



**UNIVERSITI PUTRA MALAYSIA**

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

**MAZYAR PEYDA**

**FK 2012 150**



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



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**

**December 2012**

## **COPYRIGHT**

All material contained within the thesis, including without limitation text, logos, icons, photographs, and all other artwork, is copyright material of Universiti Putra Malaysia unless otherwise stated. Use may be made of any material contained within the thesis for non-commercial purposes from the copyright holder. Commercial use of material may only be made with the express, prior, written permission of Universiti Putra Malaysia.

Copyright© Universiti Putra Malaysia



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

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

By

**MAZYAR PEYDA**

**December 2012**

**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<sup>®</sup>) 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<sub>14</sub>-C<sub>36</sub>) 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<sub>14</sub>-C<sub>18</sub>) 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<sub>20</sub>-C<sub>36</sub>) 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<sup>-1</sup>. 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 ( $72.07\pm 0.63\%$ ) of low molecular weight (2-3 ring) PAHs and *n*-alkanes ( $97.75\pm 0.26\%$ ) 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  
MENGUNAKAN PENYERAPAN SOLID-LIQUID DALAM  
PEMBAHAGIAN DUA FASA**

Oleh

**MAZYAR PEYDA**

**Disember 2012**

**Pengerusi : Profesor Fakhru-Razi Ahmadun, PhD**

**Fakulti : Kejuruteraan**

Pencemaran tanah oleh minyak mentah merupakan isu besar kerana berkaitan dengan alam sekitar dan resiko 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 penggerak. 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<sub>14</sub> - C<sub>36</sub>) dan *polycyclic aromatic hydrocarbons* (PAH). Parameter model *power law* 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<sub>14</sub> - C<sub>18</sub>) adalah fungsi langsung terhadap pekali oktanol / air dan senggatannya. Sebaliknya, kadar penyerapan (C<sub>20</sub> – C<sub>36</sub>) berhubungkait dengan isipadu molekulnya. Analisis resapan intrapartikel 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 efisiensi dapat ditentukan dengan menggunakan model *statistically significant quadratic*. Pemulihan lebih cekap apabila ejen mobilizing terhadap nisbah kaolin adalah sama kepada 3.00 mL g<sup>-1</sup>. 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 significant cubic* telah digunakan untuk memaksimumkan biodegradation dalam TPPB. Kesahan model berjaya ditentukan oleh hasil antara *predicted-model* dan eksperimental. Kajian bio-regeneration dalam lima liter reaktor menunjukkan



penurunan yang signifikan ( $72.07 \pm 0.63\%$ ) bagi berat molekul rendah (2-3 cincin) PAH dan *n-alkanes* ( $97.75 \pm 0.26\%$ ) 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.



## ACKNOWLEDGEMENTS

All praises and thanks are first due to Almighty Allah for giving me the opportunity to complete this work.

I owe my deepest gratitude to my supervisor Prof. Dr. Fakhru-Razi Ahmadun for his invaluable guidance, continuous support and encouragement throughout this study.

I would like to express my sincere appreciation to Prof. Dr. Mohamad Pauzi Zakaria, Assoc. Prof. Dr. Wan Azlina Wan Ab Karim Ghani and Assoc. Prof. Dr. Zurina Zainal Abidin for their great concern, valuable time and precious advices during the course of this study.

Special thanks are due to staff of Department of Chemical and Environmental Engineering, Faculty of Engineering for their help and cooperation during my experimental work. Thanks are extended to my friends and all my lab-mates in Analytical, Biochemical and Environmental Labs.

I would like to thank my wife and children, for their loving support, understanding, care and patience. To my beloved family, I would like to express my deepest affection for their never ending love and support.

Finally, I would like to thank Universiti Putra Malaysia (UPM) for financially supporting this project (Project number 05-05-10-1068RUGS, Research University Grant Scheme).

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)

---

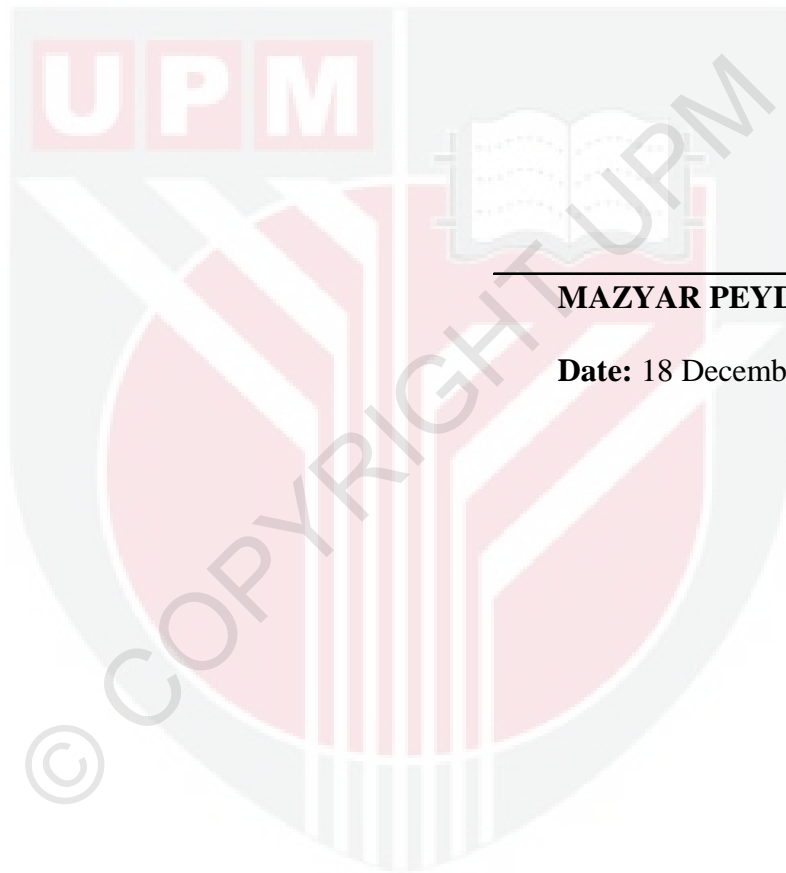
**BUJANG BIN KIM HUAT, PhD**

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

	<b>Page</b>
<b>ABSTRACT</b>	ii
<b>ABSTRAK</b>	v
<b>ACKNOWLEDGEMENTS</b>	viii
<b>APPROVAL</b>	ix
<b>DECLARATION</b>	xi
<b>LIST OF TABALES</b>	xv
<b>LIST OF FIGURES</b>	xvii
<b>LIST OF ABBREVIATIONS</b>	xx

### CHAPTER

<b>1 INTRODUCTION</b>	<b>1</b>
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
<b>2 LITERATURE REVIEW</b>	<b>12</b>
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
<b>3</b>	<b>MATERIAL AND METHODS</b>	<b>54</b>
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 <i>n</i> -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
<b>4</b>	<b>RESULTS AND DISCUSSIONS</b>	<b>83</b>
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 <i>n</i> -Alkanes	87
4.1.5	Kinetic Studies	88
4.1.6	Experimental Kinetic Data	89
4.1.7	PAHs and <i>n</i> -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
<b>5</b>	<b>CONCLUSION AND RECOMMENDATIONS</b>	<b>152</b>
5.1	Conclusion	153
5.2	Recommendations	156
	<b>REFERENCES</b>	<b>157</b>
	<b>APPENDICES</b>	<b>183</b>
	Appendix A	184
	Appendix B	189
	<b>BIODATA OF STUDENT</b>	<b>195</b>

## 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 <sup>®</sup> 5377 A	55
7. Representative engineering properties of thermoplastic polyurethane Desmopan <sup>®</sup> 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 <sup>®</sup> 5377A	95



17.	Comparison between pseudo first order, second order, and Elovich kinetic models for even carbon number <i>n</i> -alkanes (C <sub>14</sub> -C <sub>36</sub> ) absorption by Desmopan <sup>®</sup> 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 <sup>®</sup> 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 <i>n</i> -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 <sup>®</sup> )	189
33.	Partitioning coefficients of even carbon number <i>n</i> -alkanes from C <sub>14</sub> to C <sub>36</sub> between 2-propanol and thermoplastic polyurethane (Desmopan <sup>®</sup> )	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 <sup>®</sup> 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 <sup>®</sup> 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 <i>n</i> -alkanes from C <sub>14</sub> to C <sub>36</sub> into the Desmopan <sup>®</sup> 5377A at 30°C	88
7.	Sorption of crude oil, 50% diluted crude oil with 2-Propanol, and 2-propanol into the Desmopan <sup>®</sup> 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 <sup>®</sup> 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 <sup>®</sup> 5377A with octanol water partitioning coefficient at 30°C	99
10.	Comparison of pseudo-first order constant ( $k_1$ ) for even carbon number <i>n</i> -alkanes (C <sub>14</sub> -C <sub>36</sub> ) sorption into the Desmopan <sup>®</sup> 5377A with molecular volume ( $\text{\AA}^3$ ) 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 <sup>®</sup> ) 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 ( $X_2$ ), phase ratio ( $X_3$ ) on crude oil biodegradation efficiency in the TPPB; (a) NaCl concentration, 0.100 g L <sup>-1</sup> ; (b) NaCl concentration, 25.00 g L <sup>-1</sup> ; (c) NaCl concentration, 100.00 g L <sup>-1</sup>	137
24.	Biodegradation of 16 EPA priority PAHs and even carbon number <i>n</i> -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 <sup>-1</sup>	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

$\text{\AA}^3$	Cubic Angstrom
ANOVA	Analysis of Variance
ARE	Average Relative Error
ASTM	American Standard for Testing and Materials
$\alpha$	Initial sorption rate [ $\text{g (g min)}^{-1}$ ]
BCOT	Bintulu Crude Oil Terminal
BLAST	Basic Local Alignment Search Tool
$\beta$	Desorption constant ( $\text{g g}^{-1}$ ).
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 ( $\text{min}^{-1}$ )
$K_2$	Pseudo second order rate constant [ $\text{g (g min)}^{-1}$ ]
$k_i$	Intraparticle diffusion rate constant ( $\text{g g}^{-1} \text{min}^{-0.5}$ )
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
$\mu\text{L}$	Micro litre
$\mu\text{m}$	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
$q_e$	Equilibrium sorption capacity ( $\text{g g}^{-1}$ )
$q_{exp}$	Experimental sorption capacity at equilibrium
$q_{mean}$	Average of experimental values
$q_t$	Uptake at time t ( $\text{g g}^{-1}$ )
$R^2$	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<sup>®</sup>) and its hydrocarbon sorption behaviour.
2. To investigate the effects of key factors on TPH removal efficiency of thermoplastic polyurethane (Desmopan<sup>®</sup>) 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<sup>®</sup>) 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<sup>®</sup>) 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<sup>®</sup>) 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<sub>14</sub> to C<sub>36</sub> 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<sup>®</sup>) 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<sup>®</sup>) 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<sub>14</sub> to C<sub>36</sub> using GC/MS.

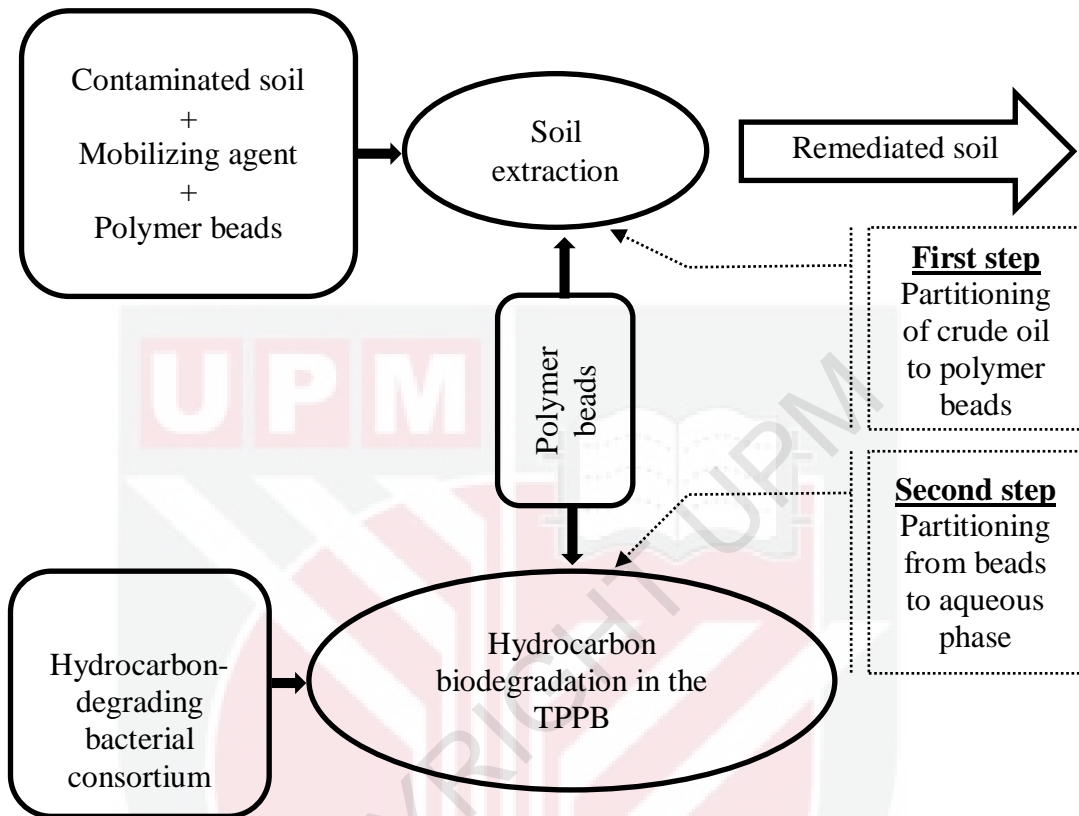
The required bio-kinetic study to proof the concept were under taken in a 5-L solid-liquid TPPB agitated with two Rushton turbines at 400 rpm for a period of 11 days.



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.**

## REFERENCES

- Abramov, O. V., Abramov, V. O., Myasnikov, S. K., & Mullakaev, M. S. (2009). Extraction of bitumen, crude oil and its products from tar sand and contaminated sandy soil under effect of ultrasound. *Ultrasonics Sonochemistry*. 16(3): 408-416.
- Abu Hamed, T., Bayraktar, E., Mehmetoglu, Ü., & Mehmetoglu, T. (2004). The biodegradation of benzene, toluene and phenol in a two-phase system. *Biochemical Engineering Journal*. 19(2): 137-146.
- Aguilera, F., Méndez, J., Pásaro, E., & Laffon, B. (2010). Review on the effects of exposure to spilled oils on human health. *Journal of Applied Toxicology*. 30(4): 291-301.
- Aithal, U. S., & Aminabhavi, T. M. (1990). Sorption and diffusion of organic solvents in polyurethane elastomers. *Polymer*. 31(9): 1757-1762.
- Al-Muhtaseb, A. a. H., Ibrahim, K. A., Albadarin, A. B., Ali-khashman, O., Walker, G. M., & Ahmad, M. N. M. (2011). Remediation of phenol-contaminated water by adsorption using poly(methyl methacrylate) (pmma). *Chemical Engineering Journal*. 168(2): 691-699.
- Alexander, M. (1975). Environmental and microbiological problems arising from recalcitrant molecules. *Microbial Ecology*. 2(1): 17-27.
- Amat-Bronnert, A., Castegnaro, M., & Pfohl-Leszkowicz, A. (2007). Genotoxic activity and induction of biotransformation enzymes in two human cell lines after treatment by erika fuel extract. *Environmental Toxicology and Pharmacology*. 23(1): 89-95.
- Amellal, N., Portal, J. M., & Berthelin, J. (2001). Effect of soil structure on the bioavailability of polycyclic aromatic hydrocarbons within aggregates of a contaminated soil. *Applied Geochemistry*. 16(14): 1611-1619.
- Aminabhavi, T. M., Harlapur, S. F., Balundgi, R. H., & Ortegoe, J. D. (1996). Sorption kinetics and diffusion of alkanes into tetrafluoroethylene/propylene copolymer membranes. *Journal of Applied Polymer Science*. 59(12): 1857-1870.
- Aminabhavi, T. M., & Khinnavar, R. S. (1993). Diffusion and sorption of organic liquids through polymer membranes: 10. Polyurethane, nitrile-butadiene rubber and epichlorohydrin versus aliphatic alcohols (C<sub>1</sub>-C<sub>5</sub>). *Polymer*. 34(5): 1006-1018.
- Amir, S., Hafidi, M., Merlina, G., Hamdi, H., & Revel, J. C. (2005). Fate of polycyclic aromatic hydrocarbons during composting of lagooning sewage sludge. *Chemosphere*. 58(4): 449-458.

- Amro, M. M. (2004). Factors affecting chemical remediation of oil contaminated water-wetted soil. *Chemical Engineering and Technology*. 27(8): 890-894.
- Amsden, B. G., Bochanysz, J., & Daugulis, A. J. (2003). Degradation of xenobiotics in a partitioning bioreactor in which the partitioning phase is a polymer. *Biotechnology and Bioengineering*. 84(4): 399-405.
- Antizar-Ladislao, B., Lopez-Real, J., & Beck, A. J. (2005). Laboratory studies of the remediation of polycyclic aromatic hydrocarbon contaminated soil by in-vessel composting. *Waste Management*. 25(3): 281-289.
- Ascon-Cabrera, M., & Lebeault, J.-M. (1993). Selection of xenobiotic-degrading microorganisms in a biphasic aqueous-organic system. *Appl. Environ. Microbiol.* 59(6): 1717-1724.
- Ascon-Cabrera, M. A., & Lebeault, J. M. (1995). Interfacial area effects of a biphasic aqueous/organic system on growth kinetic of xenobiotic-degrading microorganisms. *Applied Microbiology and Biotechnology*. 43(6): 1136-1141.
- Atalay, A., & Hwang, K. J. (1996). Extraction of light hydrocarbons from soil. *Water, Air, & Soil Pollution*. 90(3): 451-468.
- Atlas, R. M. (1981). Microbial degradation of petroleum hydrocarbons: An environmental perspective. *Microbiological Reviews*. 45(1): 180.
- Baedecker, M. J., Eganhouse, R. P., Bekins, B. A., & Delin, G. N. (2011). Loss of volatile hydrocarbons from an Inapl oil source. *Journal of Contaminant Hydrology*. 126(3-4): 140-152.
- Barron, M. G., Podrabsky, T., Ogle, S., & Ricker, R. W. (1999). Are aromatic hydrocarbons the primary determinant of petroleum toxicity to aquatic organisms? *Aquatic Toxicology*. 46(3-4): 253-268.
- Bayer (2008). Desmopan® (tpu) overview of product grades-guide values  
Bayer.
- Bayer (2012). *W89043d;desmopan developmental product* (No. 112000010958).  
Leverkusen: Bayer MaterialScience AG.
- Bayley, R., & Biggs, C. (2005). Characterisation of an attrition scrubber for the removal of high molecular weight contaminants in sand. *Chemical Engineering Journal*. 111(1): 71-79.
- Begum, M., Siddaramaiah, Kumar, H., & Aminabhavi, T. M. (2003). Molecular transport of n-alkanes into pu/pbma interpenetrating polymer network systems. *Journal of Applied Polymer Science*. 90(3): 739-746.
- Benson, D. A., Karsch-Mizrachi, I., Lipman, D. J., Ostell, J., & Wheeler, D. L. (2005). Genbank. *Nucleic Acids Research*. 33(suppl 1): D34-D38.

- Berselli, S., Benitez, E., Fedi, S., Zannoni, D., Medici, A., Marchetti, L., & Fava, F. (2006). Development and assessment of an innovative soil-washing process based on the use of cholic acid-derivatives as pollutant-mobilizing agents. *Biotechnology and Bioengineering*. 93(4): 761-770.
- Bertrand, J. C., Bianchi, M., Mallah, M. A., Acquaviva, M., & Mille, G. (1993). Hydrocarbon biodegradation and hydrocarbonoclastic bacterial communities composition grown in seawater as a function of sodium chloride concentration. *Journal of Experimental Marine Biology and Ecology*. 168(1): 125-138.
- Beškoski, V. P., Gojgić-Cvijović, G., Milić, J., Ilić, M., Miletić, S., Šolević, T., & Vrvic, M. M. (2011). Ex situ bioremediation of a soil contaminated by mazut (heavy residual fuel oil) – a field experiment. *Chemosphere*. 83(1): 34-40.
- Boehm, P. D. (2005). Polycyclic aromatic hydrocarbons (PAHs). In: D. Robert & L. M. Brian (eds.). *Environmental forensics* (pp. 313-337). Burlington: Academic Press.
- Boehm, P. D., Douglas, G. S., Burns, W. A., Mankiewicz, P. J., Page, D. S., & Bence, A. E. (1997). Application of petroleum hydrocarbon chemical fingerprinting and allocation techniques after the Exxon Valdez oil spill. *Marine Pollution Bulletin*. 34(8): 599-613.
- Boehm, P. D., Neff, J. M., & Page, D. S. (2007). Assessment of polycyclic aromatic hydrocarbon exposure in the waters of Prince William Sound after the Exxon Valdez oil spill: 1989-2005. *Marine Pollution Bulletin*. 54(3): 339-356.
- Bojes, H. K., & Pope, P. G. (2007). Characterization of EPA's 16 priority pollutant polycyclic aromatic hydrocarbons (PAHs) in tank bottom solids and associated contaminated soils at oil exploration and production sites in Texas. *Regulatory Toxicology and Pharmacology*. 47(3): 288-295.
- Bosma, T. N. P., Middeldorp, P. J. M., Schraa, G., & Zehnder, A. J. B. (1996). Mass transfer limitation of biotransformation: Quantifying bioavailability. *Environmental Science and Technology*. 31(1): 248-252.
- Bossert, I., & Bartha, R. (1984). *The fate of petroleum in soil ecosystems*. New York (USA): FAO of the United Nations.
- Bossert, I. D., & Bartha, R. (1986). Structure-biodegradability relationships of polycyclic aromatic hydrocarbons in soil. *Bulletin of Environment Contamination and Toxicology*. 37(1): 490-495.
- Boudreau, N. G., & Daugulis, A. J. (2006). Transient performance of two-phase partitioning bioreactors treating a toluene contaminated gas stream. *Biotechnology and Bioengineering*. 94(3): 448-457.
- Brown, J. L., Syslo, J., Lin, Y.-H., Getty, S., Vemuri, R., & Nadeau, R. (1998). On-site treatment of contaminated soils: An approach to bioremediation of

- weathered petroleum compounds. *Journal of Soil Contamination*. 7(6): 773-800.
- Bruce, L. J., & Daugulis, A. J. (1991). Solvent selection strategies for extractive biocatalysis. *Biotechnology Progress*. 7(2): 116-124.
- Busetti, F., Heitz, A., Cuomo, M., Badoer, S., & Traverso, P. (2006). Determination of sixteen polycyclic aromatic hydrocarbons in aqueous and solid samples from an Italian wastewater treatment plant. *Journal of Chromatography A*. 1102(1-2): 104-115.
- Canet, R., Birnstingl, J. G., Malcolm, D. G., Lopez-Real, J. M., & Beck, A. J. (2001). Biodegradation of polycyclic aromatic hydrocarbons (PAHs) by native microflora and combinations of white-rot fungi in a coal-tar contaminated soil. *Bioresource Technology*. 76(2): 113-117.
- Carlos da Silva Ramos, A., Haraguchi, L., Notrispe, F. R., Loh, W., & Mohamed, R. S. (2001). Interfacial and colloidal behavior of asphaltenes obtained from Brazilian crude oils. *Journal of Petroleum Science and Engineering*. 32(2-4): 201-216.
- Cerniglia, C. E. (1992). Biodegradation of polycyclic aromatic hydrocarbons. *Biodegradation*. 3(2): 351-368.
- Ceylan, D., Dogu, S., Karacik, B., Yakan, S. D., Okay, O. S., & Okay, O. (2009). Evaluation of butyl rubber as sorbent material for the removal of oil and polycyclic aromatic hydrocarbons from seawater. *Environmental Science and Technology*. 43(10): 3846-3852.
- Chaineau, C.-H., Morel, J.-L., & Oudot, J. (1995). Microbial degradation in soil microcosms of fuel oil hydrocarbons from drilling cuttings. *Environmental Science & Technology*. 29(6): 1615-1621.
- Chang, M.-Y., & Juang, R.-S. (2004). Adsorption of tannic acid, humic acid, and dyes from water using the composite of chitosan and activated clay. *Journal of Colloid and Interface Science*. 278(1): 18-25.
- Chen, J., Huang, P., Zhang, K., & Ding, F. (2012). Isolation of biosurfactant producers, optimization and properties of biosurfactant produced by *Acinetobacter* sp. from petroleum-contaminated soil. *Journal of Applied Microbiology*.
- Chen, J. L., Au, K. C., Wong, Y. S., & Tam, N. F. Y. (2010). Using orthogonal design to determine optimal conditions for biodegradation of phenanthrene in mangrove sediment slurry. *Journal of Hazardous Materials*. 176(1-3): 666-671.
- Cheung, W. H., Szeto, Y. S., & McKay, G. (2007). Intraparticle diffusion processes during acid dye adsorption onto chitosan. *Bioresource Technology*. 98(15): 2897-2904.



- Chew, F. N., Tan, W. S., Ling, T. C., & Tey, B. T. (2009). Single-step purification of the recombinant green fluorescent protein from intact escherichia coli cells using preparative page. *Electrophoresis*. 30(17): 3017-3023.
- Chhatre, S., Purohit, H., Shanker, R., & Khanna, P. (1996). Bacterial consortia for crude oil spill remediation. *Water Science and Technology*. 34(10): 187-193.
- Chuang, W.-Y., Young, T.-H., Wang, D.-M., Luo, R.-L., & Sun, Y.-M. (2000). Swelling behavior of hydrophobic polymers in water/ethanol mixtures. *Polymer*. 41(23): 8339-8347.
- Clayton, W., & Chien, S. (1980). Application of elovich equation to the kinetics of phosphate release and sorption in soils. *Soil Science Society of America Journal*. 44(2): 265-268.
- Collins, A. M., Woodley, J. M., & Liddell, J. M. (1995). Determination of reactor operation for the microbial hydroxylation of toluene in a two-liquid phase process. *Journal of Industrial Microbiology and Biotechnology*. 14(5): 382-388.
- Collins, L. D., & Daugulis, A. J. (1997). Characterization and optimization of a two-phase partitioning bioreactor for the biodegradation of phenol. *Applied Microbiology and Biotechnology*. 48(1): 18-22.
- Collins, L. D., & Daugulis, A. J. (1999). Benzene/toluene/ p -xylene degradation. Part ii. Effect of substrate interactions and feeding strategies in toluene/benzene and toluene/ p-xylene fermentations in a partitioning bioreactor. *Applied Microbiology and Biotechnology*. 52(3): 360-365.
- Concetta Tomei, M., Cristina Annesini, M., Prpich, G. P., & Daugulis, A. J. (2009). Biodegradation of 4-nitrophenol in a two-phase system operating with polymers as the partitioning phase. *Environmental Science and Technology*. 43(18): 7105-7110.
- Coover, M. P., & Sims, R. C. (1987). The effect of temperature on polycyclic aromatic hydrocarbon persistence in an unacclimated agricultural soil. *Hazardous waste and hazardous materials*. 4(1): 69-82.
- Costa, A. S., Romão, L. P. C., Araújo, B. R., Lucas, S. C. O., Maciel, S. T. A., Wisniewski Jr, A., & Alexandre, M. R. (2012). Environmental strategies to remove volatile aromatic fractions (BTEX) from petroleum industry wastewater using biomass. *Bioresource Technology*. 105(0): 31-39.
- Cuypers, C., Pancras, T., Grotenhuis, T., & Rulkens, W. (2002). The estimation of pah bioavailability in contaminated sediments using hydroxypropyl- $\beta$ -cyclodextrin and triton x-100 extraction techniques. *Chemosphere*. 46(8): 1235-1245.

- Daugulis, A., & Boudreau, N. (2008). Solid-liquid two-phase partitioning bioreactors for the treatment of gas-phase volatile organic carbons (VOCs) by a microbial consortium. *Biotechnology Letters*. 30(9): 1583-1587.
- Daugulis, A. J. (1997). Partitioning bioreactors. *Current Opinion in Biotechnology*. 8(2): 169-174.
- Daugulis, A. J. (2001). Two-phase partitioning bioreactors: A new technology platform for destroying xenobiotics. *Trends in Biotechnology*. 19(11): 457-462.
- Daugulis, A. J., Amsden, B. G., Bochanysz, J., & Kayssi, A. (2003). Delivery of benzene to *alcaligenes xylooxidans* by solid polymers in a two-phase partitioning bioreactor. *Biotechnology Letters*. 25(14): 1203-1207.
- de Aguiar, P. F., Bourguignon, B., Khots, M. S., Massart, D. L., & Phan-Than-Luu, R. (1995). D-optimal designs. *Chemometrics and Intelligent Laboratory Systems*. 30(2): 199-210.
- de Vasconcellos, S. P., Crespim, E., da Cruz, G. F., Senatore, D. B., Simioni, K. C. M., dos Santos Neto, E. V., . . . de Oliveira, V. M. (2009). Isolation, biodegradation ability and molecular detection of hydrocarbon degrading bacteria in petroleum samples from a brazilian offshore basin. *Organic Geochemistry*. 40(5): 574-588.
- Del Castillo, E., Montgomery, D. C., & McCarville, D. R. (1996). Modified desirability functions for multiple response optimization. *Journal of quality technology*. 28: 337-345.
- Desai, M. L., & Eisen, E. O. (1971). Salt effects in liquid-liquid equilibria. *Journal of Chemical and Engineering Data*. 16(2): 200-202.
- Di Palma, L., & Mecozzi, R. (2007). Heavy metals mobilization from harbour sediments using edta and citric acid as chelating agents. *Journal of Hazardous Materials*. 147(3): 768-775.
- Ding, L., Li, Y., Jia, D., Deng, J., & Yang, W. (2011). B-cyclodextrin-based oil-absorbents: Preparation, high oil absorbency and reusability. *Carbohydrate Polymers*. 83(4): 1990-1996.
- Douglas, G. S., Hardenstine, J. H., Liu, B., & Uhler, A. D. (2012). Laboratory and field verification of a method to estimate the extent of petroleum biodegradation in soil. *Environmental Science & Technology*. 46(15): 8279-8287.
- Dressler, M. (1979). Extraction of trace amounts of organic compounds from water with porous organic polymers. *Journal of Chromatography A*. 165(2): 167-206.



- Enneking, L., Heintz, A., & Lichtenthaler, R. N. (1996). Sorption equilibria of the ternary mixture benzene/cyclohexene/cyclohexane in polyurethane- and peba-membrane polymers. *Journal of Membrane Science*. 115(2): 161-170.
- Eriksson, L. (2008). *Design of experiments: Principles and applications*: MKS Umetrics AB.
- Fakhrul-Razi, A., Pendashteh, A., Abdullah, L. C., Biak, D. R. A., Madaeni, S. S., & Abidin, Z. Z. (2009). Review of technologies for oil and gas produced water treatment. *Journal of Hazardous Materials*. 170(2): 530-551.
- Falciglia, P. P., Giustra, M. G., & Vagliasindi, F. G. A. (2011). Low-temperature thermal desorption of diesel polluted soil: Influence of temperature and soil texture on contaminant removal kinetics. *Journal of Hazardous Materials*. 185(1): 392-400.
- Feng, D., Lorenzen, L., Aldrich, C., & Maré, P. W. (2001). Ex-situ diesel contaminated soil washing with mechanical methods. *Minerals Engineering*. 14(9): 1093-1100.
- Ferrarese, E., Andreottola, G., & Oprea, I. A. (2008). Remediation of pah-contaminated sediments by chemical oxidation. *Journal of Hazardous Materials*. 152(1): 128-139.
- Franzetti, A., Caredda, P., Ruggeri, C., Colla, P. L., Tamburini, E., Papacchini, M., & Bestetti, G. (2009). Potential applications of surface active compounds by gordonia sp. Strain bs29 in soil remediation technologies. *Chemosphere*. 75(6): 801-807.
- Franzetti, A., Di Gennaro, P., Bevilacqua, A., Papacchini, M., & Bestetti, G. (2006). Environmental features of two commercial surfactants widely used in soil remediation. *Chemosphere*. 62(9): 1474-1480.
- Frutos, F. J. G., Pérez, R., Escolano, O., Rubio, A., Gimeno, A., Fernandez, M. D., . . . Laguna, J. (2012). Remediation trials for hydrocarbon-contaminated sludge from a soil washing process: Evaluation of bioremediation technologies. *Journal of Hazardous Materials*. 199–200(0): 262-271.
- Fujita, H. (1961). *Diffusion in polymer-diluent systems* (Vol. 3/1): Springer Berlin Heidelberg.
- Gaboriau, H., & Saada, A. (2001). Influence of heavy organic pollutants of anthropic origin on pah retention by kaolinite. *Chemosphere*. 44(7): 1633-1639.
- Gallego, J. L. R., Sierra, C., Permanyer, A., Peláez, A. I., Menéndez-Vega, D., & Sánchez, J. (2011). Full-scale remediation of a jet fuel-contaminated soil: Assessment of biodegradation, volatilization, and bioavailability. *Water, Air, & Soil Pollution*. 217(1): 1-15.

- Gao, Y. F., Yang, H., Zhan, X. H., & Zhou, L. X. (2012). Scavenging of bhcs and ddts from soil by thermal desorption and solvent washing. *Environmental Science and Pollution Research*: 1-11.
- Ghazali, F. M., Rahman, R. N. Z. A., Salleh, A. B., & Basri, M. (2004). Biodegradation of hydrocarbons in soil by microbial consortium. *International Biodeterioration & Biodegradation*. 54(1): 61-67.
- Giordano, A., Stante, L., Pirozzi, F., Cesaro, R., & Bortone, G. (2005). Sequencing batch reactor performance treating pah contaminated lagoon sediments. *Journal of Hazardous Materials*. 119(1-3): 159-166.
- Gogoi, B. K., Dutta, N. N., Goswami, P., & Krishna Mohan, T. R. (2003). A case study of bioremediation of petroleum-hydrocarbon contaminated soil at a crude oil spill site. *Advances in Environmental Research*. 7(4): 767-782.
- Greenwood, P. F., Wibrow, S., George, S. J., & Tibbett, M. (2009). Hydrocarbon biodegradation and soil microbial community response to repeated oil exposure. *Organic Geochemistry*. 40(3): 293-300.
- Griffiths, R. A. (1995). Soil-washing technology and practice. *Journal of Hazardous Materials*. 40(2): 175-189.
- Guerin, T. F. (1999a). Bioremediation of phenols and polycyclic aromatic hydrocarbons in creosote contaminated soil using ex-situ landtreatment. *Journal of Hazardous Materials*. 65(3): 305-315.
- Guerin, T. F. (1999b). The extraction of aged polycyclic aromatic hydrocarbon (pah) residues from a clay soil using sonication and a soxhlet procedure: A comparative study. *J. Environ. Monit.* 1(1): 63-67.
- Ha, M., Kwon, H., Cheong, H. K., Lim, S., Yoo, S. J., Kim, E. J., . . . Chung, B. C. (2012). Urinary metabolites before and after cleanup and subjective symptoms in volunteer participants in cleanup of the hebei spirit oil spill. *Science of the Total Environment*. 429(0): 167-173.
- Hall, T. A. (1999). Bioedit: A user-friendly biological sequence alignment editor and analysis program for windows 95/98/nt. *Nucleic Acids Symposium Series*. 41: 95-98.
- Han, Y., Xia, Y., Zhu, P., Qiao, S., Zhao, R., Jin, N., . . . Wang, X. (2010). Reproductive hormones in relation to polycyclic aromatic hydrocarbon (pah) metabolites among non-occupational exposure of males. *Science of The Total Environment*. 408(4): 768-773.
- Harogoppad, S., Aithal, U., & Aminabhavi, T. (1991). Diffusion of organic solvents into polyurethane network from swelling measurements. *Journal of Applied Polymer Science*. 42(12): 3267-3270.

- Hassanshahian, M., Emtiazi, G., & Cappello, S. (2012). Isolation and characterization of crude-oil-degrading bacteria from the persian gulf and the caspian sea. *Marine Pollution Bulletin*. 64(1): 7-12.
- Hasseine, A., Meniai, A. H., & Korichi, M. (2009). Salting-out effect of single salts nacl and kcl on the lle of the systems (water + toluene + acetone), (water + cyclohexane + 2-propanol) and (water + xylene + methanol). *Desalination*. 242(1-3): 264-276.
- Hassellöv, M., Lyvén, B., Bengtsson, H., Jansen, R., Turner, D. R., & Beckett, R. (2001). Particle size distributions of clay-rich sediments and pure clay minerals: A comparison of grain size analysis with sedimentation field-flow fractionation. *Aquatic Geochemistry*. 7(2): 155-171.
- Hernandez, M., Munoz, R., & Daugulis, A. J. (2011). Biodegradation of voc mixtures of different hydrophobicities in two-phase partitioning bioreactors containing tailored polymer mixtures. *Journal of Chemical Technology & Biotechnology*. 86(1): 138-144.
- Hernández, M., Quijano, G., Thalasso, F., Daugulis, A. J., Villaverde, S., & Muñoz, R. (2010). A comparative study of solid and liquid non-aqueous phases for the biodegradation of hexane in two-phase partitioning bioreactors. *Biotechnology and Bioengineering*. 106(5): 731-740.
- Ho, Y., & McKay, G. (1999). Pseudo-second order model for sorption processes. *Process Biochemistry*. 34(5): 451-465.
- Howard, P., Meylan, W., Aronson, D., Stiteler, W., Tunkel, J., Comber, M., & Parkerton, T. F. (2005). A new biodegradation prediction model specific to petroleum hydrocarbons. *Environmental Toxicology and Chemistry*. 24(8): 1847-1860.
- Huang, L., Ma, T., Li, D., Liang, F. l., Liu, R. L., & Li, G. q. (2008). Optimization of nutrient component for diesel oil degradation by rhodococcus erythropolis. *Marine Pollution Bulletin*. 56(10): 1714-1718.
- Huesemann, M. H., Hausmann, T. S., & Fortman, T. J. (2002). Microbial factors rather than bioavailability limit the rate and extent of pah biodegradation in aged crude oil contaminated model soils. *Bioremediation Journal*. 6(4): 321-336.
- Huesemann, M. H., Hausmann, T. S., & Fortman, T. J. (2004). Does bioavailability limit biodegradation? A comparison of hydrocarbon biodegradation and desorption rates in aged soils. *Biodegradation*. 15(4): 261-274.
- Isaza, P. A., & Daugulis, A. J. (2009). Ultrasonically enhanced delivery and degradation of PAHs in a polymer-liquid partitioning system by a microbial consortium. *Biotechnology and Bioengineering*. 104(1): 91-101.

- Isaza, P. A., Daugulis, A. J., & Karan, K. (2010). Mass transport and thermodynamic analysis of PAHs in partitioning systems in the presence and absence of ultrasonication. *AIChE Journal*. 56(10): 2717-2726.
- Ivančev-Tumbas, I., Tričković, J., Karlović, E., Tamaš, Z., Rončević, S., Dalmacija, B., . . . Klačnja, M. (2004). Gc/ms-scan to follow the fate of crude oil components in bioreactors set to remediate contaminated soil. *International Biodeterioration and Biodegradation*. 54(4): 311-318.
- Jain, A., Khan, T., & Daugulis, A. (2010). Bioproduction of benzaldehyde in a solid–liquid two-phase partitioning bioreactor using *pichia pastoris*. *Biotechnology Letters*. 32(11): 1649-1654.
- Janikowski, T., Velicogna, D., Punt, M., & Daugulis, A. (2002). Use of a two-phase partitioning bioreactor for degrading polycyclic aromatic hydrocarbons by a *sphingomonas* sp. *Applied Microbiology and Biotechnology*. 59(2): 368-376.
- Jin, H. X., Dong, B., Wu, B., & Zhou, M. H. (2012). Oil absorptive polymers: Where is the future? *Polymer-Plastics Technology and Engineering*. 51(2): 154-159.
- Jing, G., Luan, M., & Chen, T. (2011). Prospects for development of oily sludge treatment. *Chemistry and Technology of Fuels and Oils*. 47(4): 312-326.
- Johnsen, A. R., Wick, L. Y., & Harms, H. (2005). Principles of microbial pah-degradation in soil. *Environmental Pollution*. 133(1): 71-84.
- Johnson, R. T., Montgomery, D. C., & Jones, B. A. (2011). An expository paper on optimal design. *Quality Engineering*. 23(3): 287-301.
- Kanaly, R. A., & Harayama, S. (2000). Biodegradation of high-molecular-weight polycyclic aromatic hydrocarbons by bacteria. *Journal of Bacteriology*. 182(8): 2059-2067.
- Karickhoff, S. W., Brown, D. S., & Scott, T. A. (1979). Sorption of hydrophobic pollutants on natural sediments. *Water Research*. 13(3): 241-248.
- Kendagannaswamy, B. (2002). Chain-extended polyurethanes—synthesis and characterization. *Journal of Applied Polymer Science*. 84(2): 359-369.
- Kerr, J., Melton, H., McMillen, S., Magaw, R., Naughton, G., & Little, A. (1999). *Polyaromatic hydrocarbon content in crude oils around the world*. Paper presented at the SPE/EPA exploration and production environmental conference: 359-368.
- Khan, T. R., & Daugulis, A. J. (2011a). The effects of polymer phase ratio and feeding strategy on solid–liquid tppbs for the production of 1-phenylacetylcarbinol from benzaldehyde using *candida utilis*. *Biotechnology Letters*. 33(1): 63-70.

- Khan, T. R., & Daugulis, A. J. (2011b). Medium composition effects on solute partitioning in solid-liquid two-phase bioreactors. *Journal of Chemical Technology & Biotechnology*. 86(1): 157-160.
- Khinnavar, R., & Aminabhavi, T. (1991). Diffusion and sorption of organic liquids through polymer membranes. I. Polyurethane versus n-alkanes. *Journal of Applied Polymer Science*. 42(8): 2321-2328.
- Khodadoust, A. P., Bagchi, R., Suidan, M. T., Brenner, R. C., & Sellers, N. G. (2000). Removal of PAHs from highly contaminated soils found at prior manufactured gas operations. *Journal of Hazardous Materials*. 80(1-3): 159-174.
- Khuri, A. I., & Mukhopadhyay, S. (2010). Response surface methodology. *Wiley Interdisciplinary Reviews: Computational Statistics*. 2(2): 128-149.
- Kim, S.-H., Chung, I.-D., Ha, C.-S., Kim, K.-J., & Cho, W.-J. (1999). Preparations and oil absorptivities of poly(stearyl methacrylate-co-cinnamoyloxyethyl methacrylate) and pet nonwoven fiber photocrosslinked with it. *Journal of Applied Polymer Science*. 73(12): 2349-2357.
- Kirby, M. F., & Law, R. J. (2008). Oil spill treatment products approval: The uk approach and potential application to the gulf region. *Marine Pollution Bulletin*. 56(7): 1243-1247.
- Korsmeyer, R. W., & Peppas, N. A. (1981). Effect of the morphology of hydrophilic polymeric matrices on the diffusion and release of water soluble drugs. *Journal of Membrane Science*. 9(3): 211-227.
- Kostka, J. E., Prakash, O., Overholt, W. A., Green, S. J., Freyer, G., Canion, A., . . . Huettel, M. (2011). Hydrocarbon-degrading bacteria and the bacterial community response in gulf of mexico beach sands impacted by the deepwater horizon oil spill. *Applied and Environmental Microbiology*. 77(22): 7962-7974.
- Kumar, K. V. (2006). Linear and non-linear regression analysis for the sorption kinetics of methylene blue onto activated carbon. *Journal of Hazardous Materials*. 137(3): 1538-1544.
- Kumar, S., Srivastava, V. C., & Badoni, R. P. (2011). Studies on adsorptive desulfurization by zirconia based adsorbents. *Fuel*. 90(11): 3209-3216.
- Kwan, K. S., Subramaniam, C. N. P., & Ward, T. C. (2003). Effect of penetrant size and shape on its transport through a thermoset adhesive: I. N-alkanes. *Polymer*. 44(10): 3061-3069.
- Laflamme, R. E., & Hites, R. A. (1978). The global distribution of polycyclic aromatic hydrocarbons in recent sediments. *Geochimica et Cosmochimica Acta*. 42(3): 289-303.



- Lagergren, S. (1898). About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademiens Handlingar*. 24(4): 1-39.
- Lahlou, M., Harms, H., Springael, D., & Ortega-Calvo, J. J. (2000). Influence of soil components on the transport of polycyclic aromatic hydrocarbon-degrading bacteria through saturated porous media. *Environmental Science & Technology*. 34(17): 3649-3656.
- Lao, L. L., Peppas, N. A., Boey, F. Y. C., & Venkatraman, S. S. (2011). Modeling of drug release from bulk-degrading polymers. *International Journal of Pharmaceutics*. 418(1): 28-41.
- Lazaridis, N. K., Karapantsios, T. D., & Georgantas, D. (2003). Kinetic analysis for the removal of a reactive dye from aqueous solution onto hydrotalcite by adsorption. *Water Research*. 37(12): 3023-3033.
- Lazić, Ž. R. (2004). *Design of experiments in chemical engineering: A practical guide*: Vch Verlagsgesellschaft Mbh.
- Leahy, J. G., & Colwell, R. R. (1990). Microbial degradation of hydrocarbons in the environment. *Microbiological reviews*. 54(3): 305-315.
- Lee, S., & Knaebel, K. S. (1997). Effects of mechanical and chemical properties on transport in fluoropolymers. I. Transient sorption. *Journal of Applied Polymer Science*. 64(3): 455-476.
- Lei, L., Khodadoust, A. P., Suidan, M. T., & Tabak, H. H. (2005). Biodegradation of sediment-bound PAHs in field-contaminated sediment. *Water Research*. 39(2-3): 349-361.
- Lei, L., Suidan, M. T., Khodadoust, A. P., & Tabak, H. H. (2004). Assessing the bioavailability of PAHs in field-contaminated sediment using xad-2 assisted desorption. *Environmental Science & Technology*. 38(6): 1786-1793.
- Lemiere, S., Cossu-Leguille, C., Bispo, A., Jourdain, M.-J., Lanhers, M.-C., Burnel, D., & Vasseur, P. (2005). DNA damage measured by the single-cell gel electrophoresis (comet) assay in mammals fed with mussels contaminated by the 'Erika' oil-spill. *Mutation Research/Genetic Toxicology and Environmental Mutagenesis*. 581(1-2): 11-21.
- Li, S., & Wei, J. (2012). Evaluation of the influence of homopolymerization on the removal of water-insoluble organics by grafted polypropylene fibers. *Marine Pollution Bulletin*. 64(6): 1172-1176.
- Li, X., Feng, Y., & Sawatsky, N. (1997). Importance of soil-water relations in assessing the endpoint of bioremediated soils. *Plant and Soil*. 192(2): 219-226.

- Li, X., Li, P., Lin, X., Zhang, C., Li, Q., & Gong, Z. (2008). Biodegradation of aged polycyclic aromatic hydrocarbons (PAHs) by microbial consortia in soil and slurry phases. *Journal of Hazardous Materials*. 150(1): 21-26.
- Li, Y., & Gupta, G. (1994). Adsorption of hydrocarbons by clay minerals from gasoline. *Journal of Hazardous Materials*. 38(1): 105-112.
- Littlejohns, J. V., & Daugulis, A. J. (2008). Response of a solid-liquid two-phase partitioning bioreactor to transient BTEX loadings. *Chemosphere*. 73(9): 1453-1460.
- Liu, R., Zhang, Y., Ding, R., Li, D., Gao, Y., & Yang, M. (2009). Comparison of archaeal and bacterial community structures in heavily oil-contaminated and pristine soils. *Journal of Bioscience and Bioengineering*. 108(5): 400-407.
- Low, M. J. D. (1960). Kinetics of chemisorption of gases on solids. *Chemical Reviews*. 60(3): 267-312.
- Lu, L., & Zhu, L. (2012). Effect of soil components on the surfactant-enhanced soil sorption of PAHs. *Journal of Soils and Sediments*. 12(2): 161-168.
- Lu, M., Zhang, Z., Sun, S., Wang, Q., & Zhong, W. (2009). Enhanced degradation of bioremediation residues in petroleum-contaminated soil using a two-liquid-phase bioslurry reactor. *Chemosphere*. 77(2): 161-168.
- Lundstedt, T., Seifert, E., Abramo, L., Thelin, B., Nyström, Å., Pettersen, J., & Bergman, R. (1998). Experimental design and optimization. *Chemometrics and Intelligent Laboratory Systems*. 42(1-2): 3-40.
- Lustig, S. R., & Peppas, N. A. (1987). Solute and penetrant diffusion in swellable polymers. Vii. A free volume-based model with mechanical relaxation. *Journal of Applied Polymer Science*. 33(2): 533-549.
- MacLeod, C. T., & Daugulis, A. J. (2005). Interfacial effects in a two-phase partitioning bioreactor: Degradation of polycyclic aromatic hydrocarbons (PAHs) by a hydrophobic mycobacterium. *Process Biochemistry*. 40(5): 1799-1805.
- Mahanty, B., Pakshirajan, K., & Dasu, V. V. (2010). A two liquid phase partitioning bioreactor system for the biodegradation of pyrene: Comparative evaluation and cost benefit analysis. *Journal of Chemical Technology & Biotechnology*. 85(3): 349-355.
- Major, D. N., & Wang, H. (2012). How public health impact is addressed: A retrospective view on three different oil spills. *Toxicological & Environmental Chemistry*. 94(3): 442-467.
- Mann, M. J. (1999). Full-scale and pilot-scale soil washing. *Journal of Hazardous Materials*. 66(1-2): 119-136.

- Marcoux, J., Déziel, E., Villemur, R., Lépine, F., Bisailon, J. G., & Beaudet, R. (2000). Optimization of high-molecular-weight polycyclic aromatic hydrocarbons' degradation in a two-liquid-phase bioreactor. *Journal of Applied Microbiology*. 88(4): 655-662.
- Margesin, R., Walder, G., & Schinner, F. (2003). Bioremediation assessment of a BTEX-contaminated soil. *Acta Biotechnologica*. 23(1): 29-36.
- Marquez, M. C., Ventosa, A., & Ruiz-Berraquero, F. (1987). A taxonomic study of heterotrophic halophilic and non-halophilic bacteria from a solar saltern. *Journal of General Microbiology*. 133(1): 45-56.
- Martinez-Jeronimo, F., Villasenor, R., Rios, G., & Espinosa-Chavez, F. (2005). Toxicity of the crude oil water-soluble fraction and kaolin-adsorbed crude oil on daphnia magna (crustacea: Anomopoda). *Archives of Environmental Contamination and Toxicology*. 48(4): 444-449.
- Mazzeo, D. E. C., Fernandes, T. C. C., & Marin-Morales, M. A. (2011). Cellular damages in the allium cepa test system, caused by BTEX mixture prior and after biodegradation process. *Chemosphere*. 85(1): 13-18.
- McAllister, L. E., & Semple, K. T. (2010). Role of clay and organic matter in the biodegradation of organics in soil *Geomicrobiology: Molecular and environmental perspective* (pp. 367-384). Springer Netherlands.
- Melbye, A. G., Brakstad, O. G., Hokstad, J. N., Gregersen, I. K., Hansen, B. H., Booth, A. M., . . . Tollefsen, K. E. (2009). Chemical and toxicological characterization of an unresolved complex mixture-rich biodegraded crude oil. *Environmental Toxicology and Chemistry*. 28(9): 1815-1824.
- Meléndez, L. V., Lache, A., Orrego-Ruiz, J. A., Pachón, Z., & Mejía-Ospino, E. (2012). Prediction of the sara analysis of colombian crude oils using atr-ftir spectroscopy and chemometric methods. *Journal of Petroleum Science and Engineering*. 90-91: 56-60.
- Mena, E., Villaseñor, J., Cañizares, P., & Rodrigo, M. A. (2011). Influence of soil texture on the electrokinetic transport of diesel-degrading microorganisms. *Journal of Environmental Science and Health, Part A*. 46(8): 914-919.
- Meo, S. A., Al-Drees, A. M., Meo, I. M. U., Al-Saadi, M. M., & Azeem, M. A. (2008). Lung function in subjects exposed to crude oil spill into sea water. *Marine Pollution Bulletin*. 56(1): 88-94.
- Meylan, W. M., & Howard, P. H. (2005). Estimating octanol-air partition coefficients with octanol-water partition coefficients and henry's law constants. *Chemosphere*. 61(5): 640-644.
- Mikkonen, A., Hakala, K. P., Lappi, K., Kondo, E., Vaalama, A., & Suominen, L. (2012). Changes in hydrocarbon groups, soil ecotoxicity and microbiology



along horizontal and vertical contamination gradients in an old landfarming field for oil refinery waste. *Environmental Pollution*. 162: 374-380.

- Minai-Tehrani, D., Minoui, S., & Herfatmanesh, A. (2009). Effect of salinity on biodegradation of polycyclic aromatic hydrocarbons (PAHs) of heavy crude oil in soil. *Bulletin of Environmental Contamination and Toxicology*. 82(2): 179-184.
- Mohajeri, L., Aziz, H. A., Isa, M. H., & Zahed, M. A. (2010). A statistical experiment design approach for optimizing biodegradation of weathered crude oil in coastal sediments. *Bioresource Technology*. 101(3): 893-900.
- Morales-Caselles, C., Kalman, J., Micaelo, C., Ferreira, A. M., Vale, C., Riba, I., & DelValls, T. A. (2008). Sediment contamination, bioavailability and toxicity of sediments affected by an acute oil spill: Four years after the sinking of the tanker prestige (2002). *Chemosphere*. 71(7): 1207-1213.
- Moretto, L., Silvestri, S., Ugo, P., Zorzi, G., Abbondanzi, F., Baiocchi, C., & Iacondini, A. (2005). Polycyclic aromatic hydrocarbons degradation by composting in a soot-contaminated alkaline soil. *Journal of Hazardous Materials*. 126(1): 141-148.
- Morrish, J. L. E., & Daugulis, A. J. (2008). Improved reactor performance and operability in the biotransformation of carveol to carvone using a solid-liquid two-phase partitioning bioreactor. *Biotechnology and Bioengineering*. 101(5): 946-956.
- Mulligan, C. N. (2005). Environmental applications for biosurfactants. *Environmental Pollution*. 133(2): 183-198.
- Mullins, O. C. (2010). The modified yen model. *Energy & Fuels*. 24(4): 2179-2207.
- Munoz, R., Chambaud, M., Bordel, S., & Villaverde, S. (2008). A systematic selection of the non-aqueous phase in a bacterial two liquid phase bioreactor treating  $\alpha$ -pinene. *Applied Microbiology and Biotechnology*. 79(1): 33-41.
- Myers, R. H., & Montgomery, D. C. (2002). *Response surface methodology: Process and product optimization using designed experiments* (2nd ed ed.). USA: John Wiley & Sons.
- Nakahara, T., Erickson, L. E., & Gutierrez, J. R. (1977). Characteristics of hydrocarbon uptake in cultures with two liquid phases. *Biotechnology and Bioengineering*. 19(1): 9-25.
- Nardella, A., Massetti, F., Sisto, R., & Tomaciello, R. (1999). Clean-up of polluted wet soils by solvent extraction. *Environmental Progress*. 18(4): 243-249.
- National research council (US) (1985). *Oil in the sea:Inputs, fates, and effects*. Washington, D.C.: The National Academies Press.

- Ncibi, M. C. (2008). Applicability of some statistical tools to predict optimum adsorption isotherm after linear and non-linear regression analysis. *Journal of Hazardous Materials*. 153(1–2): 207-212.
- Neff, J. M., Stout, S. A., & Gunster, D. G. (2005). Ecological risk assessment of polycyclic aromatic hydrocarbons in sediments: Identifying sources and ecological hazard. *Integrated Environmental Assessment and Management*. 1(1): 22-33.
- Nocentini, M., Pinelli, D., & Fava, F. (2000). Bioremediation of a soil contaminated by hydrocarbon mixtures: The residual concentration problem. *Chemosphere*. 41(8): 1115-1123.
- Occulti, F., Roda, G. C., Berselli, S., & Fava, F. (2008). Sustainable decontamination of an actual-site aged pcb-polluted soil through a biosurfactant-based washing followed by a photocatalytic treatment. *Biotechnology and Bioengineering*. 99(6): 1525-1534.
- Odermatt, J. R. (1994). Natural chromatographic separation of benzene, toluene, ethylbenzene and xylenes (btex compounds) in a gasoline contaminated ground water aquifer. *Organic Geochemistry*. 21(10–11): 1141-1150.
- Okuda, T., Alcantara-Garduno, M. E., Suzuki, M., Matsui, C., Kose, T., Nishijima, W., & Okada, M. (2007). Enhancement of biodegradation of oil adsorbed on fine soils in a bioslurry reactor. *Chemosphere*. 68(2): 281-286.
- Oren, A. (1999). Bioenergetic aspects of halophilism. *Microbiol. Mol. Biol. Rev.* 63(2): 334-348.
- OSHA, O. s. h. a. (2012). Osha technical manual (otm). 01/20/1999, 2012, from [http://www.osha.gov/dts/osta/otm/otm\\_toc.html](http://www.osha.gov/dts/osta/otm/otm_toc.html)
- Oudot, J. (1984). Rates of microbial degradation of petroleum components as determined by computerized capillary gas chromatography and computerized mass spectrometry. *Marine Environmental Research*. 13(4): 277-302.
- Palinkas, L. A., Downs, M. A., Petterson, J. S., & Russell, J. (1993). Social, cultural, and psychological impacts of the exxon valdez oil spill. *Human Organization*. 52(1): 1-13.
- Palinkas, L. A., Russell, J., Downs, M. A., & Petterson, J. S. (1992). Ethnic differences in stress, coping, and depressive symptoms after the exxon valdez oil spill. *Journal of Nervous and Mental Disease*. 180(5): 287-295.
- Palittapongarnpim, M., Pokethitiyook, P., Suchart Upatham, E., & Tangbanluekal, L. (1998). Biodegradation of crude oil by soil microorganisms in the tropic. *Biodegradation*. 9(2): 83-90.

- Park, S. W., Lee, J. Y., Yang, J. S., Kim, K. J., & Baek, K. (2009). Electrokinetic remediation of contaminated soil with waste-lubricant oils and zinc. *Journal of Hazardous Materials*. 169(1-3): 1168-1172.
- Partovinia, A., Naeimpoor, F., & Hejazi, P. (2010). Carbon content reduction in a model reluctant clayey soil: Slurry phase n-hexadecane bioremediation. *Journal of Hazardous Materials*. 181(1): 133-139.
- Pasmore, M., Todd, P., Pfiefer, B., Rhodes, M., & Bowman, C. N. (2002). Effect of polymer surface properties on the reversibility of attachment of pseudomonas aeruginosa in the early stages of biofilm development. *Biofouling*. 18(1): 65-71.
- Paudyn, K., Rutter, A., Kerry Rowe, R., & Poland, J. S. (2008). Remediation of hydrocarbon contaminated soils in the canadian arctic by landfarming. *Cold Regions Science and Technology*. 53(1): 102-114.
- Paul F, K. (2002). Long-term environmental impact of oil spills. *Spill Science and Technology Bulletin*. 7(1-2): 53-61.
- Pearl, M., Pruijn, M., & Bovendeur, J. (2006). The application of soil washing to the remediation of contaminated soils. *Land Contamination and Reclamation*. 14(3): 713-726.
- Pendashteh, A. R., Abdullah, L. C., Fakhru'l-Razi, A., Madaeni, S. S., Zainal Abidin, Z., & Awang Biak, D. R. (2012). Evaluation of membrane bioreactor for hypersaline oily wastewater treatment. *Process Safety and Environment Protection*. 90(1): 45-55.
- Peppas, N. A. (1984). Mathematical modeling of diffusion processes in drug delivery polymeric systems. *Controlled drug bioavailability*. 1: 203-237.
- Peppas, N. A., & Sahlin, J. J. (1989). A simple equation for the description of solute release. Iii. Coupling of diffusion and relaxation. *International Journal of Pharmaceutics*. 57(2): 169-172.
- Pérez-Cadahía, B., Laffon, B., Porta, M., Lafuente, A., Cabaleiro, T., López, T., . . . Méndez, J. (2008a). Relationship between blood concentrations of heavy metals and cytogenetic and endocrine parameters among subjects involved in cleaning coastal areas affected by the 'prestige' tanker oil spill. *Chemosphere*. 71(3): 447-455.
- Pérez-Cadahía, B., Laffon, B., Valdiglesias, V., Pásaro, E., & Méndez, J. (2008b). Cytogenetic effects induced by prestige oil on human populations: The role of polymorphisms in genes involved in metabolism and DNA repair. *Mutation Research-Genetic Toxicology and Environmental Mutagenesis*. 653(1-2): 117-123.

- Pineda-Flores, G., Boll-Argüello, G., Lira-Galeana, C., & Mesta-Howard, A. (2004). A microbial consortium isolated from a crude oil sample that uses asphaltenes as a carbon and energy source. *Biodegradation*. 15(3): 145-151.
- Pollard, S. J. T., Hrudehy, S. E., & Fedorak, P. M. (1994). Bioremediation of petroleum- and creosote-contaminated soils: A review of constraints. *Waste Management & Research*. 12(2): 173-194.
- Prahl, F. G., & Carpenter, R. (1983). Polycyclic aromatic hydrocarbon (PAH)-phase associations in washington coastal sediment. *Geochimica et Cosmochimica Acta*. 47(6): 1013-1023.
- Prpich, G. P., Adams, R. L., & Daugulis, A. J. (2006). Ex-situ bioremediation of phenol contaminated soil using polymer beads. *Biotechnology Letters*. 28(24): 2027-2031.
- Prpich, G. P., & Daugulis, A. J. (2004). Polymer development for enhanced delivery of phenol in a solid-liquid two-phase partitioning bioreactor. *Biotechnology Progress*. 20(6): 1725-1732.
- Prpich, G. P., & Daugulis, A. J. (2005). Enhanced biodegradation of phenol by a microbial consortium in a solid-liquid two phase partitioning bioreactor. *Biodegradation*. 16(4): 329-339.
- Prpich, G. P., & Daugulis, A. J. (2006). Biodegradation of a phenolic mixture in a solid-liquid two-phase partitioning bioreactor. *Applied Microbiology and Biotechnology*. 72(3): 607-615.
- Prpich, G. P., Rehmann, L., & Daugulis, A. J. (2008). On the use, and reuse, of polymers for the treatment of hydrocarbon contaminated water via a solid-liquid partitioning bioreactor. *Biotechnology Progress*. 24(4): 839-844.
- Rahman, K. S. M., Thahira-Rahman, J., Lakshmanaperumalsamy, P., & Banat, I. M. (2002). Towards efficient crude oil degradation by a mixed bacterial consortium. *Bioresource Technology*. 85(3): 257-261.
- Reddy, C. M., Arey, J. S., Seewald, J. S., Sylva, S. P., Lemkau, K. L., Nelson, R. K., . . . Camilli, R. (2011). Composition and fate of gas and oil released to the water column during the deepwater horizon oil spill. *Proceedings of the National Academy of Sciences*.
- Rehmann, L., & Daugulis, A. J. (2007). Biodegradation of biphenyl in a solid-liquid two-phase partitioning bioreactor. *Biochemical Engineering Journal*. 36(3): 195-201.
- Rehmann, L., & Daugulis, A. J. (2008). Biodegradation of pcbs in two-phase partitioning bioreactors following solid extraction from soil. *Biotechnology and Bioengineering*. 99(5): 1273-1280.

- Rehmann, L., Prpich, G. P., & Daugulis, A. J. (2008). Remediation of pah contaminated soils: Application of a solid-liquid two-phase partitioning bioreactor. *Chemosphere*. 73(5): 798-804.
- Rehmann, L., Sun, B., & Daugulis, A. J. (2007). Polymer selection for biphenyl degradation in a solid-liquid two-phase partitioning bioreactor. *Biotechnology Progress*. 23(4): 814-819.
- Rengasamy, R. S., Das, D., & Praba Karan, C. (2011). Study of oil sorption behavior of filled and structured fiber assemblies made from polypropylene, kapok and milkweed fibers. *Journal of Hazardous Materials*. 186(1): 526-532.
- Rhykerd, R. L., Weaver, R. W., & McInnes, K. J. (1995). Influence of salinity on bioremediation of oil in soil. *Environmental Pollution*. 90(1): 127-130.
- Riccardi, C., Di Filippo, P., Pomata, D., Incoronato, F., Di Basilio, M., Papini, M. P., & Spicaglia, S. (2008). Characterization and distribution of petroleum hydrocarbons and heavy metals in groundwater from three italian tank farms. *Science of The Total Environment*. 393(1): 50-63.
- Ritger, P. L., & Peppas, N. A. (1987a). A simple equation for description of solute release i. Fickian and non-fickian release from non-swellable devices in the form of slabs, spheres, cylinders or discs. *Journal of controlled release*. 5(1): 23-36.
- Ritger, P. L., & Peppas, N. A. (1987b). A simple equation for description of solute release ii. Fickian and anomalous release from swellable devices. *Journal of controlled release*. 5(1): 37-42.
- Robertson, S. J., McGill, W. B., Massicotte, H. B., & Rutherford, P. M. (2007). Petroleum hydrocarbon contamination in boreal forest soils: A mycorrhizal ecosystems perspective. *Biological Reviews*. 82(2): 213-240.
- Rodríguez-Trigo, G., Zock, J. P., & Montes, I. I. (2007). Health effects of exposure to oil spills. *Archivos de Bronconeumología*. 43(11): 628-635.
- Roy, T. A., Johnson, S. W., Blackburn, G. R., & Mackerer, C. R. (1988). Correlation of mutagenic and dermal carcinogenic activities of mineral oils with polycyclic aromatic compound content. *Fundamental and Applied Toxicology*. 10(3): 466-476.
- Rzeszutek, K., & Chow, A. (1998a). Extraction of phenols using polyurethane membrane. *Talanta*. 46(4): 507-519.
- Rzeszutek, K., & Chow, A. (1998b). An investigation into the sorption of benzoic acids by polyurethane membrane. *Talanta*. 47(3): 697-709.
- Sabaté, J., Viñas, M., & Solanas, A. M. (2006). Bioavailability assessment and environmental fate of polycyclic aromatic hydrocarbons in biostimulated creosote-contaminated soil. *Chemosphere*. 63(10): 1648-1659.



- Saeki, H., Sasaki, M., Komatsu, K., Miura, A., & Matsuda, H. (2009). Oil spill remediation by using the remediation agent je1058bs that contains a biosurfactant produced by *gordonia* sp. Strain je-1058. *Bioresource Technology*. 100(2): 572-577.
- Saha, M., Togo, A., Mizukawa, K., Murakami, M., Takada, H., Zakaria, M. P., . . . Tana, T. S. (2009). Sources of sedimentary PAHs in tropical asian waters: Differentiation between pyrogenic and petrogenic sources by alkyl homolog abundance. *Marine Pollution Bulletin*. 58(2): 189-200.
- Salanitro, J. P. (2001). Bioremediation of petroleum hydrocarbons in soil. *Advances in agronomy*. 72: 53-105.
- Santodonato, J. (1997). Review of the estrogenic and antiestrogenic activity of polycyclic aromatic hydrocarbons: Relationship to carcinogenicity. *Chemosphere*. 34(4): 835-848.
- Satheesh Kumar, M. N., Manjula, K. S., & Siddaramaiah (2007). Transport behavior of n-alkane penetrants into castor oil based polyurethane-polyester nonwoven fabric composites. *Journal of Hazardous Materials*. 145(1-2): 36-44.
- Sayed, S. A., & Zayed, A. M. (2006). Investigation of the effectiveness of some adsorbent materials in oil spill clean-ups. *Desalination*. 194(1-3): 90-100.
- Schmidt-Etkin, D. (2011). Spill occurrences: A world overview *Oil spill science and technology* (pp. 7-48). Boston: Gulf Professional Publishing.
- Scott Parent, J., Capela, M., Dafoe, J. T., & Daugulis, A. J. (2012). A first principles approach to identifying polymers for use in two-phase partitioning bioreactors. *Journal of Chemical Technology & Biotechnology*. 87(8): 1059–1065.
- Semer, R., & Reddy, K. R. (1996). Evaluation of soil washing process to remove mixed contaminants from a sandy loam. *Journal of Hazardous Materials*. 45(1): 45-57.
- Semple, K. T., Doick, K. J., Jones, K. C., Burauel, P., Craven, A., & Harms, H. (2004). Peer reviewed: Defining bioavailability and bioaccessibility of contaminated soil and sediment is complicated. *Environmental Science & Technology*. 38(12): 228-231.
- Sheibani, G., Naeimpoor, F., & Hejazi, P. (2011). Statistical factor-screening and optimization in slurry phase bioremediation of 2,4,6-trinitrotoluene contaminated soil. *Journal of Hazardous Materials*. 188(1–3): 1-9.
- Silva, A., erue-Matos, C., & Fiúza, A. (2005). Use of solvent extraction to remediate soils contaminated with hydrocarbons. *Journal of Hazardous Materials*. 124(1-3): 224-229.

- Singh, A., Van Hamme, J. D., & Ward, O. P. (2007). Surfactants in microbiology and biotechnology: Part 2. Application aspects. *Biotechnology advances*. 25(1): 99-121.
- Smith, J., Nakles, D., Sherman, D., Neuhauser, E., & Loehr, R. (1989). *Environmental fate mechanisms influencing biological degradation of coal-tar derived polynuclear aromatic hydrocarbons in soil systems*. Paper presented at the The Third International Conference on New Frontiers for Hazardous Waste Management. US Environmental Protection Agency, Washington, DC: 397-405.
- Soclo, H. H., Garrigues, P., & Ewald, M. (2000). Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: Case studies in cotonou (benin) and aquitaine (france) areas. *Marine Pollution Bulletin*. 40(5): 387-396.
- Sokker, H. H., El-Sawy, N. M., Hassan, M. A., & El-Anadouli, B. E. (2011). Adsorption of crude oil from aqueous solution by hydrogel of chitosan based polyacrylamide prepared by radiation induced graft polymerization. *Journal of Hazardous Materials*. 190(1-3): 359-365.
- Spaulding, M. L. (1988). A state-of-the-art review of oil spill trajectory and fate modeling. *Oil and Chemical Pollution*. 4(1): 39-55.
- Stat-Ease (2002). Design expert , user's technical manual (Version 6) [Trial version]. Minneapolis, USA: Estat Ease Inc.
- Straif, K., Baan, R., Grosse, Y., Secretan, B., El Ghissassi, F., & Coglianò, V. (2005). Carcinogenicity of polycyclic aromatic hydrocarbons. *The lancet oncology*. 6(12): 931-932.
- Suárez, B., Lope, V., Pérez-Gómez, B., Aragonés, N., Rodríguez-Artalejo, F., Marqués, F., . . . Pollán, M. (2005). Acute health problems among subjects involved in the cleanup operation following the prestige oil spill in asturias and cantabria (spain). *Environmental Research*. 99(3): 413-424.
- Tang, B., & Isacson, U. (2006). Chemical characterization of oil-based asphalt release agents and their emissions. *Fuel*. 85(9): 1232-1241.
- Tanobe, V. O. A., Sydenstricker, T., Amico, S., Vargas, J., & Zawadzki, S. (2009). Evaluation of flexible postconsumed polyurethane foams modified by polystyrene grafting as sorbent material for oil spills. *Journal of Applied Polymer Science*. 111(4): 1842-1849.
- Tibbett, M., George, S., Davie, A., Barron, A., Milton, N., & Greenwood, P. (2011). Just add water and salt: The optimisation of petrogenic hydrocarbon biodegradation in soils from semi-arid barrow island, western australia. *Water, Air, & Soil Pollution*. 216(1): 513-525.

- Tomei, M. C., Annesini, M. C., Prpich, G. P., & Daugulis, A. J. (2009). Biodegradation of 4-nitrophenol in a two-phase system operating with polymers as the partitioning phase. *Environmental Science & Technology*. 43(18): 7105-7110.
- Tomei, M. C., Annesini, M. C., Rita, S., & Daugulis, A. J. (2010). Two-phase partitioning bioreactors operating with polymers applied to the removal of substituted phenols. *Environmental Science & Technology*. 44(19): 7254-7259.
- Trindade, P. V. O., Sobral, L. G., Rizzo, A. C. L., Leite, S. G. F., & Soriano, A. U. (2005). Bioremediation of a weathered and a recently oil-contaminated soils from brazil: A comparison study. *Chemosphere*. 58(4): 515-522.
- Ulrich, A., Guigard, S., Foght, J., Semple, K., Pooley, K., Armstrong, J., & Biggar, K. (2009). Effect of salt on aerobic biodegradation of petroleum hydrocarbons in contaminated groundwater. *Biodegradation*. 20(1): 27-38.
- Urum, K., Grigson, S., Pekdemir, T., & McMenamy, S. (2006). A comparison of the efficiency of different surfactants for removal of crude oil from contaminated soils. *Chemosphere*. 62(9): 1403-1410.
- Urum, K., & Pekdemir, T. (2004). Evaluation of biosurfactants for crude oil contaminated soil washing. *Chemosphere*. 57(9): 1139-1150.
- US National Library of Medicine Isopropanol. Retrieved 2/3/2012, from US National Library of Medicine <http://toxnet.nlm.nih.gov/cgi-bin/sis/search/f?./temp/~8ZUZl6:1>
- USEPA (1996a). *Epa method 3550c: Ultrasonic extraction* (No. SW-846 ): USEPA.
- USEPA (1996b). *Epa method 8015b:Nonhalogenated organics using GC/FID* (No. SW-846 ).
- USEPA (2000). *40 cfr - code of federal regulations - title 40: Protection of environment*. from <http://cfr.vlex.com/source/code-federal-regulations-protection-environment-1089>.
- USEPA (2007). *Method 8270d semivolatile organic compounds by gas chromatography/massspectrometry (GC/MS)*. From <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/8270d.pdf>.
- USEPA (2008, April 16, 2012). Priority chemicals Retrieved May 12, 2011, 2011, from <http://www.epa.gov/osw/hazard/wastemin/priority.htm>.
- Valderrama, C., Barios, J. I., Caetano, M., Farran, A., & Cortina, J. L. (2010). Kinetic evaluation of phenol/aniline mixtures adsorption from aqueous solutions onto activated carbon and hypercrosslinked polymeric resin (mn200). *Reactive and Functional Polymers*. 70(3): 142-150.



- Valderrama, C., Cortina, J. L., Farran, A., Gamisans, X., & Lao, C. (2007a). Kinetics of sorption of polyaromatic hydrocarbons onto granular activated carbon and macronet hyper-cross-linked polymers (mn200). *Journal of Colloid and Interface Science*. 310(1): 35-46.
- Valderrama, C., Gamisans, X., Cortina, J. L., Farrán, A., & de las Heras, F. X. (2009). Evaluation of polyaromatic hydrocarbon removal from aqueous solutions using activated carbon and hyper-crosslinked polymer (macronet mn200). *Journal of Chemical Technology & Biotechnology*. 84(2): 236-245.
- Valderrama, C., Gamisans, X., de las Heras, F. X., Cortina, J. L., & Farrán, A. (2007b). Kinetics of polycyclic aromatic hydrocarbons removal using hyper-cross-linked polymeric sorbents macronet hypersol mn200. *Reactive and Functional Polymers*. 67(12): 1515-1529.
- Van Cuyk, S., Siegrist, R., Logan, A., Masson, S., Fischer, E., & Figueroa, L. (2001). Hydraulic and purification behaviors and their interactions during wastewater treatment in soil infiltration systems. *Water Research*. 35(4): 953-964.
- Vandermeer, K., & Daugulis, A. (2007). Enhanced degradation of a mixture of polycyclic aromatic hydrocarbons by a defined microbial consortium in a two-phase partitioning bioreactor. *Biodegradation*. 18(2): 211-221.
- Verma, S., Saxena, J., Prasanna, R., Sharma, V., & Nain, L. (2012). Medium optimization for a novel crude-oil degrading lipase from pseudomonas aeruginosa sl-72 using statistical approaches for bioremediation of crude-oil. *Biocatalysis and Agricultural Biotechnology*. 1(4): 321-329.
- Vila, J., & Grifoll, M. (2009). Actions of mycobacterium sp. Strain ap1 on the saturated- and aromatic-hydrocarbon fractions of fuel oil in a marine medium. *Applied and Environmental Microbiology*. 75(19): 6232-6239.
- Villar, P., Villar, M., Callejón, M., Pérez, J. L., Jiménez, J. C., Alonso, E., & Guiraúm, A. (2009). Evolution of polycyclic aromatic hydrocarbons (PAHs) and heavy metals in sludge samples from conventional activated sludge wastewater treatment plants. *Environmetrics*. 20(5): 561-574.
- Wainipee, W., Weiss, D. J., Sephton, M. A., Coles, B. J., Unsworth, C., & Court, R. (2010). The effect of crude oil on arsenate adsorption on goethite. *Water Research*. 44(19): 5673-5683.
- Walker, A., Scholz, D., Michel, J., Benggio, B., Boyd, J., & Walker, W. (2000). Selection guide for oil spill applied technologies. Volume 1: Decision-making. *EPA region III-SATA Contract(68553002)*: 131-138.
- Walker, A. H., Guard, U. S. C., Scientific, & Environmental Associates, I. (2003). *Selection guide for oil spill applied technologies*: Scientific and Environmental Associates.

- Wang, C., Li, D., & Liu, S. (2007a). Screening and identification of four PAHs-biodegrading strains. *Chinese Journal of Applied and Environmental Biology*. 13(4): 546-550.
- Wang, J. Y., Huang, X. J., Kao, J. C. M., & Stabnikova, O. (2007b). Simultaneous removal of organic contaminants and heavy metals from kaolin using an upward electrokinetic soil remediation process. *Journal of Hazardous Materials*. 144(1-2): 292-299.
- Wang, Z., Fingas, M., Blenkinsopp, S., Sergy, G., Landriault, M., Sigouin, L., . . . Westlake, D. W. S. (1998). Comparison of oil composition changes due to biodegradation and physical weathering in different oils. *Journal of Chromatography A*. 809(1-2): 89-107.
- Wang, Z., Fingas, M., Yang, C., & Christensen, J. H. (2005). Crude oil and refined product fingerprinting: Principles. In: D. Robert & L. M. Brian (eds.). *Environmental forensics* (pp. 339-407). Burlington: Academic Press.
- Ward, D. M., & Brock, T. (1978a). Hydrocarbon biodegradation in hypersaline environments. *Applied and Environmental Microbiology*. 35(2): 353-359.
- Ward, D. M., & Brock, T. D. (1978b). Hydrocarbon biodegradation in hypersaline environments. *Applied and Environment Microbiology*. 35(2): 353-359.
- Ward, O., Singh, A., & Van Hamme, J. (2003). Accelerated biodegradation of petroleum hydrocarbon waste. *Journal of Industrial Microbiology and Biotechnology*. 30(5): 260-270.
- Wardlaw, G. D., Nelson, R. K., Reddy, C. M., & Valentine, D. L. (2011). Biodegradation preference for isomers of alkylated naphthalenes and benzothiophenes in marine sediment contaminated with crude oil. *Organic Geochemistry*. 42(6): 630-639.
- Watkinson, R. J., & Morgan, P. (1990). Physiology of aliphatic hydrocarbon-degrading microorganisms. *Biodegradation*. 1(2): 79-92.
- Weber, W., & Morris, J. (1963). Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.* 89(17): 31-60.
- Weissenfels, W. D., Klewer, H. J. r., & Langhoff, J. (1992). Adsorption of polycyclic aromatic hydrocarbons (PAHs) by soil particles: Influence on biodegradability and biotoxicity. *Applied Microbiology and Biotechnology*. 36(5): 689-696.
- Whang, L. M., Liu, P. W. G., Ma, C. C., & Cheng, S. S. (2009). Application of rhamnolipid and surfactin for enhanced diesel biodegradation-effects of ph and ammonium addition. *Journal of Hazardous Materials*. 164(2-3): 1045-1050.

- Widrig, D. L., Boopathy, R., & Manning Jr, J. F. (1997). Bioremediation of tnt-contaminated soil: A laboratory study. *Environmental Toxicology and Chemistry*. 16(6): 1141-1148.
- Wilcke, W. (2007). Global patterns of polycyclic aromatic hydrocarbons (PAHs) in soil. *Geoderma*. 141(3-4): 157-166.
- Wilke, B. M. (2005). Determination of chemical and physical soil properties. *Monitoring and Assessing Soil Bioremediation*: 47-95.
- Wolinska-Grabczyk, A. (2007). Transport of liquid hydrocarbons in the polyurethane-based membranes. *Journal of Membrane Science*. 302(1-2): 59-69.
- Woolard, C. R., & Irvine, R. L. (1995). Treatment of hypersaline wastewater in the sequencing batch reactor. *Water Research*. 29(4): 1159-1168.
- Yasuda, H., Lamaze, C., & Ikenberry, L. (1968). Permeability of solutes through hydrated polymer membranes. Part i. Diffusion of sodium chloride. *Die Makromolekulare Chemie*. 118(1): 19-35.
- Yeh, C.-H., Lin, C.-W., & Wu, C.-H. (2010). A permeable reactive barrier for the bioremediation of BTEX-contaminated groundwater: Microbial community distribution and removal efficiencies. *Journal of Hazardous Materials*. 178(1-3): 74-80.
- Yeom, S., Daugulis, A., & Nielsen, D. (2010a). Estimating the cellular maintenance coefficient and its use in the design of two-phase partitioning bioscrubbers. *Bioprocess and Biosystems Engineering*. 33(6): 731-739.
- Yeom, S. H., Daugulis, A. J., & Lee, S. H. (2010b). Bioremediation of phenol-contaminated water and soil using magnetic polymer beads. *Process Biochemistry*. 45(9): 1582-1586.
- Yilmaz, H., Güler, S., & Güler, Ç. (1999). The rheological and dielectric properties of kaolinite suspensions in the presence of alcohols. *Physica Scripta*. 59(1): 77-80.
- Yoshida, N., Yagi, K., Sato, D., Watanabe, N., Kuroishi, T., Nishimoto, K., . . . Tani, Y. (2005). Bacterial communities in petroleum oil in stockpiles. *Journal of Bioscience and Bioengineering*. 99(2): 143-149.
- Youngblood, W. W., & Blumer, M. (1975). Polycyclic aromatic hydrocarbons in the environment: Homologous series in soils and recent marine sediments. *Geochimica et Cosmochimica Acta*. 39(9): 1303-1314.
- Zahed, M. A., Aziz, H. A., Isa, M. H., Mohajeri, L., Mohajeri, S., & Kutty, S. R. M. (2011). Kinetic modeling and half life study on bioremediation of crude oil dispersed by corexit 9500. *Journal of Hazardous Materials*. 185(2-3): 1027-1031.

- Zahed, M. A., Aziz, H. A., Mohajeri, L., Mohajeri, S., Kutty, S. R. M., & Isa, M. H. (2010). Application of statistical experimental methodology to optimize bioremediation of n-alkanes in aquatic environment. *Journal of Hazardous Materials*. 184(1–3): 350-356.
- Zajic, J., & Supplisson, B. (1972). Emulsification and degradation of “bunker c” fuel oil by microorganisms. *Biotechnology and bioengineering*. 14(3): 331-343.
- Zakaria, M. P., Horinouchi, A., Tsutsumi, S., Takada, H., Tanabe, S., & Ismail, A. (2000). Oil pollution in the straits of malacca, malaysia: Application of molecular markers for source identification. *Environmental Science & Technology*. 34(7): 1189-1196.
- Zappi, M. E., Rogers, B. A., Teeter, C. L., Gunnison, D., & Bajpai, R. (1996). Bioslurry treatment of a soil contaminated with low concentrations of total petroleum hydrocarbons. *Journal of Hazardous Materials*. 46(1): 1-12.
- Zhang, W., Li, J., Huang, G., Song, W., & Huang, Y. (2011a). An experimental study on the bio-surfactant-assisted remediation of crude oil and salt contaminated soils. *Journal of Environmental Science and Health, Part A: Toxic-Hazardous Substances and Environmental Engineering and Mining Journal*. 46(3): 306-313.
- Zhang, Y., Wang, F., Wang, C., Hong, Q., Kengara, F. O., Wang, T., . . . Jiang, X. (2011b). Enhanced microbial degradation of humin-bound phenanthrene in a two-liquid-phase system. *Journal of Hazardous Materials*. 186(2-3): 1830-1836.
- Zhang, Z., Hou, Z., Yang, C., Ma, C., Tao, F., & Xu, P. (2011c). Degradation of n-alkanes and polycyclic aromatic hydrocarbons in petroleum by a newly isolated pseudomonas aeruginosa dq8. *Bioresource Technology*. 102(5): 4111-4116.
- Zhou, M. H., Ha, C.-S., & Cho, W.-J. (2001). Synthesis and properties of high oil-absorptive network polymer 4-tert-butylstyrene–sbr–divinylbenzene. *Journal of Applied Polymer Science*. 81(5): 1277-1285.
- Zhou, W., & Zhu, L. (2007). Efficiency of surfactant-enhanced desorption for contaminated soils depending on the component characteristics of soil-surfactant-PAHs system. *Environmental Pollution*. 147(1): 66-73.
- Zilouei, H., Guieysse, B., & Mattiasson, B. (2008). Two-phase partitioning bioreactor for the biodegradation of high concentrations of pentachlorophenol using sphingobium chlorophenicum dsm 8671. *Chemosphere*. 72(11): 1788-1794.
- Zock, J. P., Rodríguez-Trigo, G., Pozo-Rodríguez, F., Barberà, J. A., Bouso, L., Torralba, Y., . . . Vereá, H. (2007). Prolonged respiratory symptoms in clean-up workers of the prestige oil spill. *American Journal of Respiratory and Critical Care Medicine*. 176(6): 610-616.



**APPENDICES**