembahagian bioreaktor *solid-liquid* dua fasa sebagai pemulihan minyak mentah yang tercemar oleh kaolin liat. Dalam usaha untuk mencapai matlamat ini, kajian tentang sedutan serta pengekstrakan minyak mentah dari kaolin telah dijalankan menggunakan *thermoplastic polyurethane* (Desmopan®) dengan *2-propanol* sebagai agen penggerakan . Akhirnya minyak mentah yang diperolehi dimasukkan ke dalam bekas polimer untuk proses pembahagian bioreaktor dalam cecair pepejal dua fasa (TPPB).

Kapasiti keseimbangan penyerapan (q_e) merupakan keadaan kinetik *thermoplastic polyurethane* (TPU) juga dikaji. Penyerapan polimer menunjukkan nilai q_e tertinggi dalam 50% minyak mentah cair dengan 2-propanol. Data ujikaji Penyerapan berhubungkait dengan model kinetik lain. Hasil kajian menunjukkan bahawa model

kinetik *Elovich* sepadan dengan data penyerapan minyak mentah cair, manakala model kinetik *pseudo-first* dan *pseudo-second* boleh menentukan penyerapan *n-alkanes* (C_{14} - C_{36}) dan *polycyclic aromatic hydrocarbons* (PAH). Parameter model *power low* juga telah menunjukkan bahawa mekanisme pengangkutan bagi kedua-dua minyak cair mentah dan minyak pekat mentah ke dalam TPU adalah *Fickian*. penyerapan Kinetik PAH dan *short-link n-alkanes* (C_{14} - C_{18}) adalah fungsi langsung terhadap pekali oktanol / air dan senggatannya. Sebaliknya, kadar penyerapan (C_{20} – C_{36}) berhubungkait dengan isipadu molekulnya. Analisis resapan intrapartikal menunjukkan bahawa, 2-propanol dalam minyak mentah mengurangkan rintangan kedua-dua jisim luaran dan dalaman antara struktur dalaman TPU.

Reka bentuk komposit pusat (CCD) di bawah kaedah respons permukaan (RSM) digunakan untuk rekabentuk eksperimen dalam kajian pemulihan kaolin dan analisis kdapatan kajian. Pengaruh pembolehubah bebas terhadap jumlah hidrokarbon petroleum (TPH) penurunan effiensi dapat ditentukan dengan menggunakan model *statiscally significant quadratic*. Pemulihan lebih cekap apabila ejen mobilizing terhadap nisbah kaolin adalah sama kepada 3.00 mL g^{-1}. Nisbah interaksi fasa dan kepekatan minyak mentah dalam kaolin jelas mempengaruhi penyingkiran TPH. Beban bio-Regenerasi minyak mentah TPU telah ditentukan dalam TPPB pepejal-cecair dengan menggunakan RSM berasaskan reka bentuk *D-optimal*. Pembentukan bakteria dalam konsortium itu telah dikenal pasti sebagai *brevibacillus brevis*, *Gordonia sp*, *Ochrobactrum Anthropic*, *Cellulosimicrobium terreum*, dan *Bacillus sp*. Berdasarkan rRNA 16S. faktor utama kombinasi optimum dengan model *statistically significan cubic* telah digunakan untuk memaksimumkan biodegradation dalam TPPB. Kesahan model berjaya ditentukan oleh hasil antara *precdicted-model* dan eksperimental. Kajian bio-regeneration dalam lima liter reaktor menunjukkan

penurunan yang signifikan (72.07 ± 0.63%) bagi berat molekul rendah (2-3 cincin) PAH dan *n-alkanes* (97.75 ± 0.26%) dalam minyak mentah yang dimuatkan dalam polimer pepejal. Regenerasi dan penggunaan semula minyak mentah dalam TPU juga mengesahkan dengan melemahkan penyerapan kepada kitaran serapan-regenerasi berturut-turut dalam TPPB.

Bukti-bukti ini menunjukkan bahawa pengekstrakan pepejal polimer diikuti oleh bio-regenerasi penyerapan dalam TPPB boleh digunakan untuk merawat minyak mentah yang tercemar oleh kaolin liat.

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I certify that a Thesis Examination Committee has met on 18 December 2012 to conduct the final examination of Mazyar Peyda on his thesis entitled "Remediation of Crude Oil Contaminated Kaolin by Adsorption Using Solid-Liquid Two-Phase Partitioning" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

Thamer Ahmed Mohammed Ali, PhD
Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Chuah Teong Guan @ Luqman Chuah bin Abdullah, PhD
Professor
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Sa'ari Bin Mustapha, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

David C Stuckey, PhD
Professor
Imperial College London
United Kingdom
(External Examiner)

NORITAH OMAR, PhD
Assoc. Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 26 June 2013

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the Degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Fakhru'l-Razi Ahmadun, PhD
Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Mohamad Pauzi Zakaria, PhD
Professor
Faculty of Environmental Sciences
University Putra Malaysia
(Member)

Zurina Zainal Abidin, PhD
Associate Professor
Faculty of Engineering
University Putra Malaysia
(Member)

Wan Azlina Wan Ab Karim Ghani, PhD
Associate Professor
Faculty of Engineering
University Putra Malaysia
(Member)

BUJANG BIN KIM HUAT, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

MAZYAR PEYDA

Date: 18 December 2012

TABLE OF CONTENTS

	Page
ABSTRACT	ii
ABSTRAK	v
ACKNOWLEDGEMENTS	viii
APPROVAL	ix
DECLARATION	xi
LIST OF TABALES	xv
LIST OF FIGURES	xvii
LIST OF ABBREVIATIONS	xx
CHAPTER	
1 INTRODUCTION	1
1.1 Background	1
1.2 Problem Statements	3
1.3 Objectives of the Study	6
1.4 Scope and Limitation of the Study	6
2 LITERATURE REVIEW	12
2.1 Basic in Crude Oil Chemistry	12
2.1.1 Aromatic Hydrocarbons	15
2.1.2 Polycyclic Aromatic Hydrocarbons	15
2.2 Human Health Effects Associated with Exposure to Spilled Oil	18
2.3 Fate of Spilled Oil	20
2.4 Biodegradation of Crude Oil	22
2.4.1 Susceptibility to Biodegradation	22
2.4.2 Effects of Temperature	25
2.4.3 Bioavailability of Hydrocarbons	26
2.4.4 Effects of Toxicity	26
2.4.5 Effects of Salinity	27
2.4.6 Effects of Soil Texture	28
2.5 Bioremediation of Crude Oil Contaminated Soil	29
2.5.1 Soil washing	30
2.5.2 Land farming	31
2.5.3 Electro bioremediation	31
2.5.4 Slurry phase	32
2.6 Synthetic Sorbents in Oil Spill Clean Up	33
2.7 Fundamentals of TPPB	34
2.7.1 Disadvantages of Liquid-Liquid TPPB	35
2.7.2 Advantages of Solid-Liquid TPPB	36
2.7.3 Limitations of Solid-Liquid TPPB	37
2.8 Solid–Liquid TPPB for Contaminated Soil Remediation	38
2.9 Mobilizing Agent in Soil Remediation	41
2.10 Sorption and Diffusion of Organic Compounds in Polyurethane	42
2.11 Sorption Kinetics of Organic Compounds	45
2.12 Statistical Design of Experiments	46

2.13 Response surface methodology 46
2.14 D-Optimal Design 48
2.15 Modeling and Optimization 50
2.16 Application of RSM in Bioremediation Studies 51
2.17 Summary 52

3 MATERIAL AND METHODS 54
3.1 Chemicals 54
3.2 Crude Oil 54
3.3 Model Fine Soil 54
3.4 Solid Phase in Bioreactor 55
3.5 SEM Observation 56
3.6 Fourier Transform Infrared (FTIR) Analysis 57
3.7 Particle Size Distribution Analysis 57
3.8 Statistical Analysis 58
3.9 Determination of Polymer/2-Propanol Partitioning Coefficient 62
3.10 Solid Polymer Desorption for Hydrocarbon Analysis 63
3.11 PAHs and n-Alkanes Analysis Using GC-MS 64
3.12 TPH Analysis Using GC-FID 67
3.13 Crude Oil Sorption in Kinetic Studies 68
3.14 Determination of Diffusional Exponent 69
3.15 Assessment of Fitted Kinetic Models 69
3.16 Kaolin Remediation Study Using CCFD Experimental Design 71
3.16.1 Preparation of Crude Oil Contaminated Kaolin 72
3.16.2 Extraction of TPH from Kaolin 73
3.17 Preparing Crude Oil Degrading Consortium 73
3.18 Enrichment and Isolation of Consortium Strains 74
3.19 Identification of Bacterial Strains According 16S rRNA 74
3.20 TPPB Studies Using D-optimal Experimental Design 75
3.20.1 Delivery Phase Loading 78
3.20.2 Culture Medium 78
3.20.3 Inoculation 78
3.20.4 Crude Oil Biodegradation Analysis 79
3.21 Effect of Absorbed 2-Propanol on Bacterial Growth 79
3.21.1 Bacterial Growth Analysis 80
3.22 Solid Polymer Bioavailability and Toxicity 80
3.23 Bio-regeneration of Polymeric Sorbent 81
3.23.1 Polymer Loading with Crude Oil in Bio-regeneration Studies 81
3.24 Solid Polymer Reusability Study 82

4 RESULTS AND DISCUSSIONS 83
4.1 First objective: 83
4.1.1 Distribution of Crude Oil Fractions 83
4.1.2 Alcohol Sorption Kinetic 84
4.1.3 Sorption Studies 85
4.1.4 Sorption of PAHs and *n*-Alkanes 87
4.1.5 Kinetic Studies 88
4.1.6 Experimental Kinetic Data 89
4.1.7 PAHs and *n*-Alkane Sorption Kinetics 96
4.1.8 Sorption Behaviour 100

4.1.9 Analysis of Intraparticle Diffusivity Mechanisms 101
4.2 Second objective: 105
4.2.1 Particle Size Analysis of Suspended Kaolin 105
4.2.2 Statistical Evaluation of Experimental Results 106
4.2.3 Quadratic Model Diagnostic Plots 112
4.2.4 Effect of Mobilizing Agent to Kaolin Ratio 115
4.2.5 Interaction between Factors 118
4.3 Third objective: 120
4.3.1 Effect of Absorbed Mobilizing Agent on Bacterial Growth 120
4.3.2 Solid Polymer Bioavailability and Toxicity 121
4.3.3 Identification of crude oil degrading strains 122
4.3.4 Statistical Evaluation of Experimental Results 123
4.3.5 Cubic Model Diagnostic Plots 128
4.3.6 Effect of NaCl Concentration 130
4.3.7 Effect of Crude oil Concentration in Solid Polymer 135
4.3.8 Effects of Phase Ratio 140
4.3.9 Optimum Condition and Verification 141
4.3.10 Evaluation of Degraded Compounds 142
4.3.11 Biodegradation of Crude Oil in Solid-Liquid TPPB 145
4.3.12 SEM Imaging 148
4.3.13 FTIR Analysis 149
4.3.14 Reusability of Sorbents 151

5 CONCLUSION AND RECOMMENDATIONS 152
5.1 Conclusion 153
5.2 Recommendations 156

REFERENCES 157

APPENDICES 183

Appendix A 184

Appendix B 189

BIODATA OF STUDENT 195

LIST OF TABLES

Table		Page
1.	Chemical Constituents Commonly Found in Crude Oil, values are presented as percentage	13
2.	Predicted octanol/water partitioning (k_{ow}) coefficient and geometry of even carbon number *n*-alkanes	14
3.	Predicted octanol / water partitioning (k_{ow}) coefficient and geometry of 16 EPA priority polycyclic aromatic hydrocarbons	17
4.	Solid polymers employed to construct TPPB	39
5.	Exponent *n* for different geometries	45
6.	Physical and chemical properties of thermoplastic polyurethane Desmopan®5377 A	55
7.	Representative engineering properties of thermoplastic polyurethane Desmopan®5377 A	56
8.	List of studied PAHs, monitored mass to charge ration and retention time	66
9.	Internal standards with corresponding analytes assigned for quantitation	67
10.	Summary of Kinetic Models Used in the Present Study	70
11.	Explanation of error functions in the statistical analysis	71
12.	The actual and coded values of the input variables used in the face centred response surface study, values in parentheses shows coded values	72
13.	The actual and coded (in parentheses) values of the input variables used in the D-Optimal design	77
14.	Equilibrium sorption data and kinetic rate constant of solvent TPU system	84
15.	Kinetic parameters obtained by fitting experimental data to the pseudo-first, pseudo-second order and Elovich model for single and binary 2-propanol and crude oil sorption into the thermoplastic polyurethane at 30°C	94
16.	Comparison between pseudo first order, second order, and Elovich kinetic models for 16 EPA priority PAHs absorption with Desmopan®5377A	95

17. Comparison between pseudo first order, second order, and Elovich kinetic models for even carbon number *n*-alkanes (C_{14}-C_{36}) absorption by Desmopan®5377A 97

18. Kinetic analysis of different dilution ratios of crude oil with 2-Propanol in TPU at 30°C 101

19. Intraparticle diffusion rate constants for crude oil and 2-propanol in single and binary sorption into the Desmopan®5377A at 30°C 102

20. Particle size characteristic of kaolin in distilled water and alcohols 105

21. Analysis of variance (ANOVA) for the quadratic model of TPH removal efficiency from crude oil contaminated kaolin 108

22. Summary of the statistical analysis of the quadratic model 109

23. Experimental matrix of variables and corresponding experimental and predicted crude oil removal 111

24. Results of bioavailability assessment of the thermoplastic polyurethane 121

25. Isolated species from crude oil degrading consortium enriched with crude oil 122

26. Experimental matrix of variables and results of RSM based D-optimal design 124

27. Analysis of variance (ANOVA) for the cubic model of biodegradation of crude oil using TPPB 126

28. Summary of the statistical analysis of the cubic model 127

29. Optimum values in the TPPB for maximum crude oil biodegradation efficiency 141

30. Percentage of biodegradation of *n*-Alkanes for optimum experimental conditions in the TPPB 143

31. Percentage of biodegradation of 16 EPA priority parent PAHs for optimum experimental conditions in the TPPB 145

32. Partitioning coefficients of 16 EPA priority PAHs between 2-propanol and thermoplastic polyurethane (Desmopan®) 189

33. Partitioning coefficients of even carbon number n-alkanes from C_{14} to C_{36} between 2-propanol and thermoplastic polyurethane (Desmopan®) 194

LIST OF FIGURES

Figure		Page
1.	Schematic presentation of crude oil contaminated kaolin remediation by sorption using solid-liquid two phase partitioning.	11
2.	The schematic diagram of design points central composite design for three variables (Lundstedt et al., 1998)	48
3.	Distribution of Malaysian oil field (Petronas BCOT, Sarawak) crude oil fractions	83
4.	Methanol, Ethanol, and 2-Propanol uptake experiment points with Desmopan®5377A at 30°C fitted with pseudo-first order kinetic model	85
5.	Effect of 2- Propanol content in diluted crude oil on the sorption capacity of Desmopan®5377A in equilibrium with reaction volume of 40 mL at 30°C	86
6.	Effect of 2-Propanol content in diluted crude oil on the sorption capacity of 16 EPA priority PAHs and even carbon number *n*-alkanes from C_{14} to C_{36} into the Desmopan®5377A at 30°C	88
7.	Sorption of crude oil, 50% diluted crude oil with 2-Propanol, and 2-propanol into the Desmopan®5377A as a function of immersion time at 30°C	89
8.	Sorption kinetic data of crude oil (a), 5% diluted crude oil (b) and diluted crude oil with 50% of 2-Propanol (c) with Desmopan®5377A fitted by the pseudo first-order, pseudo second-order and Elovich model at 30°C	90
9.	Comparison of pseudo-second order constant (K_2) for 16 EPA priority PAHs sorption into the Desmopan®5377A with octanol water partitioning coefficient at 30°C	99
10.	Comparison of pseudo-first order constant (k_1) for even carbon number *n*-alkanes (C_{14}-C_{36}) sorption into the Desmopan®5377A with molecular volume ($Å^3$) at 30°C	100
11.	Intraparticle diffusion kinetics for crude oil, 2-propanol, and 50% diluted crude oil with 2-propanol into the thermoplastic polyurethane (Desmopan®) at 30°C	104
12.	Particle Size Distribution kaolin suspension in (a) distilled water, (b) methanol, (c) ethanol, and 2-propanol	105
13.	Normal probability versus studentized residuals for checking normality of the TPH removal efficiency	113

14. Studentized residuals versus predicted values of TPH removal for checking constant error 114

15. The actual and predicted plot of TPH removal efficiency (%) 115

16. Effect of mobilizing agent to kaolin ratio (X_2) on total petroleum hydrocarbon (TPH) removal efficiency in kaolin, at different extraction phase to kaolin ratio (X_1) and crude oil concentration in kaolin (X_3) at 30°C 116

17. Interaction effects of solid extraction phase ratio (X_1) and crude oil concentration in kaolin (X_3) on total petroleum hydrocarbon (TPH) removal efficiency in kaolin at 30°C 118

18. Effect of crude oil dilution with 2-propanol on bacterial growth at 30°C 120

19. Normal probability versus studentized residuals for checking normality of the crude oil biodegradation in the TPPB 128

20. Studentized residuals versus predicted values of the crude oil biodegradation in the TPPB for checking constant error 129

21. The actual and predicted plot of crude oil biodegradation in the TPPB 129

22. Interaction effects of salt concentration(X_1) and crude oil concentration in solid polymer (X_2) on crude oil biodegradation efficiency in the TPPB; (a) polymer phase ratio, 2.00%; (b) polymer phase ratio, 16.00%; (c) polymer phase ratio 30.00% 131

23. Interaction effects of crude oil concentration in solid polymer (X2), phase ratio (X3) on crude oil biodegradation efficiency in the TPPB; (a) NaCl concentration, 0.100 g L^{-1}; (b) NaCl concentration, 25.00 g L^{-1}; (c) NaCl concentration, 100.00 g L^{-1} 137

24. Biodegradation of 16 EPA priority PAHs and even carbon number *n*-alkanes in solid-liquid TPPB by a microbial consortium, (C_0) initial and (C) final concentrations in the solid phase, data points are the average of three replicates and error bars represent the standard error of the mean 147

25. SEM micrograph of thermoplastic polyurethane (Desmopan®) beads: (a) Virgin beads (×1000), (b) Bio-regenerated beads (×1000), (c) Bio-regenerated (×7000), and (d) Microbial growth on the Bio-regenerated beads 148

26. FTIR spectra of crude oil at frequency between 400 and 4000 cm^{-1} 150

27. FTIR spectra of virgin and bio-regenerated thermoplastic polyurethane (Desmopan®) in solid-liquid two phase partitioning bioreactor 150

28. Bio-regeneration of oil loaded Desmopan® during five repeated cycles 151

29. Partitioning curve for Naphthalene, Acenaphthene, and Acenaphthylene 190

30. Partitioning curve for Fluoranthene, Pyrene, and Benzo (a) anthracene 190

31. Partitioning curve for Fluorene, Phenanthrene, and Anthracene 191

32. Partitioning curve for Chrysene, and Benzo (b) fluoranthene 191

33. Partitioning curve for Benzo (b) pyrene, and Indeno (1, 2, 3-cd) pyrene 192

34. Partitioning curve for Dibenzo (a, h) anthracene 192

35. Partitioning curve for Benzo (ghi) perylene 193

LIST OF ABBREVIATIONS

$Å^3$	Cubic Angstrom
ANOVA	Analysis of Variance
ARE	Average Relative Error
ASTM	American Standard for Testing and Materials
α	Initial sorption rate [g (g min)$^{-1}$]
BCOT	Bintulu Crude Oil Terminal
BLAST	Basic Local Alignment Search Tool
ß	Desorption constant (g g^{-1}).
BTEX	Benzene, Toluene, Ethyl benzene, Xylenes
CCD	central composite design
CCFD	Central Composite Face-centred Design
d(0.1)	Size of particle below which 10% of the sample lies
d(0.9)	Size of particle below which 90% of the sample lies
d[3,2]	Surface Weighted Mean, also known as the Surface Area Moment Mean Diameter or Sauter mean
d[4,3]	Volume Weighted Mean or Mass Moment Mean Diameter
DCM	Dichloromethane
DF	Degree of freedom
DNA	Deoxyribonucleic acid
EPA	Environmental Protection Agency
ev	Electron volt
FTIR	Fourier Transform Infrared
GC-FID	Gas Chromatography- Flame Ionization Detector
GC-MS	Gas Chromatography-Mass Spectrometric

ID	Internal Diameter
IFO	Intermediate fuel oil
ISO	International Organization for Standardization
K_1	Pseudo first-order rate constant (min^{-1})
K_2	Pseudo second order rate constant [g (g $min)^{-1}$]
k_i	Intraparticle diffusion rate constant (g $g^{-1}min^{-0.5}$)
kN/m	Kilo newton per meter
k_{oc}	Soil organic carbon-water partitioning coefficient
kPa	Kilopascal
LMW	Low Molecular Weight
Log k_{ow}	Logarithm of Octanol-Water partitioning coefficient
m/z	Mass to charge ratio
µL	Micro litre
µm	micrometre
MPa	Mega-Pascal
MSE	Mean Square Error
MSM	Mineral Salt Medium
n	Diffusional exponent
NCBI	National Centre for Biotechnology Information
nm	nanometre
OD	Optical Density
PAHs	Polycyclic Aromatic Hydrocarbons
PCR	Polymerase Chain Reaction
pmol	Pico mole
ppm	Parts per million

PRESS	Predicted Residual Error Sum of Squares
PSD	Particle Size Distribution
q_{cal}	Theoretically calculated sorption capacity at equilibrium
qe	Equilibrium sorption capacity (g g^{-1})
q_{exp}	Experimental sorption capacity at equilibrium
q_{mean}	Average of experimental values
q_t	Uptake at time t (g g^{-1})
R^2	The coefficient of determination
R^2	Coefficient of correlation
RMS	Root Mean Square
RMSE	Root Mean Squared Error
rpm	round per minute
RSM	Response surface methodology
SEM	Scanning electron microscopy
SIM	Selected Ion Monitoring
Span	Measurement of the width of the distribution
SSE	Sum Squares Error
TPH	Total Petroleum Hydrocarbon
TPPB	Two phase partitioning bioreactor
TPU	Thermoplastic polyurethane
USEPA	United States Environmental Protection Agency
v/v	Volume to volume ratio
w/v	Ratio of Weight to volume
16S rRNA	16 Subunit of Ribosomal ribonucleic acid

CHAPTER 1

INTRODUCTION

1.1 Background

Growth in global crude oil consumptions has led to harm the environment during all stages of exploration, producing, processing, transportation, storage and using of petroleum hydrocarbons (Boehm *et al.*, 1997; Soclo *et al.*, 2000; Boehm *et al.*, 2007; Riccardi *et al.*, 2008). Although anthropogenic oil spill rate decreased due to stringent regulations and global industrial technology improvement, but the worldwide annual amount of 1.2 million tons of oil input into our environment is a major concern. During the past two decades, the major sources of oil spill have been related to the accidental or intentional discharge from tank ships or through pipelines (Schmidt-Etkin, 2011). On the other hand, oil spilled on land from pipelines and farm tanks can contaminate soil and threatening underground water (Riccardi *et al.*, 2008).

Due to the noxious properties of a large number of compounds present in crude oil, an oil spill can cause devastating damage to marine life, terrestrial life and natural resources (Paul F, 2002), as well as acute and chronic effects on human health (Suárez *et al.*, 2005; Pérez-Cadahía *et al.*, 2008b). Therefore, removal of crude oil from contaminated soil considered as an important practice to avoid subsequent pollution of aquatic as well as soil environments.

To remove spilled crude oil on land, on inland waters (fresh and estuarine), and coastal waters, different categories of technologies proposed for various situations. Mechanical recovery and chemical agents are applicable as emergency responses to oil spill. Bioremediation is appropriate after physical oil removal techniques when

further oil removal needed in small static water bodies or contaminated soil (USEPA, 2000).

Although bioremediation is known as an economical clean up method, biological treatment of soil and wastewaters containing a high concentrations of polycyclic aromatic hydrocarbons and/or high concentrations of mono aromatic hydrocarbons is limited owing to the intrinsic toxic nature of these compounds (Collins and Daugulis, 1999; Nocentini *et al.*, 2000; Ivančev-Tumbas *et al.*, 2004; Trindade *et al.*, 2005).

Two phase partitioning bioreactor (TPPB) developed as a new platform to resolve limitations experienced with conventional bioremediation due to substrate toxicity and lack of substrate delivery (Daugulis, 1997). Application of solid polymers through a two-step polymer partitioning process is effective in ex situ bioremediation of organic contaminated soil (Prpich *et al.*, 2006). In the first step, polymer beads absorb organics from contaminated soil. In the second step, polymer beads as organic phase in a TPPB delivers a sub inhibitory level of absorbed contaminants to the cell containing aqueous phase. Because of the non-biodegradable nature of occupied solid polymers, these polymers are re-useable in the same application (Prpich *et al.*, 2006).

Although it has been shown that solid polymers in conjunction with TPPB can effectively absorb and degrade xenobiotics, application of this technology platform in case of a complex mixture of hydrocarbons such as crude oil contaminated soil have not been studied.

1.2 Problem Statements

Currently, various methods have been developed to remove organic contaminants from soil, including biological, (Chhatre *et al.*, 1996) thermal, (Minai-Tehrani *et al.*, 2009) chemical (Amro, 2004) and physical (Abramov *et al.*, 2009). Despite recent research advances in remediation of hydrocarbon contaminated soil, bioremediation of crude oil contaminated clay is still a cause for concern. Therefore, it is necessary to solve the specific technical problems outlined below.

1. The US Environmental protection Agency has proposed soil washing as one of the innovative technologies for soil remediation. In this technique, organic contaminants sorbed onto the fine soil particles are removed by aqueous chemicals augmented with chemicals like surfactants, acids, bases, chelating agents, alcohols, or other additives to dissolve or solubilised the contaminants. This solution is then treated to remove or degrade contaminants that may have become, dissolved or suspended in the aqueous phase (Griffiths, 1995). Generally, soil washing processes is not cost effective in case of treatment of soils rich in fine clay particles (Pearl *et al.*, 2006).

2. Although, soil washing is less time consuming compared with bioremediation and phytoremediation (Trindade *et al.*, 2005). Bio and phytoremediation are highly affected by climatic factors, especially in the case of weathered soil contaminated with high crude oil concentration (Paudyn *et al.*, 2008).

3. Surfactants are used to remove crude oil from contaminated soils, but the main problem is the lack of knowledge about environmental fate and toxicity of the surfactant and its metabolites, especially for in situ soil remediation (Franzetti *et al.*, 2006; Urum *et al.*, 2006). Therefore, the ability of bio-surfactants due to their inherent biodegradability and low toxicity has been studied by researchers. Comparison of bio and synthetic surfactants in remediation of weathered and non-

weathered contaminated soil with crude oil has been carried out. It was reported that the enhancement of crude oil removal using the surfactant solutions was more effective for the non-weathered soils (Urum and Pekdemir, 2004).

The results obtained demonstrated that in all surfactant solutions, crude oil removal in the weathered soil was less than 50%. On the other hand, bio and synthetic surfactants remove a much greater proportion of aliphatic than aromatic compounds. It is important to note that aromatics are more toxic and recalcitrant than aliphatic compounds (Urum *et al.*, 2006).

It was revealed that surfactants have strong effect on desorption of polycyclic aromatic hydrocarbons (PAHs) in contaminated soil. Although surfactants can promote transport of solubilised PAHs, they can also be adsorbed by solid matrix. Partitioning of PAHs in to immobile adsorbed surfactants can be led to increase the sorption of PAHs into soil (Zhou and Zhu, 2007).

4. In solvent extraction for remediation of contaminated soil with petroleum hydrocarbons, the effectiveness of extraction highly depends on intimate contact between soil and extracting agent. Therefore, it is necessary to use water miscible solvents, or use a hydrophobic solvent mixed with a hydrophilic co-solvent, otherwise it is essential to dry the soil before extraction in order to obtain an optimum soil/solvent contact (Nardella *et al.*, 1999).

5. Despite the interesting advantages of crude oil contaminated soil bioremediation such as cost effectiveness (Salanitro, 2001) and potential for soil reuse (Frutos et al., 2012); there are some obstacles that may be hindering its usefulness (Nocentini *et al.*, 2000). Success of the biological treatment of soil and wastewaters containing high concentrations of polycyclic aromatic hydrocarbons and/or high concentrations of mono aromatic hydrocarbons is limited, which results from the lack of suitable

bioavailability (Lei *et al.*, 2004) and intrinsic toxic nature of these compounds (Collins and Daugulis, 1999; Nocentini *et al.*, 2000; Ivančev-Tumbas *et al.*, 2004; Trindade *et al.*, 2005).

Although, both polar and nonpolar fractions of crude oil contribute to the toxicity (Melbye et al., 2009), role of polar fraction and volatile organic compounds such as benzene, toluene, ethyl benzene and xylene (BTEX) is dominant due to their higher water solubility (Mazzeo *et al.*, 2011). Therefore, bioremediation is effective in sub-inhibitory concentrations of toxic compounds in the aqueous phase (Yeh *et al.*, 2010). Moreover, high salinity is a common problem in most oil and gas industries (Fakhru'l-Razi et al., 2009), that adversely affects soil and water bio-remediation efforts (Zhang *et al.*, 2011a; Pendashteh *et al.*, 2012).

6. Due to high specific surface area in clay minerals (Hassellöv et al., 2001), treatment of clayey soils contaminated with hydrocarbons presents a technical challenge. High fraction of clay minerals in a hydrocarbon contaminated soil causes an obstacle for conventional remediation processes. Consequently, efficient remediation of environmentally significant hydrocarbons from clayey soils is necessary.

7. A two phase partitioning bioreactor has an ability to extract pollutants from hydrocarbon contaminated soil and to release absorbed pollutants in sub-inhibitory level for microbial growth (Amsden *et al.*, 2003; Prpich *et al.*, 2006; Rehmann *et al.*, 2008). However, application of this technology platform to treat crude oil contaminated clay has not yet been studied.

1.3 Objectives of the Study

Based on above-mentioned situation, the overall aim of this thesis was to determine whether sorption using solid polymer followed by polymer bioregeneration in a solid-liquid two phase partitioning bioreactor (TPPB) is applicable as an ex-situ remediation of crude oil contaminated kaolin.

Specific goals and objectives of the research included:

1. To evaluate the equilibrium sorption capacity of thermoplastic polyurethane (Desmopan®) and its hydrocarbon sorption behaviour.
2. To investigate the effects of key factors on TPH removal efficiency of thermoplastic polyurethane (Desmopan®) from kaolin contaminated by crude oil.
3. To evaluate the effects of key factors on bio regeneration of the crude oil loaded thermoplastic polyurethane (Desmopan®) as a delivery phase in a two-phase partitioning bioreactor (TPPB).

1.4 Scope and Limitation of the Study

The experimental hypothesis of this research is that, thermoplastic polyurethane can absorb hydrocarbons from crude oil contaminated kaolin using 2-propanol as mobilizing agent and subsequently hydrocarbon loaded thermoplastic polyurethane beads can be bio-regenerated in a two phase partitioning bioreactor.

To obtain the main goal, the specific focus of this thesis was as follows:

1. To evaluate the equilibrium sorption capacity of thermoplastic polyurethane (Desmopan®) and its hydrocarbon sorption behaviour.

To achieve this objective, sorption of crude oil (BCOT, Sarawak) as a function of dilution with 2-propanol (5, 10, 25, 50, 75, and 95%) into the thermoplastic polyurethane (Desmopan®) at particular time intervals and also in equilibrium were

studied in 100 mL glass lab bottles. The sorption behaviour of polymer was evaluated by immersion weight gain method. The polymer beads were taken out of the test solution at particular time intervals, weighed on a Sartorius balance (GD503 Class II Balance) and returned to the lab bottle. The procedure of sorption and weighting was continued until the sample achieved a constant final weight (equilibrium). Analysis of absorbed even carbon number *n*-alkanes from C_{14} to C_{36} and 16 Environmental Protection Agency (EPA) priority parent PAHs were done by GC-MS.

The experimental data were correlated with the pseudo-first order, pseudo-second order, and Elovich kinetic models. A trial-and-error nonlinear procedure was used to determine the kinetic parameters by minimizing the Mean Square Error (MSE) between experimental data and predicted values.

The power law model was also used to determine the mechanism of transport into the thermoplastic polyurethane for both diluted and undiluted crude oil. The intraparticle diffusion analysis was used to determine rate limiting step in sorption of crude oil into the polymer beads.

2. To investigate the effects of key factors on TPH removal efficiency of thermoplastic polyurethane (Desmopan®) from crude oil contaminated kaolin.

To achieve this objective, the effects of main operating parameters (polymer to kaolin ratio, mobilizing agent to kaolin ratio, and oil concentration in contaminated kaolin) on remediation of crude oil contaminated kaolin was investigated. Removal of TPH was carried out batch wise in the 100 mL capped laboratory bottles with 2.00 g of kaolin and different values of operating parameters. The performance of the polymeric sorbent was evaluated in terms of TPH removal efficiency. The TPH was analysed by GC-FID before and after treatment.

Crude oil contaminated soil and sediments with various textures may behave in different manners comparing to the artificially spiked soil samples. On the other hand, most organic and inorganic contaminants tend to bind, either chemically or physically, to fine fraction of soil particles such as clay and silt. Therefore, kaolin was used as a model soil to ensure repeatability.

Isopropyl alcohol (2-propanol) as an efficient and water miscible mobilizing agent was used in soil remediation studies in order to transfer hydrocarbons from soil particles to polymer beads.

Crude oils from different oil producing regions and even within a specific production field are vary widely in their physical and chemical properties. Despite this variation, their partitioning behaviour among environmental compartments is same, although rate of partitioning may be different. Therefore, all experiments carried out using crude oil obtained from a Malaysian oilfield; Petronas Bintulu Crude Oil Terminal (BCOT), Sarawak.

To determine the influences of the key factors on the TPH removal efficiency, a three-factor central composite face centered design (CCFD) under response surface methodology (RSM) was employed to model and optimize remediation of kaolin artificially contaminated with crude oil. Removal of total petroleum hydrocarbons (TPH) was the dependent variable. Samples were extracted and analyzed according to US-EPA protocols.

Numerical optimization was carried out for maximum TPH removal using design expert software, and the desirability-functions approach was applied to the optimization.

3. To evaluate the effects of key factors on bio-regeneration of the crude oil loaded thermoplastic polyurethane (Desmopan®) as a delivery phase in a two-phase partitioning bioreactor (TPPB).

The largest sources of oil spills in the last two decades have been related to its transportation by tankers, offshore oil exploration platforms or through pipelines. Therefore, crude oil degraders were isolated from a sediment sample collected from Strait of Malacca, alongside the shoreline in port Kelang. The isolated bacteria were, purified and identified according to morphological observation and 16S rRNA gene sequencing.

D-optimal design under response surface methodology (RSM) was employed to study the effects of key factors on biodegradation of loaded crude oil into the polymer beads in batch reactors. Erlenmeyer flasks were used as bioreactors; each containing growth medium, indigenous acclimatized microorganism and different amounts of NaCl in the aqueous phase, the concentration of crude oil in the solid polymers (crude oil/TPU), and the ratio of solid polymer to aqueous phase.

Numerical optimization based on the desirability function was done in order to determine the optimum values of independent variables and maximize the crude oil biodegradation efficiency from the model obtained through experiments. A verification check in optimum combination of independent variables was applied to the model. Samples obtained from triplicated experiments using optimum conditions were extracted and analyzed to measure removal efficiency of the parent PAHs and even carbon number n-alkanes from C_{14} to C_{36} using GC/MS.

The required bio-kinetic study to proof the concept were under taken in a 5-L solid-liquid TPPB agitated with two Rushton turbines at 400 rpm for a period of 11 days.

All the sorption and the biodegradation studies were carried out at the Biochemical laboratory, Department of Chemical and Environmental Engineering, Faculty of Engineering, Universiti Putra Malaysia. Identification of the microorganisms was done at the Microbiology laboratory, Department of Plant Protection, Faculty of Agriculture, Universiti Putra Malaysia.

It was the objective of this thesis to demonstrate the applicability of a two-step treatment process shown in Figure 1 in a lab-scale study for the remediation of kaolin contaminated with crude oil.

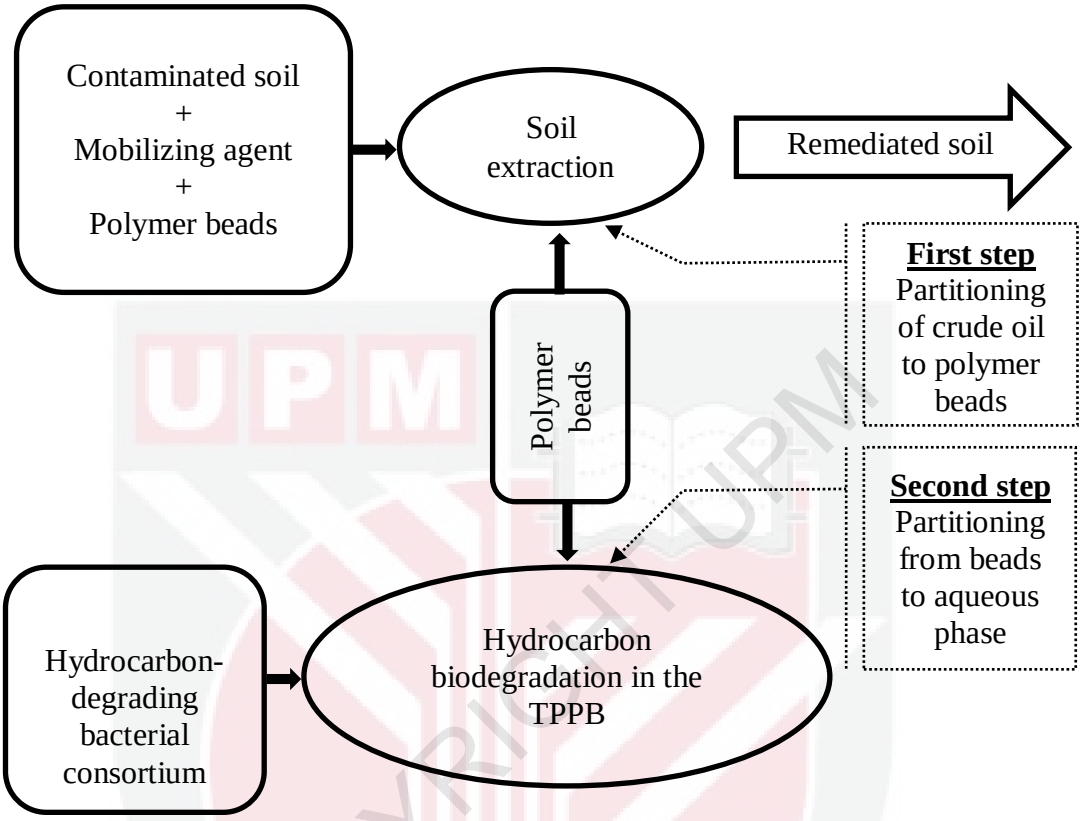

Figure 1. Schematic presentation of crude oil contaminated kaolin remediation by sorption using solid-liquid two phase partitioning.

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APPENDICES