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REMOVAL OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) FROM CONTAMINATED SOIL USING POLYMERIC NANOPARTICLES

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สารโพลีไซคลิกอะโรมาติกไฮโดรคาร์บอน (พีเอเอช) เป็นกลุ่มของสารอินทรีย์ที่ได้รับความสนใจสูงเนื่องจากมีศักยภาพความเสี่ยงต่อสุขภาพอนามัยและสิ่งแวดล้อม ด้วยเหตุที่พีเอเอชชอบที่จะจับกับดินและยากต่อการกำจัด ในการศึกษานี้ อนุภาคนาโนแอมฟิฟิลลิกโพลียูรีเทน ที่มีโพลีเอททีลีนไกลคอลมอร์ดิฟายด์ยูรีเทนอะครีเลทเป็นพรีเคอร์เซอร์เชน (ที่มีขนาด 80-110 นาโนเมตร)ได้ถูกสังเคราะห์ขึ้นเพื่อใช้ในการกำจัดการปนเปื้อนของพีเอเอชในคอลัมน์ดิน โดยใช้การทดลองแบบแบชและคอลัมน์ในการศึกษาการดูดซับของ ฟีแนนทรีนและเบนไซ(เอ)ไพรีนที่ความเข้มข้นต่างๆ ผลการทดลองสนับสนุนว่าอนุภาคดังกล่าวมีความสามารถในการกำจัดสารกลุ่มพีเอเอช ที่มีค่า log K_{ow} ระหว่าง 4.6-6.5 และยังสามารถนำอนุภาคดังกล่าวไปประยุกต์ใช้กับสารอินทรีย์กลุ่มไม่ชอบน้ำอื่นๆ ที่มีคุณสมบัติทางกายภาพเคมีที่คล้ายกันด้วย ในการศึกษาจลนศาสตร์พบว่า การดูดซับของฟีแนนทรีนและเบนไซ(เอ)ไพรีนเข้าสู่สภาวะคงที่ในอนุภาคนาโนเร็วกว่าในดินคือที่ 24 และ 48 ชั่วโมงตามลำดับ ทั้งนี้ค่าสัมประสิทธิ์ความเข้มข้นระหว่างดิน-น้ำ (K_{sw}) ของฟีแนนทรีนมีค่าต่ำกว่าเบนไซ(เอ)ไพรีนคือ 1776±88 และ 3162±363 ลิตรต่อกิโลกรัม ตามลำดับ เมื่อปรับค่าสัมประสิทธิ์ความเข้มข้นอิงตามปริมาณคาร์บอนอินทรีย์ให้อยู่ในรูปของลอกการิทึม (log K_{oc}) พบว่าค่าที่ได้คือ 4.88 และ 5.13 ตามลำดับ สอดคล้องกับผลการศึกษาอื่น ส่วนค่าสัมประสิทธิ์ระหว่างดินและอนุภาคนาโนชี้ให้เห็นว่า ทั้งฟีแนนทรีนและเบนไซ(เอ)ไพรีนดูดซับในอนุภาคนาโนได้ดีกว่าในดิน โดยค่า $K_{s,APU}$ ของฟีแนนทรีนสูงกว่าเบนไซ(เอ)ไพรีนคือ 0.55±0.03 และ 0.36±0.02 ลิตรต่อกิโลกรัม ตามลำดับ การทดลองหามวลสมดุลของอนุภาคนาโนในคอลัมน์ดินพบว่า อนุภาคนาโนกลับคืนมาได้ ร้อยละ 94 ส่วนการทดลองประสิทธิภาพของอนุภาคนาโนเพื่อกำจัดสารทั้งสองชนิดจากดินปนเปื้อนพบว่า การไหลของอนุภาคนาโนให้หยุดชะงัก 24 ชั่วโมงไว้ในคอลัมน์ สามารถกำจัดสารทดลองทั้งสองชนิดที่ปนเปื้อนอยู่ในดินออกได้ดีกว่าการไหลผ่านแบบต่อเนื่อง ทั้งนี้ ฟรีแนนทรีนร้อยละ 90 และ เบนไซ(เอ)ไพรีนร้อยละ 50 ถูกกำจัดจากดินปนเปื้อนที่ความเข้มข้นต่ำ (0.35 มิลลิกรัมต่อกิโลกรัม) ในทางตรงกันข้ามที่ความเข้มข้นสูง (1.75 มิลลิกรัมต่อกิโลกรัม) พบว่า เพียงร้อยละ 29 ของฟรีแนนทรีน และ ร้อยละ 15 ของเบนไซ(เอ)ไพรีน ถูกกำจัดออกจากดิน ซึ่งจะเห็นได้ว่า ความเข้มข้นของสารทดลองมีผลต่อประสิทธิภาพในการกำจัดของอนุภาคนาโนและลักษณะของการไหลของอนุภาคนาโนแบบหยุดชะงักที่ระยะเวลายาวนานขึ้นจะช่วยในการกำจัดด้วยเช่นกัน จากผลการทดลองในคอลัมน์แสดงให้เห็นว่า อนุภาคนาโนสามารถปล่อยฟรีแนนทรีนออกจากดินที่มีการปนเปื้อนต่ำได้อย่างมีประสิทธิภาพ อย่างไรก็ดี ปัจจัยหลักที่ลดประสิทธิภาพการกำจัดเบนไซ(เอ)ไพรีนอาจเกิดจากการดูดซับของเบนไซ(เอ)ไพรีนบนอนุภาคนาโนในการทดลองแบบคอลัมน์เข้าสู่สภาวะสมดุลช้ากว่าการทดลองแบบแบช ดังนั้นการเพิ่มเวลาในการหยุดชะงักการไหลของอนุภาคดังกล่าวไว้ในคอลัมน์นานกว่า 24 ชั่วโมงจะเป็นการเพิ่มประสิทธิภาพในการกำจัดเบนไซ(เอ)ไพรีนออกจากดินปนเปื้อน

สหสาขาวิชาการจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต..
สาขาวิชาการจัดการสิ่งแวดล้อม ลายมือชื่ออาจารย์ที่ปรึกษา..
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KEY WORD: POLYCYCLIC AROMATIC HYDROCARBONS / POLYMERIC NANOPARTICLES / REMOVAL OF PAHs FROM SOIL

ONARPAR SANTISUKKASAEM: REMOVAL OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) FROM CONTAMINATED SOIL USING POLYMERIC NANOPARTICLES. THESIS ADVISOR: BENJALAK KARNCHANASEST, Ph.D. THESIS CO-ADVISOR: WARAPONG TUNGITTIPLAKORN, Ph.D. 105 pp. ISBN 974-14-2436-1

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds of great concern due to their potential risk to human health and the environment as they are likely bound to soils and difficult to remove. In this study, the amphiphilic polyurethane (APU) nanoparticles made of poly(ethylene glycol)-modified urethane acrylate (PMUA) precursor chains (80-110 nm) were synthesized to use in remediation of PAHs contaminated soil-packed column. Through batch and column tests, the sorption ability of APU nanoparticles under various phenanthrene (PHEN) and benzo(a)pyrene (BaP) concentrations are investigated. The test results supported that the application of APU nanoparticles could be applied to remove PAHs that have the $\log K_{ow}$ ranges between 4.6 and 6.5, thereby promoted the application of APU nanoparticles to other hydrophobic organic compounds having similar physicochemical properties. The experiment on steady state attainment revealed that sorption kinetic of test compounds onto APU was more rapid than onto soil (24 and 48 hours, respectively). The partition coefficient between soil and water, $K_{s,w}$, of PHEN was lower than that of BaP (PHEN=1776±88 L/kg; BaP=3162±363 L/kg). By Normalizing $K_{s,w}$ using organic carbon content in the soil, $\log K_{oc}$ of PHEN and BaP obtained from arithmetic equation (PHEN=4.88; BaP=5.13) yielded parallel results compared to $\log K_{oc}$ from other studies. The partition coefficient between soil and APU, $K_{s,APU}$, suggested that both PHEN and BaP were likely to sorb onto APU nanoparticles rather than sorbed onto soil. The results revealed that $K_{s,APU}$ of PHEN was slightly higher than that of BaP (PHEN=0.55±0.03 L/kg; BaP=0.36±0.02 L/kg). Mass balance on APU nanoparticles mobility in soil demonstrated that 94% of the particles was recovered from the soil column. The removal of PHEN and BaP from pre-contaminated soil column evidently supported that greatest recovery of test compounds were obtained regarding 24-hous flow interruption. In low contamination soil column (0.35 mg/kg), approximately 90% and 50% of initially sorbed PHEN and BaP were recovered over the duration of the experiment. In contrast, approximately 29% and 15% of initially sorbed PHEN and BaP were recovered in high contamination soil column (1.75 mg/kg). These results showed that increase in concentration of PAHs in the soil column reduced APU nanoparticles effectiveness and longer duration of the flow interruption should be considered in APU nanoparticles-assisted remediation. The column tests demonstrated that APU nanoparticles could effectively flush PHEN from soil contaminated with low concentration. However, the significant factor that decreased the efficiency of BaP remediation may be due to the sorption of BaP onto APU in column reached its equilibrium slower than that in batch experiment. Therefore, longer duration of flow interruption than 24 hours would tentatively increase the removal efficiency of BaP from the soil.

Department Environmental Management	Student's signature..........................
Field of study Environmental Management	Advisor's signature..........................
Academic year 2006	Co-Advisor's signature......................

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At last, the author would like to dedicate this work to her family especially her beloved mother, who put all her love and care, trust and understanding to the author since she was born, during this research study, and for always.

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LIST OF ABBREVIATIONS

APU = Amphiphilic Polyurethane
BaP = Benzo(a)pyrene
CEC = Cation Exchange Capacity
DCM = Dichloromethane
DLS = Dynamic Light Scattering
DMAc = N,N-Dimethylacetamide
EC = Electrical conductivity
EPA = Environmental Protection Agency
FT-IR = Fourier Transform Infrared Spectrometer
GC-FID = Gas Chromatography with Flame Ionization Detector
HEMA = 2-hydroxyethyl methacrylate
HOCs = Hydrophobic Organic Compounds
HPCD = Hydroxypropyl-*â*-cyclodextrin
K_{d} = Sorption Coefficient
K_{oc} = Soil organic carbon-water partition coefficient
K_{ow} = Octanol-water Partition Coefficient
KPS = Potassium persulfate
NAPLs = Nonaqueous Phase Liquids
NCO = Chemical symbol for the isocyanate reactive radical/group
PAHs = Polycyclic Aromatic Hydrocarbons
PEG = Poly(ethylene glycol)
PHEN = Phenanthrene
PMUA = Poly(ethylene glycol) Modified Urethane Acrylate
ppb = Part Per Billion
ppm = Part Per Million
PTMG = Poly(tetramethylene glycol)
S = Water Solubility
TDI = 2,4-toulene diisocyanate
UAA = Polyurethane Acrylate Anionomer
UAN = Urethane Acrylate Nonionomer

CHAPTER I

INTRODUCTION

1.1 Problem Identification

Soil maybe contaminated with hydrophobic organic compounds (HOCs). Some of these organic chemicals are toxic and are of concern due to the potential risk in human health and the environment. The risk is concerned through the bio-accumulation, bio-concentration and bio-magnification in the food chain system (Roos et al., 2004; Sawyer et al., 1994; Zhou and Zhu, 2005). Among the pollutants in soil matrices, polycyclic aromatic hydrocarbons (PAHs) are organic compounds of great concern as they are likely to bind to soils and have tendency to leach to groundwater (ATSDR, 1995-1996; Manahan, 2000; Zhou and Zhu, 2005). Yet, soil and groundwater contamination has the potential to cause significant risk to environment over long periods, but are frequently overlooked and ignored.

In general, contaminated soil can be remediated by two methods: in-situ or ex-situ remediation. In-situ or on-site remediation required less investment cost, but only the topside of the soil can be cleanup. While ex-situ or off-site remediation required high investment cost on excavating the contaminated soil and transport to the cleanup site, but the cleanup is more complete (McLaughlin, n.d.). As a consequence, the manipulation on new treatment technology to cope with in-situ remediation is an economically challenge to many researchers. The in-situ remediation is done through soil drilling followed by washing, venting, or bioremediation (Andreu and Pico, 1994; Clesceri et al., 1989; Katsoyiannis and Samara, 2004).

The remediation technology for groundwater and nonaqueous phase liquids (NAPLs) by pump-and-treat technology remains the most used method although the innovative technologies such as air sparging, in situ bioremediation, electrokinetics, and treatment walls are increasingly applied to the site (Bumb, 1999). However, the conventional pump-and-treat methods are not likely to be efficient for remediation of PAHs-contaminated sites. The limitation of the methods is due to physicochemical characteristics of PAHs as their mobility in soil is reduced when they sorb to soil constituents. Hence, their characteristics will slow down the kinetics of desorption reactions and the dissolution from non-aqueous-phase mixtures (Tungittiplakorn et al., 2004). As a result, the injection of water without the addition of extracting agents to change the mobility of contaminants might not be the suitable solution for remediation of PAHs-contaminated sites (Bumb, 1999; Viglianti et al., 2005). On the other hand, bioremediation process takes a very long time and requires a suitable environment for bacteria to accomplish the complete degradation. Moreover, PAHs are recalcitrant, so bioremediation without extracting agent is unlikely to be efficient (Hinchee et al., 1994; Nazaroff and Alvarez-Cohen, 2001; Wise et al., 2000). Therefore, the use of extracting agent to enhance the mobility of PAHs in soil seems to be the most suitable solution for remediation of PAHs in soil (Bumb, 1999; Kim et al., 2003; Kim et al., 2004; Tungittiplakorn et al., 2004; Viglianti et al., 2005).

The sorption of hydrophobic organic compound, e.g. PAHs, in soil can be reduced by surfactant molecule existing in aqueous phase. The surfactant (surface active agents)-enhanced remediation technique is aimed to enhance desorption of sorbed particles from soil through solubilization of sorbed particles in surfactant micelles (Edwards et al., 1992; West and Kerr, 1992; Palmer et al., 1992; Riser-Roberts, 1998). However, some limitations of this technique such as the micelle breakage and the loss of surfactant through sorption to soil affect the remediation efficiency (Harwell, 1992; Kim et al., 2003). Moreover, the subsequent disposal of micelle-contaminated soil wash water can be a major environmental constraint (Zheng and Obbard, 2002). Therefore, the design of surfactant that is capable of minimizing their micelle breakage and losses became the focus on the surfactant-enhanced remediation technology (Kim et al., 2003; Kim et al., 2004; Tungittiplakorn et al., 2004; http://www.ksvinc.com/cmc.htm).

Biosurfactant, cyclodextrin, and synthetic nanopolymer are alternatives to synthetic surfactant which are frequently applied for solubility enhancement of contaminated soil (Jennings and Tanner, 2000; Tungittiplakorn, 2004; Viglianti et al., 2005). Although biosurfactant and cyclodextrin are considered natural and nontoxic, they might not be effective for remediation of PAHs-contaminated sites. For instance, the effectiveness of biosurfactant is affected by its CMC, while biosurfactant-producing bacteria appear to be found in soils which have not been exposed to hydrocarbon contamination (Jennings and Tanner, 2000). Even though cyclodextrin do not have CMC (Tungittiplakorn et al., 2004), but the cheapest form of cyclodextrin is far less efficient than ones with higher cost (Viglianti et al., 2005). Besides, both of them are natural compounds; therefore, it is difficult to control their physical and/or chemical properties (Tungittiplakorn et al., 2004). On the other hand, a group of researchers have developed synthetic nanopolymers that are amphiphilic and their chains are cross-linked in water. In addition, the nanopolymers react minimally with soils and should not interact with liposomes of microorganism due to the cross-linked structures that makes it possible for the particles to maintain their structure when in contact to soil or liposomes. Unlike the natural compounds, their physical/chemical properties can be controlled (Kim et al., 2003). Among the suggested enhancement methods, synthetic or engineered nanopolymer will be investigated as an alternative agent for removal PAH from soil.

Polymers are the macromolecules that have high-molecular weight which often represent as a very long linear chains, have variety of display and sometimes having an extraordinary tensile strength (Braun et al., 2005; Sperling, 2001). Amphiphilic polyurethane (APU) nanoparticles with poly(ethylene glycol) modified urethane acrylate (PMUA) precursor chains are one of the synthetic polymers that have extremely low CMC and their dispersion efficiency is retained even at extremely high dilution (Kim et al., 2004). For that reasons, APU nanoparticles can provide more stable particles compared to conventional surfactants. Besides, the residual contaminants could then be treated by an in-situ bioremediation, since the presence of APU nanoparticles does not inhibit mineralization of phenanthrene (PHEN) (Tungittiplakorn et al., 2005). In addition, the study by Tungittiplakorn et al. (2005) revealed that within the scope of their experimental conditions, APU nanoparticles are unaffected by biodegradation and so can be recycled by separation of bacteria from the nanoparticles suspension through filtration or centrifugation.

In this study, we were further investigate the sorption behavior of APU nanoparticles to another PAH compound that has significant differences in the physiochemical properties than PHEN through the analysis of gas chromatography with flame ionization detector. Apart from PHEN, BaP is selected as the indicator for the investigation as it is generally represent the group of PAHs that has very low water solubility and is relatively potent carcinogen widely prevalent in the environment. As a matter of fact that BaP is carcinogen; therefore, the removal of this compound will vitally reduce the public health risk.

1.2 Objectives

The main objective of this research is to investigate the efficiency of nanopolymers to enhance desorption of sorbed PAHs from contaminated soil.

Strategies:

1. To synthesize the nanopolymers which are suitable for PAHs sorption.
2. To investigate PAHs sorption capacity between soil and nanopolymers.
3. To investigate PAHs removal capacity from contaminated soil.

1.3 Hypothesis

Polymeric nanoparticles have higher potential to sorb PAHs than soil, thus they have higher tendency to remove PAHs from contaminated soil.

1.4 Scope of the study

The batch partitioning and column experiments were conducted in order to study the sorption process in soil. The soil used in this experiment was collected from the surrounding of coal-tar contaminated site in order to simulate the characteristics of the soil in the PAHs-contaminated site. The adsorbent, polymeric nanoparticles, were synthesized using Tungittiplakorn et al. (2004) as a guide. In this study, phenanthrene and benzo(a)pyrene were used as PAH indicators. The distribution coefficient and elution of both PAH representatives were compared. The analysis of the sorption-desorption experiment was conducted by gas chromatography with flame ionization detector (GC-FID).

CHAPTER II

LITERATURE REVIEW

2.1 Polycyclic Aromatic Hydrocarbons (PAHs)

2.1.1 Sources and environmental occurrence

PAHs are primarily formed during the oil combustion and pyrolysis of organic materials (Harvey, 1999). A minor portion also originates from discharges of non-combusted fossil fuel products. They are normally detected in the area of chemical industry sites such as coal tar, gas plants, and petroleum refinery industries. PAHs are a group of over 100 different organic compounds with varying physicochemical properties (ATSDR, 1995-1996; Khodadoust et al., 2000; Paterson et al., 1999). Several PAHs are reported on the U.S. Environmental Protection Agency (EPA) List of Priority Pollutants as they are suspected to have toxic, mutagenic, and carcinogenic potential. Moreover, the larger PAH compounds (five or more aromatic rings) are not only carcinogen, but are also difficult to degrade by microbial population. By owning those risk potentials, the remediation of PAHs-contaminated sites is becoming a significant environmental issue (Chen et al., 1996; Chowdiah et al., 1998; Hinchee, 1994; Koran et al., 2001; Wise et al., 2000).

In 1974, more than 80% of the total estimated emission of the carcinogenic hydrocarbon benzo(a)pyrene in the United States was from the combustion of fossil fuels in heat and power generation, refuse burning, and coke ovens. Despite the fact that emission from motor vehicles especially in areas adjacent to expressways and airports constitute a smaller percentage of the total emissions nationwide, they are often major contributors in local urban environments (Harvey, 1999). Apart from these sources, forest fires and volcanic activity are the primary natural sources of PAHs in the environment (Karnchanasest and Jailak, 2004). Concentrations of PAHs in soil vary relatively to the distance from the source of pollution. Normally, the concentrations in urban and industrial areas are 10-100 times higher than those in more remote regions (Harvey, 1999; Viglianti et al., 2005).

2.1.2 Physicochemical properties

PAHs are soluble in organic solvents, but have low solubilities in water. In general, their solubilities decrease with increasing molecular weight. On a molecular basis, PAHs are the least volatile hydrocarbons. Although the lowest molecular weight PAH, naphthalene, has appreciable volatility and sublimes, the higher molecular weight PAHs, benzo(a)pyrene, are much less volatile (ATSDR, 1995-1996; Donnelly and Betowski, 1999; Karnchanasest and Jailuk 2004).

PAHs consist of multiple-benzene rings. The physical properties such as melting point and retention on chromatographic phases are influenced by molecular shape of the compounds. The shape appears to affect to biological activities as the number of ring corresponds to the degree of recalcitrant of the compounds (Donnelly and Betowski, 1999). For instance, the five-and six-ring compounds such as benzo(a)pyrene and indeno(123-cd)pyrene are more resistant to degradation than naphthalene and phenanthrene which having 2 and 3 benzene rings (Khodadoust et al., 2000; Kootstra et al., 1995). For those reasons, molecular shape is a significant feature of the PAHs.

Partitioning coefficient such as octanol-water partition coefficient, K_{ow}, is a significant chemical property in soil sorption mechanism. K_{ow} provides a direct estimation of hydrophobicity of an organic compound (Hemond and Fechner-Levy, 2000). Since PAHs are water-hating compounds, they tends to partition to the octanol phase instead of water. Therefore, the K_{ow} value is directly proportional to the hydrophobicity of the compound, which corresponds to the aqueous solubility of such particular compound. For example, phenanthrene has higher aqueous solubility than benzo(a)pyrene; as a consequence, the K_{ow} of phenanthrene is lower than that of benzo(a)pyrene . Moreover, the K_{ow} of a compound can also be used to find the partition coefficient of the contaminant in the organic fraction of the soil, K_{oc}, of a particular contaminant (Ferrante, 1996).

The analysis of higher mass PAHs by Gas Chromatography (GC) is limited by their low solubilities, low volatilities, and by column temperature limitations. However, PAHs with molecular weights less than 300 are readily determined by GC.

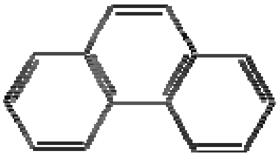
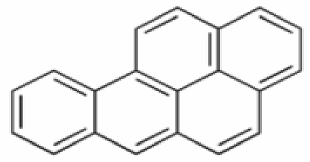
This also includes the 16 EPA target PAHs (Donnelly and Betowski, 1999). The relevant physicochemical properties of the PAHs used in this study are shown in Table 2.1.

2.1.3 Harmful effects

A number of PAHs have caused tumor in laboratory animals that were exposed to PAHs by ingestion, skin contact, and inhalation of contaminated air. Mice that were fed with high doses of PAH, such as benzo(a)pyrene, experienced reproductive problems, while their offspring showed birth defects and continuously decrease in their body weight. However, these effects have not been proven to occur in people as there is no information available from studies on humans to tell which effects can result from being exposed to individual PAHs at certain levels (ATSDR, 1995-1996).

Benzo(a)pyrene is the most cited example of a PAH compound, since the compound can reactivate the metabolism in human bodies. The two stereoisomers of this metabolite, ethylene oxide and propylene oxide, can bind covalently to DNA which later initiate mutation and carcinogenesis (Manahan, 2000). In some ways, benzo(a)pyrene is a sentinel or worst case PAH, particularly from a carcinogenic standpoint. Emphasis on this compound has increased tremendously due to its carcinogenicity, relative ease of analysis, and the belief by investigators that this compound serves as an indicator for the presence of other PAHs which contaminate the environment (Irwin et al., 1997). On the other hand, phenanthrene is widely distributed in the aquatic environment and has been identified in surface water, tap water, wastewater, and dried lake sediments although it is not classified as human carcinogenicity (ATSDR, 1990; Faust, 1993).

Table 2.1 The relevant physicochemical properties of test compounds

Properties		Phenanthrene (PHEN)	Benzo(a)pyrene (BaP)
Chemical structure			
Molecular formula		$C_{14}H_{10}$	$C_{20}H_{12}$
Molecular weight		178.23	252.31
Appearance	Color	White to yellow	Yellow
	Physical state	Crystalline solid	Crystalline solid
Melting point (℃)		101	178
Boiling point (℃)		340	496
Density (g/cm^3)		1.179	1.240
Vapor pressure (Pa)		1.6×10^{-2}	7.0×10^{-7}
Water solubility (mg/L)		1.29	0.0038
Log K_{ow}		4.6	6.5
Henry's Law constant (Pa•m^3/mol)		3.98	0.034

Source: Mackay et al., 2000
Remark: Properties were determined at 25 ℃

2.2 Soil Sorption of Organic Pollutants

2.2.1 Fate and transport of PAHs in soil

The release of PAHs to the environment is quite wide spread since it is a ubiquitous product of incomplete combustion. They are largely associated with particulate matter, soils, and sediments. The persistence and movement of hydrophobic compounds are determined by their properties such as water solubility, polarity of the compound, soil sorption constant (K_{oc}), the octanol-water partition coefficient (K_{ow}), and half life in soil. Although environmental concentrations are highest near sources, their presence in places distant from primary sources indicates that they are reasonably stable in the atmosphere and capable of long distance transport. If released to soil they will be expected to adsorb very strongly to the soil and will not be expected to leach to the groundwater (Irwin et al., 1997), unless the compounds are present in organic solvent that has higher solubility in water (Canadian council of ministers of the environment, 1999). PAHs, especially the one with higher molecular weight will not be expected to hydrolyze or significantly vaporize from soils and surfaces. Some of PAHs that have low molecular weight may be subject to appreciable biodegradation in soils, while the compounds with higher molecular weight are rather recalcitrant (Irwin et al., 1997).

The term sorption is commonly used to denote the uptake of a contaminant by soil or sediment without reference to specific mechanism. Normally, two distinguished sorption mechanisms are adsorption and absorption. Physical adsorption results from London-van der Waals forces between the adsorbate and adsorbent. The term absorption is used to describe a process in which the sorbed material dissolves in an organic phase by forces common to solution, e.g. by van der Waals forces (Chiou, 1999; Hemond and Fechner-Levy, 2000; Sawyer et al., 1994).

Sawyer et al. (1994) concluded that one of the most important factor influencing the transport and environmental fate of contaminants in soil and sediment is the sorption-desorption process. Sorption of hydrophobic compounds in soil and sediment may result from adsorption or partitioning between the compounds and soil matrices. They suggested that water solubility of organic compounds is corresponded to the persistency of the compounds. The lower the water solubility, the stronger the compound will sorb to soil. They reported the water solubility of selected PAHs, for example, naphthalene (double-ring compound) is much higher than that of benzo(a)pyrene. Thus benzo(a)pyrene are more stable in soil than naphthalene and other PAH compounds that having fewer benzene rings. The heterogeneous mixtures in soil and hydrophobicity of PAHs tend to bind soil together with the contaminants, which in turns reduce the mobility and bioavailability of those contaminants (Sawyer et al., 1994; Tungittiplakorn et al., 2004).

2.2.2 Partitioning of PAHs in soil

Partitioning is analogous to the transport of contaminants from one environmental compartment to another, for example, the extraction of an organic solute from water into an organic solvent (Chiou, 1999; Karnchanasest and Jailuk, 2004). The relationship of the concentrations of a contaminant between 2 separate phases under equilibrium at a constant system temperature is defined as isotherm. Hence, the adsorption and partition isotherm express the relation of the amount of contaminant adsorbed on a solid (e.g. soil organic matter) to the concentration of the contaminant in solution, and the relation of the contaminant between 2 solution phases (e.g. between water and organic solvent). The adsorption isotherms are normally express by 3 adsorption models as shown in Figure 2.1.

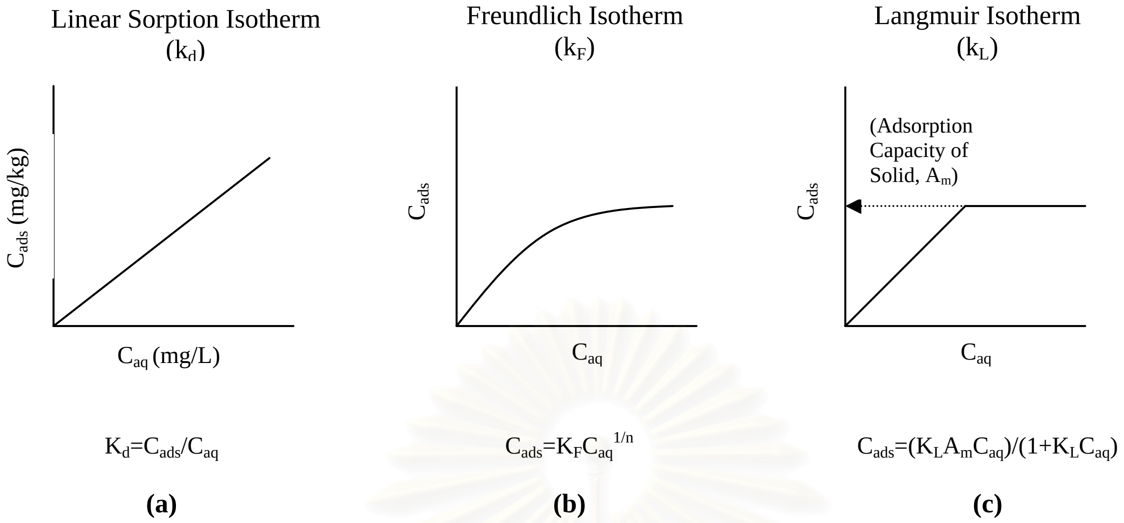


Figure 2.1 Sorption isotherms (a) Linear sorption isotherm (b) Freundlich Isotherm (c) Langmuir Isotherm (*Source: Knox and Sabatini, 1993*)

The relationship between the material being concentrated, *adsorbate*, and the adsorbing solid, *adsorbent*, can be expressed by sorption isotherm (Chiou, 1999; Evangelou, 1998; Sawyer et al., 1994). The linear sorption isotherm occurs when the concentrations of the chemical sorbed by the solid is directly proportional to the concentration of the chemical in water (Tan, 1998). The sorption isotherms of nonionic compounds on water-saturated soils are all relatively linear and are not strongly temperature dependent as it shows only small exothermic heats and a lack of contaminants competition (Chiou, 1999). The expression of linear isotherm in term of distribution coefficient of particles between solid and water is:

$$K_d = C_s/C_w \qquad (2.1)$$

where K_d is distribution coefficient of particles between water and soil (L g^{-1}, mL g^{-1}, or cm^{3}g^{-1}), while C_s and C_w are concentration of organic compound sorbed onto solid phase (mg kg^{-1}) and dissolved in aqueous phase (mg L^{-1}) respectively (Tan, 1998). When the isotherm is considered as linear, the relationship between the concentration in water and concentration in solid can be described by a single partition coefficient (Hemond and Fechner-Levy, 2000).

For non-linear isotherm, the relationship between adsorbate and adsorbent can be expressed by either Freundlich or Langmuir isotherms. The Freundlich isotherm is defined by:

$$C_s = K_f * C^{1/n} \tag{2.2}$$

where C_s and C denotes concentration in solid phase and fluid phase respectively, K_f is Freundlich adsorption constant and n is Freundlich exponent. If n is equal to 1, the Freundlich isotherm reduces to the linear isotherm. The Langmuir isotherm can be expressed by:

$$C_s = (K_l * Q * C / (1 + K_l * C) \tag{2.3}$$

where K_l is Langmuir adsorption constant and Q denotes the maximum number of sorption site (Karickhoff et al., 1979; Sawyer et al., 1994; Tan, 1998).

Sorption is directly proportional to the quantity of organic matter associated with the solid for many organic chemicals especially neutral hydrophobic organic (Chiou et al., 1979; Mean et al., 1980; Karickhoff et al., 1979). Equation (2.4) expresses the normalizing soil or sediment specific sorption coefficients to the organic carbon content of the sorbent yields a new coefficient, K_{oc}, where K_{oc} is considered as a unique property as the constant of the organic chemical being sorbed:

$$K_{oc} = \frac{Kd}{\%OC} \text{ x } 100 \tag{2.4}$$

where K_{oc} is the soil organic carbon-water partition coefficient, K_d is the linear sorption coefficient specific to particular sorbent and chemical combination and %OC is the organic carbon content of that sorbent expressed in percent (Gawlik et al., 1997).

2.2.3 Factors influencing the soil sorption

Soil that required remediation can vary widely in terms of physical properties. The primary physical characteristic is texture. Usually, soil texture is classified as sand, silt, or clay. In general, sandy soils have little attraction for contaminants like metals or synthetic organics. In contrast, soil with fine-textured such as silt and clay have a much greater affinity for all classes of contaminants (Demars et al., 1999).

A second important physical property is the organic matter content, since the extent of soil uptake for organic compounds shows a strong dependence on the organic matter content of the soil. Over the years, many researchers assumed that soil organic matter functions as a high surface area adsorbent capable of adsorbing nonionic organic compounds by hydrophobic interactions. The soil organic matter consists of a heterogeneous makeup of organic constituents such as lignins, carbohydrates, protein, fats, and waxes contains a large fraction of operationally defined as humic substance (Chiou, 1999). The humic material greatly increases the affinity of sediments for nonpolar organic contaminants and serves as an energy source for sediment microbial populations (Demars et al., 1999). Ordinary soils are rich in minerals and are referred to as mineral soils. The organic matter content for a large number of mineral soils falls between 0.5 and 3.0% by weight (Chiou, 1999). Thus, soils that have higher organic matter will bind more to hydrophobic compounds than that with lower organic matter due to more particle surface area.

The water content of the soil is the third physical property that influences soil sorption. For instance, the uptake of hydrophobic compounds from solvent solution by soil was found to be suppressed by soil moisture. The study by Chiou (1999) indicates that organic compounds and water compete for adsorption on soil minerals, which provide most of the surface area in ordinary soils. (Chiou, 1999). In addition, wet soil tends to adsorb less hydrophobic compounds as the charge of water molecules competes with the charge of the compounds for binding sites (Karickhoff et al., 1979; Manahan, 2000).

2.3 Amphiphilic Polyurethane (APU) Nanoparticles

2.3.1 Nano-networks

Nanoparticles attracted many researchers due to the ability to synthesize and manipulate the particles. Besides, their size and shape can be controlled by synthesis procedures. Nanoparticles are the particles that have one dimension smaller than 100 nm which is comparable to corona virus and protein fragments. They have very high specific surface area and their properties can be manipulated accordingly (Biswas and Chang, 2005). Nanotechnology is a tool for sustainable development rather than an environmental liability and meets many needs in environmental management; for instance, resource recovery and pollution prevention (Colvin, n.d.).

The practical use of polymers demands solving the problem of the removal between a macromolecule and a solid surface (Toth, 2002). Schmidt and Malwitz (2003) suggested that nanopolymer additives required lower loading compared to traditional ones. The surface active polymers can be designed in different ways depending on the selectivity to bound with specific functional group of the contaminant (Committee on innovative remediation technology, 1997). Moreover, the higher stability of nanopolymer is accomplished by cross-linking of the polymer chains. After the cross-linking, polymer chains are inter-linked and formed one giant covalently bonded molecule which commonly called nanopolymer-network. The synthesis of cross-linked polymer is divided into 3 main steps so called the sol-gel transition. The reaction stage of transition is called gel point. At the gel point the viscosity of the system becomes infinite, and the equilibrium modulus climbs from zero to finite values. In other words, the polymer goes from being a liquid to being a solid. The 3 steps for producing cross-linked polymers are step polymerization reaction, chain polymerization, and postpolymerization reactions (Sperling, 2001).

The sol-gel transition is also applied to this study in synthesizing APU nanoparticles. At the step polymerization reactions, the little molecules of isocyanates react with polyols with functionality greater than two to form short, branched chains, eventually condensing it into polyurethanes. Next, at chain polymerization step, the multifunctional molecules are presented. The polymer chain obtained from the first step is polymerized with the molecules. The last reaction is at postpolymerization reactions, where the polymer is cross-linked after synthesis is complete. The multifunctional molecules and initiator for the cross-linking process used in this study are poly(ethylene glycol) and potassium persulfate respectively.

2.3.2 Structure of APU nanoparticles

The APU nanoparticles consist of hydrophobic group together with hydrophilic group, which is considered as an amphipathic structure. When APU nanoparticles are dispersed in water, the outer hydrophilic groups stabilize the particles by extending into the aqueous phase. On the other hands, hydrophobic backbones make up the interior core of the particles and have high affinity for hydrophobic organic pollutants. The molecular formula of poly(ethylene glycol)-modified urethane acrylate (PMUA) precursor chain before cross-link and the structure diagram of APU nanoparticles (after cross-link) are illustrated in Figure 2.2 and 2.3 respectively. Unlike surfactant micelles that tend to break up with subsequent adsorption to the soil, the cross-linked APU nanoparticles were reported to remain intact with low adsorption to soil. PMUA chains will only disperse in water to form nano-aggregates (APU nanoparticles) even at extremely low concentrations as the whole PMUA chains are insoluble in water (Tungittiplakorn et al., 2004).

Water is a good solvent for hydrophilic segment, poly(ethylene glycol) (PEG), in PMUA chains, but is not a solvent for hydrophobic segment, poly(tetramethylene glycol) (PTMG) (Kim et al., 2003). As a result, the size of PTMG controls the hydrophobicity of the precursor chain, whereas the size of PEG reflects the hydrophilicity of the precursor chain. Hence, higher molecular weight of PTMG increases the sorption capacity. However, the higher the molecular weight may result in less stability of the nanoparticles (Tungittiplakorn et al., 2004).

2.3.3 Adsorption mechanism of APU nanoparticles

The performance of APU nanoparticles is similar to that of surfactant. APU nanoparticles represents as either ionic or nonionic depending on the functional group on the exterior. In case of non-ionic APU nanoparticles, the surface-active portion bears no apparent ionic charge. Since nonionic surfactant presents no electrical effects, there is no strong adsorption onto charged surfaces (Rosen, 1989). Likewise, adsorption of nonionic APU nanoparticles onto charged surface like soil is insignificant and thus, considered to exhibit low to very low loss to soil constituent (Kim et al., 2003; Kim et al., 2004; Tungittiplakorn et al., 2004).

The aggregation of nonpolar portions of APU nanoparticles rather than soluble in water is due to the hydrophobic bonding force. The distortion of the usual water structure that forced the water into a rigid cage of hydrogen-bonded molecules caused the hydrophobic portions to interact mainly with each other through van der Waals interactions. The result of the hydrophobic and van der Waals interactions is of great tendency for APU nanoparticles to interact with hydrophobic pollutant through adsorption, and not with water (Freeman, 2000; Kim et al., 2003; Tungittiplakorn et al., 2004; Rosen, 1989).

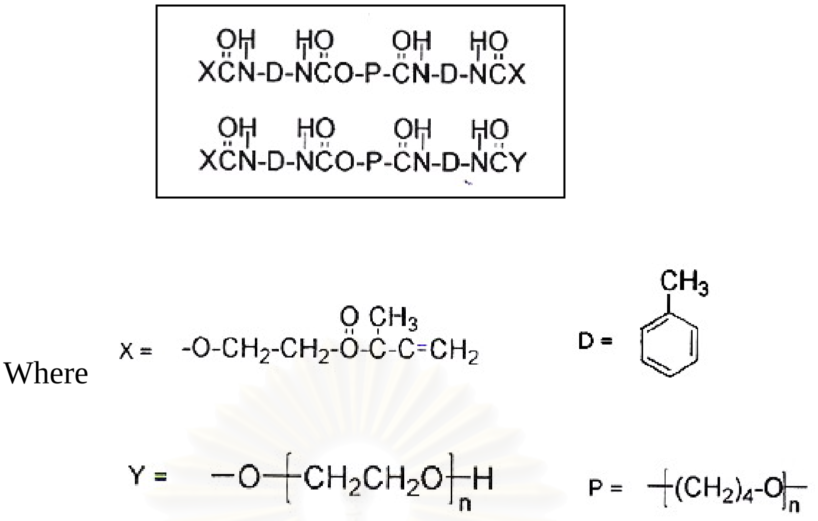


Figure 2.2 Molecular formula of PMUA precursor chain

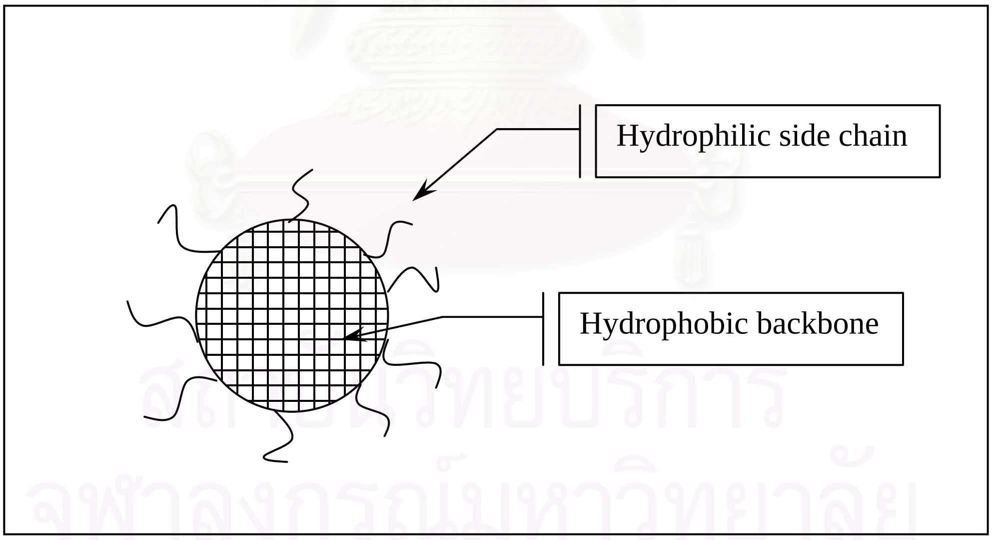


Figure 2.3 Structure of APU nanoparticles

2.3.4 Applications of APU for PAHs sorption

Ko et al. (1999) suggested that anionic surfactant, SDS (sodium dodecyl sulfate), and non-ionic surfactant, Tween80 or HPCD (hydroxypropyl-*â*-cyclodextrin) becomes relatively less effective for hydrophobic organic compounds (HOCs) partitioning with increasing HOC size and hydrophobicity. Addition of surfactants into contaminated subsurface may not enhance the removal of sorbed HOCs except at the very high surfactant doses necessary to overcome the adverse effects of surfactant sorption to the solid phase (Ko et al., 1999). The limitation of surfactant in enhancing the solubility of hydrophobic organic compounds due to the loss to soil particles leads to the distinction of an alternative surface active agent such as APU nanoparticles.

Recently, the application of polymericnanoparticles composite materials is particularly attractive to many researchers due to their synergistic and hybrid properties (Schmidt and Malwitz, 2003). From the previous researches, amphiphilic polyurethane (APU) nanoparticles that are made of polyurethane acrylate anionomer (UAA) and poly(ethylene glycol) modified urethane acrylate (PMUA) precursor chains are used to enhance the solubility and bioavailability of organic contaminant that sorbed strongly to soil in terms of their ability to enhance desorption (Kim et al., 2003; Tungittiplakorn et al., 2004).

The interesting application of this synthetic nanopolymer is for modification of solid surfaces in order to prevent adsorption of hydrophobic compounds. It is synthesized in order to adsorb hydrophobic compounds, which adsorption invariably occurs via interaction between the hydrophobic backbone and the hydrophobic surface, for example, hydrophobic interior confer a high affinity to bind with contaminant while the extension of hydrophilic surfaces promote particle mobility in soil (Holmberg, 2004; Tungittiplakorn et al., 2004).

Kim et al. 2003 compared the effects of APU nanoparticles and Triton X-100 on the sorption of PHEN on aquifer sand. In the low dose region, APU nanoparticles exhibited a greater reduction of PHEN sorption compared to Triton X-100. However, in the higher concentration region, APU nanoparticles and Triton X-100 showed almost the same reduction of PHEN sorption. The reason contributed to this is due to the microstructural difference of APU nanoparticles and surfactant micelles. As when the concentration of surfactant is equal to or greater its CMC, surfactant molecules form micelles via aggregation of surfactant monomers. But at surfactant concentrations below its CMC, surfactant monomers are completely dissolve in the aqueous phase which leads to the reduction of sorption efficiency due to the loss to soil particles (Edwards et al., 1992; Harwell, 1992; Holmberg, 2004; Kim et al., 2003; Palmer et al., 1992; Rosen, 1989; Zhou and Zhu, 2005). The potential of the novel APU nanoparticles for the in-situ extraction of sorbed PAHs was reported by Kim et al. (2003) that a very high recovery rate (95%) of the PHEN from aquifer sand was achieved with extremely low loss of the applied nanoparticles with UAA precursor chain (Kim et al., 2003).

The study by Tungittiplakorn et al. (2004) evaluated the mobility of APU nanoparticles with ionic (UAA) and nonionic (PMUA) precursor chain in soil. The adsorption of APU nanoparticles with both precursor chains had relatively low affinity for soil compared to the APU nanoparticles affinity for PHEN. The discussion of the stability testing for APU nanoparticles with UAA and PMUA precursor chains demonstrated that the stability and particle size of PMUA suspension remained essentially constant when compared with UAA that are greatly affected by electrolyte.

Their results showed that nonionic polymer with PMUA precursor chain woks better than UAA in water with high ionic strength and seem to be a more versatile choice for use in soil remediation. The column experiment also shown that, the PMUA precursor polymer is capable of removing PHEN from contaminated sand column. The mass balance revealed that 100% recovery rate were obtained during the second application for PMUA while the rate of recovery of UAA chain reached only 62% due to the trapping of aggregated particles in the column. (Tungittiplakorn et al., 2004).

The comparison of APU nanoparticles to nonionic surfactants such as Brij 30, Tween 80 and Triton X-100 for flushing PHEN from soil revealed that APU nanoparticles washed out a larger amount of PHEN (about 40%) from soil column than those surfactants which washed out only 18%, 4.5%, and 18% of PHEN. The research group hypothesized that the higher in situ extraction performance of APU nanoparticles compared with the tested surfactants was because of the lower degree of sorption of APU nanoparticles onto aquifer caused the better extraction efficiency (Kim et al., 2004).

CHAPTER III

METHODOLOGY

3.1 Apparatus

3.1.1 Synthesis of polymeric nanoparticles

- Synthesis glass reactor
- Mechanical stirrer (with adjustable speed, <100 rpm)
- Water bath (with adjustable temperature meter)
- Condenser
- Silicone bath
- Magnetic stirrer
- Hot plate
- Round-bottom 3 neck vessel
- Thermometer

3.1.2 Batch partitioning experiments

- Platform shaker (GFL 3017)
- Vacuum pump
- Isolation glass columns

3.1.3 Column experiments

- Glass column with teflon cap and glass filter (2.5 cm i.d. x 10 cm length)
- Peristaltic pump (Watson Marlow SciQ 323)
- Fraction collector (Amersham Biosciences Frac-920)

3.1.4 Instruments

- Analytical balance
- Fourier Transform Infrared Spectrometer (FT-IR) (PerkinElmer, Spectrum One)
- Particle size distribution analyzer (Malvern Instruments)
- Ultrasonics (Transsonic 700/H Elma)
- Oven (AAF 1100 Carbolite)
- Oven (FD115 (E2) WTB Binder)
- Rotary vacuum evaporator (Heidolph Instruments Laborota 4001)
- Microwave extraction system (Milestone ETHOS SEL)
- Gas chromatography with FID detector (Agilent Technologies 6890N)

3.2 Materials

3.2.1 Chemicals and solvents

- Poly(tetramethylene glycol), MW=1000 (PTMG, Aldrich Chemical Co.)
- 2,4-toulene diisocyanate (TDI, Aldrich Chemical Co.)
- 2-hydroxyethyl methacrylate (HEMA, Fluka)
- Poly(ethylene glycol), MW=2000 (PEG, Fluka)
- N,N-Dimethylacetamide (DMAc, Acros)
- Potassium persulfate (KPS, Acros)
- Solvent: Analytical grade Hexane (J.B Beaker) , Acetone (J.B. Beaker), and Dichloromethane (DCM, Mallinkrodt)
- Sodium sulfate anhydrous (Na_2SO_4, Merck)
- Silica gel (Merck)
- Calcium sulfate ($CaSO_4$, Carlo)
- Sodium azide (NaN_3, Aldrich Chemical Co.)

3.2.2 Test compounds: Phenanthrene 98% (Fluka) and benzo(a)pyrene 98% (Dr. Ehrenstorfer)

3.2.3 Internal standard: Pyrene 98% (Fluka)

3.2.4 Glassware and others: Erlenmeyer flask, volumetric flask, suction flask, glass separatory funnel, beaker, glass bottle with cap (Duran), test tube, syringe, micro-pipette, glass fiber filter (Whatman GF/C), Nitrogen gas 99.99%.

3.2.5 Distilled Deionized (DDI) water

The glassware used in this experiment were washed and soaked in Extran MA 03 Phosphate-free overnight in order to cleanup heavily contaminated items, which required for microdetermination purposes. Then all the glassware were washed and rinsed with DDI water, dried at 105°C for an hour, and rinsed with hexane prior to use.

3.3 Method evaluations

3.3.1 Confirmation of PAHs identity

The standard solution was injected to GC for the identification of retention time of each test compounds and internal standard in order to overcome the interference of other contaminants that might present in the experimental procedures. In this case, the chromatogram was used to represent the retention time of the test compounds and internal standard.

The illustration of the chromatogram demonstrated the retention time on the x-axis whereas the peak area on the y-axis. The peak area of the PAHs detected by the GC was corresponded to the concentration of each PAHs spiked, i.e. higher peak area of PHEN than BaP due to higher working concentration of PHEN compare to that of

BaP. A mixture of PAHs in hexane was injected into GC/FID column under the optimal condition for five replicates to determine the retention time of each test compounds. The mean retention times of test compounds (PHEN and BaP) and internal standard (PYR) were 12.32 min (SD = 0.03), 16.37 min (SD = 0.007), and 22.55 min (SD = 0.05) respectively. The typical chromatogram of standard PAHs used in this study and their mean retention times is shown in Appendix A.

3.3.2 Contamination in the experimental procedures

Soil, water, and APU nanoparticles were analyzed for any contaminations. Blank analyses were determined in the same manner as the sample determination, but with the absence of PAH standards. The blank procedures were carried out in triplicate. Three g soil, 1-L water, and 50 mL APU nanoparticles were used for blank analysis. Then the samples were extracted according to their extraction procedures described in section 3.4.6, and preceded for concentration to 2-mL volumetric flask and later transferred to GC vials. The chromatograms of each blank analysis were shown in Appendix B. The chromatographs verified that there were no evidence of trace test compounds and internal standard presence in all media.

3.3.3 Calibration

The calibration curves for soil, water and APU nanoparticles were developed by spiking PAHs at five working concentrations on the soil, water, and APU nanoparticles separately. Then the samples obtained from extraction procedures were injected to GC-FID. A fixed concentration of the internal standard was also added to each working concentrations. The standard curves, regression equations and regression coefficients of the calibration curves were obtained.

The calibration curves of good linear regression equations between the compound concentrations and peak area ratio (peak area of the test compound over peak area of an internal standard) in soil, water, and APU nanoparticles were presented in Appendix C1-C3. The concentration of the test compounds in the sample were obtained using calibration curve which were constructed based on the peak area ratio. The slope, y-intercept and r^2 of the each compound were presented in Table 3.1.

Table 3.1 The regression equations and regression coefficients of the calibration curves

Samples	**PHEN**	**BaP**
Soil	$y = 0.34x + 0.03$ (r^2=0.99)	$y = 1.13x + 0.06$ (r^2=0.91)
Water	$y= 11.62x + 1.52$ (r^2=0.94)	$y = 12.64x – 0.01$ (r^2=0.96)
APU	$y = 0.97x – 0.07$ (r^2=0.97)	$y = 0.80x + 0.01$ (r^2=0.93)

3.3.4 Recovery

Recoveries of each PAH were determined and repeated 3 times to find out the efficiency of the extraction procedure for column experiment. Where recovery is defined as the ratio of amount PAHs recovered to original amount spiked. The PAHs standards at 0.5, 1, 5, 10, and 15 ppm with identical amount of internal standard were injected to GC in order to construct the calibration curve for column experiment (shown in Appendix C4). Where APU nanoparticles were mixed with different concentration of PAHs standards and extracted according to the extraction method (described in section 3.4.6). Then find out the percent recovery by the following equation:

$$\%\ \text{recovery} = \frac{\text{Amount recovered}}{\text{Original amount spiked}} \times 100 \qquad (3.1)$$

The average percentage recoveries from APU extraction for each test compounds were reported in Table 3.2. From the table, extraction of PHEN and BaP from nanoparticles yielded approximately 81% and 77% respectively. The results revealed that recovery of the compound decrease with higher molecular weight of the compound. The chart illustrated in Figure 3.1 showed that the salinity (addition of $CaCl_2$) to APU nanoparticles contaminated with PAHs neither increase nor decrease the extraction efficiency. The results demonstrated that the present of $CaCl_2$ did not affect the percent recovery for both PAHs.

Table 3.2 Average percent recoveries of the test compounds from APU nanoparticles

Conc (mg/L)	**% Recovery**	
	PHEN	**BaP**
0.5	87	78
1	84	70
5	82	82
Average	84	77

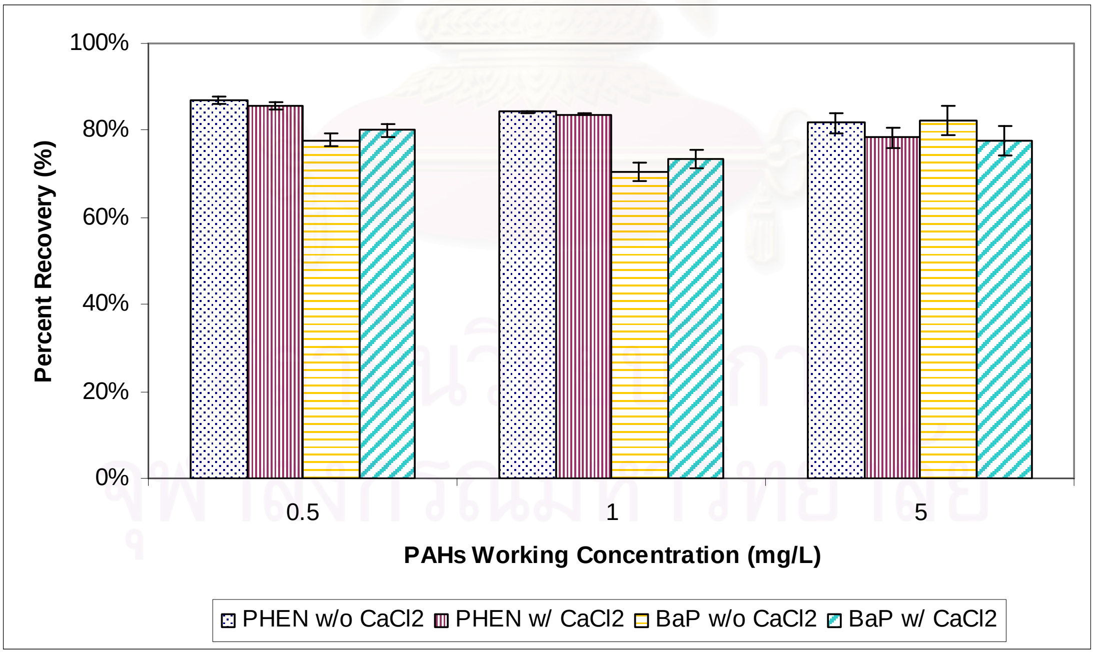


Figure 3.1 Average percent recoveries of test compounds

3.3.5 Detection limit

The detection limit was determined from the injection of various concentrations of test compounds. The results obtained reflect the minimum level at which the analyte can be reliably detected by GC. The standard deviation (σ) was determined from triplicate analyses of each compound in each media. The equation used for determination of the limit of detection is as follows:

$$\text{Detection limit} = \frac{2 \text{ x initial conc. x } \sigma}{\text{Average signal detected in GC}} \qquad (3.2)$$

The results of detection limit were determined and reported in Table 3.3.

Table 3.3 Detection limits of the experimental procedures

Compounds	Detection limit		
	Soil (mg/kg)	Water (µg/L)	APU (µg/L)
PHEN	0.15	30	0.5
BaP	0.04	0.13	0.1

3.4 Methods

3.4.1 Synthesis of the precursor polymer

The synthesis experiment was modified from Tungittiplakorn et al. (2004) and was conducted to obtain the desired property of APU nanoparticles that is suitable for sorption of PHEN and BaP. The synthesis reactor is shown in Figure 3.2. The synthesis was divided into 3 steps: Mixed TDI with PTMG, added HEMA, and added PEG dissolved in 0.25% DMAc. The 99.99% nitrogen gas is purged to the reactor at each addition of chemicals to prevent oxygen in the system. The composition of the chemical used in the study was shown in Table 3.4. The completion of the reaction was verified by the Fourier Transform Infrared Spectrometer, FT-IR. The reaction was completed when there was a disappearance of NCO functional group at the wavelength of 2270 cm^{-1}.

Table 3.4 Chemical Composition of APU nanoparticles with PMUA precursor chain

Chemical	Molar Ratio	FW	Mole	Weight Theory (g)	Weight (g)
TDI	2	174.16	0.04	6.9664	6.9540
PTMG	1	1000	0.02	20.0000	20.0020
HEMA	1	130.15	0.02	2.6030	2.6000
PEG	1	2000	0.02	40.0000	40.0000

3.4.2 Formation and characterization of nanoparticles

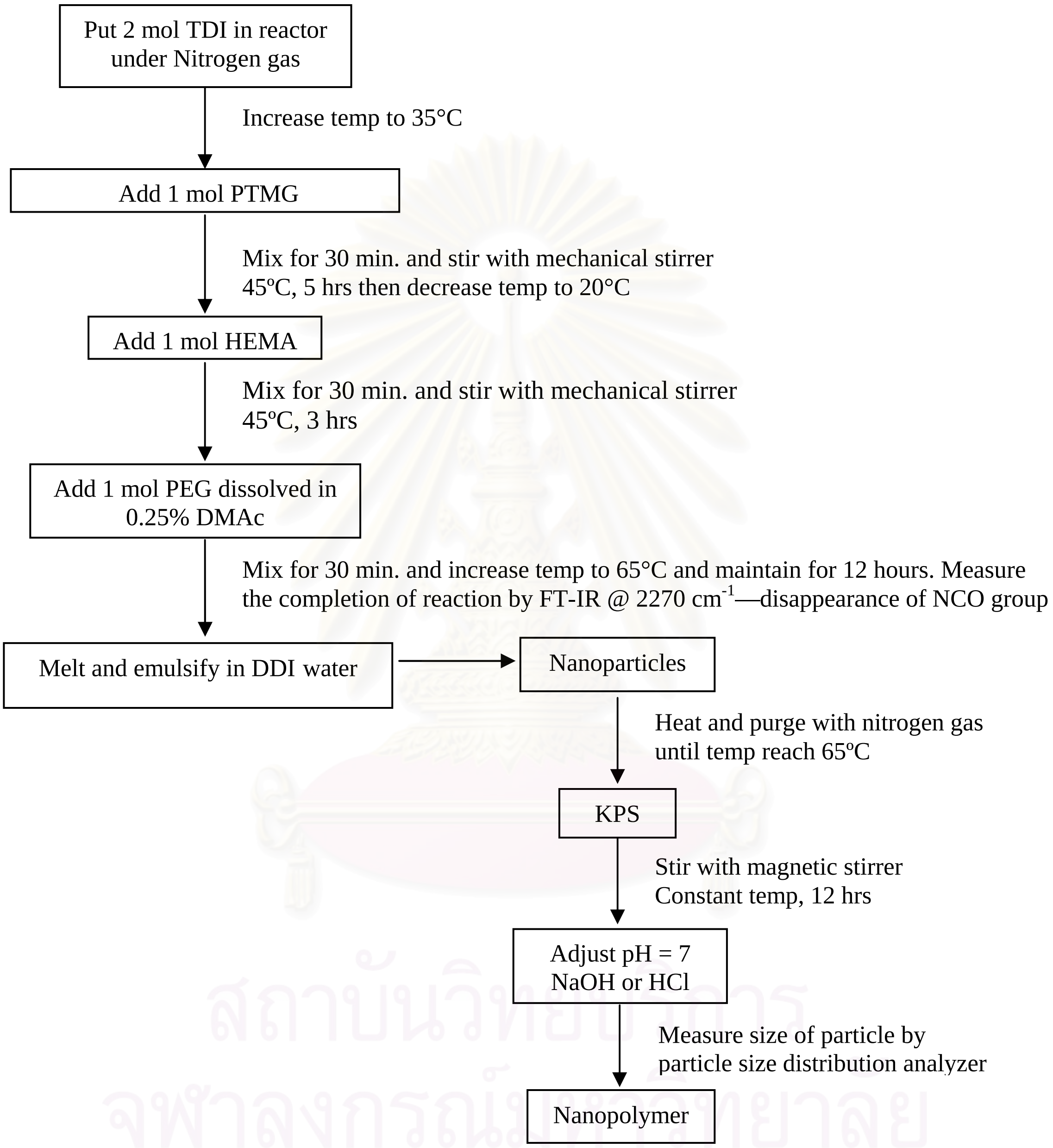
The emulsion was formed by adding DI water droplets to the precursor at 35ºC with vigorous stirring using a spetula. The formation of nano-sized micelle-like colloidal particles occurred by the interaction between amphiphilic polymer (PMUA) and water molecules with the vigorous stirring using mechanical stirrer at very high rpm as shown in Figure 3.3. Then the precursor chains were cross-linked by adding the initiator, KPS (5% by weight), into the emulsion. The cross-link reaction was carried out in a round-bottom flask with magnetic stirrer and continuous purging of nitrogen at 65ºC as shown in Figure 3.4. The particle size distribution analyzer was used to verify the size distribution of nanoparticles. The sequence of the synthesis of amphiphilic polyurethane (APU) nanoparticles with poly(ethylene) glycol modified urethane acrylate (PMUA) precursor chain is illustrated in Figure 3.5.

Figure 3.2 Synthesis reactor

Figure 3.3 Formation of nano-sized particles

Figure 3.4 Cross-link reactor

Figure 3.5 Sequence in the preparation of PMUA precursor chains and nanoparticles



3.4.3 Collection and preparation of soil sample

The soil samples were obtained from the surrounding of coal-tar burning site in Ramkamhaeng, Bangkok. The area of the site is approximately 0.64 hectare and has been used as the coal-tar burning site for a decade. Since coal burning site was one major location for PAHs contamination; therefore, the soil sample collected from the site could represent the characteristics of soil that was contaminated with PAHs. There was no evidence that the site had been fertilized and/or contaminated with pesticides or herbicides. The collection of 15 soil core samples was randomly dug. The plow depth was approximately 5 inches from the soil surface. The soil samples were homogeneously mixed and kept in an air-tight glass container. Part of the sample was kept in the air tight container for determination of moisture content. The rest of the sample was air-dried and sieved with 2mm sieve size for determination of soil texture and pH, and 0.5mm sieve size for determination of organic carbon content. The soil samples used in batch and column experiment were sieved to 0.5mm prior to use.

3.4.4 Determination of soil characteristics

The soil sample was analyzed for physicochemical properties including soil texture, pH, moisture content, organic carbon content, cation exchange capacity and electroconductivity. Moreover, the background existence of PAH test compounds existence in soil sample was also determined. The soil characteristics determination methods are presented in Table 3.5.

Table 3.5 The soil characteristics determination methods

Parameters	Methods
Soil texture	Sieve analysis
pH	pH meter (soil:water, 1:1)
Moisture content	Gravimetric method
Organic carbon content	Walkley-Black method
Cation exchange capacity	Ammonium saturation and distillation
Electroconductivity	EC meter (soil:water, 1:5)
PAHs test compounds	U.S. EPA Method 3546

3.4.5 Preparation of standard solutions

- ***PAH test compounds***

PHEN and BaP were prepared in mixture for determination of recoveries, calibration curves and partitioning experiments. The stock solution of test compounds were prepared in hexane and made up in a volumetric flask. Since PHEN and BaP were hardly dissolved in water, they were first dissolved in hexane at concentration of 1,000(S) and 10,000(S) respectively, where S denotes aqueous solubility of each compound. The stock solutions were kept at 4 ℃. The stock solutions were diluted to 100(S) and 1,000(S) in acetone. Then the solutions were diluted again in DDI water to obtain the desired working concentrations. In this experiment, hexane and acetone would not influence any effects in the experiment, because the volume spiked were in micrometer level. The five working concentrations in different proportion to S as 1S, 0.75S, 0.5S, 0.25S, and 0.15S were used in the experiments.

- ***Internal standard solution***

Pyrene was used as internal standard. The internal standard was weighed at 1000 times the concentration of its aqueous solubility, 1000(0.135 mg/L), dissolved in hexane and made up in a volumetric flask. The stock solutions were kept at 4 ℃. Every samples were spiked with 500 µL at the same concentration before the samples were passed to the extraction procedures.

3.4.6 Extraction

The method for extraction of PAHs from soil and water samples was modified from the work of Karnchanasest and Jailuk (2004) and Karnchanasest and Satayavibul (2005). The soil samples were extracted using microwave-assisted extraction method U.S. EPA Method 3546. Thirty milliliter of 1:1 hexane: acetone was used as a solvent prior to extraction. The extraction conditions were as followed: an ambient temperature raised to 120℃ for 10 minutes, then held the temperature at 120℃ for 20 minutes. The procedures were vented for 5 minutes. The power supplied was at 500 watts. The resulting solutions were combined and proceeded for isolation step (U.S. EPA, 2000). The water samples were extracted using liquid-liquid extraction method. The extraction process was carried out in a 2-L separatory funnel. In this study, 30 mL hexane was used as a solvent to extract PAHs out of 1 liter of water. The resulting solution from isolation step and liquid-liquid extraction was concentrated at 66℃ to 2 mL using rotary evaporator. The APU nanoparticles samples were extracted using liquid-liquid extraction by mixing 50 mL solvent with the ratio of hexane:acetone 9:1 and reduced the volume to 2 mL by evaporation using rotary evaporator at 66℃. Then the samples were transferred to GC auto sample vials for analysis.

3.4.7 Isolation

Since the sample analyzed by GC must be crystal clear in appearance and color, so isolation step is required for the sample extracted from soil. The interaction of solvent and soil particles caused the extracted sample became yellowish color; therefore, it was necessary to clean the sample before further to next experimental steps. A glass column with 40 cm in length and 2 cm in diameter was used for isolation of extracted soil samples. The columns were packed with glass wool, sodium sulfate anhydrous, and 15 g of silica gel respectively. The packed glass columns are illustrated in Figure 3.6. The silica gel was activated in the oven at 500℃ for 4 hours, while sodium sulfate was treated in the oven at 105℃ for 2 hours prior to use. Both absorbents were allowed to cool at room temperature in a desiccator. After the columns were packed, 50 mL of eluent, 20% DCM in hexane, was used to clean up PAHs solution in the extracted samples. First, hexane was drained until it stayed just above the silica gel layer. Then, the column was washed with 10 mL of eluent followed by half portion of the extracted sample. Next, 15 mL of the eluent and another portion of extracted sample was transferred to the column followed by 15 mL of the eluent simultaneously. The last 10 mL of eluent was passed through the column before the cleaned up solution was collected. After that the cleaned up samples were concentrated to 2 mL using rotary evaporator (Karnchanasest and Jailuk, 2004) prior to analyze by GC.

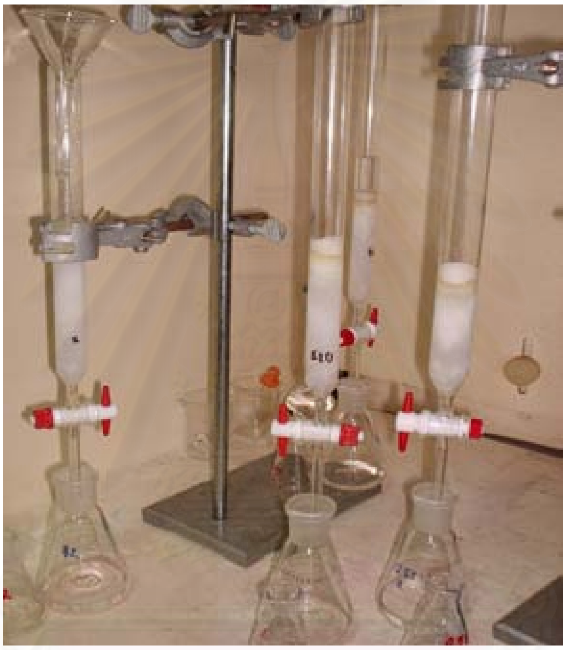


Figure 3.6 Isolation glass columns

3.4.8 Gas chromatographic analysis

Gas chromatography with flame ionization detector was used to qualify the concentration of phenanthrene and benzo(a)pyrene with the absence and presence of the nanoparticles. The analysis was conducted by GC- FID using Hewlett Packard HP 6890 autosample injector 7683 series with HP-5 capillary column (30m x 320µm id) 5% phenyl methyl siloxane with a film thickness of 0.25µm. The optimal condition of GC-FID was as followed: an initial column temperature of 80℃ ramped to 160℃ at a rate of 25℃/min. The temperature was held at 160℃ for 5 minutes, and then ramped to 300℃ at 5℃/min and held at this final temperature for 5 minutes. The total run time of the program was 30 minutes. Injection was made in the splitless mode.

3.5 Batch partitioning experiments

3.5.1 Steady state attainment

The experiment was conducted in triplicate using 3 g of soil in 1-L of water and 3 g of soil in 50 mL of 0.5g/L APU nanoparticles at highest working concentration (at PAH's water solubility) of test compounds. Three bottles of sample were collected at the end of shaking time at 6, 12 hours, 1, 2, and 4 days. The samples were extracted according to the extraction procedure explained previously. The amounts of PAHs in systems with soil and water and in soil and APU suspension were analyzed. The plot of the PAHs concentration in soil against the shaking time and PAHs concentration in APU against the shaking time indicated that the system already reached the steady state. The soil-water system and soil-APU system reached steady state at 48 and 24 hr respectively as shown in Appendix D.

3.5.2 Partition coefficient of PAHs between soil and water

Partitioning experiments between soil and water were conducted using 3g of soil in 1-L of standard solution at 5 working PAH concentrations (S, 0.75S, 0.5S, 0.25S, and 0.15S). The samples were shaken until the steady state was reached. Then they were filtered by GF/C. The soil and water samples were extracted according to extraction method explained in the previous sections. The supernatants was analyzed by GC-FID. The concentrations of PAHs on soil versus the concentrations in water were plotted. From the plot, the behavior of sorption isotherm was investigated and the partition coefficient, K_d was determined. The K_d obtained from this experiment was later expressed as $K_{s,w}$.

3.5.3 Partition coefficient of PAHs between soil and APU

The partitioning experiment was conducted in a similar manner to the previous experiment; however, 50mL of 3 different APU concentrations (0.5, 2.5, and 5g/L) were introduced into each batch instead of water. The samples were shaken until the steady state was reached. Then they were filtered by GF/C. DDI water was rinsed through the soil residue remained on filter paper in order to wash out APU that may bind to the soil particles. The soil and water samples were extracted according to extraction method explained in the previous sections. The concentration of PAHs adsorbed onto nanopolymer and soil were analyzed by GC-FID. The relationship of PAHs concentration in soil versus the PAHs concentration on APU nanoparticles indicated the sorption coefficient of PAHs between soil and APU, $K_{\mathrm{s,APU}}$.

3.6 Column experiments

3.6.1 Determination of APU nanoparticles mobility in the soil sample

The flow behavior of the washing materials within the soil matrix has been evaluated using soil column experiment. The soil sample was packed into the glass column (2.5 cm i.d. x 10 cm length) and equilibrated with 5 mM $CaSO_4$ and 0.02% NaN_3, which were employed as a mobile phase to simulate a groundwater electrolyte and to inhibit microbial growth, respectively. Then APU emulsion (12g/L) were introduced into the column as a suspension in 5 mM $CaSO_4$ and 0.02% NaN_3 for approximately 0.5 pore volume followed by elution with the electrolyte solution. The electrolyte solution was fed until there were no further changes in concentration of particles. Five milliliter samples were collected by a fraction collector at constant flow rate (20mL/hr) and dried at 50°C for 48 hours to determine the final weight of the particles.

3.6.2 Determination of APU nanoparticles' ability to remove PAHs

Column experiments were performed to test the ability of APU nanoparticles to remove PHEN and BaP from contaminated soil. To investigate the efficiency of APU nanoparticles solution to remove test compounds from the soil column, 1 and 5 mg/L of each test compounds were mixed with the soil. Then the samples were shaken on a platform shaker for 24 hours. The contaminated soil was then packed in glass column (2.5 cm i.d. x 10 cm length). The apparatus for column experiment included a 1-L glass bottle with cap, a peristaltic pump, a soil column connected by Teflon tube in order to minimize the adsorption of PAHs on the tube surface. The apparatuses are shown in Figure 3.7.

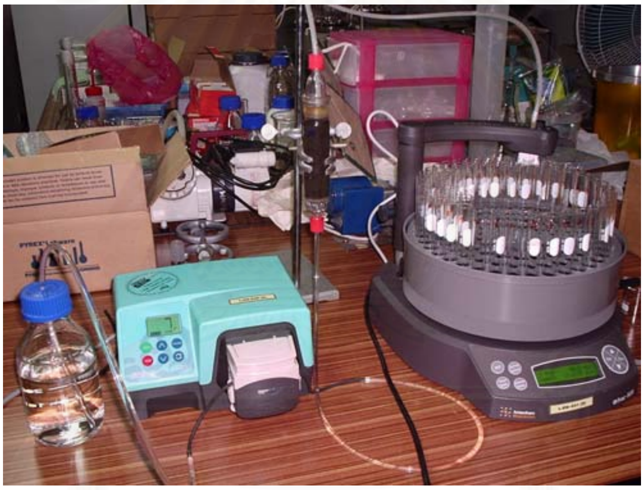


Figure 3.7 Column experiment apparatuses

After column preparation, the columns were subjected to be tested with 4 conditions. Properties of the test columns are summarized in Table 3.6. The experiment was conducted at room temperature (25±3°C). The concentration of APU nanoparticles were at 12g/L for every soil column tests. The flow rate of the experiment was kept constant at 20 mL/hr. The flow interruption at every 24 hours was also performed to investigate the performance of APU nanoparticles to remove test compounds compared to the experiment without flow interruption. It is expected that flow interruption would prolong the contact time, which provided adequate time for APU to extract test compounds from the soil column.

Table 3.6 Soil column test condition

Column No.	Flow Interrupt	Mass dry soil (g)	Total PAHs in column (mg), [mg/L, mg/kg]	Inlet APU conc. (g/L), [duration,days]	Water pore volume (mL)
1	×	68.93	0.025, [1, 0.36]	12, [3]	33.48
2	/	70.83	0.025, [1, 0.35]	12, [6]	31.05
3	×	71.50	0.125, [5, 1.75]	12, [3]	30.12
4	/	70.12	0.125, [5, 1.78]	12, [6]	31.64

First, 10 pore volume of the electrolyte solution ($CaSO_4$ and 0.02% NaN_3) was initially fed to the soil column without APU nanoparticles solution to ensure that the soil was completely saturate and to flush out dissolved PAHs. Then APU nanoparticles in electrolyte solution was pumped into the column instead of electrolyte alone. Effluent samples (30mL) were continuously collected using fraction collector, and transferred into 125 mL Erlenmeyer flask. Then 30mL of hexane has been used to extract PAHs from the collected samples. The supernatant was then transferred to evaporating flask and concentrated the volume to 2mL at 66°C (appropriate temperature to evaporate hexane out of the system) before transferred into GC-vials. Since PAHs have very high boiling point and very low pressure vapor as shown in Table 2.1; therefore they are not likely to evaporate at this evaporation condition. The experiment was continued until the PAHs removal rate appeared to decline. Duplicate experiments were performed for each test analysis.

3.7 Data analysis

Statistical analysis in this study was processed in Graphpad, Microsoft Excel 2003 and a Ti-89 Texas Instruments calculator. The software provided a wide range of statistical analyses that were mostly essential to this study including mean, standard deviation, linear regression, equations and correlation coefficient, etc.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characteristics of APU nanoparticles

The molar proportions of reactants (TDI:PTMG:HEMA:PEG) used for the synthesis of the precursor chains are 2:1:1:1. The completion of synthesis reaction was measured by FT-IR before and after PEG was added into the mixture. According to the FT-IR results shown in Appendix E, the disappearance of NCO group at wavelength of 2270 cm^{-1} has been discovered after 2 hours of introducing PEG into the mixture. The disappearance of NCO group indicates that all the double bond structures have bonding. The pH of the APU nanoparticles (reported to be acidic, pH=2) was neutralized with NaOH, since nanoparticles formulated using neutral hydrophilic pendent chains greatly increased the removal rate of PHEN from a contaminated soil column (Tungittiplakorn et al., 2004).

The size of the APU nanoparticles was measured by particle size distribution analyzer using wet analysis system and polydisperse analysis model. The statistical results reported that the particle sizes ranged from 50nm to 150nm. The particle size distribution is illustrated in Figure 4.1.

The average diameter of the particles was approximately 80-110nm which was slightly larger than the size reported in the previous study by Tungittiplakorn et al. (2004) (60-80nm measured by dynamic light scattering (DLS) system). The detection limit of the analyzer (50nm to 190μm), stirring speed and stirring duration are the controlling factors for difference of particle size. Table 4.1 reports the diameter size with respect to the % volume of the particles in the solution. The highest volume (12%) of the particles had the size of 90nm. The particles size of 80 and 110nm had the volume of 11%. The particles size ranged between 50 to 80nm and 110 to 150nm had 16% and 13% total volume, respectively. Large particles were filtered out using 0.45μm glass micro-fiber filter. The comparison between particle sizes of different synthesized APU nanoparticles was reported in Table 4.2.

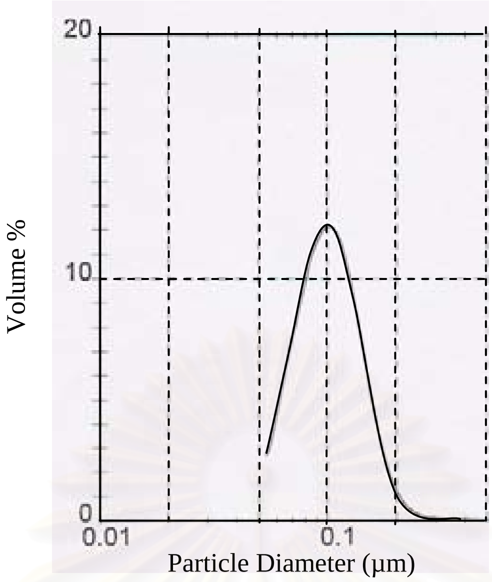


Figure 4.1 APU particle size distributions

Table 4.1 Size of APU particles synthesized in this study

Size (nm)	Volume %
50	2.66
60	5.45
70	8.28
80	10.77
90	12.07
110	11.29
130	8.45
150	4.88

Table 4.2 Comparison of APU particles size to other studies

Type of APU particles	Particle Size (nm)	References
APU 700 with UAN chain	Aggregated - 32.10	Kim et al. (2003) Kim et al. (2004)
APU 1000 with UAN chain	23.40	Kim et al. (2003)
APU with UAA chain	15-60	Tungittiplakorn et al. (2004)
APU with PMUA chain	60-80	Tungittiplakorn et al. (2004)
APU with PMUA chain	80-110	This study

APU: amphiphilic polyurethane nanoparticles; UAN: urethane acrylate nonionomer; UAA: urethane acrylate anionomer; PMUA: poly(ethylene glycol)-modified urethane acrylate

4.2 Characteristics of soil

Probably the single most important feature of a soil is texture. Many physical, chemical, and biological characteristics of a soil are related to texture, making textural determination one of the most basic of soil analysis. Soil from the surrounding of a coal burning site was used in this study. Analysis revealed that the soil composed of 67.8% sand, 20.2% silt, and 12% clay. The soil texture, the relative proportion of the various grain sizes in a soil, was accounted to be sandy loam soil which sand is dominant. Thus, in this study, soil texture may have less influence to soil sorption as most of sandy soil will have little attraction for contaminants such as synthetic organics. The moisture content of the soil was measured to be 8.46%. The pH of the soil sample was slightly basic (pH=7.9), and is described as moderately alkaline. Soil CEC, cation exchange capacity, is normally expressed in units of charge per weight of soil. Two different, but numerically equivalent sets of units are used: meq/100 g (milliequivalents of element per 100 g of dry soil) or cmolc/kg (centimoles of charge per kilogram of dry soil). Normal CEC ranges in soils would be from less than 1 meq/100 g, for sandy soils low in organic matter, to more than 25 meq/100 g for soils high in certain types of clay or organic matter (www.soils.agri.umn.edu). In this study, the soil sample has cation exchange capacity (CEC) and electrical conductivity (EC) of 7.9 cmolc/kg and 1.5 aS/m, respectively. The organic matter of the soil sample was determined to be 4.03%, which was corresponded to 2.34% organic carbon content. The organic carbon content represents the fertility of the soil. The soil that has organic carbon content of less than 1.5% is considered to have low fertility (Karnchanasest and Jailak, 2004). Chiou (1999) suggested that soil that has organic matter content between 0.5-3.0% are considered to have high affinity for hydrophobic compounds. Therefore, the significant factor that influences sorption in this study may be due to soil organic matter.

4.3 Partitioning coefficients

4.3.1 Comparison of steady state attainment

Partitioning coefficients of PAHs between soil-water system and APU-soil system were determined by batch partitioning experiment at 5 PAH concentrations at their steady state. Individual steady state attainments for each compound in each system were shown in Appendix D. The steady state attainment for both systems were compared and illustrated in Figures 4.2 and 4.3. PHEN and BaP in soil-water system and soil-APU system reached their equilibrium at 24 and 48 hours, respectively. From the figures, both test compounds in soil-APU system approached their steady states faster than that of soil-water system. The major reason for this was that the particle size of APU is much smaller than that of soil; for instance, APU nanoparticles having average particle size of 80-110 nm while the soil used in this study was sieved to 0.5 mm. The much smaller particle size of APU nanoparticles resulted in a tremendous surface area, which caused APU to have higher tendency to sorb more of test compound at the same period of time. The more rapid steady state of both test compounds in soil-APU system partially fulfilled our assumption that APU nanoparticles having higher potential to sorb PAHs than soil.

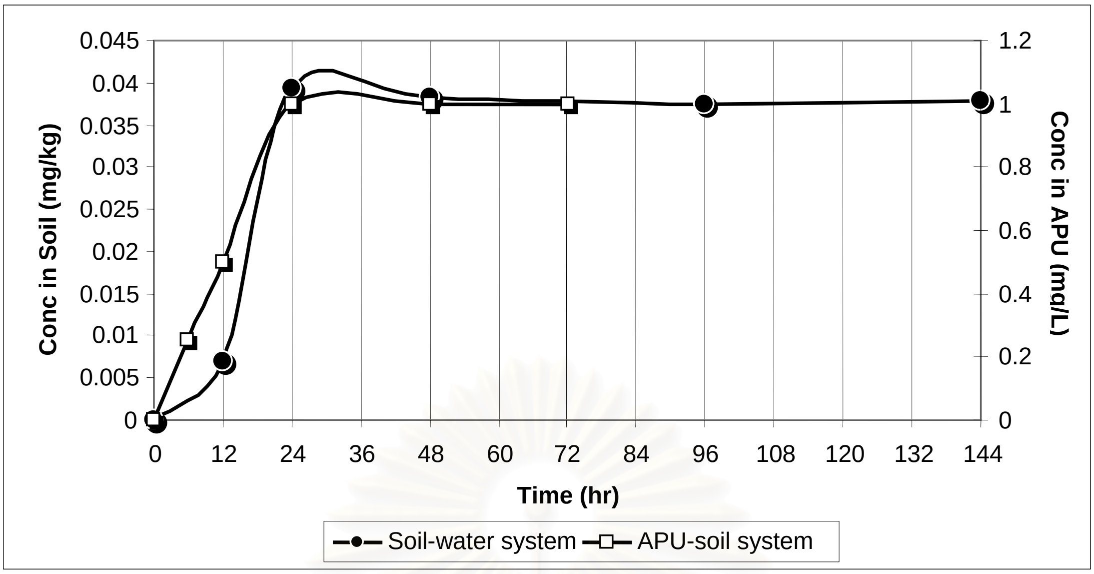


Figure 4.2 Comparison of steady state attainment for PHEN in soil-water system (conc. in soil, mg/kg) and APU-soil system (conc. in APU, mg/L)

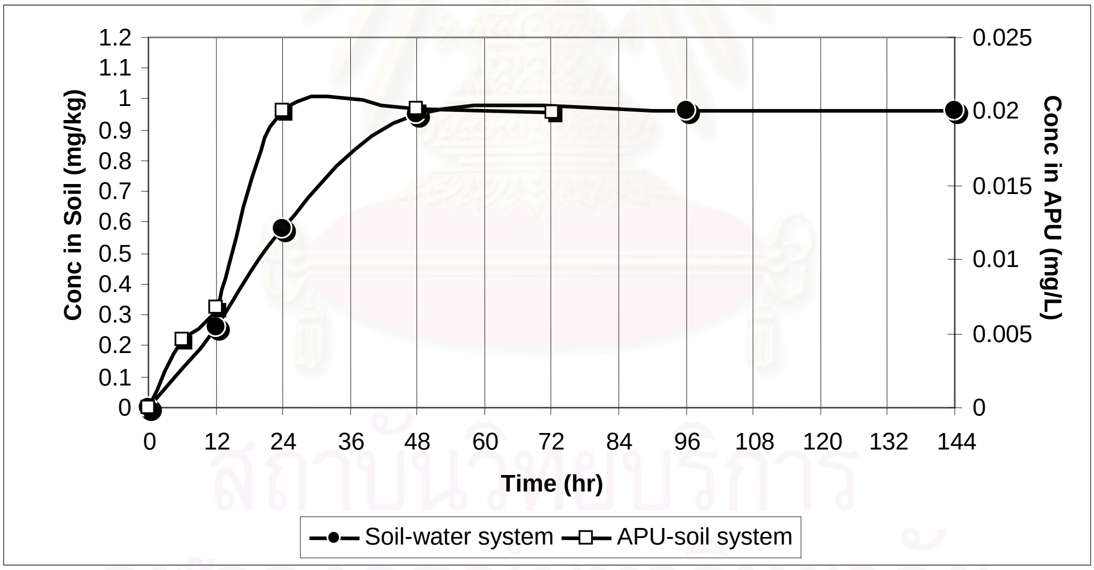


Figure 4.3 Comparison of steady state attainment for BaP in soil-water system (conc. in soil, mg/kg and APU-soil system (conc. in APU, mg/L)

Remarks**:** The concentrations of PAHs are not on the same scale due to different ranges of working concentration. The aim of these figures is to compare the time when both system reached their equilibrium.

4.3.2 Partition coefficient of PAHs in soil-water system

The concentration detected in soil and water at each working concentrations were reported in Appendix F1. The amount of sorbed PAHs on soil was fitted to the linear isotherm where the equilibrium concentration of PAHs in water (mg/L) is plotted on the x-axis and the adsorbed PAH in soil (mg/kg) is plotted on the y-axis. The linear isotherm of PHEN and BaP are illustrated in Figures 4.4, 4.5, and 4.6.

In this experiment, $K_{s,w}$ is the partitioning coefficient of PAHs between soil and water phase. The $K_{s,w}$ value can be obtained from the slope of the linear isotherm, which are 1457±124 L/kg for PHEN and 3162±363 L/kg for BaP. It is evident from the arithmetic result that BaP has much higher $K_{s,w}$ value than PHEN. This may be due to the fact that BaP has significantly higher lipophilicity; therefore BaP has higher tendency to sorb on the soil (Mackay et al., 2004).

Since the organic carbon content in soil sample was theoretically adequate for 3 g of soil to adsorb all test compounds concentrations, the point deviated in Figure 4.4 may possibly result from the experimental error. As the experiment was designed to conduct with very low working concentration; occasionally, error from the experimental procedure was hardly avoided. So, the partition coefficient was simply calculated from the linear portion of the isotherm. By excluding the last data point, the partition coefficient increase to 1776±88 L/kg as shown in Fiugre 4.5.

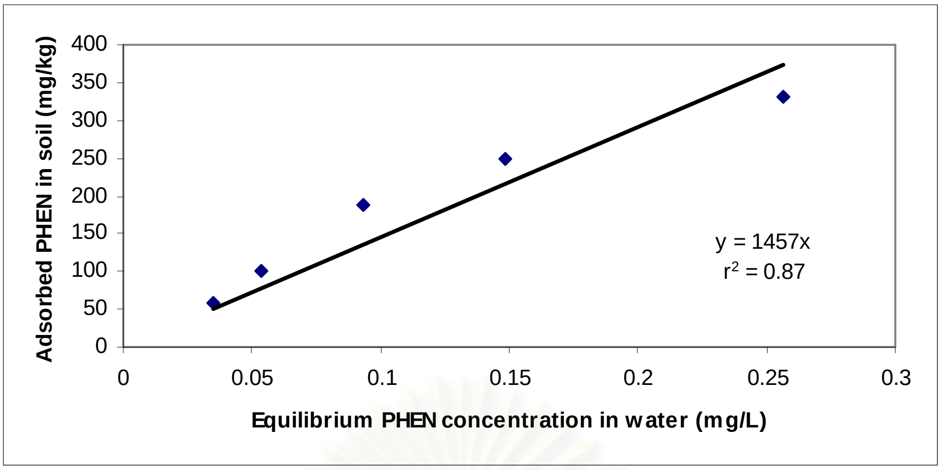


Figure 4.4 Sorption isotherm of PHEN on soil

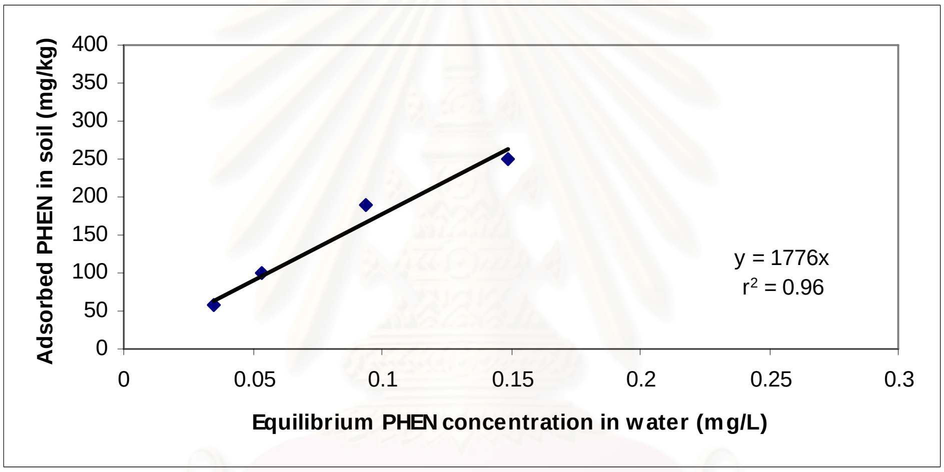


Figure 4.5 Sorption isotherm of PHEN on soil excluding outliner

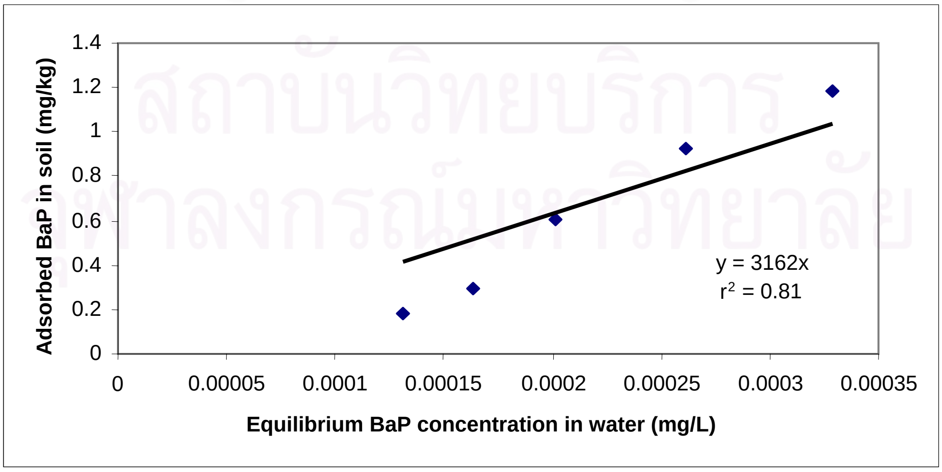


Figure 4.6 Sorption isotherm of BaP on soil

The $K_{s,w}$ values were then normalized by organic carbon content to the soil organic carbon-water partition coefficients, K_{oc}, (Equation 2.4) in order to determine the partition coefficient in relation to organic carbon content. After normalized by 2.34% orgnic carbon content, K_{oc} for PHEN and BaP were reported to be 75,897 and 135,128 L/kg respectively. The K_{oc} values were calculated to obtain log K_{oc} as shown in Table 4.3. The similar results were found in other literatures related to partition coefficient of PAHs.

The values of K_{oc} obtained from the study were parallel to the literatures; however, many factors could affect the measured value of K_{oc}. Beside the different laboratory procedures, factors under actual environmental conditions such as particle size distribution and surface area of solids, temperature, concentration of dissolved or colloidal organic matter in water, loss of chemical due to volatilization, degradation, photodegradation, and adsorption to test flask walls could affect the K_{oc} value. Also, non-equilibrium adsorption mechanisms or failure to reach equilibrium conditions may contribute to the variation of K_{oc} values.

For instance, the difference in experimental procedures may yield a different partition coefficient, which resulted in different K_{oc} values. Krauss and Wilcke (2000) concluded that the log K_{oc} values of PAHs and PCB were different among the different particle size fractions. Hulscher and Cornelissen (1996) suggested that partition coefficient for most of the compounds decrease with increasing temperature. However, partition coefficient may increase at higher temperature for the compounds in which their solubility decreases at higher temperature (Chiou et al., 1979). Moreover, Hegeman et al. (1995) found that dissolved organic matter could affect the partition coefficients of PHEN and BaP. The study revealed that the presence of dissolved or colloidal organic matter result in a higher apparent solubility of both compounds in the liquid phase. In this study, the soil is sieved to 0.5mm, the temperature is constant at room temperature throughout the experiment, and the dissolved organic matter is not present in the sample.

Table 4.3 Comparison of log K_{oc} to the literatures

Compounds	log K_{oc}	
	This study	Literatures
PHEN	4.88	$3.72^{(a)}$ $4.36^{(b)}$ $4.56^{(c)}$ $4.72^{(d)}$
BaP	5.13	$5.70^{(d)}$ $5.90^{(e)}$

(a) Abdul et al. (1987); Aquifer materials-water
(b) Karickhoff et al. (1979); Natural sediments-water
(c) Sabljic et al. (1995); N/A
(d) Karnchanasest and Jailuk (2004); Soil-water
(e) Meylan et al. (1992); Soil-water

In addition, log K_{oc} could be varied accordingly due to biodegradation and photodegradation. PAHs with up to four aromatic rings are biodegradable under aerobic conditions, but the biodegradation rate of PAH with more aromatic rings is very slow. The rate of biodegradation in soil depends on several factors including the characteristic of the soil, its microbial population and the properties of the different PAH compounds. Nagpal (1993) discovered that some PAH could be degraded through the process of photodegradation. For example, lower aromatic rings compound such as PHEN was sensitive to photodegradation; whereas BaP that has higher aromatic ring was relatively resistant to photodegradation. However, the experiments were conducted in the dark with the use of bacterial inhibitor. So, biodegradation and photodegradation of PAHs were eventually restrained.

4.3.3 Partition coefficient of PAHs in soil-APU system

The concentrations detected in soil and APU at each working concentrations were reported in Appendix F2. The amount of sorbed PAHs on soil was fitted to the linear isotherm where the equilibrium concentration of PAHs in APU solution (mg/L) is plotted on the x-axis and the adsorbed PAHs in soil (mg/kg) is plotted on the y-axis. The linear isotherm of PHEN and BaP are illustrated in Figures 4.7 and 4.8, respectively.

The $K_{s,APU}$ is the partition coefficient between soil and APU solution phases. The $K_{s,APU}$ value can be obtained from the slope of the linear isotherm, which are 0.55±0.03 L/kg for PHEN and 0.36±0.02 L/kg for BaP. It is evident from the arithmetic result that BaP has slightly lower $K_{s,APU}$ value than PHEN. The low $K_{s,APU}$ implied that BaP has stronger affinity for APU nanoparticles than soil. Moreover, more actual sorptive sites, due to larger surface area of APU than soil surface, of APU nanoparticles than soil particles caused the test compounds to have higher affinity to APU than soil. This can be discussed due to the fact that BaP has significantly lower water solubility than PHEN; therefore BaP has higher tendency to partition into the APU phase, which is considered to have stronger affinity for hydrophobic compounds.

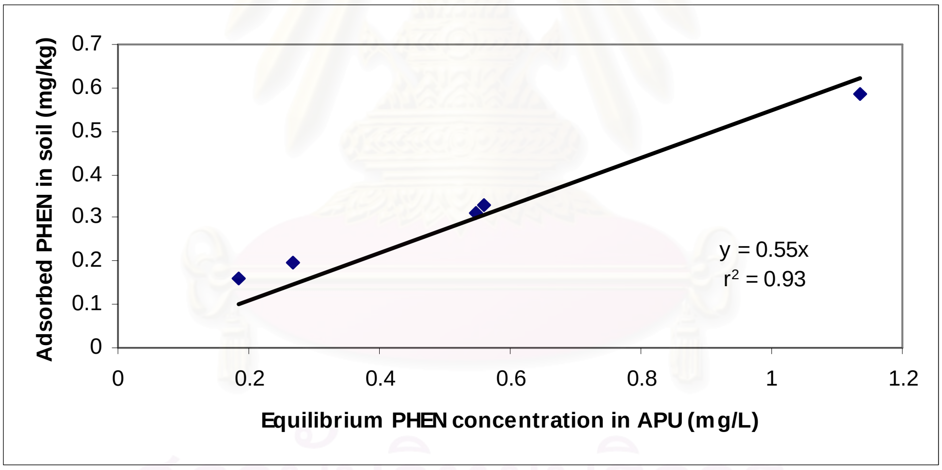


Figure 4.7 Sorption isotherm of PHEN on APU

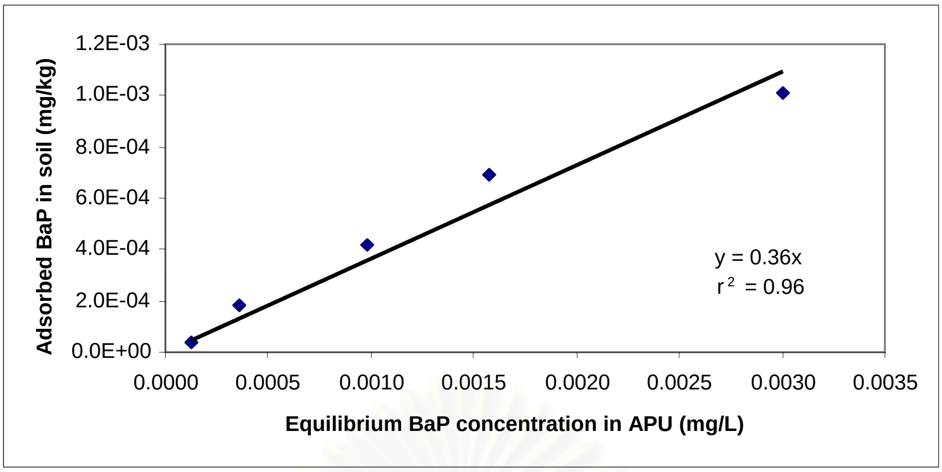


Figure 4.8 Sorption isotherm of BaP on APU

As APU nanoparticles are amphiphile molecules, the hydrophilic groups are responsible for stabilizing the particles in an aqueous phase while the hydrophobic backbone in the interior has high affinity for hydrophobic pollutants. The cross-linked structure of APU nanoparticles largely reduced their sorption onto soil matters. The study of Tungittiplakorn et al (2004) supported this assumption as the isotherm experiment showed that the adsorption of APU nanoparticles on the sandy aquifer material followed a Langmuir-type isotherm, which is based on four hypotheses: 1) The surface of the adsorbent is uniform, that is, all the adsorption sites are equal 2) Adsorbed molecules do not interact 3) All adsorption takes place through the same mechanism, and 4) At the maximum adsorption only a monolayer is formed (Sawyer et al., 2004; en.wikipedia.org/wiki/Langmuir). As a result, Tungittiplakorn et al (2004) and Kim et al (2003) tentatively concluded that the subsequent adsorption of APU nanoparticles to the soil was remarkably low compared to the adsorption of PHEN to APU nanoparticles. Thus, the results showed from the partitioning experiment suggested that both PHEN and BaP are likely to sorb onto the APU nanoparticles rather than sorb onto soil.

However, the $K_{s,APU}$ of PHEN is slightly higher than that of BaP that is more hydrophobic. This indicates that APU nanoparticles caused a decrease of $K_{s,APU}$ value of more hydrophobic compound. Therefore, it can be concluded that APU nanoparticles exhibited better extraction performance and had a greater reduction of BaP sorption in soil. The major reason for this is evidence from the value of $K_{s,w}$ and

$K_{s,APU}$ (with 95% confidence intervals summarized in Table 4.4), which implied that sorption kinetic of test compounds onto APU is more rapid than onto soil. Additionally, more hydrophobic compound is highly sorb onto APU. Thus, sorption of BaP onto APU is better than onto soil when compared with sorption of PHEN. As a consequence, the observation from the linear isotherm of BaP indicates that the hydrophobic property is dominant in the sorption of PAHs onto APU nanoparticles.

Table 4.4 Partition coefficients of PHEN and BaP between soil and water ($K_{s,w}$) and partition coefficient of PHEN and BaP between soil and APU nanoparticles ($K_{s,APU}$)

Test compounds	$K_{s,w}$ (L/kg)	$K_{s,APU}$ (L/kg)
PHEN	1776 ± 88	0.55 ± 0.03
BaP	3162 ± 363	0.36 ± 0.02

Other investigation on partition coefficients of PAHs between soil and other system has been determined. Paterson et al. (1999) studied the efficiency and kinetics of various nonionic surfactants facilitated extraction of PHEN from coal tar-contaminated soil. The soil characteristics reported in the literatures were similar to this study. The partition coefficients obtained from system with ethylene oxide-propylene oxide (EO-PO) copolymers and Triton X-100 were 8.6-47.6 L/kg and 10.5 L/kg, respectively. The comparison between the study of Peterson et al. (1999) with this study implied that APU nanoparticles may have higher extraction efficiency of PHEN from the soil, since the partition coefficient of PHEN between soil and APU is much lower than that between soil and EO-PO copolymers or soil and Triton X-100. Therefore, the partition coefficient obtained from the experiment suggested that sorption ability of APU nanoparticles was higher than some types of polymer and some commercial surfactants.

4.3.4 Partition coefficient of PAHs in APU-water system

The partition coefficient of PAHs between APU and water can be calculated from the relationship between $K_{s,w}$ and $K_{s,APU}$ reported in previous chapter. The expression of the relationship is as follow:

$$K_{APU,w} = (C_{APU}/C_s) \times (C_s/C_w) \qquad (4.1)$$

where $K_{APU,w}$ is the parition coefficient of PAHs between APU and water (dimensionless), C_{APU}/C_s denotes the reciprocal of $K_{s,APU}$ (kg/L), and C_s/C_w denotes the $K_{s,w}$ value (L/kg).

By substituting the reciprocal of $K_{s,APU}$ and $K_{s,w}$ to Equation 4.1, $K_{APU,w}$ values for PHEN and BaP were calculated to be 2,665 and 15,581 respectively. The logarithms of partition coefficient were 3.51 for PHEN and 3.94 for BaP and are shown in Table 4.5.

Table 4.5 Partitioning coefficient of PAHs between APU and water

Compounds	$K_{s,w}$ (L/kg)	$K_{APU,s}$ (kg/L)	$K_{APU,w}$	Log$K_{APU,w}$
PHEN	1776	1.82	3229.09	3.51
BaP	3162	2.78	8783.33	3.94

The logarithms of octanol-water partition coefficient, logK_{ow}, of PHEN and BaP were reported to be 4.57 and 6.04 respectively (Abdul et al., 1987; Weiss, 2000). Therefore, log$K_{APU,w}$ of both test compounds are lower than logK_{ow}. The lower log$K$ in APU-water system than in octanol-water system suggested that APU nanoparticles have lower potential to sorb PHEN and BaP than octanol. This implied that sorption ability of octanol is stronger than APU. The result is analogous to the theory that octanol is purely hydrophobic, while APU is amphiphile particles.

4.4 APU nanoparticles mobility in the soil

The number of pore volume has been determined by feeding water to soil-packed column until the soil was saturated. It was found that 1 pore volume conferred approximately 30mL of water. The porosity of the column was determined to be approximately 0.61 from the weight of the column before and after saturation of the pore space with the water. Theoretically, the range of soil porosity, the volume percentage of the total soil bulk not occupied by solid particles, is equal to the ratio of pore volume to volume of soil column. Therefore, an increased in soil porosity results in higher amount of water per 1 pore volume. The soil porosity generally ranged from 25% to 50% for compact soils to ideal case. However, the well aggregated (granulated) soil with high organic matter may have approximately 65% soil porosity (www.uwm.edu/~fredlund/www.475/05PoreWaterEnergy2003.htm). As a result, the slightly high sample volume obtained from the experiment may be due to the high value of organic matter content in the soil.

The column breakthrough curve of 12g/L APU nanoparticles is shown in Figure 4.9. The relative concentration (C/C_o) of APU nanoparticles solution flowing through the soil column is plotted against the number of pore volume. C is the concentration of APU nanoparticles of a sample eluted from the soil column. C_o is the initial concentration of APU nanoparticles in the elutant. After adding 0.5 pore volumes (15mL) of APU nanoparticles solution to the soil column, electrolyte was fed to rinse out the particles from the column. The electrolyte capacity for removing applied nanoparticles was achieved after 1 pore volumes were fed to the column. The data obtained from the experiment were reported in Appendix G.

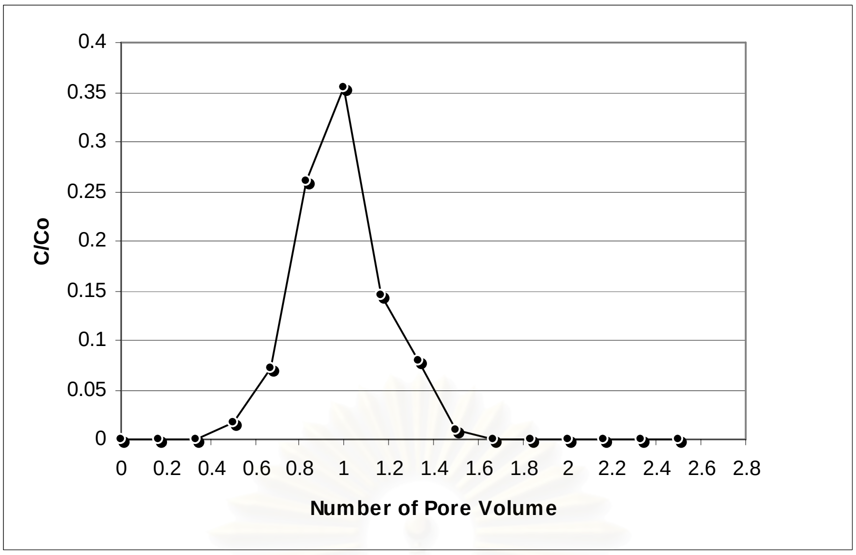


Figure 4.9 Breakthrough curve of APU nanoparticles

In Figure 4.10, the mass recovery of the APU nanoparticles from the soil column is plotted as a function of the volume of the aqueous solution added to the soil column. In this graph, M_t represents the total mass of APU nanoparticles to the column, and M is the accumulated mass of APU nanoparticles eluted from the column. The recovery rate determined from mass balance revealed that 94% of the particles was recovered. The recovery rate in this experiment is slightly lower than the previous study by Tungittiplakorn et al (2004). In the previous study, 100% of APU nanoparticles with PMUA precursor chain was achieved. Loss of particles in this experiment is possibly ascribed to adsorption on soil organic and the trap of particles in the micropore. The soil used in this study has significantly higher organic carbon content compared to the previous study (2.34% to 0.57%). High organic carbon content may increase degree of sorption of APU nanoparticles onto soil.

Another possible cause of loss of particles may due to the silt and clay contents of the soil. Demars et al (1999) stated that soil with fine-textured such as silt and clay have a much greater affinity for all classes of contaminants especially hydrophobic organics. The sandy aquifer used in the study of Tungittiplakorn et al (2004) consisted of 4.32% silt and 1.77% clay; however, the soil used in this study consisted of 20.2% silt and 12% clay. So it can be anticipated that APU nanoparticles has an interaction with higher % silt and clay of the soil, which tentatively affect the mobility of the particles in the soil column.

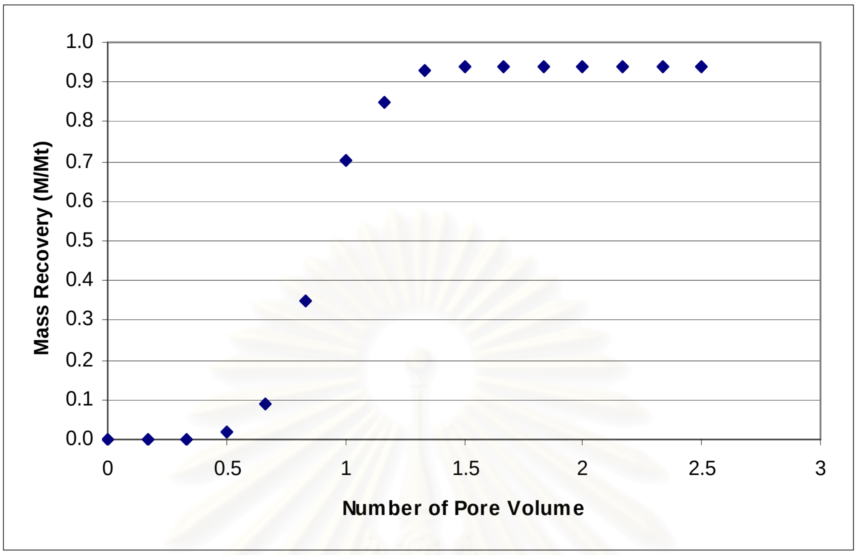


Figure 4.10 Mass recovery of APU nanoparticles from a soil column

4.5 Removal of PAHs from precontaminated soil column

APU nanoparticles were also tested in column experiments for their ability to remove PHEN and BaP from precontaminated soil column. The raw data for 4 test conditions were shown in Appendix H, I, J and K. The results for each test conditions are described below.

4.5.1 PAHs removal from 1mg/L pre-contaminated soil column without flow interruption

The extent that aqueous solution of APU nanoparticles washed PAHs from soil initially contaminated with 1mg/L (approximately 0.35mg/kg$_{soil}$) demonstrated that, without APU nanoparticles the effluent from the soil-packed column had shown insignificant removal of PAHs. Insignificant PAHs concentrations are likely due to PAHs sorption to soil particles. This can be the evident that the test compounds were really sorbed to soil and were difficult to remove by water or electrolyte alone. In this experiment, fluctuation of the concentrations of PAHs eluted from the column occured because there is no interruption of the flow within this experiment. Since the electrolyte and APU nanoparticles were continuously fed into the column, it might not be an adequate contact time for APU nanoparticles to wash out PAHs from the soil.

The cumulative mass removal of the test compounds has been calculated and reported in Figure 4.11. The total of 0.025mg of PHEN and BaP (1mg/L dissolved in 25mL water) were initially added into soil column. The result shows that PHEN and BaP extraction became insignificant after 36 and 38 pore volume, respectively. Approximately 0.0181 mg of PHEN and 0.0088 mg of BaP were totally removed from the soil column. Thus, flushing with 12g/L APU nanoparticles removed approximately 72% of PHEN and 35% of BaP from the soil columns. The lower amount of removed BaP is likely due to its stronger sorption potential compared to that of PHEN. Figure 4.12 shows the percent of mass remaining in soil for PHEN and BaP. The results revealed that at the end of the experiment, the mass of PHEN and BaP remaining in the soil column were 27.7% and 64.6%, respectively.

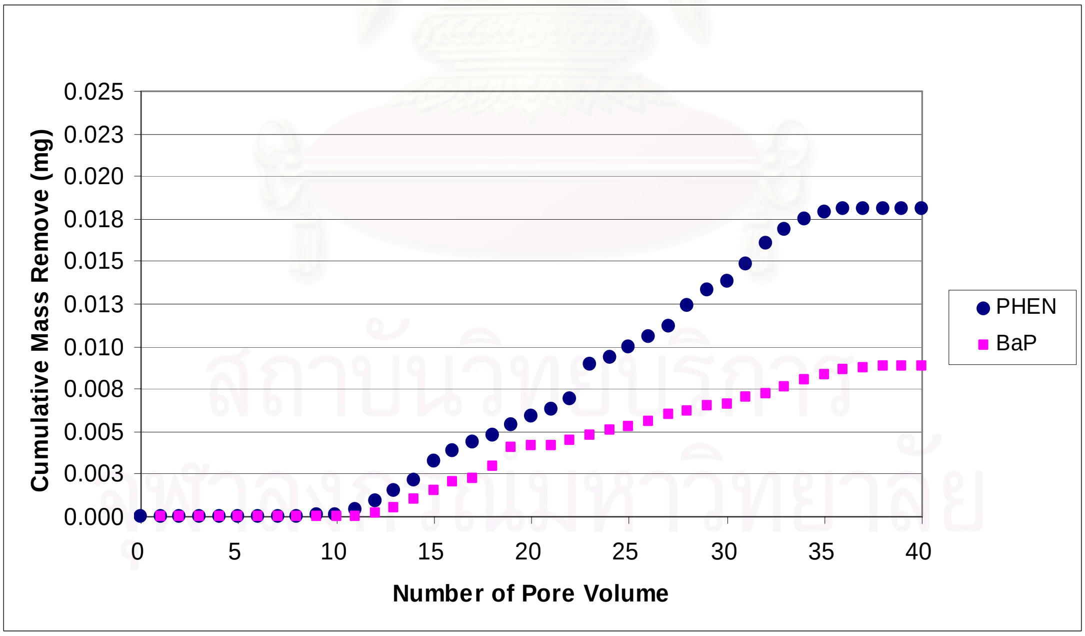


Figure 4.11 Cumulative PAHs mass removed from 0.025mg spiked soil using 12g/L inlet APU nanoparticles without flow interruption

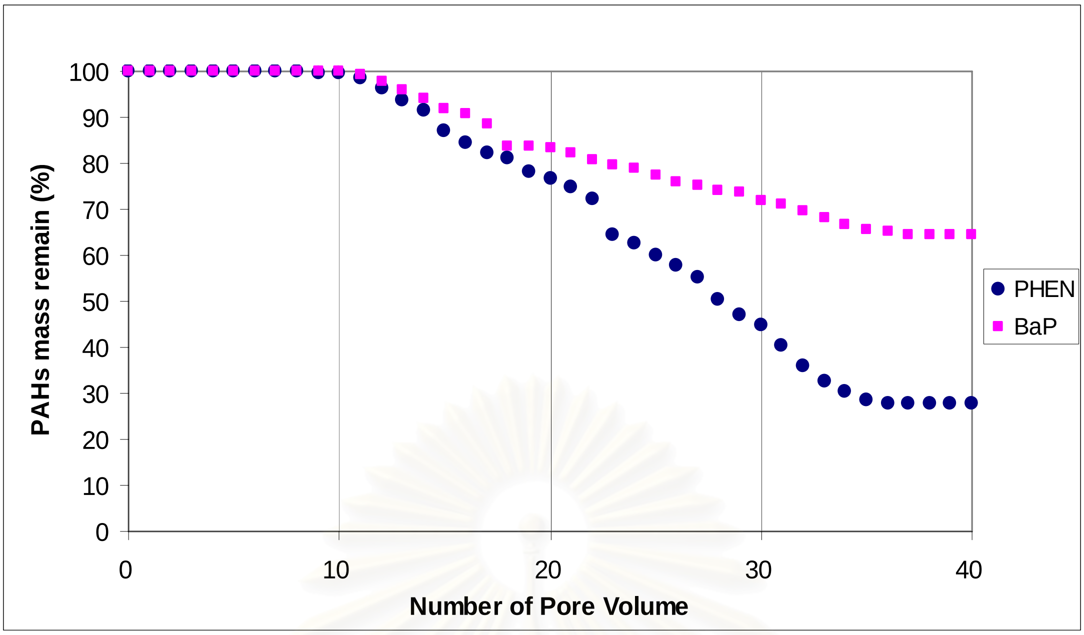


Figure 4.12 Washing of PAHs from soil pre-spiked with 0.025mg using 12g/L inlet APU concentration without flow interruption

4.5.2 PAHs removal from 1mg/L pre-contaminated soil column with 24 hours flow interruption

At the first 10 pore volume of applying electrolyte solution, the effluent PAHs concentration was less than 0.0014mg/L. During 12g/L APU nanoparticles applied to the column, the effluent PAHs concentrations rapidly increased, stabilized, then eventually decreased. This indicates that the interruption of the flow prevented the fluctuation of the effluent PAHs concentrations.

The cumulative mass removal of the test compounds was showed in Figure 4.13. The result shows that continuously increasing of PHEN and BaP extraction became insignificant after 32 and 30 pore volume, respectively. The higher number of pore volumes of APU nanoparticles required to extract BaP at the same rate and duration than PHEN demonstrated that BaP sorbed stronger to soil particles. Although the batch partitioning experiment concluded that BaP has higher tendency to partition into the APU phase than soil; yet, the soil-sorbed with BaP is more likely to be difficult to remove than soil-sorbed with PHEN. So, the more number of APU nanoparticles pore volumes were required to wash out BaP from soil column.

Approximately 0.0226 mg of PHEN and 0.0125 mg of BaP were totally removed from the soil column. Thus, flushing with 12g/L APU nanoparticles removed approximately 90% of PHEN and 50% of BaP from the soil columns. Figure 4.14 shows the percent of mass remaining in the soil versus the pore volumes of washing. Percent of mass remaining in soil for PHEN and BaP were 9.5% and 49.9%, respectively.

Figure 4.15 illustrates the percent PAHs remove versus time for 0.35mg/kg contaminated columns. In the primary 12 hours, the effluent from both test columns are recognized as very low to no contamination of PAHs as only electrolyte solution was passed to the soil columns. After 12g/L APU nanoparticles suspension was fed to the columns, less than 20% of the initially sorbed PHEN and BaP were recovered during 12 hours of flushing. Highest amount of PHEN and BaP for both test conditions were recovered within 2 days of experiment; not account for the day of interruptions.

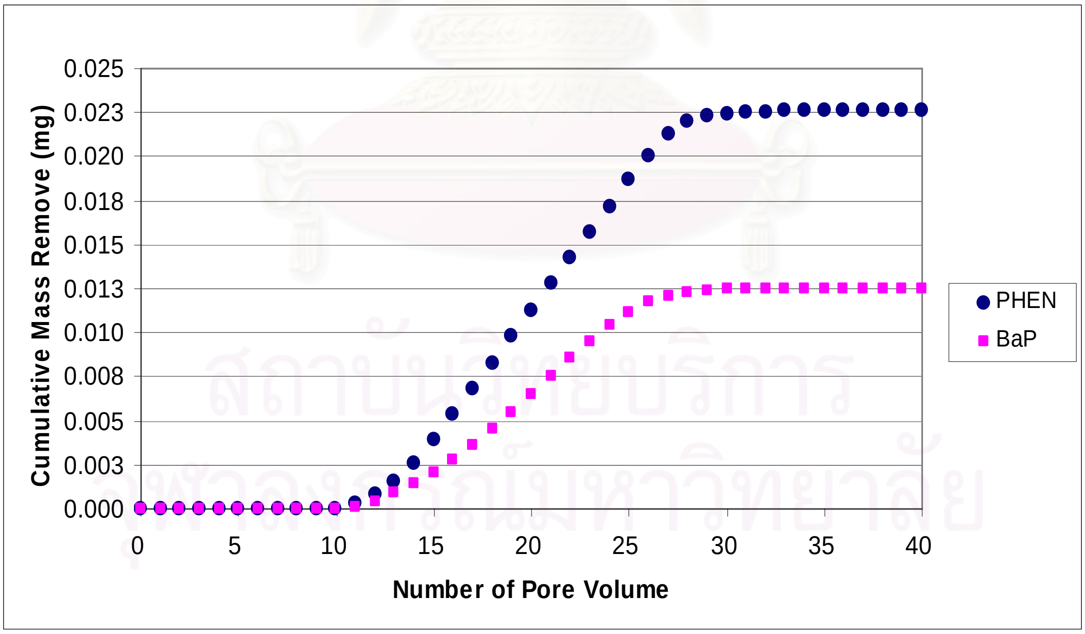


Figure 4.13 Cumulative PAHs mass removed from 0.025mg spiked soil using 12g/L inlet APU nanoparticles with flow interruption

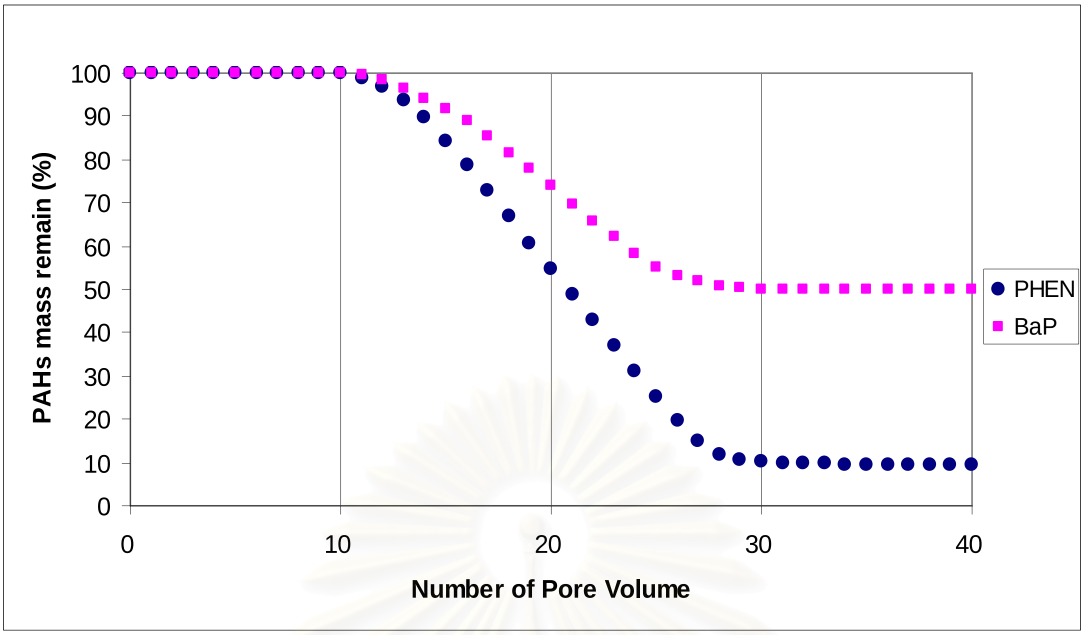


Figure 4.14 Washing of PAHs from soil pre-spiked with 0.025mg using 12g/L inlet APU concentration with flow interruption

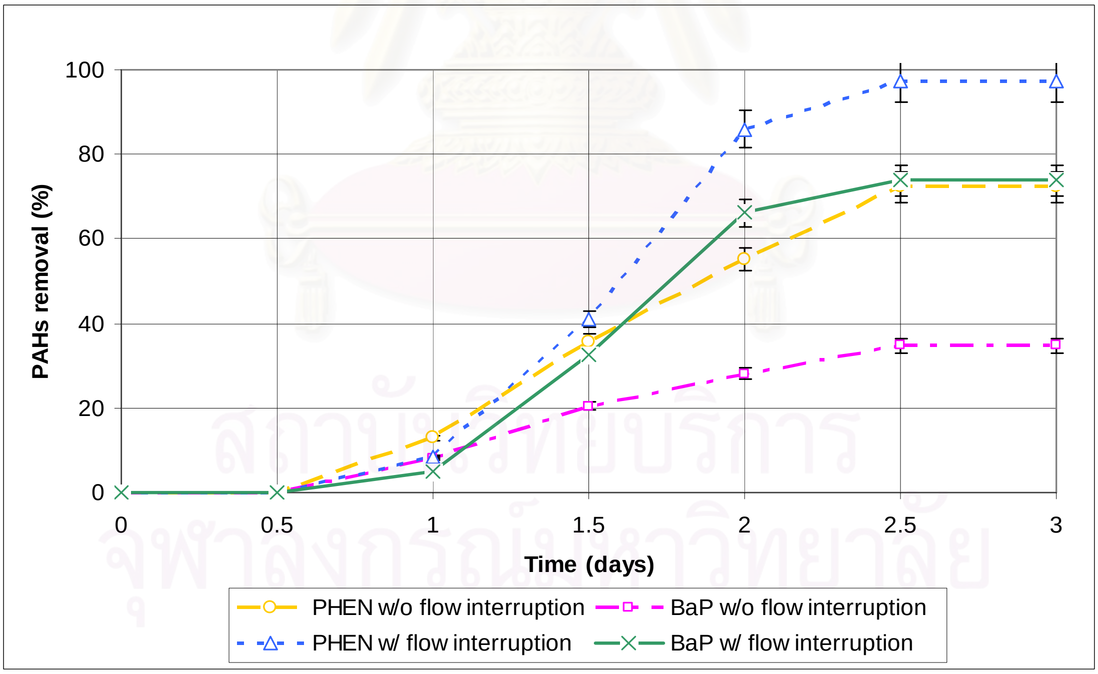


Figure 4.15 Removal of 0.35mg/kg PAHs contaminated soil column versus time

4.5.3 PAHs removal from 5mg/L pre-contaminated soil column without flow interruption

The higher concentration of PAHs was also prepared for the soil column test. The experiment was conducted to investigate the removal rate of 12g/L APU nanoparticles with higher PAHs contamination. The result from 5mg/L contaminated soil column (approximately 1.75mg/kg$_{soil}$) yielded similar manner to that of 1mg/L contaminated soil column. It was also noticed that APU nanoparticles increased the amount of PHEN and BaP removed from the contaminated soil from approximately 1% after 10 pore volumes of the electrolyte solution was passed through the column.

The cumulative removal of the test compounds from 5mg/L contaminated soil-packed column was showed in Figure 4.16. The initial amount of 0.125 mg PHEN and BaP (5mg/L dissolved in 25mL water) were added into soil column. The result shows that PHEN and BaP extraction insignificantly change after 34 pore volumes. Approximately 0.0221 mg of PHEN and 0.0047 mg of BaP were totally removed from the soil column. Thus, approximately 17.7 % of PHEN and 3.8% of BaP were extracted from the soil column. Its obvious percentage of extraction indicates that percentage of PHEN residues remains in soil is lower than BaP similar to the column test with low PAHs contamination.

Figure 4.17 shows that higher extraction efficiency again falls to PHEN extraction; although, the soil was contaminated with higher PAHs concentration. Percent of mass remaining in soil for PHEN and BaP were 82.3% and 96.2%, respectively. As a result, concentration of 12g/L APU nanoparticles is not likely to be efficient to remove 0.125mg PAHs contaminated soil.

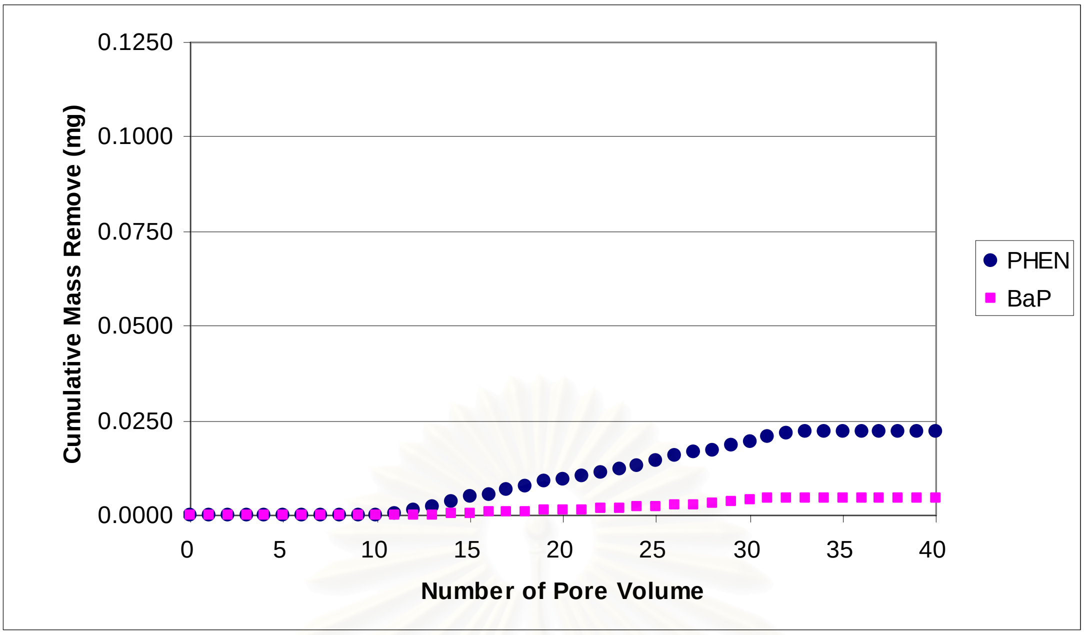


Figure 4.16 Cumulative PAHs mass removed from 0.125mg spiked soil using 12g/L inlet APU nanoparticles without flow interruption

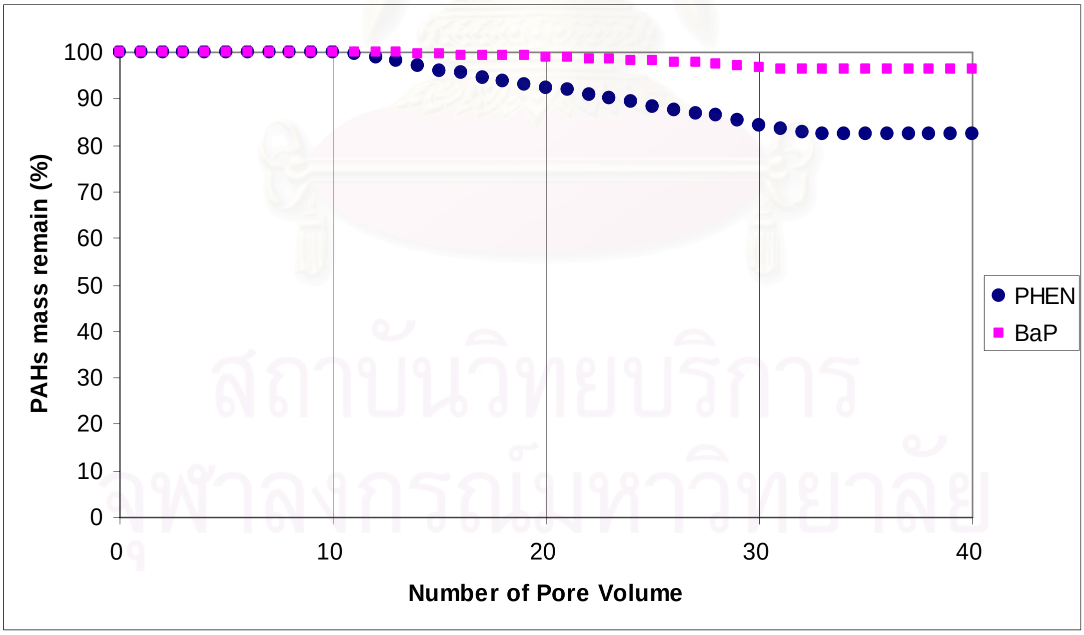


Figure 4.17 Washing of PAHs from soil pre-spiked with 0.125mg using 12g/L inlet APU concentration without flow interruption

4.5.4 PAHs removal from 5mg/L pre-contaminated soil column with 24 hours flow interruption

At the first 10 pore volume of applying electrolyte solution, the effluent PAHs concentration was unable to be detected by GC. During 12g/L APU nanoparticles was applied to the column, the effluent PAHs concentrations rapidly increased, stabilized, then eventually decreased. In case of high PAHs contamination, the interruption of the flow also prevented the fluctuation of PAHs in effluent. The saturation of APU nanoparticles for 24 hours before releasing the effluent from the soil column provides an adequate contact time for the particles to extract the test compounds.

The cumulative mass removal of the test compounds was showed in Figure 4.18. PHEN and BaP extraction was insignificantly change after 32 and 26 pore volume, respectively. Approximately 0.0363 mg of PHEN and 0.0191mg of BaP were totally removed from the soil column, while approximately 29% of PHEN and 15% of BaP were removed from the soil column. Figure 4.19 shows the calculated percent of PAHs mass remaining in the soil versus the pore volumes of washing. Percent of mass remaining in soil for PHEN and BaP were 70.9% and 84.7%, respectively.

Figure 4.20 illustrates the percent PAHs remove versus time for 1.75mg/kg contaminated columns. The similar trend of removal was observed compared to 1mg/L contaminated columns. The highest amount of PHEN and BaP were also recovered within 2 days of experiment not account for the day of interruptions.

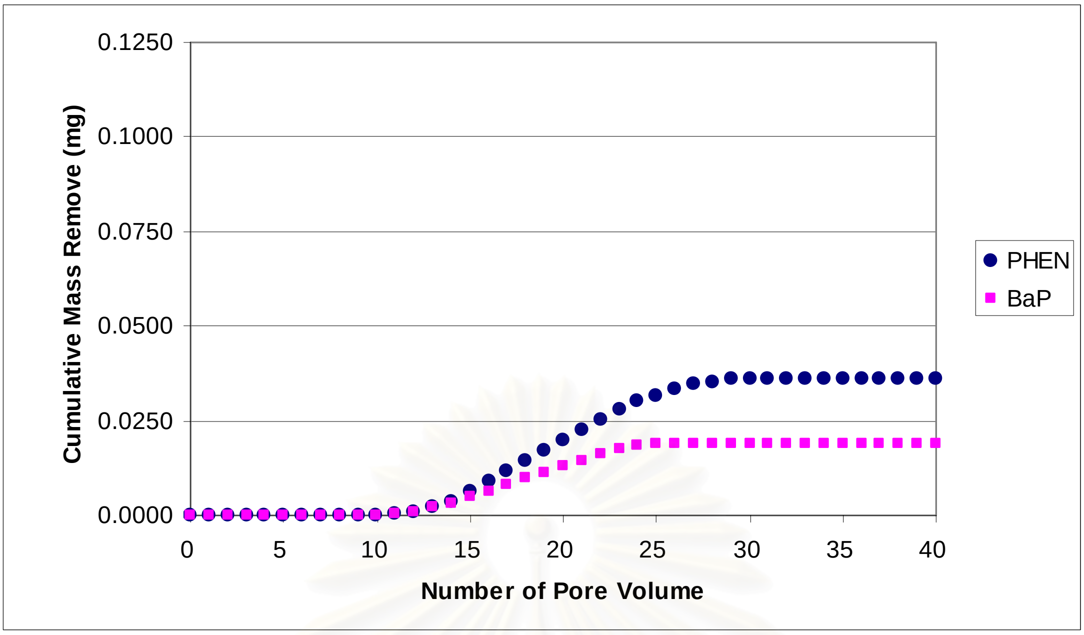


Figure 4.18 Cumulative PAHs mass removed from 0.125mg spiked soil using 12g/L inlet APU nanoparticles with flow interruption

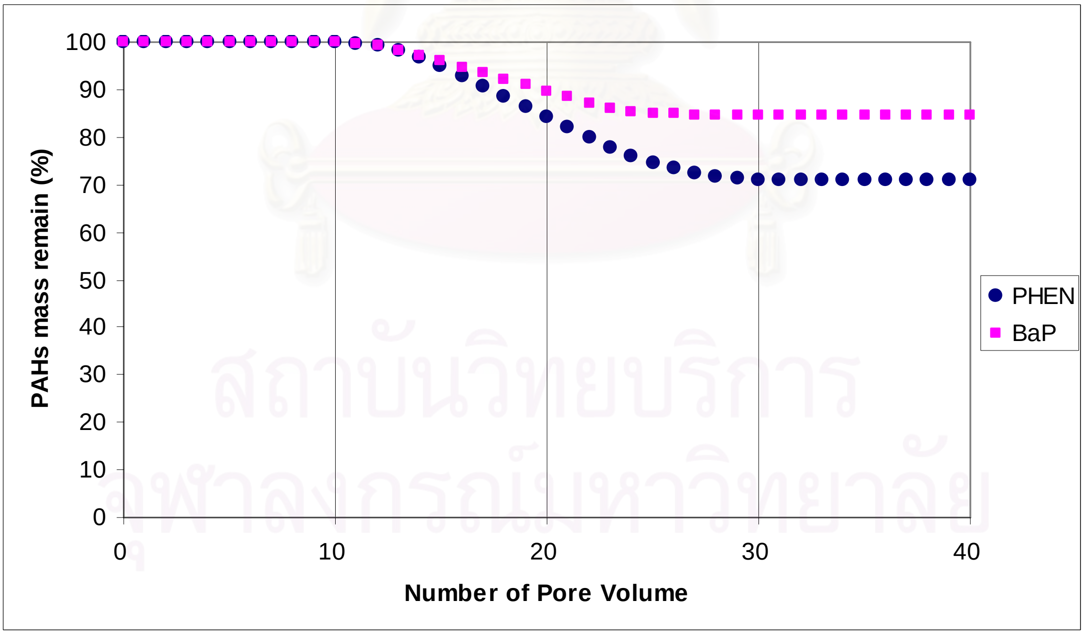


Figure 4.19 Washing of PAHs from soil pre-spiked with 0.125mg using 12g/L inlet APU concentration with flow interruption

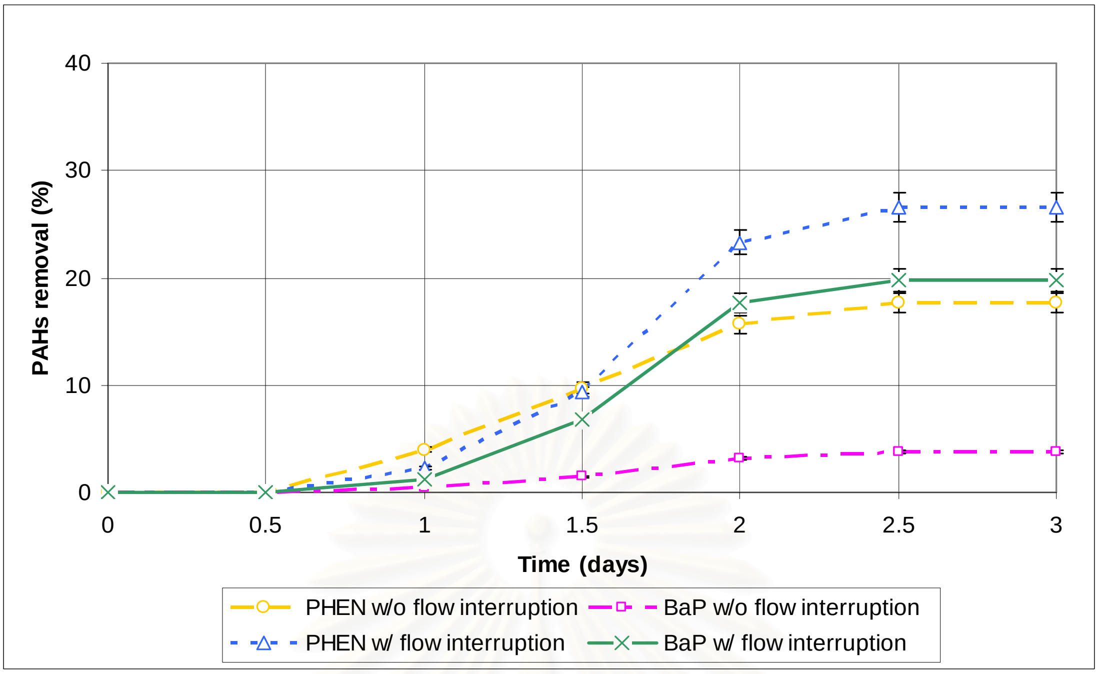


Figure 4.20 Removal of 1.75mg/kg PAHs contaminated soil column versus time

4.5.5 Comparison of PHEN and BaP elution from the soil columns

The ratios of the amount of PAHs remaining (M) to the initial amount of PAHs (M_o) in the soil column when eluted with electrolyte solution without PMUA (phase A), followed by a 12g/L PMUA suspension (phase B) versus number of pore volume are illustrated in Figures 4.21 and 4.22. The results indicate that the flow interruption is effective for further reducing the level of contamination for low (1mg/L) and high (5mg/L) PAHs contamination. Therefore, it can be tentatively concluded that the slow desorption kinetics due to an inadequate desorption duration, high organic matter content in soil, and PAHs exposure time could overcome by longer intervals of flow interruption.

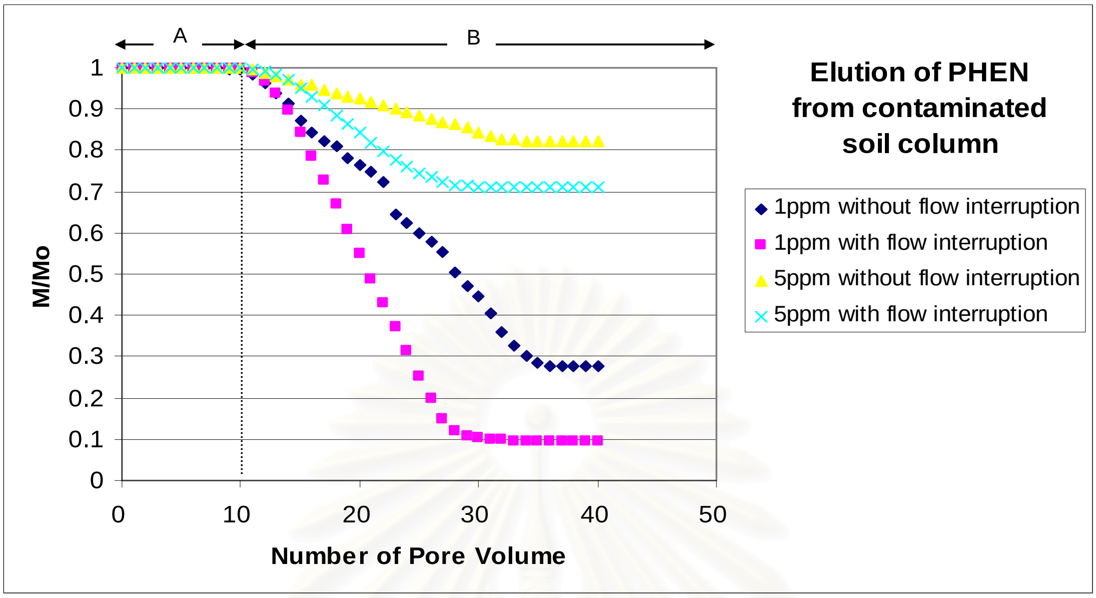


Figure 4.21 PHEN elution from the contaminated soil column

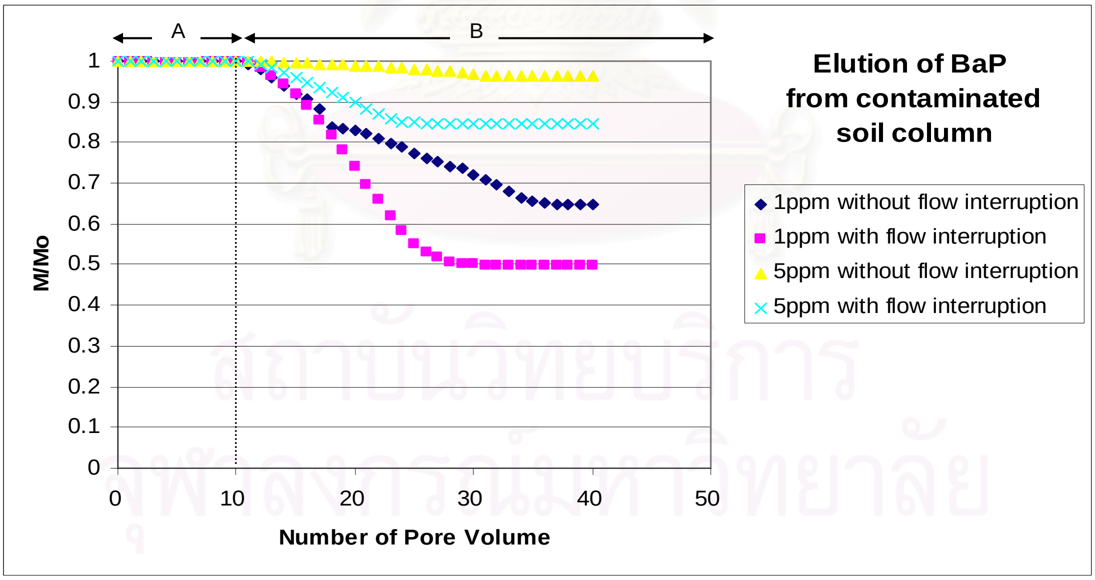


Figure 4.22 BaP elution from the contaminated soil column

The experiment with 24 hours flow interruptions yielded higher extraction efficiency for both test compounds compared to the experiment without flow interruption. For low contaminated soil column, the percent PHEN removed from the soil column without flow interruptions versus test column influence by flow interruptions are 72% and 90%, respectively. Meanwhile, the similar trend is also observed from BaP extraction. The flow interruptions increased the percent BaP mass removed from 35% to 50%. Likewise, the percent PHEN and BaP removed from the high contaminated soil column without flow interruptions and with influence of flow interruptions are increased from 17.7% to 29% and 3.8% to 15%, respectively. The comparison of both low and high contaminated column tests revealed similar extraction behavior for both with and without flow interruptions. For instance, the extraction efficiencies of PHEN in low and high contamination conditions for both with and without flow interruption were higher than that of BaP.

The removal of BaP in all test conditions was lower than removal of PHEN; although, the partition coefficient of both test compounds between APU and soil of batch experiment shown in Table 4.5 indicated that BaP has higher affinity for APU than PHEN. This may be due to the sorption of PHEN and BaP onto APU in column reached its equilibrium slower than that in batch experiment. This may possibly due to the fact that column experiment was statically conducted while vigorously shaking was involved in batch experiment. The shaking could assist the rate of adsorption, which caused the test compounds to reach their equilibrium in batch faster than in column experiment.

The Figures suggested that the higher recovery of both test compounds, especially BaP was achieved by flow interruption. For instance, the continuous feeding of APU nanoparticles without interruption may not provide enough contact time for the particles to extract test compounds from the soil pore. Because BaP is more hydrophobic and tends to sorb stronger to soil particles, the continuously feed of APU nanoparticles resulted in considerably low percent removal of BaP as compared to the discontinuous feeding via 24 hours of flow interruption. Comparison of Figures 2.21 and 2.22 shows that concentration of APU nanoparticles used in this study is sufficient to remove 0.35mg/kg PHEN contaminated soil columns. Even though lower BaP is recovered by APU nanoparticles, but flow interruption could assist the extraction of 0.35mg/kg BaP contaminated soil. In contrast, APU nanoparticles is considered to be inefficient to remove higher concentration of test compounds from soil columns, since less than 30% of initially sorbed PAHs was recovered from the soil columns.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The resulting particles were of colloidal size (80-110 nm). The highest volume (12%) of total particles was 90 nm. Both of 80 and 110 nm particles size had similar volume of 11%. The size of the particles was controlled by detection limit of the analyzer, and speed and duration of stirring during emulsification. The sensitivity of the analyzer could affect the size distribution and volume of each detected particles size. The vigorous interaction between the amphiphilic polymers (APU nanoparticles with PMUA precursor chain) and water by high speed and longer duration of stirring could reduce the size of the larger particles.

The batch experiment on steady state attainment revealed that PHEN and BaP rapidly reach their equilibrium in soil-APU system. Test compounds in soil-water system and soil-APU system reached their steady state at 48 and 24 hours, respectively. The partition coefficient between soil and water, $K_{s,w}$, of PHEN is lower than that of BaP (PHEN=1776±88 L/kg; BaP=3162±363 L/kg). By Normalizing $K_{s,w}$ using organic carbon content in the soil, $\log K_{oc}$ of PHEN and BaP obtained from arithmetic equation (PHEN=4.88 L/kg; BaP=5.13 L/kg) yielded parallel results compared to $\log K_{oc}$ from other literatures. The partitioning coefficient between soil and APU, $K_{s,APU}$, suggested that both PHEN and BaP were likely to sorb onto APU nanoparticles rather than sorb onto soil. The results revealed that $K_{s,APU}$ of PHEN is slightly higher than that of BaP (PHEN=0.55±0.03 L/kg; BaP=0.36±0.02 L/kg). The partitioning experiment showed that sorption kinetic of test compounds onto APU was more rapid than onto soil. In addition, more hydrophobic compound was highly sorb onto APU. Thus, sorption of BaP onto APU is better than onto soil when compared with sorption of PHEN.

The relationship between $K_{s,w}$ and $K_{APU,s}$ expressed the partition coefficient between APU and water phase, $K_{APU,w}$. The $\log K_{APU,w}$ of PHEN is slightly lower than that of BaP (PHEN=3.51; BaP=3.94), which corresponded to the fact that compound with lower water solubility will drastically partition to APU phase rather than water.

The comparison between log$K_{APU,w}$ (this study) and logK_{ow} (other literatures) revealed that log$K_{APU,w}$ of both test compounds are slightly lower than logK_{ow} . The lower log$K$ in APU-water system than in octanol-water system suggested that APU nanoparticles have lower potential to sorb PHEN and BaP than octanol. This implied that sorption kinetic of octanol is more rapid than APU.

Mass balance on mobility of APU nanoparticles demonstrated that 94% of APU nanoparticles was recovered from the soil column. The medium capacity for removing applied particles was equaled 1.4 mg of PMUA/g of soil. Loss of particles is tentatively due to adsorption of particles onto high organic carbon and particles trap in the micropore. Accordingly, the mobility of APU nanoparticles is corresponded to characteristic of the soil. For instance, specified soil parameters, organic carbon content, could increase degree of sorption of APU nanoparticles onto soil. So application of APU nanoparticles for soil remediation should be used regarding the soil characteristics.

The removal of PHEN and BaP from pre-contaminated soil column revealed that greatest recovery of PHEN and BaP of low and high contaminated soil-packed column were obtained regarding the 24-hous flow interruption. In low contaminated soil column (0.35mg/kg), approximately 90% and 50% of initially sorbed PHEN and BaP were recovered over the duration of the experiment. In contrast, approximately 29% and 15% of initially sorbed PHEN and BaP were recovered in high contaminated soil column (1.75mg/kg). These results show that increase in concentration of PAHs in the soil column reduces APU nanoparticles effectiveness and longer duration of the flow interruption should be considered in APU nanoparticles-assisted remediation. The significant factor that decreases the efficiency of PAHs remediation in higher PAHs contaminated soil columns may be due to the sorption of PHEN and BaP onto APU in column reached its equilibrium slower than that in batch experiment. Therefore, longer duration of flow interruption than 24 hours would tentatively increase the removal efficiency of both compounds especially BaP from the soil.

Regional and national environmental regulations are legitimated to limit amount of carcinogenic chemicals such as BaP in the environment. In Thailand, the soil that is applicable for residential and agricultural purposes should not have concentration of BaP over 0.6 mg/kg. In addition, the concentration of BaP should not exceed 2.9 mg/kg for the soil that is applicable for other purposes (www.pcd.go.th). The column tests demonstrated that APU nanoparticles can effectively flush PHEN from soil although the soil sample is considered to have high organic matter, and may be a good candidate for in-situ soil washing. On the other hand, removal of BaP in 5 mg/l was inefficient to reduce the concentration of BaP below the standard in order to utilize the soil for residential and agricultural purposes. The experimental results revealed that 1.51 mg/kg of BaP still remained after 12 g/L APU nanoparticles was applied to the soil column. As a consequence, higher concentrations of APU nanoparticles in the wash solution will increase the removal efficiency of BaP in 5 mg/l contaminated soil column, which will certainly reduce the concentration of BaP under the standard. Moreover, the appropriate concentration of APU nanoparticles could be further study to reduce BaP concentration under the standard for maximum BaP in groundwater and Safe Drinking Water Act (SDWA) (0.0002 mg/l) (www.epa.gov), due to the fact that BaP that trapped in NAPLs have tendency to leach to groundwater.

In conclusion, the whole point of introducing APU nanoparticles is to remove contaminants that are in the soil and pose a risk to groundwater that is used for drinking water supply. In the absence of some sort of cleanup by APU nanoparticles or some other means, the groundwater would likely not be suitable for drinking. Although, Kim et al. (2003), Kim et al., 2004, Tungittiplakorn et al., 2004 and this study show that high recoveries of particles from soil column could be achieved, still more information about the recovery of the particles from different soil types are required. Since some low level of nanoparticles will not be recovered and may appear in water destined for human consumption, the toxicology of the nanoparticles before they are put to use for cleaning up soil are also an essential subject to be study. In short, there are more to learn before APU nanoparticles could be considered as a viable treatment option for soil remediation.

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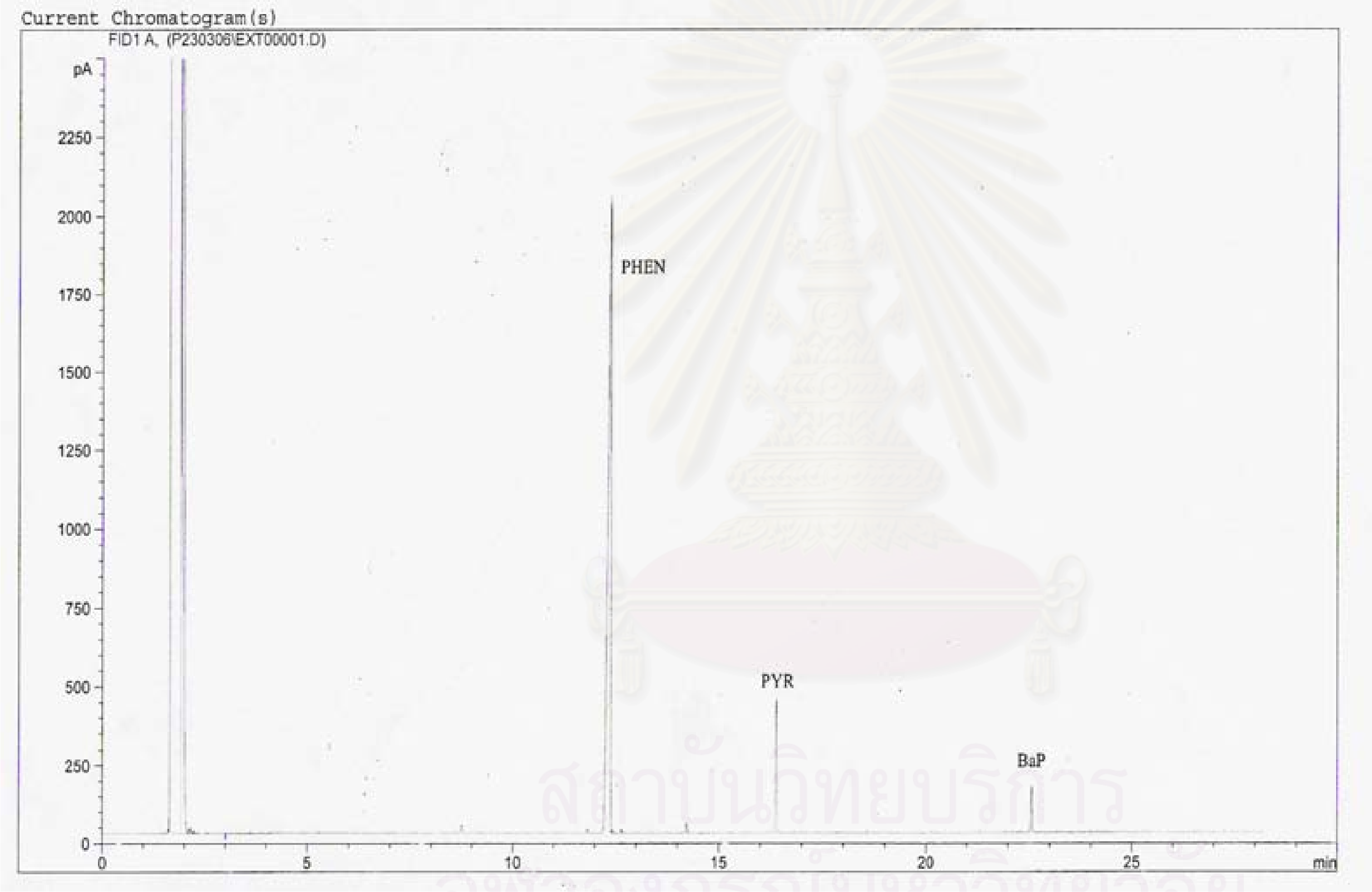
APPENDICES

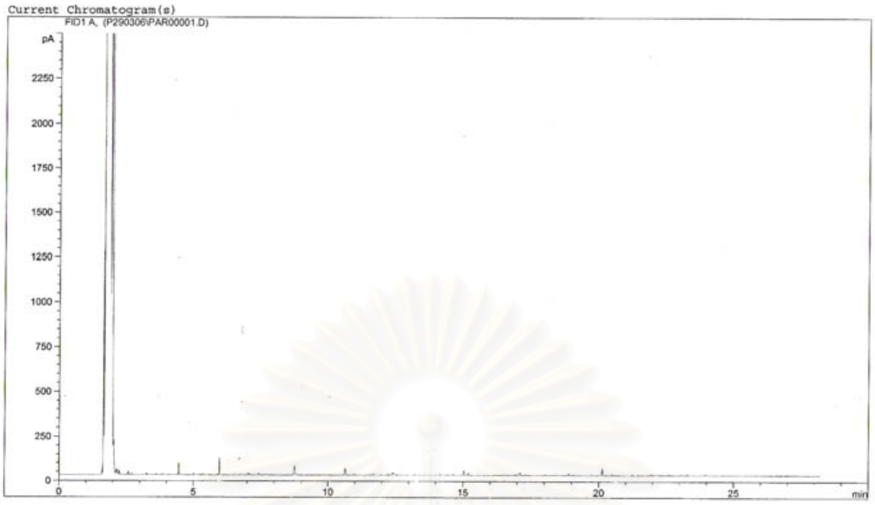
APPENDIX A—Chromatogram of PAH standards and their retention times



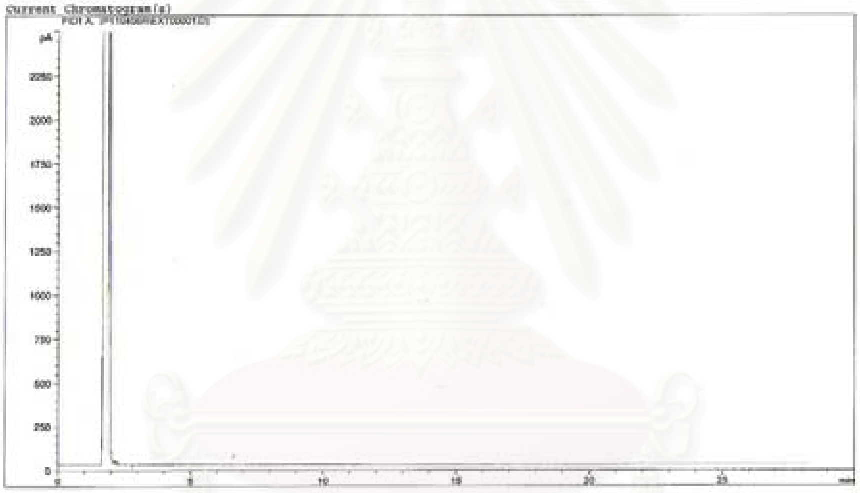
	PHEN	PYR	BaP
Mean Retention Time (min)	12.32	16.37	22.55
Standard Deviation	0.03	0.007	0.01

APPENDIX B—Chromatogram of blank analysis

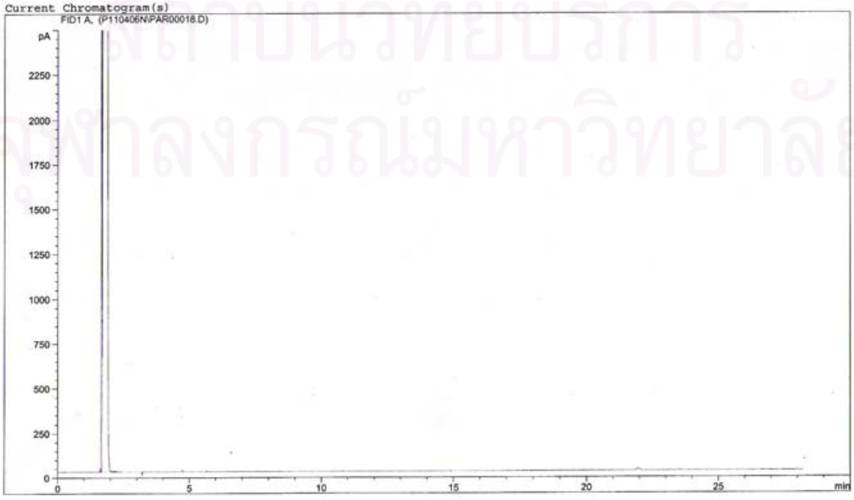
B1 Soil



B2 Water

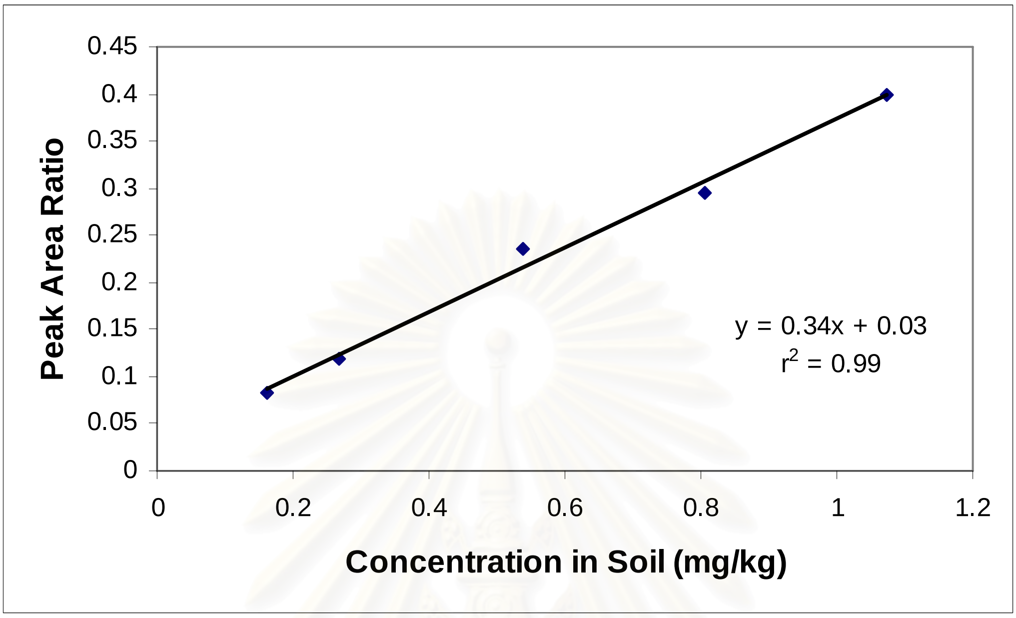


B3 APU nanoparticles

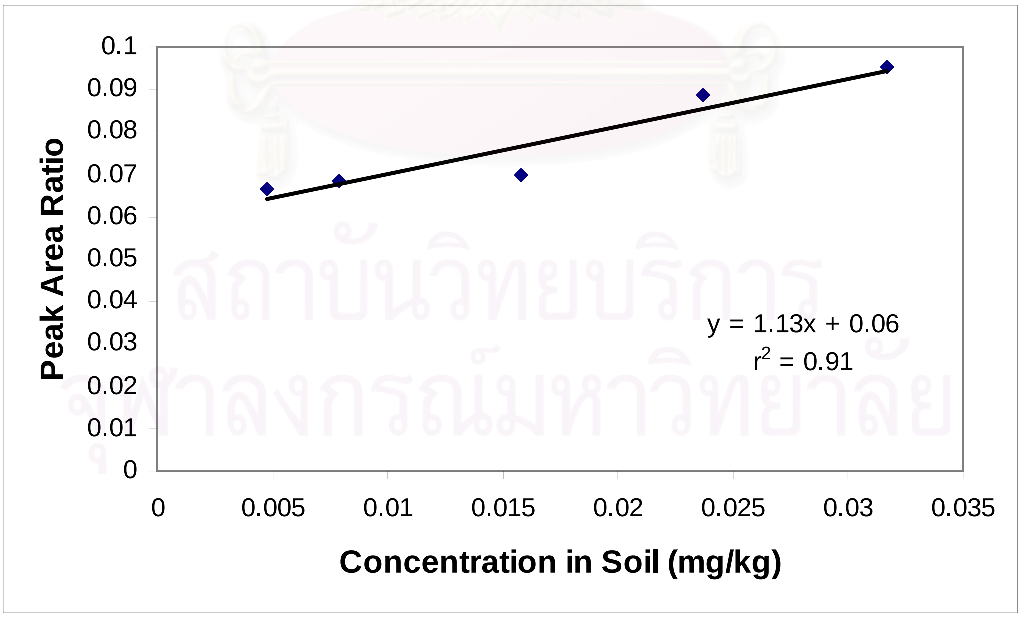


APPENDIX C—Calibration curves

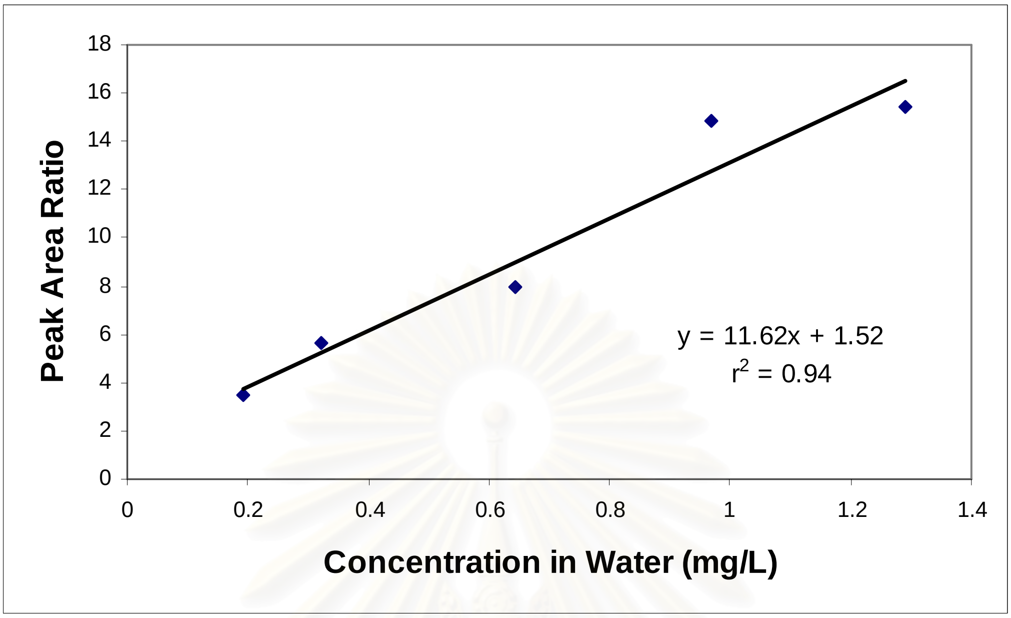
C1.1 Calibration curve for PHEN in soil



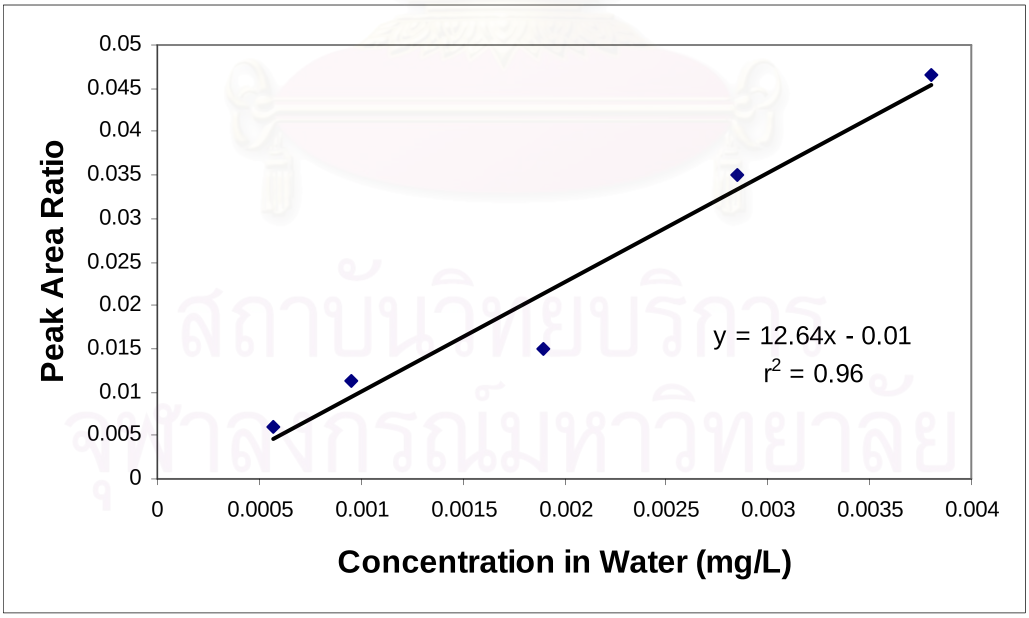
C1.2 Calibration curve for BaP in soil



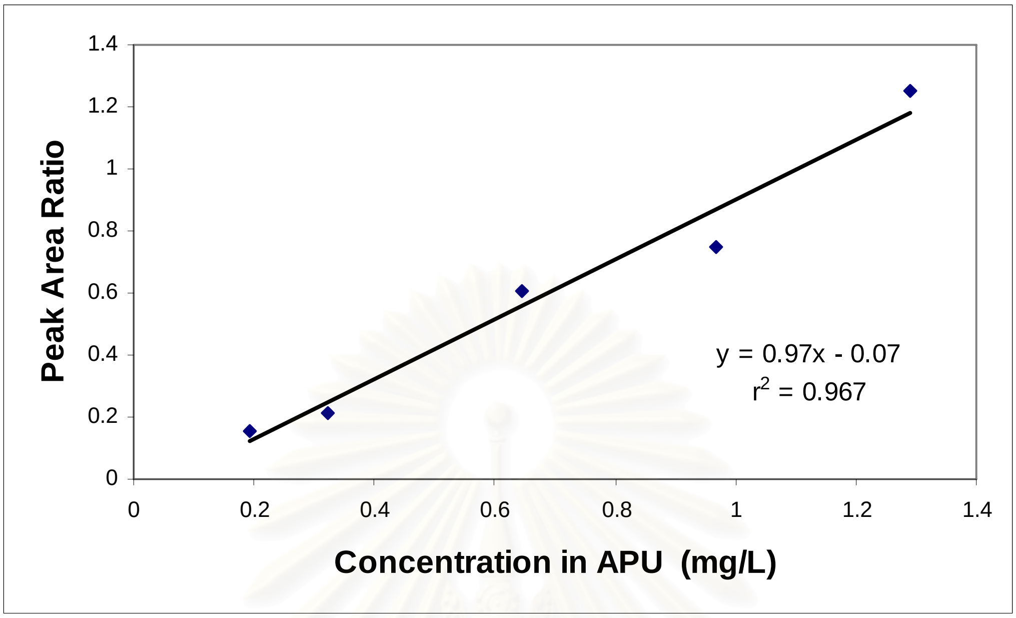
C2.1 Calibration curve for PHEN in water



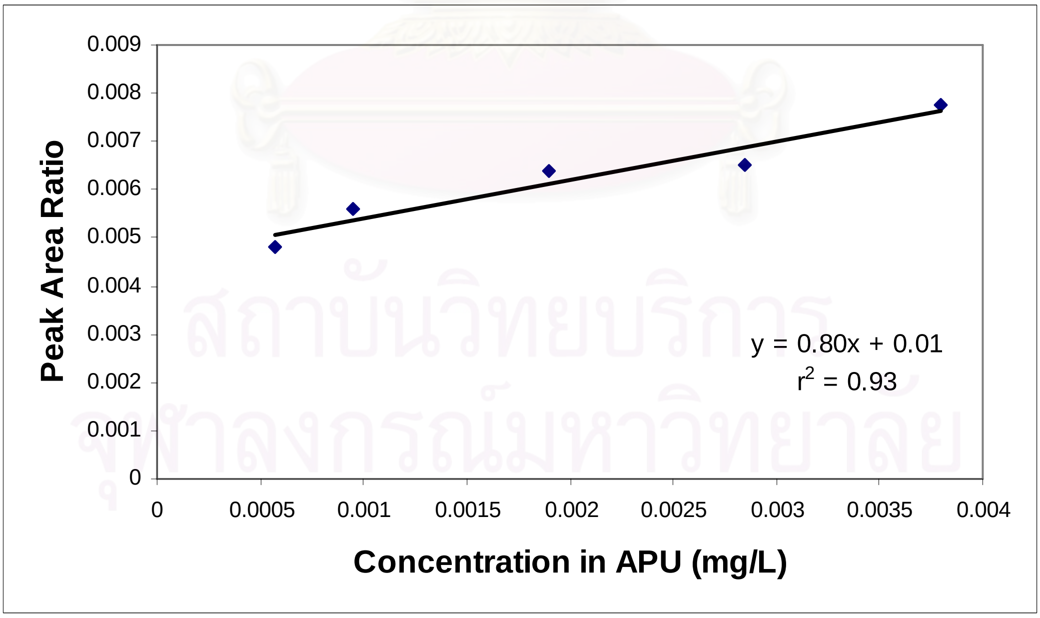
C2.2 Calibration curve for BaP in water



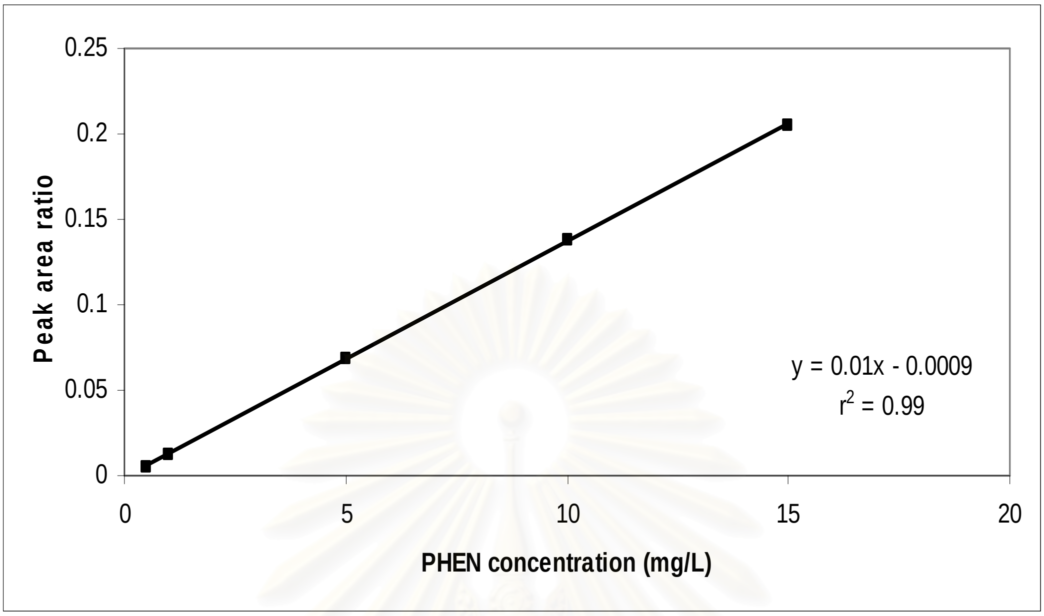
C3.1 Calibration curve for PHEN in APU



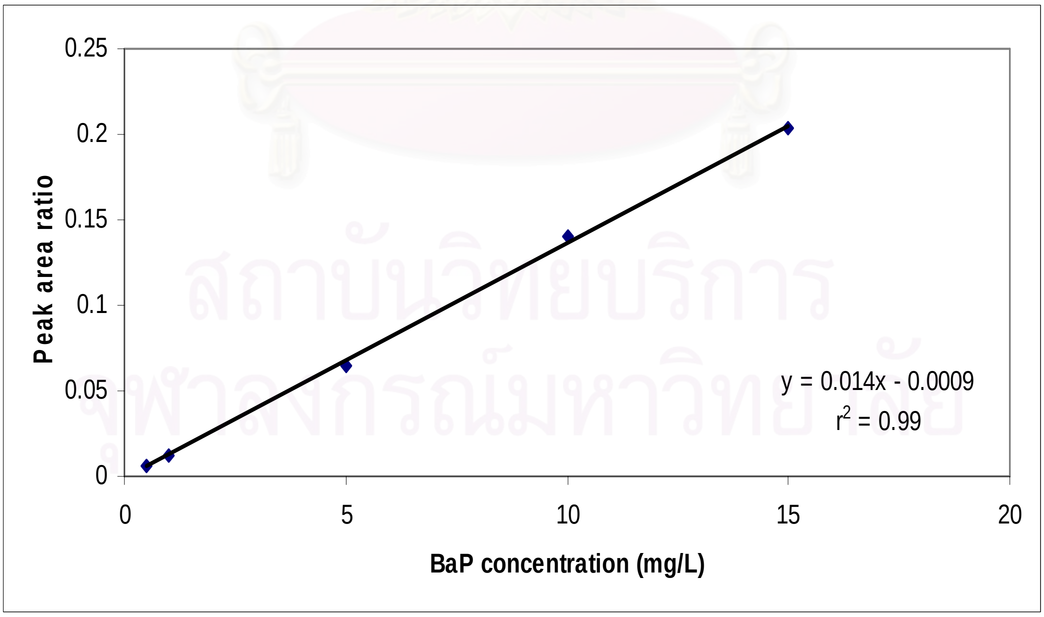
C3.2 Calibration curve for BaP in APU



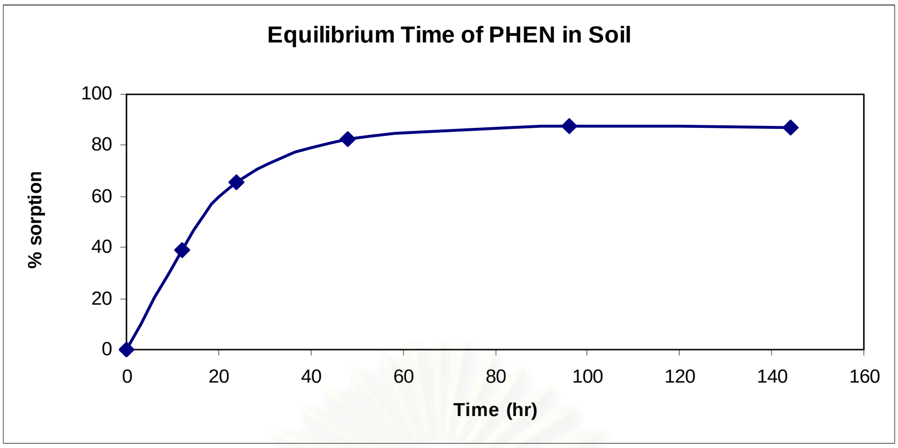
C4.1 Calibration curve for PHEN (column experiment)

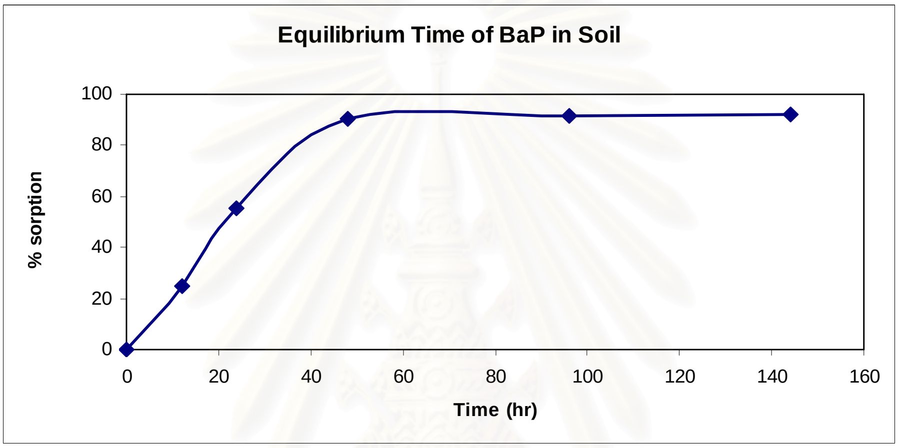


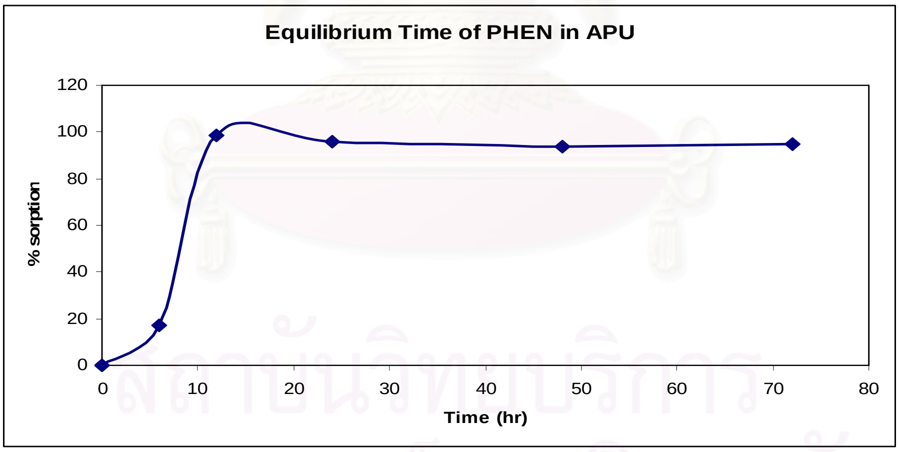
C4.2 Calibration curve for BaP (column experiment)

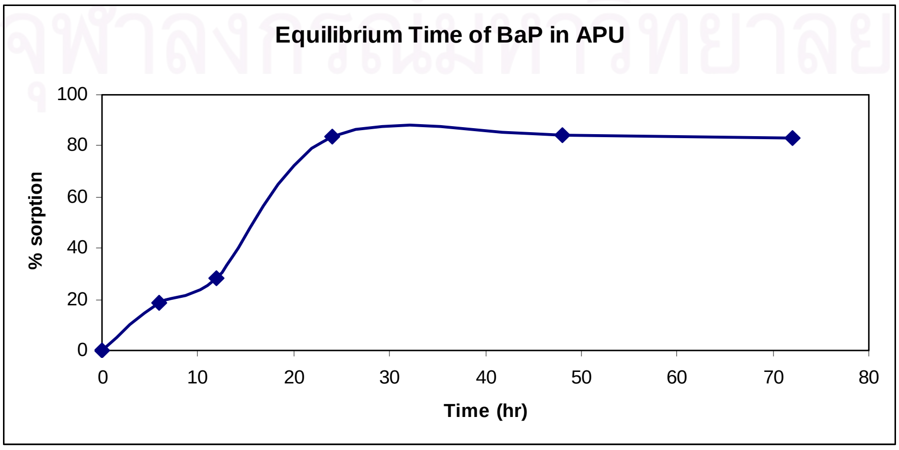


APPENDIX D—Equilibrium time

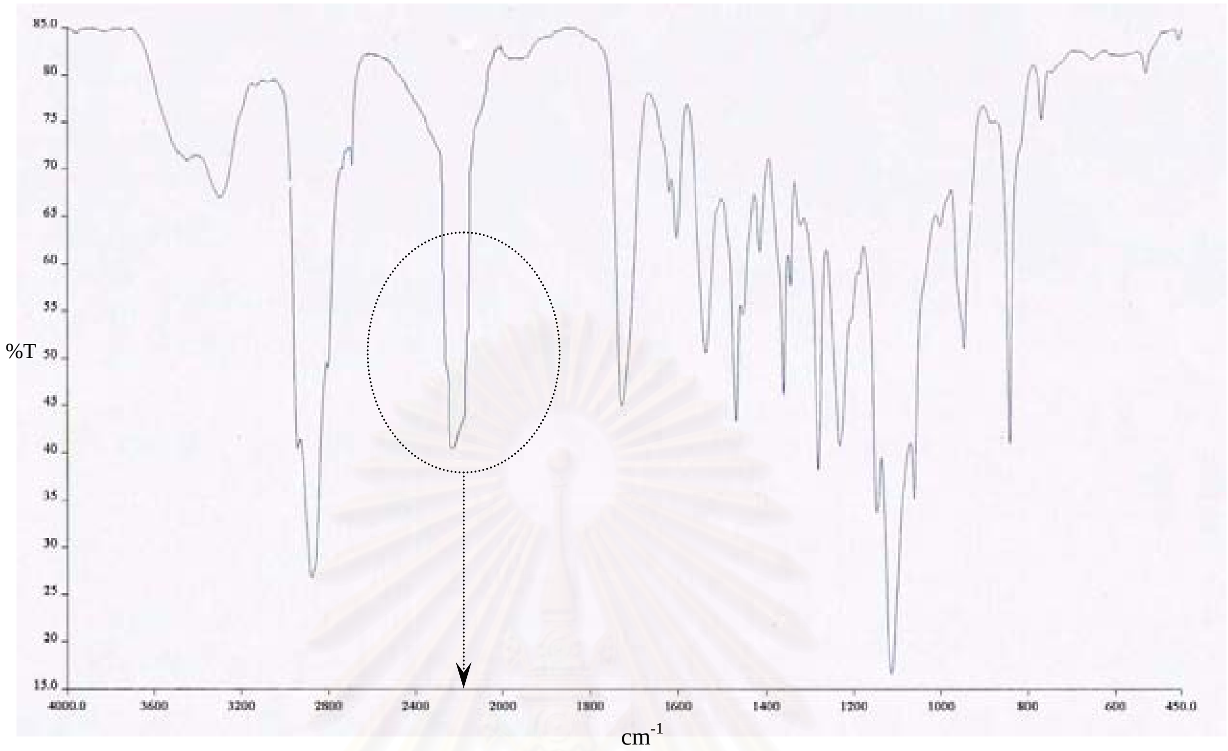




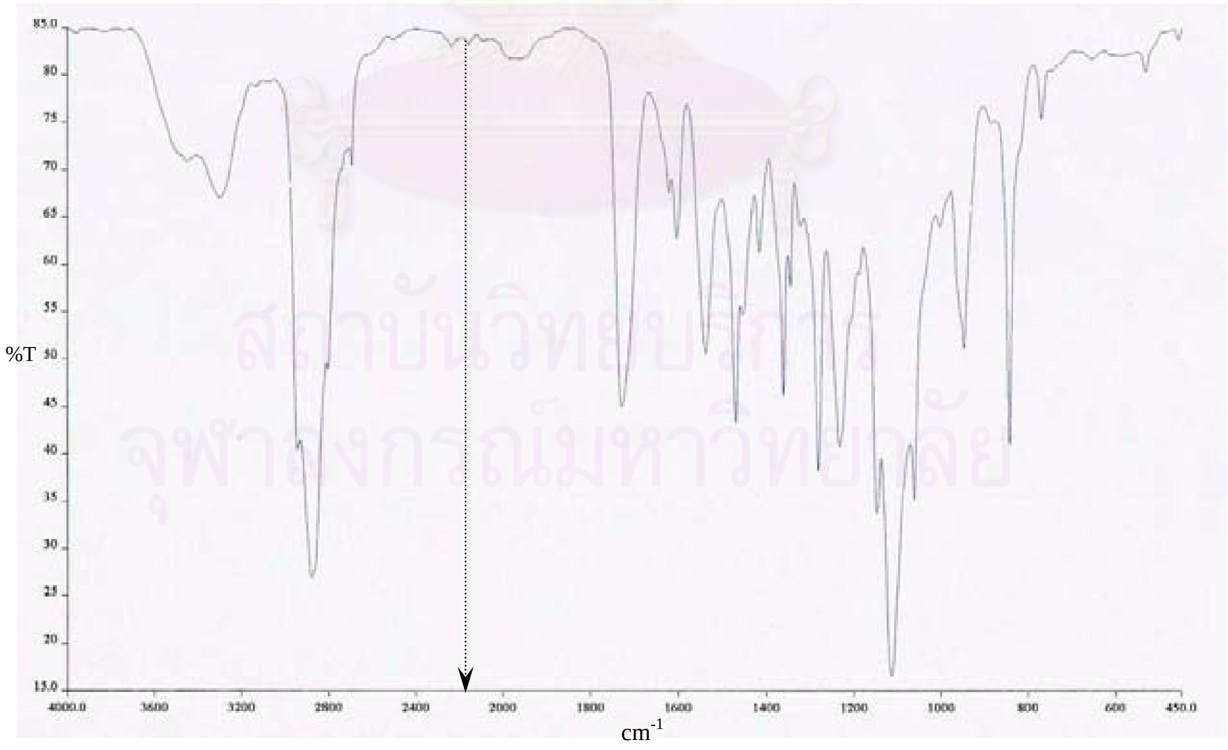




APPENDIX E—Disappearance of NCO group at wavelength 2270 cm^{-1}



Before the reaction is completed



After the reaction is completed

APPENDIX F—Partitioning Experiment

F1 Soil-Water partitioning

Phenanthrene (PHEN)

Working Concentration	Concentration in Soil, Cs						Concentration in Water, Cw					
	sample 1	sample 2	sample 3	Average	SD	%RSD	sample 1	sample 2	sample 3	Average	SD	%RSD
S	329.80	331.50	330.90	330.73	0.8622	0.2607	0.2550	0.2583	0.2568	0.2567	0.0017	0.6437
0.75S	249.20	249.80	248.10	249.03	0.8622	0.3462	0.1485	0.1477	0.1498	0.1487	0.0011	0.7129
0.5S	189.80	188.30	188.90	189.00	0.7550	0.3995	0.0936	0.0929	0.0939	0.0935	0.0005	0.5490
0.25S	99.40	100.60	99.80	99.93	0.6110	0.6114	0.0535	0.0531	0.0538	0.0535	0.0004	0.6568
0.15S	57.20	57.50	57.00	57.23	0.2517	0.4397	0.0355	0.0348	0.0352	0.0352	0.0004	0.9986

Benzo(a)pyrene (BaP)

Working Concentration	Concentration in Soil, Cs						Concentration in Water, Cw					
	sample 1	sample 2	sample 3	Average	SD	%RSD	sample 1	sample 2	sample 3	Average	SD	%RSD
S	1.1869	1.1855	1.1870	1.1865	0.0008	0.0707	0.000331	0.000325	0.000329	0.000328	0.000003	0.9305
0.75S	0.9250	0.9180	0.9290	0.9240	0.0056	0.6026	0.000260	0.000262	0.000263	0.000262	0.000002	0.5838
0.5S	0.6100	0.5990	0.6008	0.6033	0.0059	0.9781	0.000199	0.000201	0.000203	0.000201	0.000002	0.9950
0.25S	0.2924	0.2908	0.2890	0.2907	0.0017	0.5851	0.000165	0.000162	0.000164	0.000164	0.000002	0.9333
0.15S	0.1852	0.1840	0.1838	0.1843	0.0008	0.4108	0.000130	0.000130	0.000132	0.000131	0.000001	0.8091

F2 Soil-APU partitioning

Phenanthrene (PHEN)

Working Concentration	Concentration in Soil, Cs (mg/kg)						Concentration in APU, C_{APU} (mg/L)					
	sample 1	sample 2	sample 3	Average	SD	%RSD	sample 1	sample 2	sample 3	Average	SD	%RSD
S	0.5864	0.5855	0.5890	0.5870	0.0018	0.3096	1.1320	1.1387	1.1353	1.1353	0.0034	0.2951
0.75S	0.3278	0.3297	0.3254	0.3276	0.0022	0.6577	0.5612	0.5589	0.5602	0.5601	0.0012	0.2059
0.5S	0.3080	0.3110	0.3080	0.3090	0.0017	0.5605	0.5420	0.5540	0.5500	0.5487	0.0061	1.1136
0.25S	0.1980	0.1966	0.1990	0.1979	0.0012	0.6093	0.2656	0.2710	0.2655	0.2674	0.0031	1.1725
0.15S	0.1580	0.1595	0.1592	0.1589	0.0008	0.4995	0.1871	0.1852	0.1859	0.1861	0.0010	0.5164

Benzo(a)pyrene (BaP)

Working Concentration	Concentration in Soil, Cs						Concentration in APU, C_{APU}					
	sample 1	sample 2	sample 3	Average	SD	%RSD	sample 1	sample 2	sample 3	Average	SD	%RSD
S	0.001020	0.001000	0.001010	0.00101	0.00001	0.99010	0.002988	0.003025	0.002990	0.003001	0.000021	0.6934
0.75S	0.000680	0.000700	0.000690	0.00069	0.00001	1.44928	0.001550	0.001581	0.001598	0.001576	0.000024	1.5440
0.5S	0.000410	0.000419	0.000415	0.00041	0.00000	1.08744	0.000970	0.000980	0.000993	0.000981	0.000012	1.1751
0.25S	0.000183	0.000182	0.000183	0.00018	0.00000	0.31607	0.000365	0.000362	0.000364	0.000364	0.000002	0.4200
0.15S	0.000040	0.000040	0.000041	0.00004	0.00000	1.43145	0.000130	0.000130	0.000132	0.000131	0.000001	0.8091

F3 APU-Water Partitioning (From calculation)

Compound	$K_{s,w}$	LogKs,w	K_{oc}	$LogK_{oc}$	$K_{s,APU}$	$LogK_{s,APU}$	$K_{APU,s}$	$LogK_{APU,s}$	$K_{APU,w}$	$LogK_{APU,w}$
PHEN	1776.00	3.25	75897.44	4.88	0.55	-0.26	1.82	0.26	3229.09	3.51
BaP	3162.00	3.50	135128.21	5.13	0.36	-0.44	2.78	0.44	8783.33	3.94

APPENDIX G—APU nanoparticles mobility in soil

PV	Mo (g)	Co=Mo/V	M (g)	C=M/V	C/Co	M Acc	Mass recovery	% Recovery
0.0000	0.1041	0.0021	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
0.1667	0.1041	0.0021	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
0.3333	0.1041	0.0021	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
0.5000	0.1041	0.0021	0.0017	0.0000	0.0167	0.0017	0.0167	1.67
0.6667	0.1041	0.0021	0.0075	0.0002	0.0720	0.0092	0.0887	8.87
0.8333	0.1041	0.0021	0.0271	0.0006	0.2605	0.0363	0.3492	34.92
1.0000	0.1041	0.0021	0.0370	0.0008	0.3556	0.0733	0.7048	70.48
1.1667	0.1041	0.0021	0.0151	0.0003	0.1451	0.0884	0.8499	84.99
1.3333	0.1041	0.0021	0.0083	0.0002	0.0799	0.0967	0.9297	92.97
1.5000	0.1041	0.0021	0.0010	0.0000	0.0096	0.0977	0.9394	93.94
1.6667	0.1041	0.0021	0.0000	0.0000	0.0000	0.0977	0.9394	93.94
1.8333	0.1041	0.0021	0.0000	0.0000	0.0000	0.0977	0.9394	93.94
2.0000	0.1041	0.0021	0.0000	0.0000	0.0000	0.0977	0.9394	93.94
2.1667	0.1041	0.0021	0.0000	0.0000	0.0000	0.0977	0.9394	93.94
2.3333	0.1041	0.0021	0.0000	0.0000	0.0000	0.0977	0.9394	93.94
2.5000	0.1041	0.0021	0.0000	0.0000	0.0000	0.0977	0.9394	93.94

APPENDIX H1--Extraction of 1ppm PAHs contaminated soil column using 12g/L APU nanoparticles without flow interruption

			Phenanthrene Concentration (ppm)					**Benzo(a)pyrene Concentration (ppm)**				
No.	**Time (min)**	**PV**	**Sample 1**	**Sample 2**	**Average**	**SD**	**%RSD**	**Sample 1**	**Sample 2**	**Average**	**SD**	**%RSD**
1	0	0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
2	99	1.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
3	198	2.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
4	297	3.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
5	396	4.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
6	495	5.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
7	594	6.0	0.0013	0.0013	0.0013	0.0000	1.12	0.0000	0.0000	0.0000	0.0000	0.00
8	693	7.0	0.0057	0.0056	0.0057	0.0001	1.25	0.0000	0.0000	0.0000	0.0000	0.00
9	792	8.0	0.0088	0.0087	0.0088	0.0001	0.81	0.0000	0.0000	0.0000	0.0000	0.00
10	891	9.0	0.0148	0.0157	0.0153	0.0006	4.17	0.0009	0.0009	0.0000	0.0000	0.00
11	990	10.0	0.0106	0.0110	0.0108	0.0003	2.62	0.0054	0.0062	0.0058	0.0006	9.75
12	1089	11.0	0.1650	0.1630	0.1640	0.0014	0.86	0.0970	0.1080	0.1025	0.0078	7.59
13	1188	12.0	0.2610	0.2560	0.2585	0.0035	1.37	0.1400	0.1560	0.1480	0.0113	7.64
14	1287	13.0	0.3040	0.3060	0.3050	0.0014	0.46	0.2295	0.2310	0.2303	0.0011	0.46
15	1386	14.0	0.3040	0.2980	0.3010	0.0042	1.41	0.2609	0.2640	0.2625	0.0022	0.84
16	1485	15.0	0.5260	0.5430	0.5345	0.0120	2.25	0.2590	0.2630	0.2610	0.0028	1.08
17	1584	16.0	0.3370	0.3360	0.3365	0.0007	0.21	0.1318	0.1290	0.1304	0.0020	1.52
18	1683	17.0	0.2610	0.2580	0.2595	0.0021	0.82	0.3083	0.3140	0.3112	0.0040	1.30
19	1782	18.0	0.1870	0.1770	0.1820	0.0071	3.89	0.5630	0.5740	0.5685	0.0078	1.37
20	1881	19.0	0.3290	0.3350	0.3320	0.0042	1.28	0.0368	0.0390	0.0379	0.0016	4.10
21	1980	20.0	0.2110	0.2210	0.2160	0.0071	3.27	0.0443	0.0420	0.0432	0.0016	3.77
22	2079	21.0	0.2310	0.2460	0.2385	0.0106	4.45	0.1102	0.1180	0.1141	0.0055	4.83
23	2178	22.0	0.3030	0.2980	0.3005	0.0035	1.18	0.1797	0.1740	0.1769	0.0040	2.28
24	2277	23.0	0.9990	0.9780	0.9885	0.0148	1.50	0.1584	0.1620	0.1602	0.0025	1.59
25	2376	24.0	0.2330	0.2350	0.2340	0.0014	0.60	0.0790	0.0860	0.0825	0.0049	6.00
26	2475	25.0	0.2950	0.3020	0.2985	0.0049	1.66	0.1772	0.1850	0.1811	0.0055	3.05
27	2574	26.0	0.3080	0.2930	0.3005	0.0106	3.53	0.1874	0.1960	0.1917	0.0061	3.17
28	2673	27.0	0.3070	0.3120	0.3095	0.0035	1.14	0.0821	0.0970	0.0896	0.0105	11.77
29	2772	28.0	0.6170	0.6130	0.6150	0.0028	0.46	0.1230	0.1370	0.1300	0.0099	7.61
30	2871	29.0	0.4220	0.4150	0.4185	0.0049	1.18	0.0675	0.0720	0.0698	0.0032	4.56
31	2970	30.0	0.2770	0.2690	0.2730	0.0057	2.07	0.1996	0.2190	0.2093	0.0137	6.55
32	3069	31.0	0.5270	0.5330	0.5300	0.0042	0.80	0.1245	0.1270	0.1258	0.0018	1.41

			Phenanthrene Concentration (ppm)					Benzo(a)pyrene Concentration (ppm)				
No.	**Time (min)**	**PV**	**Sample 1**	**Sample 2**	**Average**	**SD**	**%RSD**	**Sample 1**	**Sample 2**	**Average**	**SD**	**%RSD**
33	3168	32.0	0.5890	0.5740	0.5815	0.0106	1.82	0.1772	0.1850	0.1811	0.0055	3.04
34	3267	33.0	0.4220	0.4150	0.4185	0.0049	1.18	0.1790	0.1900	0.1845	0.0078	4.22
35	3366	34.0	0.2950	0.2780	0.2865	0.0120	4.20	0.1880	0.1940	0.1910	0.0042	2.22
36	3465	35.0	0.2040	0.1960	0.2000	0.0057	2.83	0.1140	0.1230	0.1185	0.0064	5.37
37	3564	36.0	0.1070	0.1120	0.1095	0.0035	3.23	0.0440	0.0520	0.0480	0.0057	11.79
38	3663	37.0	0.0087	0.0082	0.0085	0.0004	4.18	0.0675	0.0720	0.0698	0.0032	4.55
39	3762	38.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
40	3861	39.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
41	3960	40.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00

APPENDIX H2--Cumulative extraction of 1ppm PAHs contaminated soil column using 12g/L APU nanoparticles without flow interruption

			Phenanthrene				Benzo(a)pyrene			
No.	Time (min)	PV	Conc (mg)	Cum (mg)	% Mass Remove	%Mass Remain	Conc (mg)	Cum (mg)	% Mass Remove	%Mass Remain
1	0	0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
2	99	1.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
3	198	2.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
4	297	3.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
5	396	4.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
6	495	5.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
7	594	6.0	0.0000	0.0000	0.0101	99.9899	0.0000	0.0000	0.0000	100.0000
8	693	7.0	0.0000	0.0000	0.0553	99.9447	0.0000	0.0000	0.0000	100.0000
9	792	8.0	0.0000	0.0000	0.1253	99.8747	0.0000	0.0000	0.0000	100.0000
10	891	9.0	0.0000	0.0001	0.2473	99.7527	0.0000	0.0000	0.0000	100.0000
11	990	10.0	0.0000	0.0001	0.3337	99.6663	0.0000	0.0000	0.0464	99.9536
12	1089	11.0	0.0003	0.0004	1.6457	98.3543	0.0002	0.0002	0.8664	99.1336
13	1188	12.0	0.0005	0.0009	3.7137	96.2863	0.0003	0.0005	2.0504	97.9496
14	1287	13.0	0.0006	0.0015	6.1537	93.8463	0.0005	0.0010	3.8924	96.1076
15	1386	14.0	0.0006	0.0021	8.5617	91.4383	0.0005	0.0015	5.9920	94.0080
16	1485	15.0	0.0011	0.0032	12.8377	87.1623	0.0005	0.0020	8.0800	91.9200
17	1584	16.0	0.0007	0.0039	15.5297	84.4703	0.0003	0.0023	9.1232	90.8768
18	1683	17.0	0.0005	0.0044	17.6057	82.3943	0.0006	0.0029	11.6124	88.3876
19	1782	18.0	0.0004	0.0048	19.0617	80.9383	0.0011	0.0040	16.1604	83.8396
20	1881	19.0	0.0007	0.0054	21.7177	78.2823	0.0001	0.0041	16.4636	83.5364
21	1980	20.0	0.0004	0.0059	23.4457	76.5543	0.0001	0.0042	16.8088	83.1912
22	2079	21.0	0.0005	0.0063	25.3537	74.6463	0.0002	0.0044	17.7216	82.2784
23	2178	22.0	0.0006	0.0069	27.7577	72.2423	0.0004	0.0048	19.1364	80.8636
24	2277	23.0	0.0020	0.0089	35.6657	64.3343	0.0003	0.0051	20.4180	79.5820
25	2376	24.0	0.0005	0.0094	37.5377	62.4623	0.0002	0.0053	21.0780	78.9220
26	2475	25.0	0.0006	0.0100	39.9257	60.0743	0.0004	0.0056	22.5268	77.4732
27	2574	26.0	0.0006	0.0106	42.3297	57.6703	0.0004	0.0060	24.0604	75.9396
28	2673	27.0	0.0006	0.0112	44.8057	55.1943	0.0002	0.0062	24.7768	75.2232
29	2772	28.0	0.0012	0.0124	49.7257	50.2743	0.0003	0.0065	25.8168	74.1832
30	2871	29.0	0.0008	0.0133	53.0737	46.9263	0.0001	0.0066	26.3748	73.6252
31	2970	30.0	0.0005	0.0138	55.2577	44.7423	0.0004	0.0070	28.0492	71.9508
32	3069	31.0	0.0011	0.0149	59.4977	40.5023	0.0003	0.0073	29.0552	70.9448

			Phenanthrene				Benzo(a)pyrene			
No.	**Time (min)**	**PV**	**Conc (mg)**	**Cum (mg)**	**% Mass Remove**	**%Mass Remain**	**Conc (mg)**	**Cum (mg)**	**% Mass Remove**	**%Mass Remain**
33	3168	32.0	0.0012	0.0160	64.1497	35.8503	0.0004	0.0076	30.5041	69.4959
34	3267	33.0	0.0008	0.0169	67.4977	32.5023	0.0004	0.0080	31.9801	68.0199
35	3366	34.0	0.0006	0.0174	69.7897	30.2103	0.0004	0.0084	33.5081	66.4919
36	3465	35.0	0.0004	0.0178	71.3897	28.6103	0.0002	0.0086	34.4561	65.5439
37	3564	36.0	0.0002	0.0181	72.2657	27.7343	0.0001	0.0087	34.8401	65.1599
38	3663	37.0	0.0000	0.0181	72.3333	27.6667	0.0001	0.0088	35.3981	64.6019
39	3762	38.0	0.0000	0.0181	72.3333	27.6667	0.0000	0.0088	35.3981	64.6019
40	3861	39.0	0.0000	0.0181	72.3333	27.6667	0.0000	0.0088	35.3981	64.6019
41	3960	40.0	0.0000	0.0181	72.3333	27.6667	0.0000	0.0088	35.3981	64.6019

APPENDIX I1--Extraction of 5ppm PAHs contaminated soil column using 12g/L APU nanoparticles without flow interruption

			Phenanthrene Concentration (ppm)					**Benzo(a)pyrene Concentration (ppm)**				
No.	**Time (min)**	**PV**	**Sample 1**	**Sample 2**	**Average**	**SD**	**%RSD**	**Sample 1**	**Sample 2**	**Average**	**SD**	**%RSD**
1	0	0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
2	99	1.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
3	198	2.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
4	297	3.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
5	396	4.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
6	495	5.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
7	594	6.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
8	693	7.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
9	792	8.0	0.0046	0.0045	0.0046	0.0001	1.55	0.0000	0.0000	0.0000	0.0000	0.00
10	891	9.0	0.0086	0.0088	0.0087	0.0001	1.63	0.0001	0.0001	0.0001	0.0000	0.00
11	990	10.0	0.0960	0.0990	0.0975	0.0021	2.18	0.0021	0.0021	0.0021	0.0000	1.08
12	1089	11.0	0.1740	0.1860	0.1800	0.0085	4.71	0.0124	0.0125	0.0125	0.0000	0.40
13	1188	12.0	0.4894	0.4780	0.4837	0.0081	1.67	0.0624	0.0620	0.0622	0.0003	0.45
14	1287	13.0	0.4057	0.4150	0.4104	0.0066	1.60	0.0330	0.0340	0.0335	0.0007	2.11
15	1386	14.0	0.5667	0.5470	0.5569	0.0139	2.50	0.0997	0.1030	0.1014	0.0023	2.30
16	1485	15.0	0.7388	0.7440	0.7414	0.0037	0.50	0.0562	0.0561	0.0562	0.0001	0.13
17	1584	16.0	0.2034	0.2140	0.2087	0.0075	3.59	0.1030	0.1010	0.1020	0.0014	1.39
18	1683	17.0	0.6299	0.6450	0.6375	0.0107	1.68	0.0654	0.0670	0.0662	0.0012	1.75
19	1782	18.0	0.5312	0.5420	0.5366	0.0076	1.42	0.0602	0.0590	0.0596	0.0008	1.42
20	1881	19.0	0.5366	0.5420	0.5393	0.0038	0.71	0.0751	0.0760	0.0756	0.0006	0.84
21	1980	20.0	0.3117	0.3220	0.3169	0.0073	2.30	0.1005	0.0997	0.1001	0.0006	0.57
22	2079	21.0	0.3564	0.3610	0.3587	0.0033	0.91	0.0996	0.1010	0.1003	0.0010	0.99
23	2178	22.0	0.5407	0.5340	0.5374	0.0047	0.88	0.1000	0.1010	0.1005	0.0007	0.70
24	2277	23.0	0.4617	0.4690	0.4654	0.0052	1.11	0.0589	0.0579	0.0584	0.0007	1.21
25	2376	24.0	0.5265	0.5330	0.5298	0.0046	0.87	0.1297	0.1330	0.1314	0.0023	1.78
26	2475	25.0	0.6865	0.6990	0.6928	0.0088	1.28	0.1178	0.1190	0.1184	0.0008	0.72
27	2574	26.0	0.4793	0.4860	0.4827	0.0047	0.98	0.0989	0.1010	0.1000	0.0015	1.49
28	2673	27.0	0.4688	0.4710	0.4699	0.0016	0.33	0.1672	0.1680	0.1676	0.0006	0.34
29	2772	28.0	0.2211	0.2270	0.2241	0.0042	1.86	0.1810	0.1880	0.1845	0.0049	2.68
30	2871	29.0	0.6615	0.6710	0.6663	0.0067	1.01	0.1921	0.1930	0.1925	0.0007	0.35
31	2970	30.0	0.6122	0.6230	0.6176	0.0076	1.24	0.1854	0.1840	0.1847	0.0010	0.54
32	3069	31.0	0.5704	0.5810	0.5757	0.0075	1.30	0.1913	0.1890	0.1902	0.0016	0.86

			Phenanthrene Concentration (ppm)					**Benzo(a)pyrene Concentration (ppm)**				
No.	**Time (min)**	**PV**	**Sample 1**	**Sample 2**	**Average**	**SD**	**%RSD**	**Sample 1**	**Sample 2**	**Average**	**SD**	**%RSD**
33	3168	32.0	0.4230	0.4320	0.4275	0.0064	1.49	0.0189	0.0192	0.0191	0.0002	1.22
34	3267	33.0	0.1980	0.1960	0.1970	0.0014	0.72	0.0790	0.0810	0.0800	0.0014	1.77
35	3366	34.0	0.0630	0.0620	0.0625	0.0007	1.13	0.0496	0.0500	0.0498	0.0003	0.57
36	3465	35.0	0.0096	0.0085	0.0091	0.0008	0.00	0.0088	0.0074	0.0081	0.0010	0.00
37	3564	36.0	0.0068	0.0053	0.0061	0.0011	0.00	0.0003	0.0001	0.0002	0.0001	0.00
38	3663	37.0	0.0007	0.0007	0.0007	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
39	3762	38.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
40	3861	39.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
41	3960	40.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00

APPENIDX I2--Cumulative extraction of 5ppm PAHs contaminated soil column using 12g/L APU nanoparticles without flow interruption

			Phenanthrene				Benzo(a)pyrene			
No.	**Time (min)**	**PV**	**Conc (mg)**	**Cum (mg)**	**%Mass Remove**	**%Mass Remain**	**Conc (mg)**	**Cum (mg)**	**%Mass Remove**	**%Mass Remain**
1	0	0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
2	99	1.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
3	198	2.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
4	297	3.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
5	396	4.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
6	495	5.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
7	594	6.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
8	693	7.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
9	792	8.0	0.0000	0.0000	0.0073	99.9927	0.0000	0.0000	0.0000	100.0000
10	891	9.0	0.0000	0.0000	0.0212	99.9788	0.0000	0.0000	0.0002	99.9998
11	990	10.0	0.0002	0.0002	0.1772	99.8228	0.0000	0.0000	0.0035	99.9965
12	1089	11.0	0.0004	0.0006	0.4652	99.5348	0.0000	0.0000	0.0235	99.9765
13	1188	12.0	0.0010	0.0015	1.2391	98.7609	0.0001	0.0002	0.1230	99.8770
14	1287	13.0	0.0008	0.0024	1.8957	98.1043	0.0001	0.0002	0.1766	99.8234
15	1386	14.0	0.0011	0.0035	2.7866	97.2134	0.0002	0.0004	0.3388	99.6612
16	1485	15.0	0.0015	0.0050	3.9729	96.0271	0.0001	0.0005	0.4286	99.5714
17	1584	16.0	0.0004	0.0054	4.3068	95.6932	0.0002	0.0007	0.5918	99.4082
18	1683	17.0	0.0013	0.0067	5.3267	94.6733	0.0001	0.0009	0.6977	99.3023
19	1782	18.0	0.0011	0.0077	6.1853	93.8147	0.0001	0.0010	0.7931	99.2069
20	1881	19.0	0.0011	0.0088	7.0482	92.9518	0.0002	0.0011	0.9139	99.0861
21	1980	20.0	0.0006	0.0094	7.5551	92.4449	0.0002	0.0013	1.0741	98.9259
22	2079	21.0	0.0007	0.0102	8.1290	91.8710	0.0002	0.0015	1.2346	98.7654
23	2178	22.0	0.0011	0.0112	8.9888	91.0112	0.0002	0.0017	1.3954	98.6046
24	2277	23.0	0.0009	0.0122	9.7334	90.2666	0.0001	0.0019	1.4888	98.5112
25	2376	24.0	0.0011	0.0132	10.5810	89.4190	0.0003	0.0021	1.6990	98.3010
26	2475	25.0	0.0014	0.0146	11.6894	88.3106	0.0002	0.0024	1.8884	98.1116
27	2574	26.0	0.0010	0.0156	12.4616	87.5384	0.0002	0.0026	2.0483	97.9517
28	2673	27.0	0.0009	0.0165	13.2134	86.7866	0.0003	0.0029	2.3165	97.6835
29	2772	28.0	0.0004	0.0170	13.5719	86.4281	0.0004	0.0033	2.6117	97.3883
30	2871	29.0	0.0013	0.0183	14.6379	85.3621	0.0004	0.0036	2.9197	97.0803
31	2970	30.0	0.0012	0.0195	15.6261	84.3739	0.0004	0.0040	3.2153	96.7847
32	3069	31.0	0.0012	0.0207	16.5472	83.4528	0.0004	0.0044	3.5195	96.4805

			Phenanthrene					Benzo(a)pyrene		
No.	**Time (min)**	**PV**	**Conc (mg)**	**Cum (mg)**	**%Mass Remove**	**%Mass Remain**	**Conc (mg)**	**Cum (mg)**	**%Mass Remove**	**%Mass Remain**
33	3168	32.0	0.0009	0.0215	17.2312	82.7688	0.0000	0.0044	3.5500	96.4500
34	3267	33.0	0.0004	0.0219	17.5464	82.4536	0.0002	0.0046	3.6780	96.3220
35	3366	34.0	0.0001	0.0221	17.6464	82.3536	0.0001	0.0047	3.7577	96.2423
36	3465	35.0	0.0000	0.0221	17.6609	82.3391	0.0000	0.0047	3.7706	96.2294
37	3564	36.0	0.0000	0.0221	17.6706	82.3294	0.0000	0.0047	3.7710	96.2290
38	3663	37.0	0.0000	0.0221	17.6717	82.3283	0.0000	0.0047	3.7710	96.2290
39	3762	38.0	0.0000	0.0221	17.6717	82.3283	0.0000	0.0047	3.7710	96.2290
40	3861	39.0	0.0000	0.0221	17.6717	82.3283	0.0000	0.0047	3.7710	96.2290
41	3960	40.0	0.0000	0.0221	17.6717	82.3283	0.0000	0.0047	3.7710	96.2290

APPENDIX J1--Extraction of 1ppm PAHs contaminated soil column using 12g/L APU nanoparticles with 24 hour flow interruption

			Phenanthrene Concentration (ppm)					**Benzo(a)pyrene Concentration (ppm)**				
No.	**Time (min)**	**PV**	**Sample 1**	**Sample 2**	**Average**	**SD**	**%RSD**	**Sample 1**	**Sample 2**	**Average**	**SD**	**%RSD**
1	0	0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
2	99	1.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
3	198	2.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
4	297	3.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
5	396	4.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
6	495	5.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
7	594	6.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
8	693	7.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
9	792	8.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
10	891	9.0	0.0014	0.0014	0.0014	0.0000	0.66	0.0000	0.0000	0.0000	0.0000	0.00
11	990	10.0	0.0055	0.0055	0.0055	0.0000	0.65	0.0007	0.0007	0.0007	0.0000	0.20
12	1089	11.0	0.1481	0.1490	0.1485	0.0007	0.44	0.0442	0.0446	0.0444	0.0003	0.59
13	1188	12.0	0.2538	0.2541	0.2540	0.0002	0.07	0.1481	0.1475	0.1478	0.0004	0.26
14	1287	13.0	0.3654	0.3642	0.3648	0.0008	0.23	0.2577	0.2608	0.2593	0.0022	0.85
15	1386	14.0	0.4954	0.4924	0.4939	0.0021	0.43	0.2712	0.2731	0.2721	0.0014	0.51
16	1485	15.0	0.6847	0.6886	0.6866	0.0028	0.40	0.3105	0.3090	0.3097	0.0011	0.34
17	1584	16.0	0.7144	0.7131	0.7137	0.0009	0.13	0.3462	0.3496	0.3479	0.0024	0.70
18	1683	17.0	0.7442	0.7455	0.7449	0.0009	0.12	0.4442	0.4475	0.4458	0.0024	0.53
19	1782	18.0	0.7459	0.7417	0.7438	0.0030	0.40	0.4615	0.4672	0.4644	0.0040	0.86
20	1881	19.0	0.7448	0.7449	0.7448	0.0000	0.00	0.4620	0.4605	0.4613	0.0010	0.22
21	1980	20.0	0.7550	0.7498	0.7524	0.0037	0.49	0.5049	0.5082	0.5065	0.0023	0.46
22	2079	21.0	0.7592	0.7600	0.7596	0.0005	0.07	0.5238	0.5271	0.5254	0.0023	0.44
23	2178	22.0	0.7115	0.7162	0.7139	0.0033	0.46	0.4769	0.4760	0.4765	0.0007	0.14
24	2277	23.0	0.7308	0.7212	0.7260	0.0068	0.93	0.4759	0.4770	0.4764	0.0007	0.16
25	2376	24.0	0.7385	0.7392	0.7388	0.0005	0.07	0.4692	0.4702	0.4697	0.0007	0.15
26	2475	25.0	0.7346	0.7376	0.7361	0.0021	0.28	0.3885	0.3891	0.3888	0.0005	0.12
27	2574	26.0	0.7030	0.7085	0.7058	0.0039	0.55	0.2808	0.2801	0.2804	0.0005	0.17
28	2673	27.0	0.6133	0.6155	0.6144	0.0015	0.25	0.1500	0.1499	0.1500	0.0001	0.05
29	2772	28.0	0.3708	0.3710	0.3709	0.0002	0.05	0.1442	0.1446	0.1444	0.0002	0.16
30	2871	29.0	0.1519	0.1510	0.1515	0.0007	0.44	0.0404	0.0398	0.0401	0.0004	1.03
31	2970	30.0	0.0423	0.0427	0.0425	0.0003	0.64	0.0327	0.0330	0.0329	0.0002	0.68
32	3069	31.0	0.0424	0.0423	0.0424	0.0001	0.22	0.0173	0.0174	0.0174	0.0001	0.38

			Phenanthrene Concentration (ppm)					Benzo(a)pyrene Concentration (ppm)				
No.	**Time (min)**	**PV**	**Sample 1**	**Sample 2**	**Average**	**SD**	**%RSD**	**Sample 1**	**Sample 2**	**Average**	**SD**	**%RSD**
33	3168	32.0	0.0212	0.0214	0.0213	0.0002	0.79	0.0017	0.0017	0.0017	0.0000	0.40
34	3267	33.0	0.0145	0.0143	0.0144	0.0001	0.84	0.0016	0.0016	0.0016	0.0000	0.17
35	3366	34.0	0.0152	0.0153	0.0152	0.0001	0.49	0.0013	0.0014	0.0013	0.0000	0.20
36	3465	35.0	0.0005	0.0005	0.0005	0.0000	0.05	0.0005	0.0004	0.0004	0.0000	0.16
37	3564	36.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
38	3663	37.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
39	3762	38.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
40	3861	39.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
41	3960	40.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00

APPENDIX J2--Cumulative extraction of 1ppm PAHs contaminated soil column using 12g/L APU nanoparticles with 24 hour flow interruption

			Phenanthrene				Benzo(a)pyrene			
No.	Time (min)	PV	Conc (mg)	Cum (mg)	% Mass Remove	%Mass Remain	Conc (mg)	Cum (mg)	% Mass Remove	% Mass Remain
1	0	0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
2	99	1.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
3	198	2.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
4	297	3.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
5	396	4.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
6	495	5.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
7	594	6.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
8	693	7.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
9	792	8.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
10	891	9.0	0.0000	0.0000	0.0111	99.9889	0.0000	0.0000	0.0000	100.0000
11	990	10.0	0.0000	0.0000	0.0549	99.9451	0.0000	0.0000	0.0057	99.9943
12	1089	11.0	0.0003	0.0003	1.2432	98.7568	0.0001	0.0001	0.3610	99.6390
13	1188	12.0	0.0005	0.0008	3.2751	96.7249	0.0003	0.0004	1.5434	98.4566
14	1287	13.0	0.0007	0.0015	6.1935	93.8065	0.0005	0.0009	3.6175	96.3825
15	1386	14.0	0.0010	0.0025	10.1444	89.8556	0.0005	0.0014	5.7945	94.2055
16	1485	15.0	0.0014	0.0039	15.6372	84.3628	0.0006	0.0021	8.2722	91.7278
17	1584	16.0	0.0014	0.0053	21.3472	78.6528	0.0007	0.0028	11.0552	88.9448
18	1683	17.0	0.0015	0.0068	27.3061	72.6939	0.0009	0.0037	14.6218	85.3782
19	1782	18.0	0.0015	0.0083	33.2567	66.7433	0.0009	0.0046	18.3368	81.6632
20	1881	19.0	0.0015	0.0098	39.2154	60.7846	0.0009	0.0055	22.0269	77.9731
21	1980	20.0	0.0015	0.0113	45.2345	54.7655	0.0010	0.0065	26.0792	73.9208
22	2079	21.0	0.0015	0.0128	51.3114	48.6886	0.0011	0.0076	30.2825	69.7175
23	2178	22.0	0.0014	0.0143	57.0224	42.9776	0.0010	0.0085	34.0942	65.9058
24	2277	23.0	0.0015	0.0157	62.8302	37.1698	0.0010	0.0095	37.9057	62.0943
25	2376	24.0	0.0015	0.0172	68.7409	31.2591	0.0009	0.0104	41.6635	58.3365
26	2475	25.0	0.0015	0.0187	74.6296	25.3704	0.0008	0.0112	44.7738	55.2262
27	2574	26.0	0.0014	0.0201	80.2756	19.7244	0.0006	0.0118	47.0173	52.9827
28	2673	27.0	0.0012	0.0213	85.1908	14.8092	0.0003	0.0121	48.2169	51.7831
29	2772	28.0	0.0007	0.0220	88.1578	11.8422	0.0003	0.0123	49.3720	50.6280
30	2871	29.0	0.0003	0.0223	89.3695	10.6305	0.0001	0.0124	49.6927	50.3073
31	2970	30.0	0.0001	0.0224	89.7094	10.2906	0.0001	0.0125	49.9555	50.0445
32	3069	31.0	0.0001	0.0225	90.0484	9.9516	0.0000	0.0125	50.0944	49.9056

			Phenanthrene				Benzo(a)pyrene			
No.	**Time (min)**	**PV**	**Conc (mg)**	**Cum (mg)**	**% Mass Remove**	**%Mass Remain**	**Conc (mg)**	**Cum (mg)**	**%Mass Remove**	**% Mass Remain**
33	3168	32.0	0.0000	0.0226	90.2189	9.7811	0.0000	0.0125	50.1079	49.8921
34	3267	33.0	0.0000	0.0226	90.3343	9.6657	0.0000	0.0125	50.1204	49.8796
35	3366	34.0	0.0000	0.0226	90.4563	9.5437	0.0000	0.0125	50.1312	49.8688
36	3465	35.0	0.0000	0.0226	90.4604	9.5396	0.0000	0.0125	50.1348	49.8652
37	3564	36.0	0.0000	0.0226	90.4604	9.5396	0.0000	0.0125	50.1348	49.8652
38	3663	37.0	0.0000	0.0226	90.4604	9.5396	0.0000	0.0125	50.1348	49.8652
39	3762	38.0	0.0000	0.0226	90.4604	9.5396	0.0000	0.0125	50.1348	49.8652
40	3861	39.0	0.0000	0.0226	90.4604	9.5396	0.0000	0.0125	50.1348	49.8652
41	3960	40.0	0.0000	0.0226	90.4604	9.5396	0.0000	0.0125	50.1348	49.8652

APPENDIX K1--Extraction of 5ppm PAHs contaminated soil column using 12g/L APU nanoparticles with 24 hour flow interruption

			Phenanthrene Concentration (ppm)					Benzo(a)pyrene Concentration (ppm)				
No.	**Time (min)**	**PV**	**Sample 1**	**Sample 2**	**Average**	**SD**	**%RSD**	**Sample 1**	**Sample 2**	**Average**	**SD**	**%RSD**
1	0	0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
2	99	1.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
3	198	2.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
4	297	3.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
5	396	4.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
6	495	5.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
7	594	6.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
8	693	7.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
9	792	8.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
10	891	9.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0001	0.0001	0.0001	0.0000	0.00
11	990	10.0	0.0960	0.0954	0.0957	0.0004	0.00	0.0000	0.0000	0.0000	0.0000	0.00
12	1089	11.0	0.1580	0.1586	0.1583	0.0004	0.27	0.1243	0.1250	0.1247	0.0005	0.40
13	1188	12.0	0.2394	0.2380	0.2387	0.0010	0.41	0.3624	0.3662	0.3643	0.0027	0.74
14	1287	13.0	0.5851	0.5905	0.5878	0.0038	0.65	0.5330	0.5340	0.5335	0.0007	0.13
15	1386	14.0	0.8307	0.8367	0.8337	0.0042	0.51	0.6650	0.6685	0.6667	0.0025	0.37
16	1485	15.0	1.2949	1.2845	1.2897	0.0074	0.57	0.7923	0.7855	0.7889	0.0048	0.61
17	1584	16.0	1.2911	1.2854	1.2883	0.0040	0.31	0.7831	0.7931	0.7881	0.0071	0.90
18	1683	17.0	1.3167	1.3054	1.3110	0.0074	0.56	0.8173	0.8184	0.8179	0.0008	0.10
19	1782	18.0	1.3612	1.3543	1.3577	0.0040	0.30	0.7845	0.7741	0.7793	0.0074	0.94
20	1881	19.0	1.3606	1.3661	1.3634	0.0080	0.58	0.7921	0.7954	0.7938	0.0023	0.29
21	1980	20.0	1.3878	1.3809	1.3844	0.0048	0.35	0.7973	0.7903	0.7938	0.0049	0.62
22	2079	21.0	1.3617	1.3669	1.3643	0.0039	0.28	0.7956	0.7985	0.7971	0.0021	0.26
23	2178	22.0	1.3817	1.3733	1.3775	0.0049	0.35	0.8021	0.8000	0.8011	0.0015	0.19
24	2277	23.0	1.2725	1.2694	1.2710	0.0037	0.29	0.7757	0.7758	0.7757	0.0001	0.01
25	2376	24.0	1.1743	1.1738	1.1740	0.0059	0.50	0.4297	0.4273	0.4285	0.0017	0.40
26	2475	25.0	0.804	0.812	0.8080	0.0022	0.27	0.1818	0.1812	0.1815	0.0004	0.23
27	2574	26.0	0.7134	0.7122	0.7128	0.0004	0.05	0.0689	0.0699	0.0694	0.0007	1.01
28	2673	27.0	0.6429	0.6507	0.6468	0.0055	0.86	0.0302	0.0305	0.0304	0.0002	0.70
29	2772	28.0	0.4435	0.4397	0.4416	0.0027	0.60	0.0111	0.0112	0.0112	0.0001	0.63
30	2871	29.0	0.2402	0.2367	0.2384	0.0024	1.02	0.0090	0.0091	0.0091	0.0001	0.78
31	2970	30.0	0.1154	0.1152	0.1153	0.0001	0.12	0.0034	0.0034	0.0034	0.0000	0.83
32	3069	31.0	0.0435	0.0435	0.0435	0.0000	0.01	0.0016	0.0016	0.0016	0.0000	0.45

			Phenanthrene Concentration (ppm)					Benzo(a)pyrene Concentration (ppm)				
No.	**Time (min)**	**PV**	**Sample 1**	**Sample 2**	**Average**	**SD**	**%RSD**	**Sample 1**	**Sample 2**	**Average**	**SD**	**%RSD**
33	3168	32.0	0.0423	0.0426	0.0424	0.0002	0.45	0.0013	0.0013	0.0013	0.0000	0.55
34	3267	33.0	0.0108	0.0107	0.0107	0.0001	0.72	0.0004	0.0004	0.0004	0.0000	0.88
35	3366	34.0	0.0043	0.0043	0.0043	0.0000	0.66	0.0000	0.0000	0.0000	0.0000	0.00
36	3465	35.0	0.0026	0.0025	0.0026	0.0000	0.42	0.0000	0.0000	0.0000	0.0000	0.00
37	3564	36.0	0.0006	0.0006	0.0006	0.0000	0.87	0.0000	0.0000	0.0000	0.0000	0.00
38	3663	37.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
39	3762	38.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
40	3861	39.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00
41	3960	40.0	0.0000	0.0000	0.0000	0.0000	0.00	0.0000	0.0000	0.0000	0.0000	0.00

APPENDIX K2--Cumulative extraction of 5ppm PAHs contaminated soil column using 12g/L APU nanoparticles with 24 hour flow interruption

			Phenanthrene				Benzo(a)pyrene			
No.	**Time (min)**	**PV**	**Conc (mg)**	**Cum (mg)**	**%Mass Remove**	**%Mass Remain**	**Conc (mg)**	**Cum (mg)**	**%Mass Remove**	**% Mass Remain**
1	0	0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
2	99	1.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
3	198	2.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
4	297	3.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
5	396	4.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
6	495	5.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
7	594	6.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
8	693	7.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
9	792	8.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0000	100.0000
10	891	9.0	0.0000	0.0000	0.0000	100.0000	0.0000	0.0000	0.0002	99.9998
11	990	10.0	0.0002	0.0002	0.1531	99.8469	0.0000	0.0000	0.0002	99.9998
12	1089	11.0	0.0003	0.0005	0.4064	99.5936	0.0002	0.0002	0.1996	99.8004
13	1188	12.0	0.0005	0.0010	0.7883	99.2117	0.0007	0.0010	0.7825	99.2175
14	1287	13.0	0.0012	0.0022	1.7288	98.2712	0.0011	0.0020	1.6361	98.3639
15	1386	14.0	0.0017	0.0038	3.0627	96.9373	0.0013	0.0034	2.7029	97.2971
16	1485	15.0	0.0026	0.0064	5.1262	94.8738	0.0016	0.0050	3.9651	96.0349
17	1584	16.0	0.0026	0.0090	7.1874	92.8126	0.0016	0.0065	5.2261	94.7739
18	1683	17.0	0.0026	0.0116	9.2851	90.7149	0.0016	0.0082	6.5346	93.4654
19	1782	18.0	0.0027	0.0143	11.4575	88.5425	0.0016	0.0097	7.7815	92.2185
20	1881	19.0	0.0027	0.0170	13.6389	86.3611	0.0016	0.0113	9.0515	90.9485
21	1980	20.0	0.0028	0.0198	15.8539	84.1461	0.0016	0.0129	10.3216	89.6784
22	2079	21.0	0.0027	0.0225	18.0368	81.9632	0.0016	0.0145	11.5969	88.4031
23	2178	22.0	0.0028	0.0253	20.2407	79.7593	0.0016	0.0161	12.8785	87.1215
24	2277	23.0	0.0025	0.0278	22.2743	77.7257	0.0016	0.0176	14.1197	85.8803
25	2376	24.0	0.0023	0.0302	24.1527	75.8473	0.0009	0.0185	14.8053	85.1947
26	2475	25.0	0.0016	0.0318	25.4455	74.5545	0.0004	0.0189	15.0957	84.9043
27	2574	26.0	0.0014	0.0332	26.5860	73.4140	0.0001	0.0190	15.2067	84.7933
28	2673	27.0	0.0013	0.0345	27.6209	72.3791	0.0001	0.0191	15.2553	84.7447
29	2772	28.0	0.0009	0.0354	28.3274	71.6726	0.0000	0.0191	15.2731	84.7269
30	2871	29.0	0.0005	0.0359	28.7089	71.2911	0.0000	0.0191	15.2876	84.7124
31	2970	30.0	0.0002	0.0361	28.8933	71.1067	0.0000	0.0191	15.2931	84.7069
32	3069	31.0	0.0001	0.0362	28.9630	71.0370	0.0000	0.0191	15.2956	84.7044

			Phenanthrene					Benzo(a)pyrene		
No.	Time (min)	PV	Conc (mg)	Cum (mg)	%Mass Remove	%Mass Remain	Conc (mg)	Cum (mg)	%Mass Remove	% Mass Remain
33	3168	32.0	0.0001	0.0363	29.0308	70.9692	0.0000	0.0191	15.2977	84.7023
34	3267	33.0	0.0000	0.0363	29.0480	70.9520	0.0000	0.0191	15.2983	84.7017
35	3366	34.0	0.0000	0.0363	29.0549	70.9451	0.0000	0.0191	15.2983	84.7017
36	3465	35.0	0.0000	0.0363	29.0590	70.9410	0.0000	0.0191	15.2983	84.7017
37	3564	36.0	0.0000	0.0363	29.0599	70.9401	0.0000	0.0191	15.2983	84.7017
38	3663	37.0	0.0000	0.0363	29.0599	70.9401	0.0000	0.0191	15.2983	84.7017
39	3762	38.0	0.0000	0.0363	29.0599	70.9401	0.0000	0.0191	15.2983	84.7017
40	3861	39.0	0.0000	0.0363	29.0599	70.9401	0.0000	0.0191	15.2983	84.7017
41	3960	40.0	0.0000	0.0363	29.0599	70.9401	0.0000	0.0191	15.2983	84.7017

BIOGRAPHY

Ms. Onarpar Santisukkasaem was born on September 30, 1982 in Bangkok, Thailand. She attended Ekamai International School and graduated in 2000. She received her Bachelor Degree in Science, Department of Energy Technology from Sinrindhorn International Institute of Technology, Thammasat University in 2004. She pursued her Master Degree study in the International Postgraduate Programs in Environmental and Hazardous Waste Management, Inter-Department of Environmental Management, Chulalongkorn University in May 2004. She was awarded Master Degree of Science in Environmental Management in September 2006.