UNIVERSITI PUTRA MALAYSIA

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

MAZYAR PEYDA

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By

MAZYAR PEYDA

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

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

REMEDIATION 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®) and 2-propanol as a mobilizing agent followed by bio-regeneration of crude oil loaded polymer beads in the TPPB. The equilibrium sorption capacity ($q_e$) as well as the kinetic behaviour of the thermoplastic polyurethane (TPU) was determined as a function of the crude oil dilution with 2-propanol. The polymeric sorbent exhibited the highest $q_e$ value when immersed in a 50% diluted crude oil. The sorption experimental data correlated well with different kinetic models. The Elovich kinetic model correlated accurately with the diluted crude oil experimental data; while the pseudo-first order and pseudo-second order kinetic models could also
predict the sorption of $n$-alkanes ($C_{14}$-$C_{36}$) and polycyclic aromatic hydrocarbons (PAHs) into the polymeric sorbent, respectively.

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

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

Bio-regeneration of crude oil loaded TPU was optimized in a solid-liquid TPPB by applying a RSM based D-optimal design. The bacterial strains in the consortium were identified as *Brevibacillus brevis*, *Gordonia* sp., *Ochrobactrum anthropic*, *Cellulosimicrobium terreum*, and *Bacillus* sp through analysis of the 16S rRNA gene. Optimum combinations of key factors with a statistically significant cubic model were used to maximize biodegradation in the TPPB. The validity of the model was successfully verified by the agreement between the model-predicted results and the
experimental results. The bio-regeneration studies in a 5L reactor showed a significant reduction (72.07±0.63%) of low molecular weight (2-3 ring) PAHs and \(n\)-alkanes (97.75±0.26%) present in the crude oil loaded solid polymers. Regeneration and reusability of the crude oil loaded TPU were also confirmed by subjecting the sorbent to successive sorption-regeneration cycles in the TPPB. These findings show that solid polymer extraction followed by bio-regeneration of sorbents in a TPPB is applicable to treat crude oil contaminated kaolin.
Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

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

Oleh

MAZYAR PEYDA

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Pencemaran tanah oleh minyak mentah merupakan isu besar kerana berkaitan dengan alam sekitar dan resikio kesihatan. Matlamat utama kajian ini adalah untuk mengkaji kemungkinan penggunaan pembahagian bioreaktor solid-liquid dua fasa sebagai pemulihan minyak mentah yang tercemar oleh kaolin liat. Dalam usaha untuk mencapai matlamat ini, kajian tentang sedutan serta pengekstrakan minyak mentah dari kaolin telah dijalankan menggunakan thermoplastic polyurethane (Desmopan®) dengan 2-propanol sebagai agen 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\textsubscript{14} - C\textsubscript{36}) dan *polycyclic aromatic hydrocarbons* (PAH). Parameter model *power low* juga telah menunjukkan bahawa mekanisme pengangkutan bagi kedua-dua minyak cair mentah dan minyak pekat mentah ke dalam TPU adalah *Fickian*. Penyerapan Kinetik PAH dan *short-link n-alkanes* (C\textsubscript{14} - C\textsubscript{18}) adalah fungsi langsung terhadap pekali oktan / air dan senggatannya. Sebaliknya, kadar penyerapan (C\textsubscript{20} – C\textsubscript{36}) berhubungkait dengan isipadu molekulnya. Analisis resapan intrapartikel menunjukkan bahawa, 2-propanol dalam minyak mentah mengurangkan rintangan kedua-dua jisim luaran dan dalaman antara struktur dalam TPU.

Reka bentuk komposit pusat (CCD) di bawah kaedah respons permukaan (RSM) digunakan untuk rekabentuk eksperimen dalam kajian pemulihan kaolin dan analisis kdatapatan kajian. Pengaruh pembolehubah bebas terhadap jumlah hidrokarbon petroleum (TPH) penurunan effiensi dapat ditentukan dengan menggunakan model *statistically significant quadratic*. Pemulihan lebih cekap apabila ejen mobilizing terhadap nisbah kaolin adalah sama kepada 3.00 mL g\textsuperscript{-1}. Nisbah interaksi fasa dan kepekatan minyak mentah dalam kaolin jelas mempengaruhi penyingkiran TPH.

Beban bio-Regenerasi minyak mentah TPU telah ditentukan dalam TPPB pepejal-ceair dengan menggunakan RSM berasaskan reka bentuk D-optimal. Pembentukan bakteria dalam konsortium itu telah dikenal pasti sebagai *brevibacillus brevis*, *Gordonia sp*, *Ochrobactrum Anthropic*, *Cellulosimicrobium terreum*, dan *Bacillus sp*. Berdasarkan rRNA 16S, faktor utama kombinasi optimum dengan model *statistically significan cubic* telah digunakan untuk memaksimumpkan 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 ± 0.63%) bagi berat molekul rendah (2-3 cincin) PAH dan *n-alkanes* (97.75 ± 0.26%) dalam minyak mentah yang dimuatkan dalam polimer pepejal. Regenerasi dan penggunaan semula minyak mentah dalam TPU juga mengesahkan dengan melemahkan penyerapan kepada kitaran serapan-regenerasi berturut-turut dalam TPPB.

Bukti-bukti ini menunjukkan bahawa pengekstrakan pepejal polimer diikuti oleh bio-regenerasi penyerapan dalam TPPB boleh digunakan untuk merawat minyak mentah yang tercemar oleh kaolin liat.
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I certify that a Thesis Examination Committee has met on 18 December 2012 to conduct the final examination of Mazyar Peyda on his thesis entitled "Remediation of Crude Oil Contaminated Kaolin by Adsorption Using Solid-Liquid Two-Phase Partitioning" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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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
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<th>Description</th>
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# LIST OF ABBREVIATIONS

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<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>Å³</td>
<td>Cubic Angstrom</td>
</tr>
<tr>
<td>ANOVA</td>
<td>Analysis of Variance</td>
</tr>
<tr>
<td>ARE</td>
<td>Average Relative Error</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Standard for Testing and Materials</td>
</tr>
<tr>
<td>α</td>
<td>Initial sorption rate ([g ,(g \text{ min})^{-1}])</td>
</tr>
<tr>
<td>BCOT</td>
<td>Bintulu Crude Oil Terminal</td>
</tr>
<tr>
<td>BLAST</td>
<td>Basic Local Alignment Search Tool</td>
</tr>
<tr>
<td>β</td>
<td>Desorption constant ((g ,g^{-1}).)</td>
</tr>
<tr>
<td>BTEX</td>
<td>Benzene, Toluene, Ethyl benzene, Xylenes</td>
</tr>
<tr>
<td>CCD</td>
<td>central composite design</td>
</tr>
<tr>
<td>CCFD</td>
<td>Central Composite Face-centred Design</td>
</tr>
<tr>
<td>d(0.1)</td>
<td>Size of particle below which 10% of the sample lies</td>
</tr>
<tr>
<td>d(0.9)</td>
<td>Size of particle below which 90% of the sample lies</td>
</tr>
<tr>
<td>d[3,2]</td>
<td>Surface Weighted Mean, also known as the Surface Area Moment Mean Diameter or Sauter mean</td>
</tr>
<tr>
<td>d[4,3]</td>
<td>Volume Weighted Mean or Mass Moment Mean Diameter</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DF</td>
<td>Degree of freedom</td>
</tr>
<tr>
<td>DNA</td>
<td>Deoxyribonucleic acid</td>
</tr>
<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>ev</td>
<td>Electron volt</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>GC-FID</td>
<td>Gas Chromatography- Flame Ionization Detector</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas Chromatography-Mass Spectrometric</td>
</tr>
<tr>
<td>ID</td>
<td>Internal Diameter</td>
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<tr>
<td>------------</td>
<td>----------------------------------</td>
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<tr>
<td>IFO</td>
<td>Intermediate fuel oil</td>
</tr>
<tr>
<td>ISO</td>
<td>International Organization for Standardization</td>
</tr>
<tr>
<td>$K_1$</td>
<td>Pseudo first-order rate constant (min$^{-1}$)</td>
</tr>
<tr>
<td>$K_2$</td>
<td>Pseudo second order rate constant [g (g min)$^{-1}$]</td>
</tr>
<tr>
<td>$k_i$</td>
<td>Intraparticle diffusion rate constant (g g$^{-1}$min$^{-0.5}$)</td>
</tr>
<tr>
<td>kN/m</td>
<td>Kilo newton per meter</td>
</tr>
<tr>
<td>$k_{oc}$</td>
<td>Soil organic carbon-water partitioning coefficient</td>
</tr>
<tr>
<td>kPa</td>
<td>Kilopascal</td>
</tr>
<tr>
<td>LMW</td>
<td>Low Molecular Weight</td>
</tr>
<tr>
<td>Log $k_{ow}$</td>
<td>Logarithm of Octanol-Water partitioning coefficient</td>
</tr>
<tr>
<td>m/z</td>
<td>Mass to charge ratio</td>
</tr>
<tr>
<td>µL</td>
<td>Micro litre</td>
</tr>
<tr>
<td>µm</td>
<td>micrometre</td>
</tr>
<tr>
<td>MPa</td>
<td>Mega-Pascal</td>
</tr>
<tr>
<td>MSE</td>
<td>Mean Square Error</td>
</tr>
<tr>
<td>MSM</td>
<td>Mineral Salt Medium</td>
</tr>
<tr>
<td>$n$</td>
<td>Diffusional exponent</td>
</tr>
<tr>
<td>NCBI</td>
<td>National Centre for Biotechnology Information</td>
</tr>
<tr>
<td>nm</td>
<td>nanometre</td>
</tr>
<tr>
<td>OD</td>
<td>Optical Density</td>
</tr>
<tr>
<td>PAHs</td>
<td>Polycyclic Aromatic Hydrocarbons</td>
</tr>
<tr>
<td>PCR</td>
<td>Polymerase Chain Reaction</td>
</tr>
<tr>
<td>pmol</td>
<td>Pico mole</td>
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<tr>
<td>ppm</td>
<td>Parts per million</td>
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xxi
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>PRESS</td>
<td>Predicted Residual Error Sum of Squares</td>
</tr>
<tr>
<td>PSD</td>
<td>Particle Size Distribution</td>
</tr>
<tr>
<td>$q_{cal}$</td>
<td>Theoretically calculated sorption capacity at equilibrium</td>
</tr>
<tr>
<td>$q_e$</td>
<td>Equilibrium sorption capacity (g g$^{-1}$)</td>
</tr>
<tr>
<td>$q_{exp}$</td>
<td>Experimental sorption capacity at equilibrium</td>
</tr>
<tr>
<td>$q_{mean}$</td>
<td>Average of experimental values</td>
</tr>
<tr>
<td>$q_t$</td>
<td>Uptake at time t (g g$^{-1}$)</td>
</tr>
<tr>
<td>$R^2$</td>
<td>The coefficient of determination</td>
</tr>
<tr>
<td>$R^2$</td>
<td>Coefficient of correlation</td>
</tr>
<tr>
<td>RMS</td>
<td>Root Mean Square</td>
</tr>
<tr>
<td>RMSE</td>
<td>Root Mean Squared Error</td>
</tr>
<tr>
<td>rpm</td>
<td>round per minute</td>
</tr>
<tr>
<td>RSM</td>
<td>Response surface methodology</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SIM</td>
<td>Selected Ion Monitoring</td>
</tr>
<tr>
<td>Span</td>
<td>Measurement of the width of the distribution</td>
</tr>
<tr>
<td>SSE</td>
<td>Sum Squares Error</td>
</tr>
<tr>
<td>TPH</td>
<td>Total Petroleum Hydrocarbon</td>
</tr>
<tr>
<td>TPPB</td>
<td>Two phase partitioning bioreactor</td>
</tr>
<tr>
<td>TPU</td>
<td>Thermoplastic polyurethane</td>
</tr>
<tr>
<td>USEPA</td>
<td>United States Environmental Protection Agency</td>
</tr>
<tr>
<td>v/v</td>
<td>Volume to volume ratio</td>
</tr>
<tr>
<td>w/v</td>
<td>Ratio of Weight to volume</td>
</tr>
<tr>
<td>16S rRNA</td>
<td>16 Subunit of Ribosomal ribonucleic acid</td>
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</tbody>
</table>
CHAPTER 1
INTRODUCTION

1.1 Background

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

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

To remove spilled crude oil on land, on inland waters (fresh and estuarine), and coastal waters, different categories of technologies proposed for various situations. Mechanical recovery and chemical agents are applicable as emergency responses to oil spill. Bioremediation is appropriate after physical oil removal techniques when
further oil removal needed in small static water bodies or contaminated soil (USEPA, 2000).

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

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

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

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

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

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

3. Surfactants are used to remove crude oil from contaminated soils, but the main problem is the lack of knowledge about environmental fate and toxicity of the surfactant and its metabolites, especially for in situ soil remediation (Franzetti et al., 2006; Urum et al., 2006). Therefore, the ability of bio-surfactants due to their inherent biodegradability and low toxicity has been studied by researchers. Comparison of bio and synthetic surfactants in remediation of weathered and non-
weathered contaminated soil with crude oil has been carried out. It was reported that the enhancement of crude oil removal using the surfactant solutions was more effective for the non-weathered soils (Urum and Pekdemir, 2004).

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

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

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

5. Despite the interesting advantages of crude oil contaminated soil bioremediation such as cost effectiveness (Salanitro, 2001) and potential for soil reuse (Frutos et al., 2012); there are some obstacles that may be hindering its usefulness (Nocentini et al., 2000). Success of the biological treatment of soil and wastewaters containing high concentrations of polycyclic aromatic hydrocarbons and/or high concentrations of mono aromatic hydrocarbons is limited, which results from the lack of suitable
bioavailability (Lei et al., 2004) and intrinsic toxic nature of these compounds (Collins and Daugulis, 1999; Nocentini et al., 2000; Ivančev-Tumbas et al., 2004; Trindade et al., 2005).

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

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

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

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

Specific goals and objectives of the research included:

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

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

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

1.4 Scope and Limitation of the Study

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

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

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

To achieve this objective, sorption of crude oil (BCOT, Sarawak) as a function of dilution with 2-propanol (5, 10, 25, 50, 75, and 95%) into the thermoplastic polyurethane (Desmopan®) at particular time intervals and also in equilibrium were
studied in 100 mL glass lab bottles. The sorption behaviour of polymer was evaluated by immersion weight gain method. The polymer beads were taken out of the test solution at particular time intervals, weighed on a Sartorius balance (GD503 Class II Balance) and returned to the lab bottle. The procedure of sorption and weighting was continued until the sample achieved a constant final weight (equilibrium). Analysis of absorbed even carbon number \( n \)-alkanes from \( \text{C}_{14} \) to \( \text{C}_{36} \) and 16 Environmental Protection Agency (EPA) priority parent PAHs were done by GC-MS.

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

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

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

To achieve this objective, the effects of main operating parameters (polymer to kaolin ratio, mobilizing agent to kaolin ratio, and oil concentration in contaminated kaolin) on remediation of crude oil contaminated kaolin was investigated. Removal of TPH was carried out batch wise in the 100 mL capped laboratory bottles with 2.00 g of kaolin and different values of operating parameters. The performance of the polymeric sorbent was evaluated in terms of TPH removal efficiency. The TPH was analysed by GC-FID before and after treatment.
Crude oil contaminated soil and sediments with various textures may behave in
different manners comparing to the artificially spiked soil samples. On the other
hand, most organic and inorganic contaminants tend to bind, either chemically or
physically, to fine fraction of soil particles such as clay and silt. Therefore, kaolin
was used as a model soil to ensure repeatability.

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

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

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

Numerical optimization was carried out for maximum TPH removal using design
expert software, and the desirability-functions approach was applied to the
optimization.
3. To evaluate the effects of key factors on bio-regeneration of the crude oil loaded thermoplastic polyurethane (Desmopan®) as a delivery phase in a two-phase partitioning bioreactor (TPPB).

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

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

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

The required bio-kinetic study to proof the concept were under taken in a 5-L solid-liquid TPPB agitated with two Rushton turbines at 400 rpm for a period of 11 days.
All the sorption and the biodegradation studies were carried out at the Biochemical laboratory, Department of Chemical and Environmental Engineering, Faculty of Engineering, Universiti Putra Malaysia. Identification of the microorganisms was done at the Microbiology laboratory, Department of Plant Protection, Faculty of Agriculture, Universiti Putra Malaysia.

It was the objective of this thesis to demonstrate the applicability of a two-step treatment process shown in Figure 1 in a lab-scale study for the remediation of kaolin contaminated with crude oil.
Figure 1. Schematic presentation of crude oil contaminated kaolin remediation by sorption using solid-liquid two phase partitioning.
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