

การกำจัดสารประกอบโพลีไซคลิกอะโรมาติกไฮโดรคาร์บอนจากน้ำท่าโดยใช้เส้นใยธรรมชาติ



นางสาว ปรีตดา ใจจนวิรุฬห์

สถาบันวิทยบริการ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชาการจัดการสิ่งแวดล้อม (สหสาขาวิชา)

บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย


ปีการศึกษา 2547

ISBN 974-17-6741-2

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

REMOVAL OF POLYCYCLIC AROMATIC HYDROCARBONS FROM RUNOFF BY
NATURAL FIBERS

Miss Paritta Rotwiroon



สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science
in Environmental Management (Inter-Department)

Graduate School
Chulalongkorn University
Academic Year 2004
ISBN 974-17-6741-2

Thesis Title Removal of Polycyclic Aromatic Hydrocarbons from Runoff
by Natural Fibers
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Field of study Environmental Management
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นางสาว ปรีตตา โรจนวิรุฬห์ : การกำจัดสารประกอบโพลีไซคลิกอะโรมาติกไฮโดรคาร์บอนจากน้ำท่าโดยใช้เส้นใยธรรมชาติ. (REMOVAL OF POLYCYCLIC AROMATIC HYDROCARBONS FROM RUNOFF USING NATURAL FIBERS) อ. ที่ปรึกษา : ผศ.ดร. เอกลักษณ์ คาน, อ.ที่ปรึกษาร่วม : ผศ. ดร. สุธา ขาวเขียว 58 หน้า. ISBN 974-17-6741-2.

สารประกอบโพลีไซคลิกอะโรมาติกไฮโดรคาร์บอน (พีเอเอช) ในน้ำท่าเป็นสารมลพิษที่มีผลกระทบต่อสิ่งมีชีวิตในแหล่งน้ำ และเป็นสารก่อมะเร็งในมนุษย์ กระบวนการดูดซับเป็นแนวทางหนึ่งในการกำจัดพีเอเอชออกจากน้ำท่า ซึ่งสามารถทำได้โดยติดตั้งอุปกรณ์ดูดซับสารพิษในระบบระบายน้ำ งานวิจัยนี้ได้ศึกษาการใช้วัสดุดูดซับที่เป็นเส้นใยธรรมชาติจากพืช 2 ชนิด คือ ฐปฤาษี และนุ่น ซึ่งมีราคาถูกและหาได้ง่ายในธรรมชาติ เปรียบเทียบกับเส้นใยสังเคราะห์โพลีเอสเตอร์ โดยทำการทดลองแบบแบตช์ และคอลัมน์เพื่อศึกษาความสามารถในการดูดซับพีเอเอชของเส้นใยทั้งสามชนิดภายใต้สภาวะการดูดซับแบบแข่งขัน และไม่แข่งขัน จากผลการทดลองพบว่า เส้นใยทั้งสามชนิดมีความสามารถกำจัดพีเอเอชออกจากน้ำเสียได้ดี ในการทดลองแบบแบตช์พบว่า ฟรอนดิลิโซไซเทอรัมสามารถอธิบายการดูดซับพีเอเอชของเส้นใยทั้งสามชนิดได้ดี และเส้นใยของฐปฤาษีมีประสิทธิภาพในการดูดซับสูงที่สุด นอกจากนี้ประสิทธิภาพในการกำจัดพีเอเอชมีแนวโน้มสูงขึ้นเมื่อความเข้มข้นของพีเอเอชลดลง จากผลการทดลองการชะตัวของพีเอเอชออกจากวัสดุที่ดูดซับแล้วพบว่า เส้นใยของนุ่นเป็นวัสดุที่พีเอเอชถูกชะออกมามากที่สุด ขณะที่เส้นใยโพลีเอสเตอร์มีความสามารถในการกักพีเอเอชสูงกว่าเส้นใยของฐปฤาษีเล็กน้อย ภายใต้สภาวะการดูดซับแบบแข่งขันในน้ำเสียที่มีพีเอเอชสองชนิดเป็นตัวถูกละลายพบว่า การดูดซับพีเอเอชทั้งสองชนิดมีการแข่งขันกันเพียงเล็กน้อย สำหรับการทดลองแบบคอลัมน์ เมื่อพิจารณากราฟแสดงผลการดูดซับและการชะพีเอเอชของเส้นใยทั้งสามชนิดพบว่า ผลการทดลองส่วนใหญ่มีลักษณะใกล้เคียงกัน โดยส่วนใหญ่ประสิทธิภาพในการกำจัดพีเอเอชของเส้นใยโพลีเอสเตอร์ และเส้นใยของฐปฤาษี มีค่าสูงกว่าประสิทธิภาพของเส้นใยของนุ่น ผลจากการวิจัยครั้งนี้พบว่าเส้นใยของฐปฤาษีมีความสามารถในการนำมาใช้เป็นตัวดูดซับเพื่อกำจัดพีเอเอชออกจากน้ำท่า

สาขาวิชาการจัดการสิ่งแวดล้อม
ปีการศึกษา 2547

ลายมือชื่อนิสิต.....

ลายมือชื่ออาจารย์ที่ปรึกษา.....

ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

4589440820 : MAJOR ENVIRONMENTAL MANAGEMENT

KEY WORD: Natural Fibers / PAHs / Removal / Runoff / Sorption

PARITTA ROTWIROON : REMOVAL OF POLYCYCLIC AROMATIC HYDROCARBONS FROM RUNOFF BY NATURAL FIBERS. THESIS

ADVISOR : ASST. PROF. EAKALAK KHAN, Ph.D., THESIS COADVISOR :

ASST. PROF. SUTHA KHAODHIAR, Ph.D., 58 pp. ISBN 974-17-6741-2.

Polycyclic aromatic hydrocarbons (PAHs) in runoff are of concern because they are generally toxic to aquatic organisms and many of them are carcinogenic to human. One of the alternatives for treating PAHs in runoff is to use sorption process, which can be engineered through catch basin inserts. This study investigated the application of two natural sorbents, cattail and kapok fibers, and a commercial sorbent, polyester fiber, for PAH removal from the runoff. Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene and fluoranthene were the PAHs studied. The PAH sorption and desorption of cattail, kapok, and polyester fibers were determined using laboratory scale batch reactors and a continuous flow column under non-competitive and competitive conditions. Results showed that cattail, kapok, and polyester fibers efficiently removed PAHs from the aqueous solutions. For the batch test, the sorption data could be described well by the Freundlich isotherm. Cattail fiber exhibited the highest sorption capacity and the removal tended to increase with increasing hydrophobicity of the PAHs. Kapok fiber had the lowest PAH retention capability while cattail fiber had slightly less PAH retention capability than polyester fiber. There was a weak degree of competitive sorption between PAHs in bi-solute systems in the competitive sorption test. For the column test, based on the shape of the breakthrough curves, most compounds exhibited similar sorption and desorption characteristics. Cattail and polyester fibers showed higher sorption capacities than kapok fiber for most PAHs. Cattail fiber can potentially be used as an effective catch basin insert sorbent for removing PAHs from runoff.

Field of study Environmental Management

Academic year 2004

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ACKNOWLEDGMENTS

I would like to express my gratefulness to my thesis advisor and co-advisor, Assist. Prof. Eakalak Khan and Assist. Prof. Sutha Khaodhiar, who always give me the valuable guidance and suggestions and also train me to deal with the problems all the way through the course of this research. I appreciate several advices and constructive comments from the committee members, Dr. Manaskorn Rachakornkij, Dr. Khemarath Osathapan, and Dr. Punjaporn Weschayanwiwat.

This study was supported by a grant from the Asian Development Bank through the National Research Center-Environmental and Hazardous Waste Management (NRC-EHWM) Center. I am grateful to Mr. J. M. Brownstein, at the Xextex Corporation for providing the polyester fiber used in this study.

I also would like to acknowledge all NRC-EHWM staffs and students, especially Miss Ramnaree Netvichien and Miss Chantana Imtim for their friendship and kind assistances in providing research instrument and a lot of technical advices and Mr. Thunyalux Ratpakdi for his valuable suggestion and assistance. I thank all my friends especially Natapol, Darin, Pongsabutr, Kullapa, and Trakarn for their friendship, encouragement, and kind helps.

Finally, I wish to express my deep gratitude to my father, my mother, and my sister for their love, encouragement, and hearty understanding throughout my study.

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ABBREVIATIONS

HPLC	high performance liquid chromatography
IAST	ideal adsorbed solution theory
MW	molecular weight
NOM	natural organic matter
PAHs	polycyclic aromatic hydrocarbons
SOM	soil organic matter



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GLOSSARY

C	concentration in the liquid phase
C°_i	equilibrium concentration in the liquid phase for component i
K_F	Freundlich constant
K_i	Freundlich constant for component i
K_L	Langmuir constant
K_{oc}	partitioning coefficient for organic carbon
K_{ow}	octanol/water partition coefficient
n_j	inverse of the Freundlich exponent for component j
q	the concentration of the sorbate
q_e	the concentration of the sorbate from experiment
q_c	the concentration of the sorbate from IAST calculation
q_m	the average concentration of the sorbate from experiment
q_T	total surface loading concentration
q°_i	surface loading concentration of single-solute system for component i
Z_i	mole fraction on the surface of the sorbent for component i
$1/n$	Freundlich exponent
Γ_{max}	total number of surface sites per mass of sorbent
π°_j	spreading pressures of the single-solute systems
π_m	spreading pressure of the mix-solute system

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CHAPTER I

INTRODUCTION

1.1 Background and Motivation

Stormwater runoff, which contributes significant quantities of pollutants to surface water, has been identified as an important cause of surface water quality degradation. Pollutants in stormwater runoff are from atmospheric fallout of air pollution, accumulation of pollutants on impervious surfaces followed by flushing of stormwater from those surfaces, and erosion on impervious surfaces. A wide variety of constituents can be found in stormwater runoff such as suspended solids, nutrients, heavy metals, oxygen demanding substances, pathogens, oils, greases and hydrocarbons (Harper, 1998).

Hydrocarbons are major pollutants concerned in stormwater runoff because many of them are not easily biodegraded and are persistent in environment. Many of these compounds are toxic to aquatic lives and some are also toxic to human (Harper, 1998). Polycyclic aromatic hydrocarbons (PAHs) are a class of hydrocarbon compounds that have been detected in aquatic environment. PAHs in the environment are of concern because they are toxic to aquatic organisms. They may inhibit the growth and reduce the life span and brood size of aquatic organisms (Neff, 1985). Many of them are mutagenic and carcinogenic to human (IARC, 1973; NAS, 1972) and are included in the U.S. EPA priority pollutants lists. Primary routes of entry of PAHs into aquatic environment include spillage and seepage of fossil fuels, atmospheric fallout, domestic and industrial sewage effluents, and stormwater runoff from land (Neff, 1985). Asphalt leaching, particles from tire abrasion, exhausts from automobiles and other combustion processes and spillage of petroleum on land surfaces, especially, gas stations, parking lots and motorways are the sources of PAHs in stormwater runoff (Korhonen *et al.*, 1998; Latimer *et al.*, 1990).

One of the alternatives for treating PAHs in the runoff is to use sorption process, which can be engineered through catch basin inserts. Catch basin insert is a treatment device installed at the inlet of stormwater catch basin to capture the

contaminants such as trash and debris, aliphatic and aromatic hydrocarbons and heavy metals by many mechanisms including filtration, settling or sorption, depending on types of the catch basin inserts (<http://www.kristar.com/level2/info/infoG.html>; <http://www.ci.chula-vista.ca.us>). Most sorbents used in catch basin inserts are synthetic and costly. This study investigated the application of local biomass as a sorbent for PAH removal from the runoff. Biomass is normally less expensive and easily found in environment. Some biomass and PAHs are hydrophobic and therefore should form hydrophobic interactions (Ribeiro *et al.*, 2000). One example of the sorption process by biomass is the sorption of dissolved PAHs to aspen wood fibers (Boving and Zhang, 2004). The sorption experiment was investigated by using PAH solutions containing between 2 ppb and 50 ppb of one of the following four PAHs: naphthalene, pyrene, anthracene and fluorene. The results demonstrated that aspen wood fibers could effectively remove PAHs from aqueous solutions and the sorption followed linear isotherm.

Ratpukdi (2002) studied the removal of used engine oil from water runoff by using biomass sorbents. The results showed that removal efficiencies of kapok fiber and cattail fiber were greater than 80% and were not much different from a commercial polyester sorbent. In this study, the two biomass sorbents were investigated for their PAH removal capacities compared to that of polyester fiber. According to Upshall *et al.* (1993), used motor oil contains as high as 200 ppm of PAHs. Both kapok and cattail fibers, which efficiently removed oil from runoff, may efficiently remove PAHs. Seven PAHs, naphthalene, anthracene, acenaphthylene, acenaphthene, phenanthrene, fluoranthene, and fluorene were studied. They are a group of PAHs, which have high water solubilities and are commonly found in stormwater runoff. The water samples containing PAHs at 10 – 40 % of their solubilities were prepared in single-solute system and bi-solute system for studying both non-competitive sorption and competitive sorption.

1.2 Objectives

The main objective of this study is to determine the effectiveness of kapok and cattail fibers as sorbents to remove PAHs from the runoff. The specific objectives are:

1. To determine the PAH sorption capacity of kapok and cattail fibers by using batch tests under non-competitive and competitive conditions,
2. To evaluate the effectiveness of kapok and cattail fibers in removing PAHs in a laboratory scale continuous test,
3. To compare the PAH removal performances of kapok, cattail, and polyester fiber.



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CHAPTER II

LITERATURE REVIEW

2.1 Polycyclic Aromatic Hydrocarbons in Stormwater Runoff

Stormwater runoff is identified as a significant cause of receiving water quality degradation because it contains many different contaminants such as suspended solids, nutrients, metals, oxygen demanding substances, pathogens, and oil, grease, and hydrocarbons. The major sources of these pollutants include components of road surface degradation, motor vehicles, atmospheric fallout, vegetation, land surfaces, litter, anti-skid compounds and chemicals, and construction sites (Harper, 1998).

Hydrocarbons in stormwater runoff are concerned because they cannot be easily degraded and may persist in environment for a long time. They cause acute or chronic effects on aquatic lives; for example, some compounds affect the growth and reproduction of fishes and/or hinder the photosynthesis in aquatic plants. Some compounds can bioaccumulate in fish tissues and then may transfer to human through the food chain (Harper, 1998). PAHs, composed of two or more fused benzene rings, are a group of hydrocarbons, which have been received attention because of their toxicity and carcinogenicity. PAHs, including benzo(a)pyrene, benz(a)anthracene, dibenz(a,h)anthracene, indeno(123-c,d)pyrene, benzo(b)fluoranthene, chrysene, benzo(j)fluoranthene, and benzo(k)fluoranthene, have been found that inducing tumors in laboratory animals. Some PAHs may inhibit the growth and reduce the life span and brood size of aquatic organisms (Neff, 1985). Some PAHs can cause cancer in human. According to EPA, benz(a)anthracene, chrysene, dibenz(a,h)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene and indeno(123-c,d)pyrene are probable human carcinogens.

Sources of PAHs in stormwater runoff are from impervious areas, such as roads, parking lots, roofs, sidewalk, and gas stations, and pervious areas, for instance, gardens and construction sites. Consequently, stormwater runoff is contaminated by

PAH deposited on surfaces, such as PAHs from automobile exhausts, asphalt leaching, oil spills, and tire abrasion (Manoli and Samara, 1999). Table 2.1 shows range of concentrations of three to six-ring PAHs in stormwater runoff in South Carolina.

Table 2.1 Concentrations of Σ PAHs in stormwater runoff in South Carolina (Ngabe *et al.*, 2000)

Sources	Σ PAHs ^a (ng/l)
Columbia	400 – 16,300
Georgetown	40 – 3,790
Murrells inlet	35 – 1,410

^a Σ PAHs consisted of 14 PAHs which are fluorene, phenanthrene, anthracene, 2-methylphenanthrene, fluoranthene, pyrene, chrysene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(e)pyrene and indeno(123-c,d)pyrene, benzo(ghi)perylene.

2.2 Properties of PAHs

At ambient temperatures, PAHs are in a solid state and have no color to yellow color. Generally, the characteristics of PAHs are high melting and boiling points, low vapor pressures, and low water solubilities. Their physical and chemical characteristics tend to be related their molecular weights. The characteristics and structure of some PAHs are shown in Table 2.2 and Figure 2.1, respectively. When the molecular weights of PAHs increase, their resistances to oxidation, reduction, and vaporization increase, whereas the water solubility tends to decrease. For example, higher molecular weight PAHs are more hydrophobic and have greater environmental persistence than lower molecular weight PAHs. PAHs with four or more aromatic rings are very persistent in the environment.

Table 2.2 Physical-chemical characteristics of some PAHs (Neff, 1979; LeGrega *et al.*, 2001)

PAH	M. W. (g/mol)	Solubility at 25°C (µg/L)	Vapor Pressure at 25°C (mm Hg)	Log K _{ow} ^a (Log K _{oc} ^b)	Benzene (total) rings
Naphthalene	128.2	12500 to 34000	1.8×10^{-2}	3.37	2
Acenaphthylene	152.2	3930	$10^{-3} - 10^{-4}$	4.07 (3.40)	2
Acenaphthene	154.2	3420	1.55×10^{-3}	3.98 (3.66)	2
Fluorene	166.2	1690	7.10×10^{-4}	4.18 (3.86)	2 (3)
Anthracene	178.2	45	2.4×10^{-4}	4.5 (4.15)	3
Phenanthrene	178.2	435	6.8×10^{-4}	4.46 (4.15)	3
Fluoranthene	202.3	206	5.0×10^{-6}	4.90 (4.58)	3 (4)
Pyrene	202.3	130	6.9×10^{-7}	4.88 (4.58)	4

^aK_{ow} = octanol/water partition coefficient

^bK_{oc} = partitioning coefficient for organic carbon

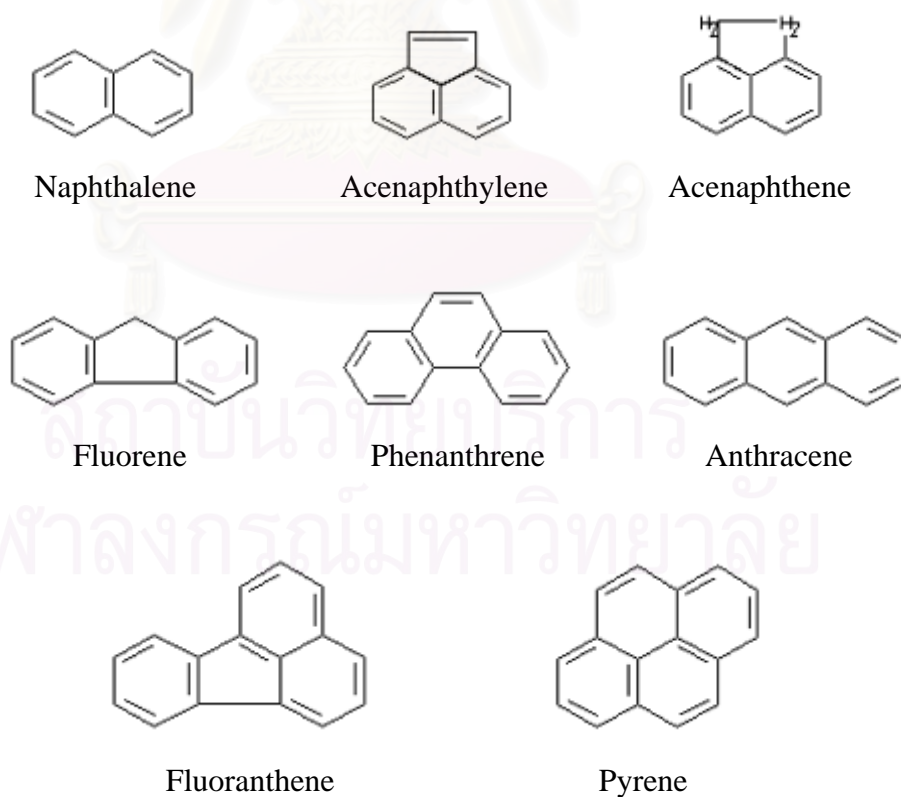


Figure 2.1 Structures of PAHs

Biodegradation of PAHs under aerobic conditions occurred very slowly. The degradation of PAHs in air and water occurred mainly via indirect photolysis under the influence of hydroxyl radicals. Moreover, PAHs tend to strongly adsorb to the organic fraction of sediments and soils. Sediments and soils are the main sinks for PAHs in the environment. Based on their physical, chemical, and biological properties, PAHs can be separated into two groups, the low molecular weight PAHs containing two to three benzene rings, for example, naphthalene, fluorene, phenanthrene and anthracene and the high molecular weight PAHs containing four to seven rings, such as chrysene, benzo(a)pyrene and coronene (Neff, 1979).

2.3 PAHs in Aquatic Environment

PAHs can enter the aquatic environment many ways: fallout and rainout from atmosphere and washing by stormwater runoff (runoff from paved roads, parking lots, gas station and the grounds of wood preservation plants). PAHs also come from various types of human activities such as industrial and domestic wastewater discharges, spillage and leakage of petroleum, and leaching and disposal of refinery effluents (Latimer *et al.*, 1990; <http://www.ns.ec.gc.ca/epb/envfacts/pah.html>; http://www.who.int/water_sanitation_health/GDWQ/Chemicals/pahfull.html; Takada *et al.*, 1991).

Fuels used by motor vehicles are the major sources of PAHs in stormwater runoff from parking lots and gas stations. There are many studies that determined the concentration of PAHs in vehicle fuels. For examples, naphthalene, fluorene, and phenanthrene were found to be the principal PAHs in French diesel fuel used by motor vehicles (Pointet *et al.*, 1997). In addition, the predominant PAHs in gasoline and diesel fuel samples collected in San Francisco Bay area was naphthalene, with concentrations of up to 2,600 mg/l in gasoline and 1,600 mg/l in diesel fuel. Comparing the average concentrations of the sixteen PAHs in gasoline and diesel fuel in this area (Figure 2.2), naphthalene, phenanthrene, fluorene, acenaphthene and pyrene are the most abundant PAHs (Marr *et al.*, 1999).

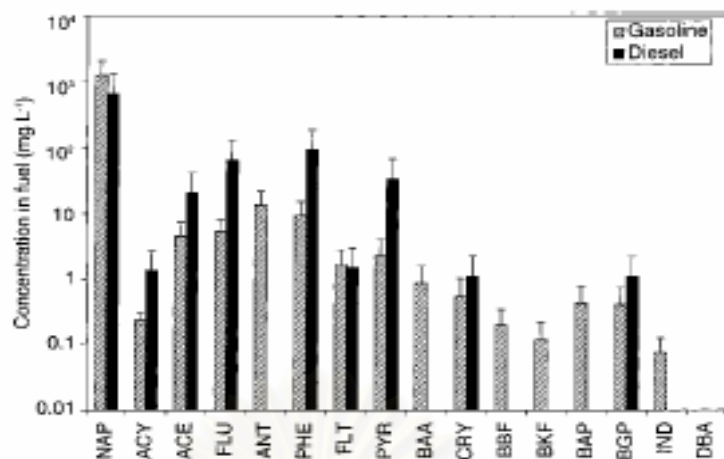


Figure 2.2 The average concentrations of the sixteen PAHs in gasoline and diesel fuel (Marr *et al.*, 1999).

For distribution of PAHs in water, most of them are adsorbed on suspended particles. Then they settle and accumulate in the bottom sediments. Since the water solubilities of PAHs tend to be lower as their molecular weights increase, most of PAHs dissolved in water are the group that has low molecular weights. Table 2.3 illustrates the relationship between the molecular weights of PAHs and their concentrations in Lincoln Creek, Milwaukee County, Wisconsin.

Table 2.3 Average concentrations of dissolved PAHs in Lincoln Creek, Milwaukee County, Wisconsin (Crunkilton and DeVita, 1997).

Compound	Molecular weight (g/mol)	Concentration (ng/l)
Acenaphthylene	152.2	<8,200
Acenaphthene	154.2	<3,400
Fluorene	166.2	<600
Phenanthrene	178.2	200
Anthracene	178.2	<120
Fluoranthene	202.3	116
Pyrene	202.3	71
Chrycene	228.3	65
Ideno(1,2,3-cd)pyrene	276.3	65
Benzo(b)fluoranthene	252.3	37
Benzo(g,h,i)perylene	276.3	37
Benzo(k)fluoranthene	252.3	22
Benzo(a)pyrene	252.3	22

The low molecular weight PAHs, containing two to three benzene rings, are acutely toxic to aquatic organisms than the high molecular weight PAHs containing four to seven rings. In general, the acute toxicity of PAHs increases with increasing molecular weight and $\log K_{ow}$; however, as $\log K_{ow}$ increases, the solubility of PAHs decreases and they tend to bind more strongly with particles. Thus higher molecular weight PAHs are less in their bioavailability and toxicity (Oris *et al.*, 1990). PAHs could be transferred from sediments into aquatic food chain through accumulation of PAHs in benthic organisms.

2.4 Natural Fibers

The major composition of a living plant is water. However, plant cell walls, which are composed mainly of carbohydrates and the mixtures of lignin and minor amounts of protein, lipids, starch, and inorganics, are a major portion of their dry mass. The chemical composition of the plant cell walls varies among different types of plants, and within various parts of the same plant.

2.4.1 Composition of Plant Cell Wall

The composition of plant cell wall can be divided into two parts (Rowell *et al.*, 2000): carbohydrates and lignin.

2.4.1.1. Carbohydrates

The carbohydrate portion of several plants consists of cellulose and hemicellulose polymers with lesser amounts of other sugar polymers such as starch and pectins. The combination of cellulose and hemicelluloses are called holocellulose. These chemicals are polymers of sugar molecules containing a lot of hydroxyl groups that are responsible for moisture sorption by hydrogen bonding.

Cellulose is the major structural component of plants. The structure of cellulose is a linear chain of glucose units attached together by $\beta(1,4)$ linkages. Cellulose contains both high packing and low packing density molecules, which are

referred to crystalline region and amorphous region, respectively. Most plants mainly consist of crystalline region that may be as much as 80% of the whole cellulose. Figure 2.3 shows a partial structure of cellulose.

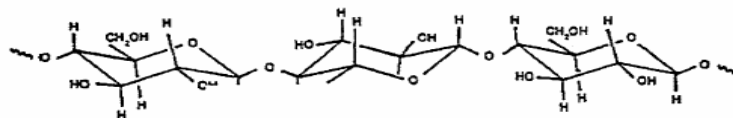


Figure 2.3 Partial structure of cellulose

Hemicellulose is a term used to describe a wide variety of heteropolysaccharides. They are often made up of more than one type of sugar unit and are sometimes referred to by the sugars they contain. Their structures contain more branches and are lower in molecular weight than cellulose as shown in Figure 2.4.

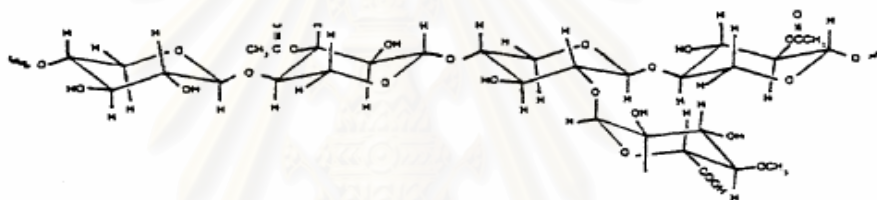


Figure 2.4 Partial structure of a hardwood hemicellulose

2.4.1.2. Lignin

Lignins are amorphous and mainly aromatic polymers of phenylpropane units that are very complex in chemical structure. The three basic building blocks of all plant lignins include guaiacyl, syringyl, and *p*-hydroxyphenyl moieties (Figure 2.5). Lignin is a class of compounds that comprises the woody parts of plants, such as cobs, hulls, and the woody portions of trees and shrubs.

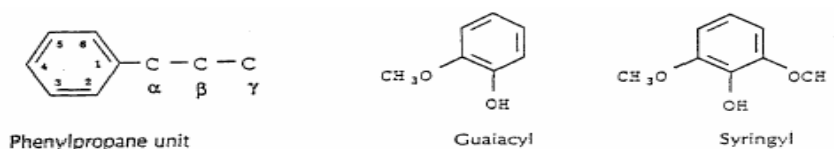


Figure 2.5 Building blocks of lignin

2.4.2 Cattail

Cattail or narrow leaf cattail is a common name of *Typha angustifolia* L. which is in Typhaceae family (Cattail family). It is an erect, rhizomatous, semiaquatic or aquatic, perennial herb. It has narrow leaves and inconspicuous flowers borne in a terminal spike composed of two separate parts of male flowers and female flowers. Figure 2.6 shows photographs of cattail and its flower. Cattail can be found nearly worldwide. Their habitats include wet meadows, marshes, ponds, seacoast estuaries, and roadside ditches (<http://www.rook.org/earl/bwca/nature/aquatics/typhalat.html>).

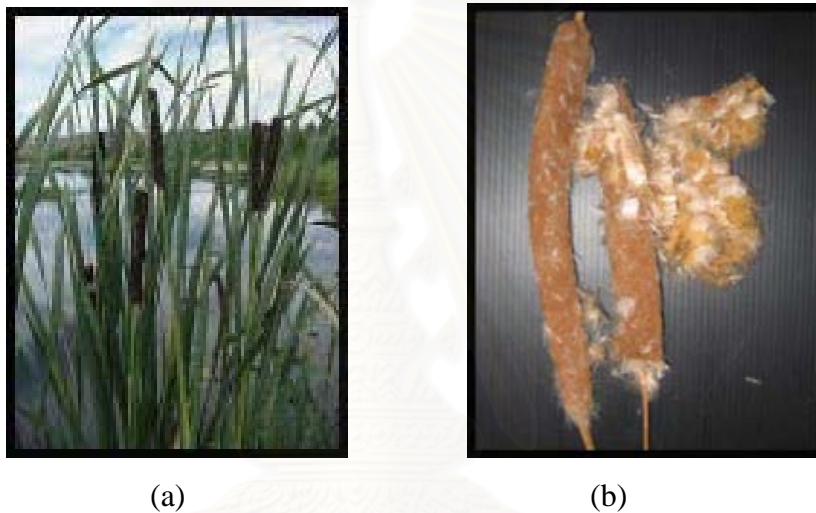


Figure 2.6 (a) Feature of cattail (<http://sunnisan.com/ppr/harvesting.html>) and (b) flowers of cattail

2.4.3 Kapok

Ceiba pentandra (L.) Gaertn is a scientific name of kapok tree, which is a member of Bombacaceae family. It is a very large tree with widely spreading braches. Kapok tree is originally native to South America but now it can be found in all tropical regions. Kapok fibers are plant hairs that are 10-35 mm. in length and consist of almost pure cellulose. They are water-repellent and have a low density because of the large air-filled lumen (http://www.tis-gdv.de/tis_e/ware/fasern/kapok/kapok.htm; <http://www.tropilab.com/ceiba-pen.html>). Figure 2.7 shows photographs of kapok fibers and tree.



Figure 2.7 (a) Kapok tree (www.cpc.unc.edu/projects/ecuador/photos.html) (b) fruit of kapok tree (www.terebess.hu/kereskedelem/img/kapok.jpg)

2.5 Sorption Theory

Sorption is referred to a process that chemicals in gas phases or liquid phases have an interaction with solid phases. These solid phases are called sorbents and the associated chemicals are called sorbates. It is adsorption if the sorbates attach on the surface of the sorbents, whereas it is absorption if the sorbates get into the sorbents. The presentation of the equilibrium distribution of a chemical between the solid phase and the liquid phase is generally termed sorption isotherm. It is a relationship between the equilibrium concentration in the liquid phase, C (e.g., $\text{mg}\cdot\text{L}^{-1}$) and the concentration of the sorbate (mass of solute sorbed per unit of sorbent), q (e.g., $\text{mg}\cdot\text{g}^{-1}$) at constant temperature (Faust, 1987).

Freundlich isotherm is the mathematical model used to describe the sorption process. The Freundlich equation is an empirical equation based on the assumption that the sorption occurs in multiple sites of the sorbent. The relationship of this model is as follow:

$$q = K_F \cdot C^{1/n} \quad (1)$$

where K_F is the Freundlich constant or capacity factor (e.g., $(\text{mg}\cdot\text{g}^{-1}) (\text{mg}\cdot\text{L}^{-1})^{-1/n}$); and $1/n$ is the Freundlich exponent.

If this model does not match the experimental data, the assumption behind Freundlich isotherm is not suitable, the other model, *Langmuir isotherm*, may be more

appropriate. The Langmuir isotherm is based on the assumption that the sorbent has limited sorption sites, therefore q cannot increase continually with increasing C . The relationship of this model is as follow:

$$q = \frac{\Gamma_{\max} \cdot K_L \cdot C}{1 + K_L \cdot C} \quad (2)$$

where Γ_{\max} represents the total number of surface sites per mass of sorbent; and K_L is the Langmuir constant or capacity factor.

2.5.1 Batch Systems

In batch systems, wastewater and sorbents are mixed together for some periods of time until they are in equilibrium then the sorbents are separated from the water. The sorption equilibrium is a condition which concentration of solution does not change with contact time. Therefore, a primary step of the batch system is to determine the contact time for the sorption process. Figure 2.8 shows a rate of sorption plotting to determine the equilibrium time (Faust, 1987).

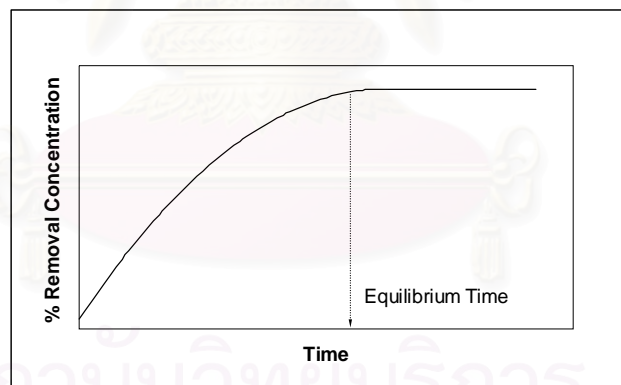


Figure 2.8 Rate of the sorption

2.5.2 Column Systems

In column systems, wastewater flows continuously through a pack bed of sorbent. The sorption process occurs as a solution passes through a series of sorbent layers. Thus, the solute is quickly sorbed on the top layers of the column until the sorption is in equilibrium. At this time, these layers are saturated with solute and the sorption is occurring in the lower layers. This second zone, the zone that the solute is

being transferred from liquid phase to solid phase, is called mass transfer zone. The mass transfer zone will move down through the column. When it reaches the bottom of the column the effluent concentration will increase. This stage is called breakthrough. Figure 2.9 illustrates a breakthrough curve, relationship between the effluent concentration and time operation, which shows a typical sorption column performance (Faust, 1987).

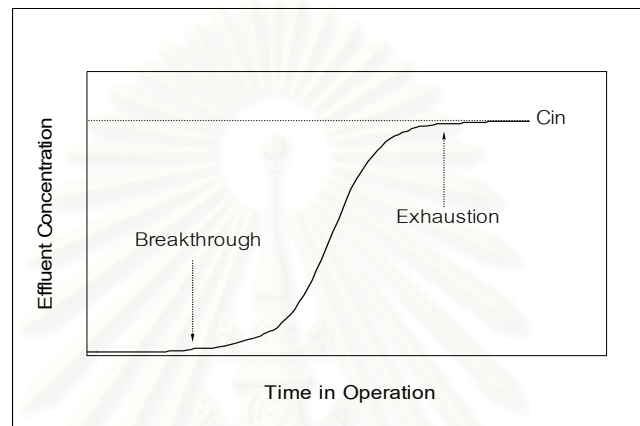


Figure 2.9 Breakthrough curve

2.5.3 Competitive Sorption

In practice, a variety of organic compounds would be found in stormwater runoff; there would be more than just a single compound sorbed in the treatment process. This situation is known as competitive sorption. The sorption of compounds in competitive or mixed-solute systems may enhance or reduce or may sorb independently. To predict the sorption of the compounds in the mixtures, the ideal adsorbed solution theory (IAST) was developed. The IAST is an approach used to predict the sorption equilibria of mixtures based on the single-solute isotherms of each component. The IAST model is based on the assumption that all sorptive sites are available to any component in the mixtures (Kilduff and Wigton, 1995; Crittenden *et al.*, 1985).

The following five basic equations are used in the IAST model.

$$q_T = \sum_{i=1}^N q_i \quad (3)$$

$$Z_i = q_i/q_T \quad i = 1 \text{ to } N \quad (4)$$

$$C_i = Z_i C_i^\circ \quad i = 1 \text{ to } N \quad (5)$$

$$1/q_T = \sum_{i=1}^N Z_i/q_i^\circ \quad (6)$$

$$\frac{\pi_m A}{RT} = \frac{\pi_1^\circ A}{RT} = \frac{\pi_j^\circ A}{RT} = \dots \quad \text{for } j = 2 \text{ to } N \quad (7)$$

Equation 3 defines q_T , the total surface loading concentration (the total concentration of sorbate). Z_i in equation 4 is the mole fraction on the surface of the sorbent for component i . C_i° and q_i° in equations 5 and 6 are the equilibrium concentration in the liquid phase and the surface loading concentration of single-solute system, respectively. Equation 6 shows no area change per mole upon mixing in the mixture from the single-solute isotherms at the spreading pressure of the mixture. Equation 7 compares that the spreading pressures of the single-solute systems (π_j°) are equal to the spreading pressure of the mix-solute system (π_m).

When the Freundlich equation is used to express the single-solute sorption of the sorbates in a system, equation 7 can be simplify to the following:

$$n_1 q_1^\circ = n_j q_j^\circ \quad j = 2 \text{ to } N \quad (8)$$

n_j in equation 8 is an inverse of the Freundlich exponent.

After an arithmetical calculation, the equation for each sorbate was derived as the following equation.

$$C_i = \frac{q_i \left[\sum_{j=1}^N n_j q_j \right] n_i}{\sum_{j=1}^N q_j n_i K_i} \quad i = 1 \text{ to } N \quad (9)$$

Equation 9 defines K_i , Freundlich constant for component i .

Crittenden *et al.* (1985) studied the performance of the IAST to predict multi-component adsorption equilibria of the following volatile organic chemicals: chloroform, bromoform, trichloroethene, tetrachloroethene, 1,2-dibromoethane, and chlorodibromomethane. The mixtures contained various combinations of 2, 3, and 6 solutes were tested using activated carbons. The experiment demonstrated that the IAST was sufficiently accurate to predict multicomponent competitive interactions between these chemicals. However, the results are acceptable for relatively similar molecules.

When the mixture contains chemicals, which have different sizes, it is possible that some sorptive sites are not involved in competition. The larger molecules may not be able to access small pores of the sorbent. Kilduff and Wigton (1995) studied the effect of natural organic matter (NOM) on sorption of trichloroethylene (TCE) on activated carbon. They developed the IAST model to predict the sorption of bisolute system between TCE and humic acid. The IAST was modified based on the hypothesis that TCE, which is a smaller molecule, could access small pores of activated carbon which humic acid could not.

2.6 Sorption of Organic Substances other than PAHs by Natural Sorbents

Biomass can be used as sorbents for contaminant removal from water. They are inexpensive and easily degraded in environment. There are several studies using biomass for removal of organic compounds. For example, various plants such as cotton, kenaf, *Salvinia sp.* and rice straw were investigated for oil sorption (Lee *et al.*, 1999; Riebiro *et al.*, 2000; Sun *et al.*, 2002).

Severson and Banerjee (1996), and Mackey and Gschwend (2000) studied the sorption of organic compounds on wood. The studies exhibited that the sorption of hydrophobic organic compounds by wood is primarily controlled by the lignin portion. The polarity of cellulose and hemicellulose is higher than the polarity of lignin. Lignin structure, that is more hydrophobic than other components, may play a major role in sorption of hydrophobic organic compounds. Lee *et al.* (1999) suggested that natural sorbents such as kenaf, cotton and milkweed have hydrophobic characteristics because of the large amount of wax on their fiber surfaces. Riebiro *et*

al. (2000) also showed that *Salvinia sp.*, a hydrophobic biomass, had high sorption capacities for oil and emulsified oil due to the hydrophobic interaction between the sorbent and organic compounds in the oils.

2.7 Sorption of PAHs by Natural Sorbents

Appert-Collin *et al.* (1999) studied the sorption of two PAHs (naphthalene and phenanthrene) on natural organic sand and mineral sand impregnated with heptamethylnonane. The result showed that sorption of PAH on mineral material was very weak, whereas a strong sorption was found on organic material.

Several studies on the sorption of PAHs by various types of NOM have showed that characteristics of sorbents, such as polarity or aromaticity, may have an effect on sorptive behavior. There are some studies showing a strong positive correlation between PAH sorption and aromatic content of NOM (Xing, 1994; Chin *et al.*, 1997; Chiou *et al.*, 1998). For instance, Chiou *et al.* (1998) found that the high partitioning of PAHs (naphthalene, phenanthrene, and pyrene) related with aromatic content more than aliphatic constituent of NOM. However, a few recent reports showed that aliphatic components of NOM could contribute significantly to PAH sorption (Chefetz *et al.*, 2000 and Salloum *et al.*, 2002).

Salloum *et al.* (2002) investigated the sorption of phenanthrene to aliphatic-rich soil organic matter (SOM) samples that included SOM precursors (algae, degraded algae, cellulose, collagen, leaf cuticle, and lignin), two kerogen samples, and a highly aromatic humic acid. The result showed that the samples containing high aliphatic component had the capability to sorb phenanthrene more than the highly aromatic components. They indicated that paraffinic carbon content in SOM samples contributes significantly to phenanthrene sorption. Chefetz *et al.* (2000) studied the sorption of pyrene on different types of NOM. The study showed that aliphatic component in NOM had an important role in pyrene sorption. Cuticle and humin samples, containing large amounts of aliphatic structure, exhibited the highest pyrene sorption capacities. However, they found that the sorption mechanisms did not associate only aliphatic structures because the degraded lignin sample, very low in aliphaticity, also had high pyrene sorption capacity. They suggested that the sorption

of pyrene on NOM surfaces in aqueous systems was controlled by many C-containing functional groups. Moreover, synthetic polymers such as polyethylene, polyvinylchloride, and rubber and many others are well known to sorb nonionic organic compounds.

Boving and Zhang (2004) investigated the potential of aspen wood as a sorbent for treating PAHs in stormwater runoff. The experiment was conducted by using the following PAHs: naphthalene, pyrene, anthracene and fluorene. Concentrations of PAH solutions are between 2 ppb and 50 ppb. The study demonstrated that aspen wood fibers could effectively remove PAHs from aqueous solutions. In addition, they found that removal efficiency of aspen wood increased with increasing molecular weight and hydrophobicity of the PAHs.

2.8 Applications of Cattail and Kapok in Wastewater Treatment

Kapok has been investigated in many studies for oil sorption. Choi and Cloud (1992) reported that kapok fiber, which has hydrophobic property, exhibited high oil sorption capacity. Kapok fiber is effective in oil sorption due to large amounts of wax on the fiber surfaces and noncollapsing lumen of the fiber. Ratpukdi (2002) examined the oil sorption efficiencies of various natural sorbents. Kapok fiber was the best sorbent for chemically emulsified oil removal.

Cattail has been studied for treatment of different types of wastewater. Groudev *et al.* (2001) investigated treatment of acid mine drainage from a uranium deposit by means of a natural wetland having cattail as one of the major species. The results exhibited that the treatment of mine waters polluted with radioactive elements, heavy metals and arsenic can be effectively treated by natural wetlands. Inthorn *et al.* (2004) studied the removal of basic, direct, and reactive dyes from water by cattail biomass powder. Cattail biomass treated with 37% formaldehyde mixed with 0.2 N sulfuric acid showed good performance for removing basic dyes at any pH and direct and reactive dyes at low pH.

2.9 Sorbent Materials in Stormwater Applications

Lately, sorbents have been used in stormwater applications to improve water quality. They will be inserted in stormwater catch basins, sumps, and other components of stormwater system in order to capture contaminants, such as hydrocarbons, oil and grease, and other toxic compounds (U.S. EPA, 2002). Three basic types of the sorbents consist of natural organic, natural inorganic, and synthetic materials. Natural organic sorbents include straw, corncobs, leaf compost, sawdust, feathers, and other carbon-based products. Clay, glass wool, sand, perlite, and volcanic ash are example of natural inorganic sorbents. For synthetic sorbents, they are man-made materials produced to obtain high pollutant removal efficiencies (U.S. EPA, 2002). For example, X-TEX made from synthetic fibers has a selective affinity for lipophilic and can efficiently remove hydrocarbons from water (UltraTech International, Inc.). Applications of sorbents in stormwater systems have both advantages and disadvantages as shown in Table 2.4.

Table 2.4 Advantages and disadvantages of the sorbents (U.S. EPA, 2002).

Advantages	Disadvantages
Sorbents can be placed in many stormwater systems, both existing and new systems.	Used sorbents require proper handling and disposal
Many of them are easy to install, operate and maintain.	Inspection of the sorbent capacities is usually required.
Most synthetic sorbents can maintain their shapes and not easily damage.	The sorbents can be clogged by debris and their capacities will decrease.

CHAPTER III

MATERIAL AND METHODS

3.1 PAH Water Samples

PAH water samples (aqueous solutions) were prepared for both single-solute and bi-solute systems for using in noncompetitive and competitive sorption tests, respectively. For the single-solute system, PAH water samples were divided in two groups. The first group included naphthalene, acenaphthylene, acenaphthene, fluorene, and phenanthrene solutions. They were initially prepared by dissolving dry PAHs in methanol. The PAH methanolic solutions were added with dechlorinated tap water and stirred for a few days. Methanol concentrations in the water samples were less than 0.1%. The other group consisted of anthracene and fluoranthene solutions. They were prepared in the same manner as the first group except dechlorinated tap water contained 40% of methanol since the two PAHs hardly dissolved in water. The initial PAH concentrations in the samples used in all sorption experiments were between 10% and 40% of their water solubilities. For the competitive sorption test, two mixtures of two PAHs were studied. The first mixture was between acenaphthylene and acenaphthene for studying the competitive sorption of mixture containing compounds that are similar in their properties (molecular weight, water solubility, and K_{ow}). The other mixture was between acenaphthene and naphthalene for investigating the competitive sorption of compounds that are different in their properties. The samples of the bi-solute system were prepared in the same manner as for the single-solute system except that the two methanolic PAH solutions were mixed before the addition of dechlorinated tap water. PAHs in the mixtures were prepared at the same concentration, 1000 ppb. pH of all samples were adjusted to 7 using either sulfuric acid or sodium hydroxide.

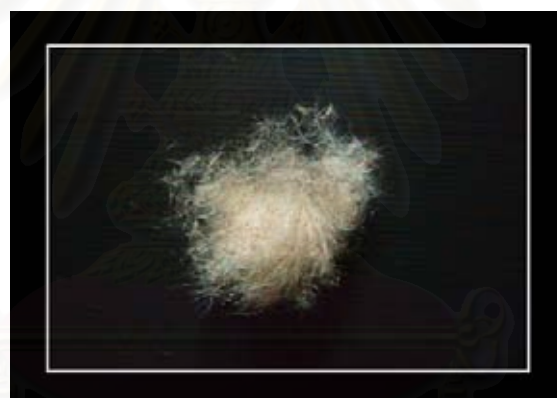
3.2 Sorbents

Local biomass sorbents used in this study were kapok fiber and cattail fiber. Polyester fiber, a commercial synthetic sorbent was tested for comparison purpose.

The fresh plants were washed with water to remove dust and other impurities. Then, they were dried at 60°C for 24 hours (Ribeiro *et al.*, 2000). Both kapok and polyester were in fiber form already, whereas; cattail had to be crushed by hand to obtain its fiber from the core. Figure 3.1 shows the photographs of the three fibers.



(a)



(b)



(c)

Figure 3.1 Sorbents used in this study: (a) Kapok fiber, (b) Cattail fiber, and (c) Polyester fiber

3.3 Experimental Procedures

3.3.1 Batch Experiment

3.3.1.1 Preliminary Test

Preliminary test was conducted to determine the time to reach sorption equilibrium for naphthalene, acenaphthylene, acenaphthene, fluorene, and phenanthrene (group 1 PAHs) solutions. The experiments were run in duplicate. Amber vials with Teflon cap seal containing 25 ml of the water samples and the biomass were shaken at room temperature (30 °C) using a rotary agitator at 50 rpm as shown in Figure 3.2. Note that the vials were in the plastic bottles. One vial was removed every 6 hours to obtain the sample that was measured for the residual PAH concentration. The equilibrium time was justified when the change in the concentration with time was less than 1%. The equilibrium time for every sorbent and every PAH was determined using the minimum mass of sorbent used in the isotherm test described in the next section. This minimum sorbent mass took the longest time to achieve the equilibrium.



Figure 3.2 Experimental setup for preliminary batch test

3.3.1.2 Sorption Isotherm Test

Sorption isotherm tests were conducted in order to determine the PAH sorption capacity of the sorbents. All of the tests were performed in duplicate. The tests followed a 9-point-isotherm technique by varying the mass of sorbent and keeping the initial concentrations of PAHs constant (10% - 40% of their water solubilities, which were 12 mg/l, 1.5 mg/l, 1.5mg/l, 0.15 mg/l, 0.045 mg/l, 0.005 mg/l, and 0.020 mg/l for naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, and fluoranthene, respectively). The mixtures between the PAH solutions and the sorbents were shaken in the same manner as in the preliminary sorption test. The equilibrium sorption of the anthracene and fluoranthene (group 2 PAHs) solutions was justified by measuring the PAH concentrations at 72, 78 and 84 hours and not having changes in the concentration. A control sample, a water sample with out the sorbent, was included to account for the loss of PAH due to activities other than sorption onto biomass. After the sorption reached equilibrium, the sorbent was removed from water by filtration while the filtrate was analyzed for PAH. The amount of PAH sorbed could be determined from the difference between the initial and residual concentrations. For the competitive sorption, two mixtures of two PAHs were performed following the same procedure as in the noncompetitive sorption.

3.3.1.3 Desorption Test

PAH desorption tests were performed to study the PAH retention capability of the sorbents. All desorption tests were conducted in duplicate. Two grams of sorbents were saturated with PAHs by immersing them in high concentration PAH solutions for 24 hours. To ensure that the sorbents were saturated with PAHs, they were immersed in PAH solutions two or three times. The PAH concentration in the solutions were measured before and after adding the sorbents in the solutions. When there was no difference between the two concentrations, the sorbents were saturated. Subsequently the saturated sorbents were added to one liter of dechlorinated tapwater and the mixture was shaken at 200 rpm (Figure 3.3). Water samples were collected every ten minutes for one hour to examine the amount of desorbed PAH.



Figure 3.3 Experimental setup for desorption test

3.3.2 Column Experiment

The column experiments were conducted to study the sorption capacity of the sorbents in a continuous system, which is similar to the field condition. One gram of each sorbent was packed in a glass column, which is 2.5 cm in diameter and 40 cm in length. Then, the columns were operated continuously by pumping the water sample through at a flow rate of 1 ml/min. Figures 3.4 and 3.5 illustrate a schematic diagram and the actual setup of the column experiment, respectively. In order to monitor for the breakthrough, the effluent sample was collected and measured for PAH every four hours. Both non-competitive sorption and competitive sorption were studied in the column experiments. For non-competitive sorption, PAH solutions contained approximately 9,000 ppb, 1,300 ppb, 1,000 ppb, 100 ppb, 50 ppb, and 20 ppb of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and fluoranthene, respectively. The concentration of each PAH in the mixture was approximately 1,000 ppb for the competitive sorption test.

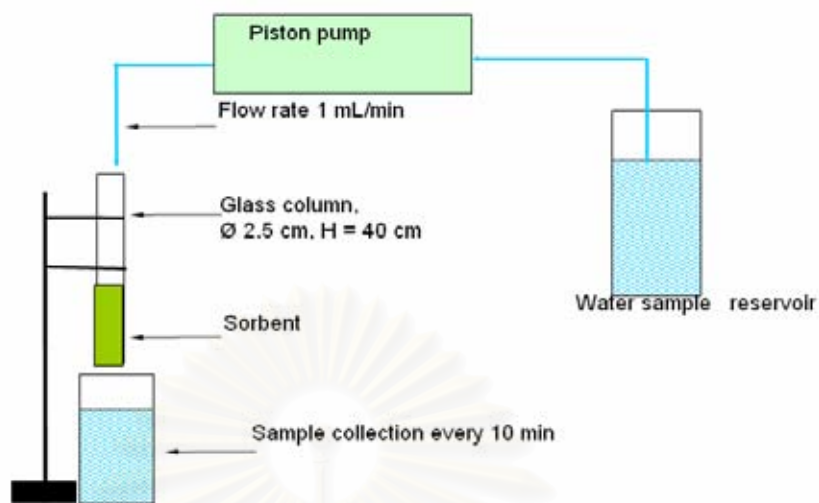


Figure 3.4 Schematic diagram of the setup of the column experiment



Figure 3.5 Actual setup of the column experiment

3.3 Analyses

pH was measured by a pH meter (Hach, Sension 3). PAH concentrations were determined according to the EPA method 550 using a high performance liquid chromatography (Shimadzu, LC-10 AD VP) equipped with a UV detector.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Batch Experiment

4.1.1 Preliminary Test

Figures 4.1 - 4.3 present the relationships between percent of PAH removal and the contact time. The compounds with higher MW required longer time to reach equilibrium. Faust (1987) stated that the configuration of the molecule has an effect on its adsorption rate; larger molecules have a lower adsorption rate than smaller molecules. The minimum times required to reach the equilibrium are summarized in Table 4.1. It should be reminded that anthracene and fluoranthene were not included in this test. Their sorption equilibrium was verified using a different method as described in Section 3.3.1.2. Excluding acenaphthylene, the equilibrium times of the three sorbents were not much different.

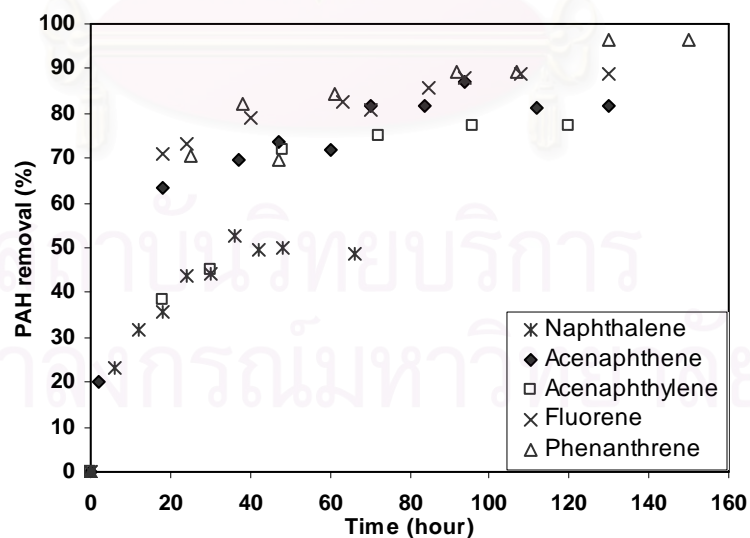


Figure 4.1 Sorption kinetic of cattail sorbent

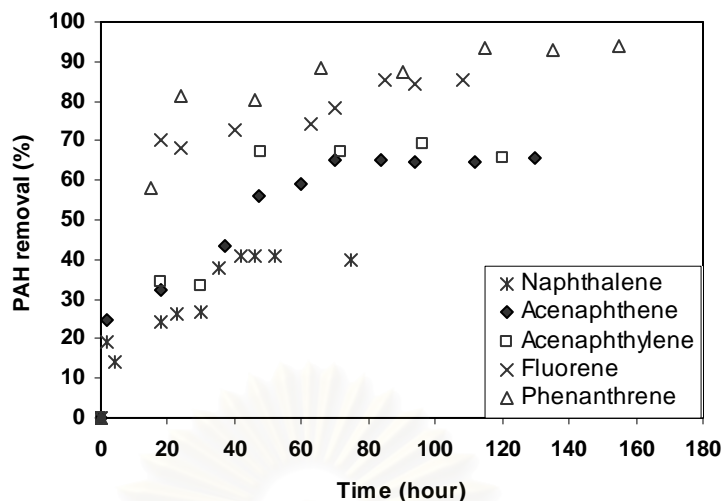


Figure 4.2 Sorption kinetic of kapok sorbent

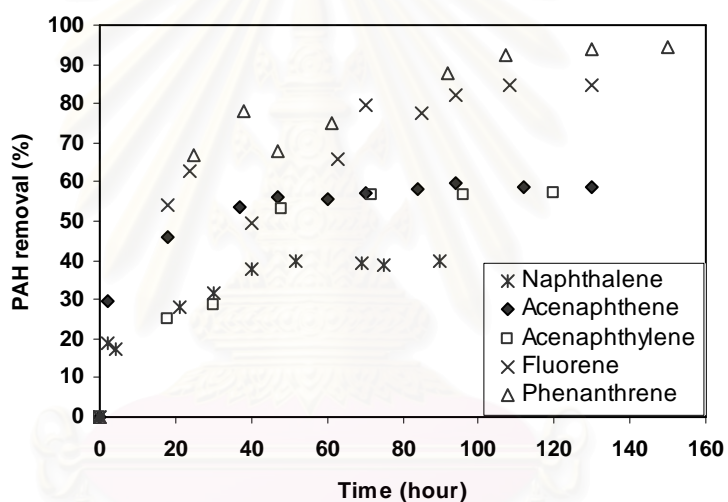


Figure 4.3 Sorption kinetic of polyester sorbent

Table 4.1 Sorption equilibrium time of PAHs on cattail, kapok, and polyester fibers

Compounds	Sorption equilibrium times (hours)		
	Cattail	Kapok	Polyester
Naphthalene	42	42	40
Acenaphthene	70	70	70
Acenaphthylene	96	80	72
Fluorene	94	85	94
Phenanthrene	130	115	130

4.1.2 Sorption Isotherm Test

4.1.2.1 Non-Competitive Sorption Test

Sorption isotherms of the sorbents for 7 PAHs are presented in Figures 4.4 - 4.10. Results of the control samples showed some loss of PAH due to activities other than sorption onto the sorbents. The PAH loss was between 1 and 12%, much lower than the PAH removal by the sorption process. For all seven PAH solutions, cattail fiber exhibited much higher sorption capacities than the other two sorbents. For acenaphthylene, anthracene, and fluoranthene solutions, polyester fiber showed higher sorption capacities than kapok fiber while the sorption capacity for naphthalene solution of kapok fiber was higher than that of polyester fiber. However, they showed similar sorption capacities for the other PAH solutions. The curves in the figures are the Freundlich model fittings of the data. Table 4.2 summarizes the characteristics of the fittings, the Freundlich constant (K_F), Freundlich exponent ($1/n$), and coefficient of determination (r^2). The sorption data tended to agree the Freundlich model. The r^2 value tended to be higher for PAHs with lower molecular weights. The isotherm tests of the low molecular weight PAHs were prepared at higher concentrations (due to high water solubilities) than the high molecular weight PAHs and in turn may be more accurate. Since the $1/n$ values were closed to 1.00, the sorption isotherms slightly deviated from linear sorption. Cattail fiber presented the highest K_F values in all cases agreeing the results shown in the figures. This indicates that cattail fiber had the highest PAH sorption capacities among the tested sorbents.

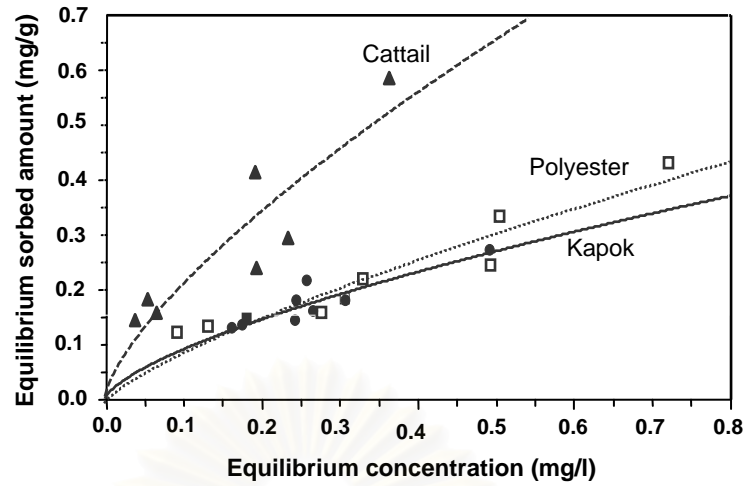


Figure 4.4 Sorption isotherms for naphthalene solution

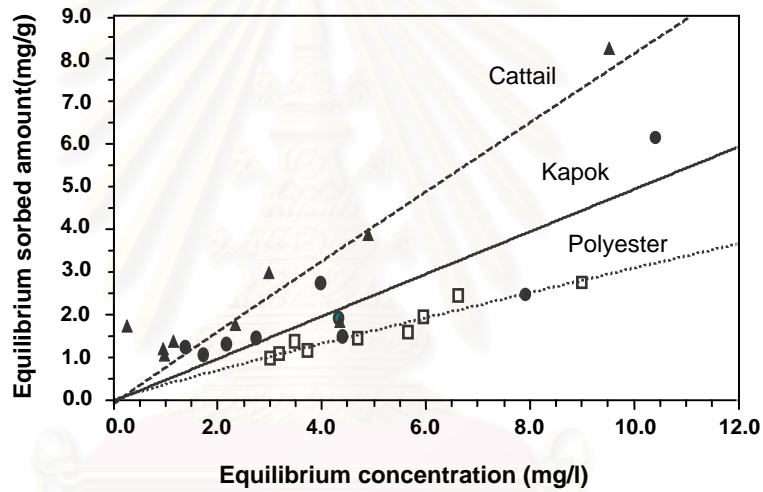


Figure 4.5 Sorption isotherms for acenaphthene solution

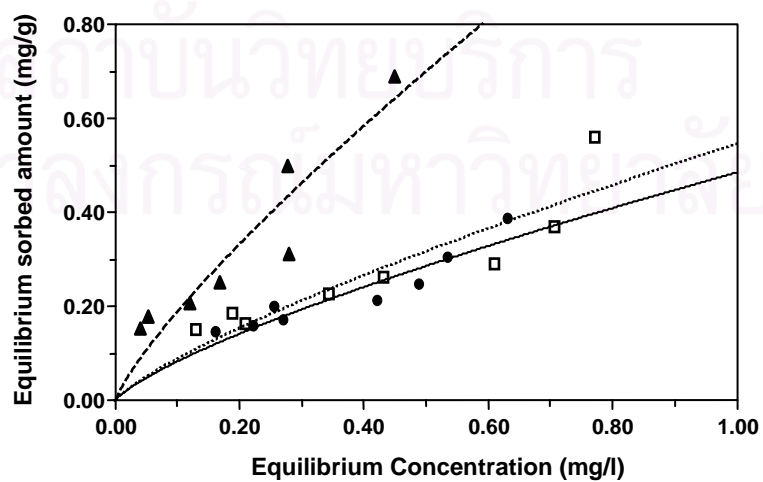


Figure 4.6 Sorption isotherms of acenaphthylene solution

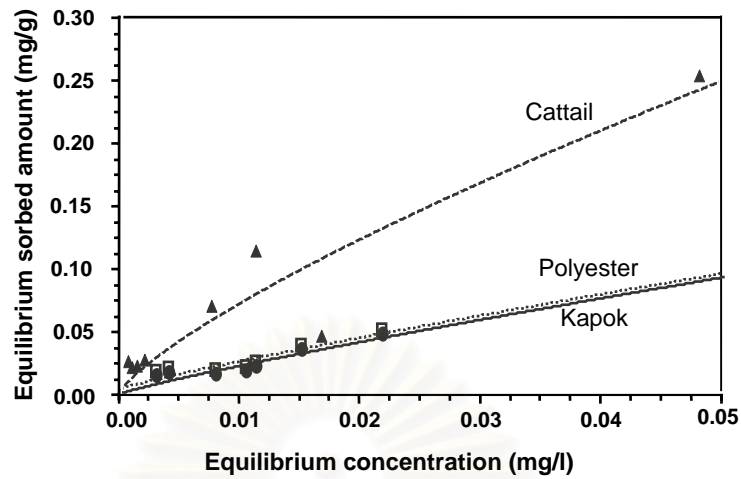


Figure 4.7 Sorption isotherms for fluorene solution

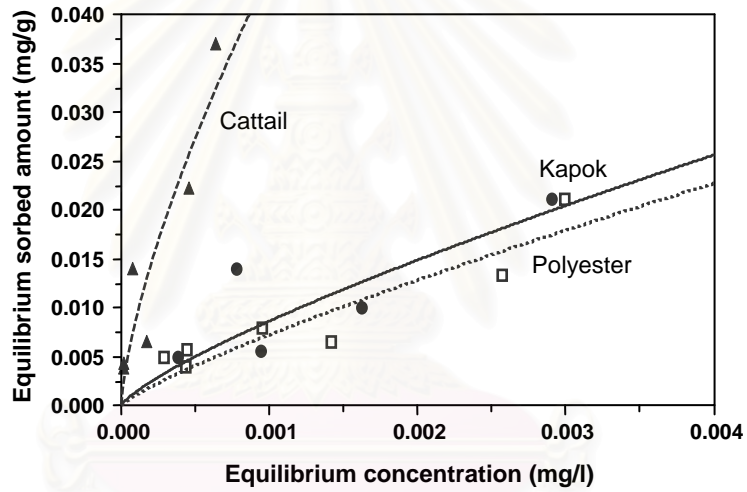


Figure 4.8 Sorption isotherms for phenanthrene solution

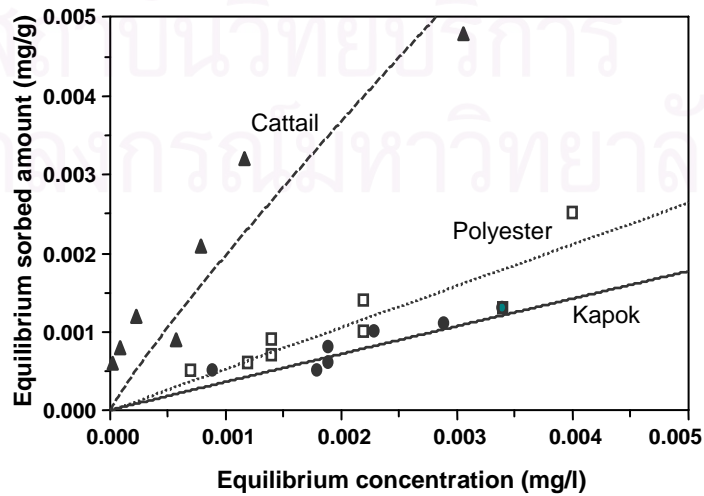


Figure 4.9 Sorption isotherms for anthracene solution

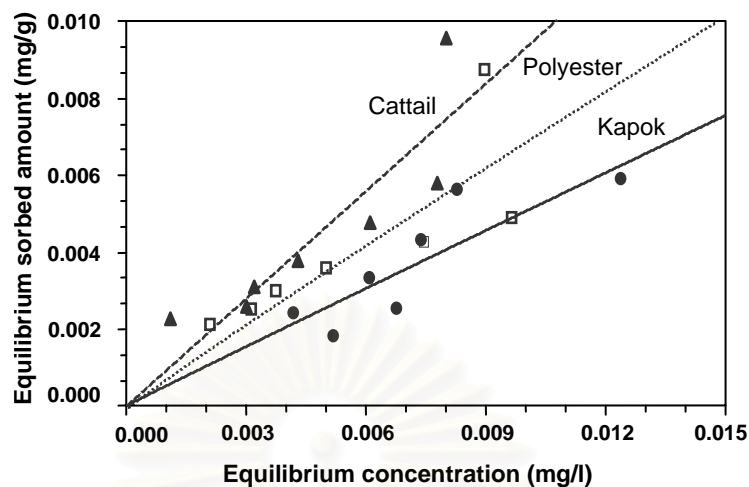


Figure 4.10 Sorption isotherms for fluoranthene solution

Table 4.2 K_{ow} of tested PAHs and sorption coefficients from the Freundlich isotherm

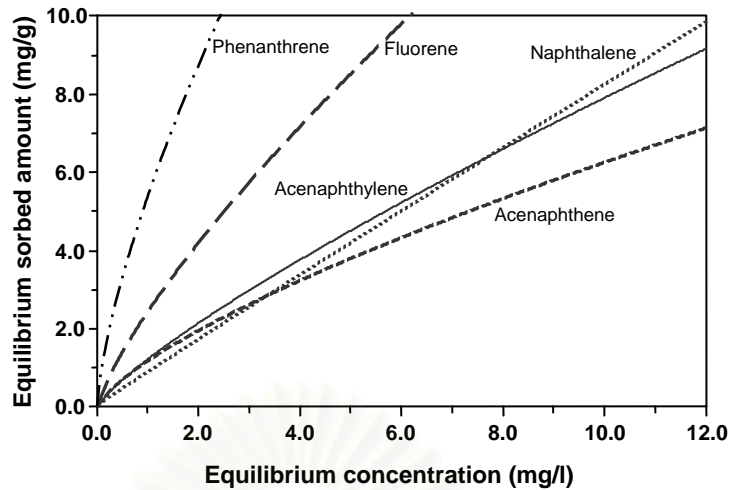
Sorbents	PAHs	Log K_{ow}	K_F	1/n	r^2
Cattail	Naphthalene	3.37	0.86	0.98	0.85
	Acenaphthene	3.98	1.21	0.71	0.81
	Acenaphthylene	4.07	1.23	0.81	0.86
	Fluorene	4.18	2.49	0.77	0.88
	Phenanthrene	4.46	5.41	0.70	0.86
	Anthracene	4.50	0.96	0.89	0.83
	Fluoranthene	4.90	0.93	1.00	0.76
Polyester	Naphthalene	3.37	0.37	0.93	0.92
	Acenaphthene	3.98	0.52	0.76	0.90
	Acenaphthylene	4.07	0.55	0.78	0.81
	Fluorene	4.18	1.34	0.81	0.88
	Phenanthrene	4.46	2.15	0.82	0.85
	Anthracene	4.50	0.51	0.99	0.83
	Fluoranthene	4.90	0.57	0.96	0.64
Kapok	Naphthalene	3.37	0.50	0.99	0.77
	Acenaphthene	3.98	0.43	0.67	0.81
	Acenaphthylene	4.07	0.49	0.76	0.86
	Fluorene	4.18	1.26	0.88	0.83
	Phenanthrene	4.46	1.95	0.78	0.71
	Anthracene	4.50	0.33	0.98	0.81
	Fluoranthene	4.90	0.48	0.99	0.74

The PAH sorption of cattail and kapok fibers was possible because of their hydrophobic characteristics. PAH molecules have high octanol-water partition coefficient (K_{ow}) and tend to sorb on hydrophobic surfaces. The sorption mechanism

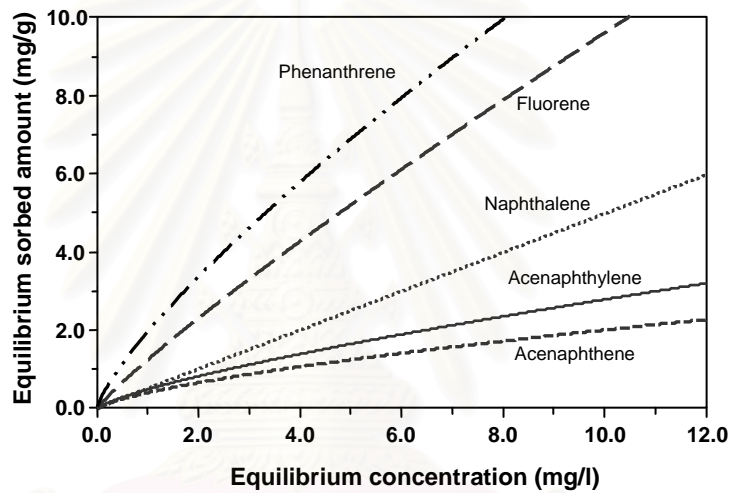
occurs through the interaction between the surface wax of cattail and kapok fibers and PAH molecules (Ratpukdi, 2002). The PAH sorption by polyester fiber was expected because it is a commercial sorbent. The higher affinity between PAHs and cattail fiber may be because the fiber has a higher specific area (surface area per mass) than the other two sorbents. Cattail fiber used in this study was the pollen part, which was very small in size compared to the other two fibers.

Figure 4.11 compares the sorption isotherms of PAHs in group 1, namely naphthalene, acenaphthylene, acenaphthene, fluorene, and phenanthrene, for each sorbent. It can be observed that the PAH sorption capacities of all three sorbents tended to increase with increasing K_{ow} of the PAHs. Boving and Zhang (2004) also reported that the PAH removal efficiency of aspen wood increased as PAH hydrophobicity increased. Same for group 2, fluoranthene, which has higher K_{ow} , also had a higher sorption capacity than anthracene for all sorbents (Figure 4.12). These results concur with K_F reported in Table 4.2.

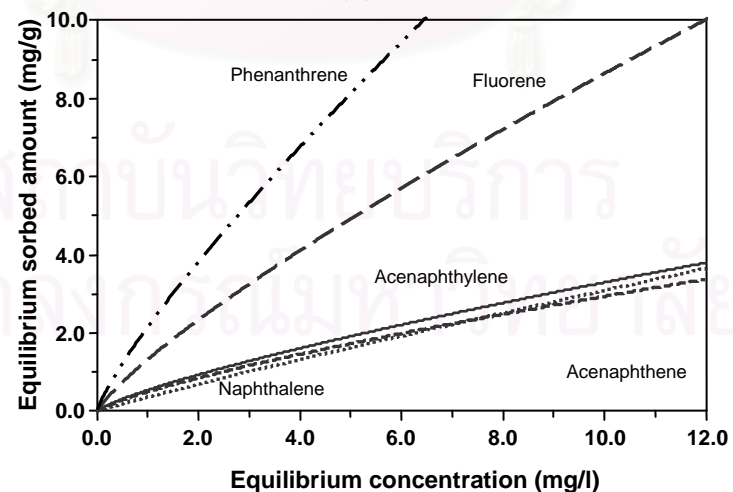
Group 2 PAHs have higher K_{ow} values than group 1 PAHs but their sorption capacities were lower than those of group 1. This may be because of the difference in experiment procedures. As mentioned in Chapter 3, the group 2 PAHs did not readily dissolve in water thus their samples were prepared in 40% methanol. The high amount of methanol in the water sample may affect on the sorption characteristics of the PAHs. The affinities between PAHs and methanol are higher than those between PAHs and water. As a result, the partitioning of PAHs to the sorbents decreased with increasing methanol in the solutions.



(a)

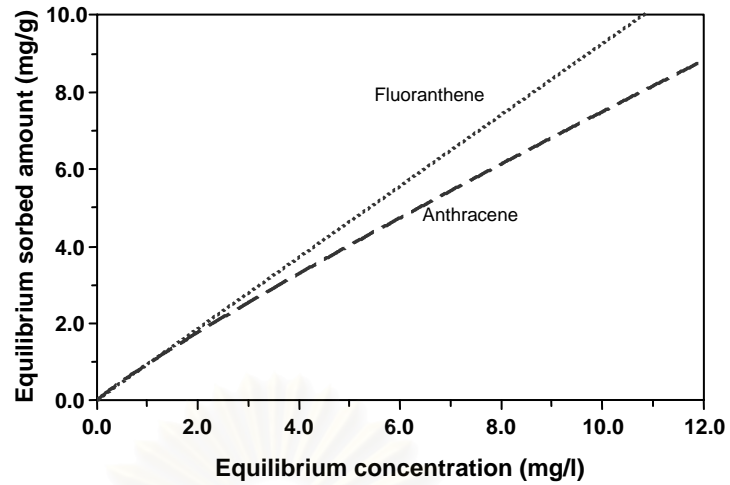


(b)

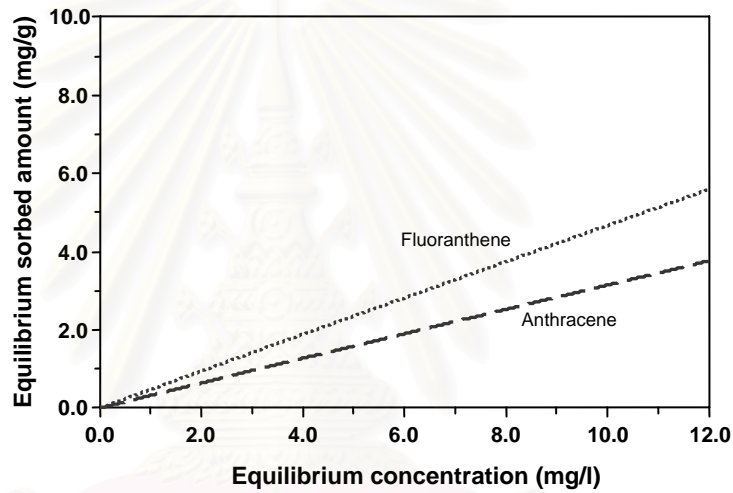


(c)

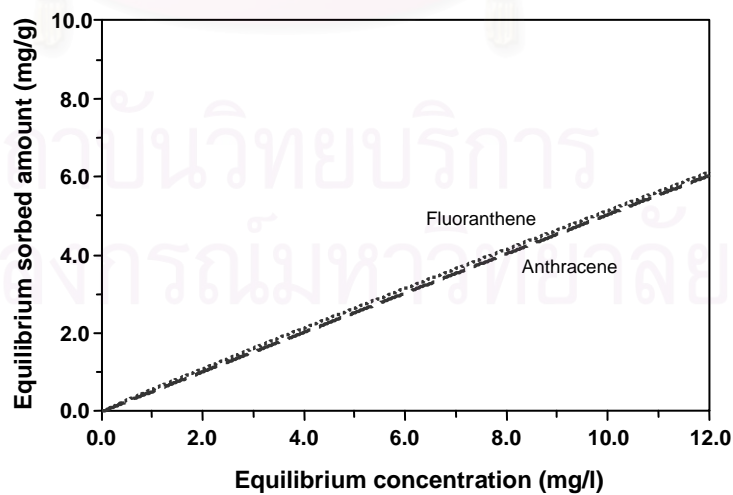
Figure 4.11 Comparison of sorption isotherms among naphthalene, acenaphthylene, acenaphthene, fluorene, and phenanthrene (group 1 PAHs) of (a) Cattail, (b) Kapok, and (c) Polyester fibers



(a)



(b)



(c)

Figure 4.12 Comparison of sorption isotherms between fluoranthene and anthracene (group 2 PAHs) of (a) Cattail, (b) Kapok, and (c) Polyester fibers

4.1.2.2 Competitive Sorption Test

Experimental data for the binary solute sorption of the acenaphthylene-acenaphthene system of cattail, kapok, and polyester sorbents are shown in Figures 4.13-4.15, respectively. Figures 4.16-4.18 present the same type of data for the naphthalene-acenaphthene system. The IAST model was used to predict the competitive sorption isotherm in comparison to the experimental isotherm. The model predictions are shown along with the experimental data in Figures 4.13-4.18. The model underestimated the PAH sorption capacities for all cases. However, the differences in the sorption capacities between each pair of PAHs predicted by the model were comparable to the experimental results for most cases. The IAST model is based on the assumption that all sorptive sites are available to any components in the mixtures. The difference between the model prediction and experimental data was observed because the sorbate molecules do not have equal access to the same sorption site as the IAST model assumes. Some sites of the tested sorbents might have small pores that were available for only small molecules. Thus, some sorption sites might not experience the competitive effect.

For the acenaphthylene-acenaphthene system, the sorption capacities for the two PAHs were not much different for all three sorbents. This may be because acenaphthylene and acenaphthene are close in their hydrophobicity. Cattail and polyester fibers exhibited more sorption capacities for acenaphthene than naphthalene in the naphthalene-acenaphthene system while the two PAHs had similar affinities to kapok fiber. These observations are consistent with the results from the noncompetitive sorption test. As mentioned in Section 4.1.2.1, acenaphthene had higher sorption capacity than naphthalene because it was more hydrophobic. Therefore, in the competitive sorption system, acenaphthene outcompeted naphthalene.

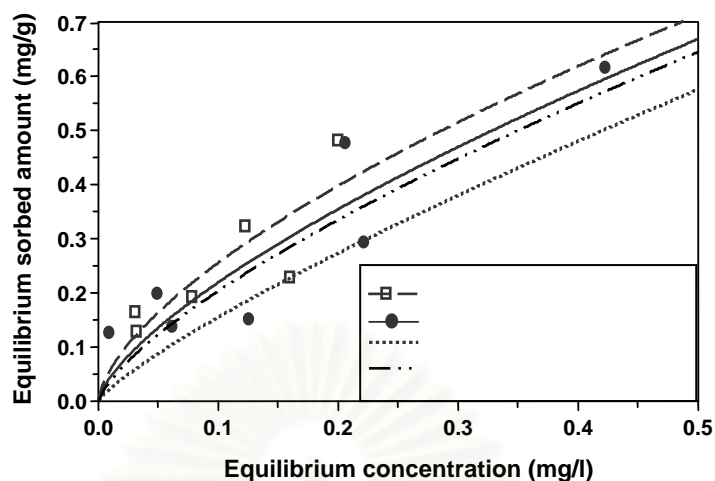


Figure 4.13 Comparison between the experimental and IAST model predicted isotherms of the cattail sorbent in the acenaphthylene–acenaphthene system

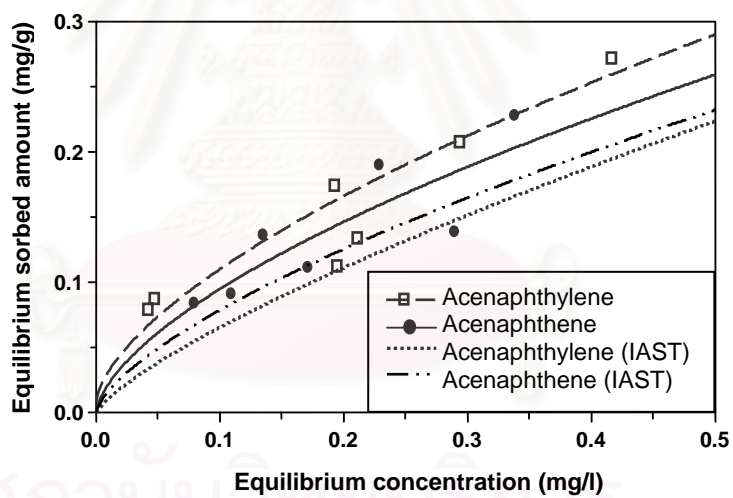


Figure 4.14 Comparison between the experimental and IAST model predicted isotherms of the kapok sorbent in the acenaphthylene–acenaphthene system

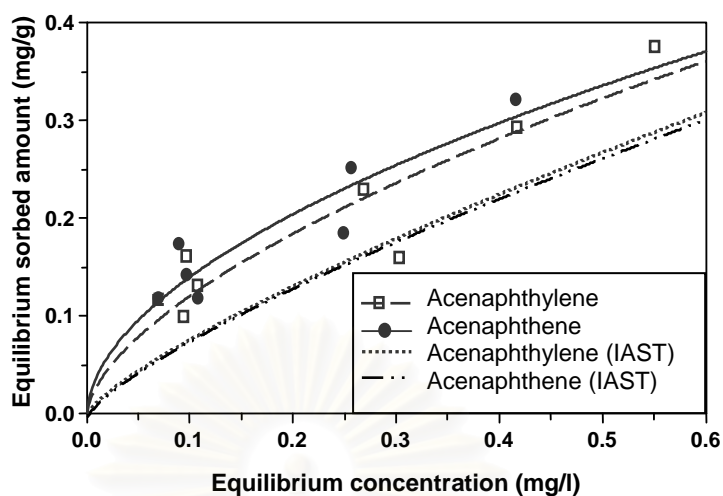


Figure 4.15 Comparison between the experimental and IAST model predicted isotherms of the polyester sorbent in the acenaphthylene–acenaphthene system

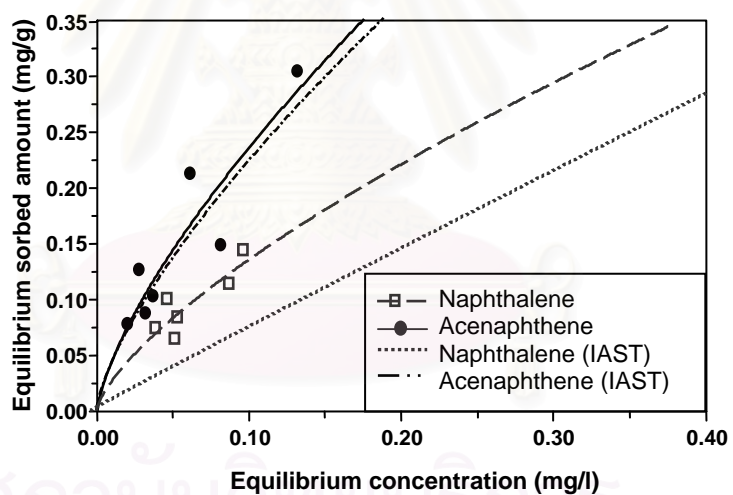


Figure 4.16 Comparison between the experimental and IAST model predicted isotherms of the cattail sorbent in the naphthalene–acenaphthene system

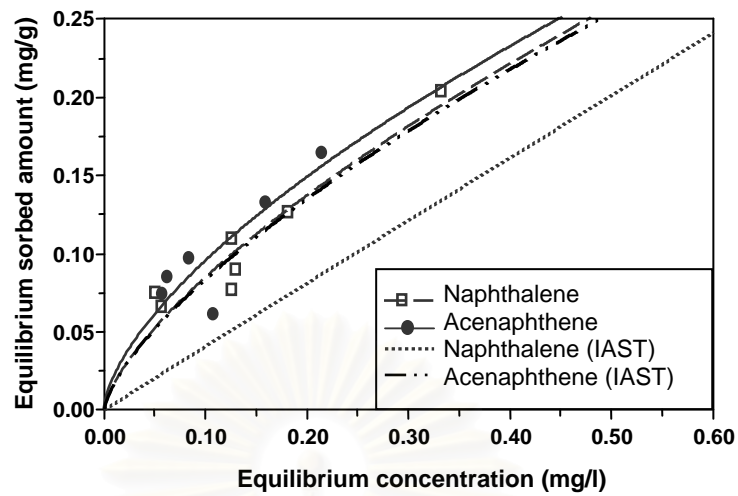


Figure 4.17 Comparison between the experimental and IAST model predicted isotherms of the kapok sorbent in the naphthalene–acenaphthene system

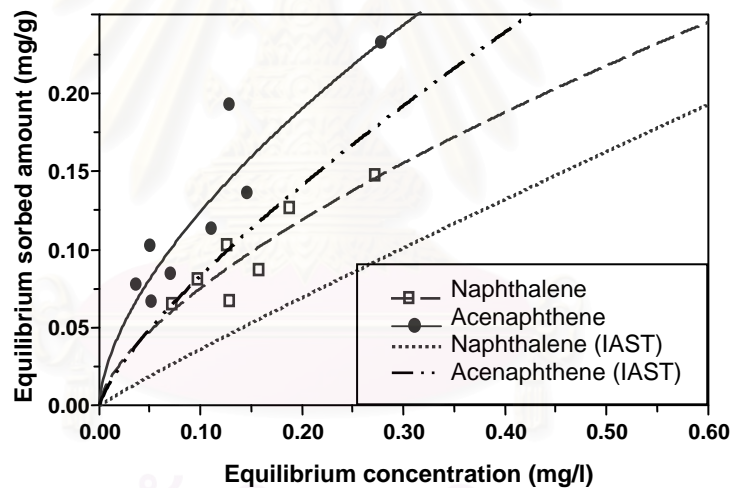


Figure 4.18 Comparison between the experimental and IAST model predicted isotherms of the polyester sorbent in the naphthalene–acenaphthene system

The fit of the IAST model to the experimental data was determined using the r^2 . The equation is defined as:

$$r^2 = 1 - [\Sigma(q_e - q_c)^2 / \Sigma(q_e - q_m)^2] \quad (1)$$

where q_e , q_c , and q_m are the experimental and predicted data, and the average of the experimental values, respectively.

Most predicted results showed not good fitness to the experimental data. These concurred with the discussion above that the model underestimated the PAH sorption capacities. However the calculated data in the sorption of acenaphthene by cattail fiber in both naphthalene-acenaphthene and acenaphthylene-acenaphthene systems showed good agreement with the experimental data as their r^2 quite high (0.81 and 0.79, respectively).

Tables 4.3 and 4.4 present the sorption coefficients of the acenaphthylene–acenaphthene and naphthalene–acenaphthene systems, respectively. The sorption capacities of all three sorbents in the bi-solute systems were slightly lower than those in the single-solute systems suggesting there were a weak degree of competitive sorption between the PAHs in the bi-solute systems. As $1/n$ values of the bi-solute systems were lower than those in the single-solute system, the sorption isotherms of the bi-solute systems tend to have higher degrees of nonlinearity. The sorption coefficient calculated from the IAST model ($K_{F,IAST}$) showed a similar trend. They tended to be slightly lower than the sorption coefficients from the bi-solute system test (K_F) for most PAHs. The difference between $K_{F,IAST}$ and K_F were close among the three sorbents. This suggests that the capability of the IAST model to predict the sorption coefficient for the three sorbents were comparable.

Table 4.3 Sorption coefficients of the acenaphthylene–acenaphthene system

Sorbent	PAH	Bi-solute system			Single-solute system			$K_{F,IAST}^a$
		K_F	$1/n$	r^2	K_F	$1/n$	r^2	
Cattail	Acenaphthylene	1.11	0.64	0.71	1.23	0.81	0.86	1.01
	Acenaphthene	1.08	0.69	0.79	1.21	0.71	0.81	1.06
Polyester	Acenaphthylene	0.49	0.61	0.85	0.55	0.78	0.81	0.46
	Acenaphthene	0.49	0.54	0.85	0.52	0.76	0.90	0.45
Kapok	Acenaphthylene	0.44	0.63	0.85	0.49	0.76	0.86	0.38
	Acenaphthene	0.40	0.62	0.71	0.43	0.67	0.81	0.37

^a $K_{F,IAST}$ is the calculated Freundlich constant from the IAST model

Table 4.4 Sorption coefficients of the naphthalene–acenaphthene system

Sorbent	PAH	Bi-solute system			Single-solute system			$K_{F,IAST}^a$
		K_F	1/n	r^2	K_F	1/n	R^2	
Cattail	Naphthalene	0.70	0.70	0.74	0.86	0.98	0.85	0.71
	Acenaphthene	1.20	0.70	0.83	1.21	0.71	0.81	1.15
Polyester	Naphthalene	0.34	0.66	0.79	0.37	0.93	0.92	0.31
	Acenaphthene	0.5	0.61	0.83	0.52	0.76	0.90	0.48
Kapok	Naphthalene	0.42	0.69	0.90	0.50	0.99	0.77	0.40
	Acenaphthene	0.42	0.64	0.74	0.43	0.67	0.81	0.41

^a $K_{F,IAST}$ is the calculated Freundlich constant from the IAST model

4.1.3 Desorption Test

Figures 4.19 – 4.23 show the PAH desorption test results for naphthalene, acenaphthene, acenaphthylene, fluorene, and phenanthrene, respectively. The degree of desorption is represented by the mass of desorbed PAH divided by the mass of PAH on sorbent. Only the data for 5 PAHs are presented because fluoranthene and anthracene did not desorb from all three sorbents. Acenaphthene desorbed substantially more than the other four PAHs. The desorption tended to be less for PAHs with higher hydrophobicity (K_{ow}). Naphthalene was excluded from this trend. The reason may be due to the small size of naphthalene molecule (two-benzene ring compound), which may fit well in the small pore size of the fibers. The PAH retention ability of polyester fiber was the best but was not much higher than that of cattail fiber except for naphthalene. The desorption of PAHs increased with increasing desorption time. The desorption rates of most PAHs from kapok fiber were higher than those of the other two sorbents. PAHs tended to increasingly desorb from kapok fiber with time.

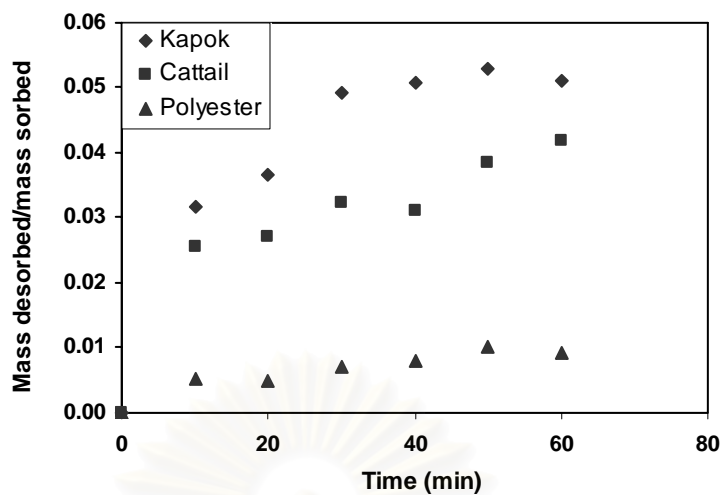


Figure 4.19 Desorption of naphthalene

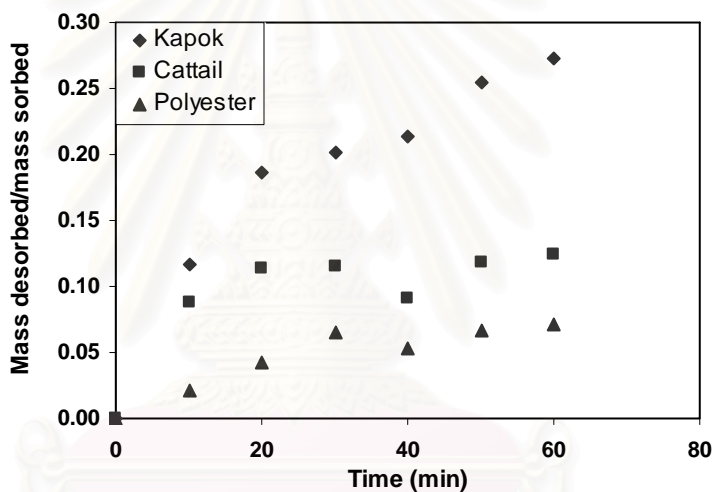


Figure 4.20 Desorption of acenaphthene

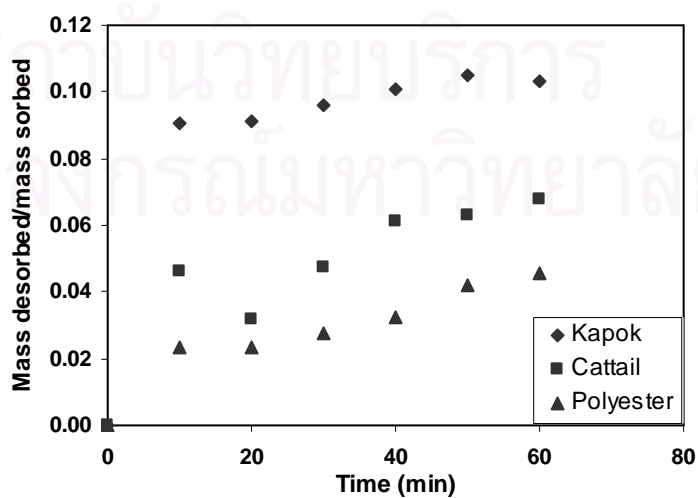


Figure 4.21 Desorption of acenaphthylene

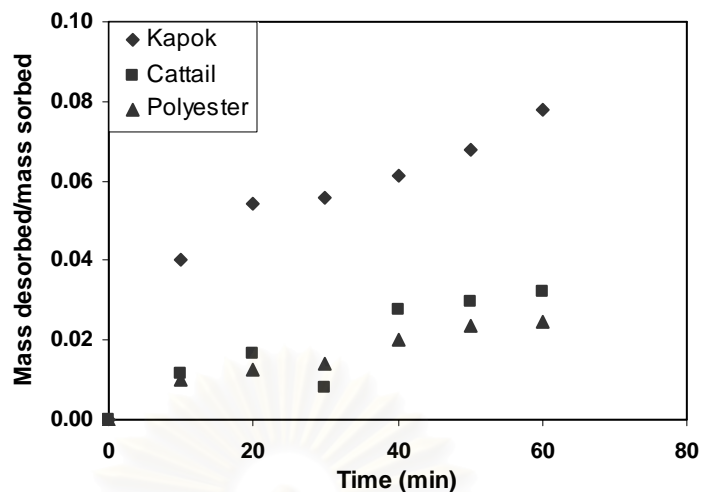


Figure 4.22 Desorption of fluorene

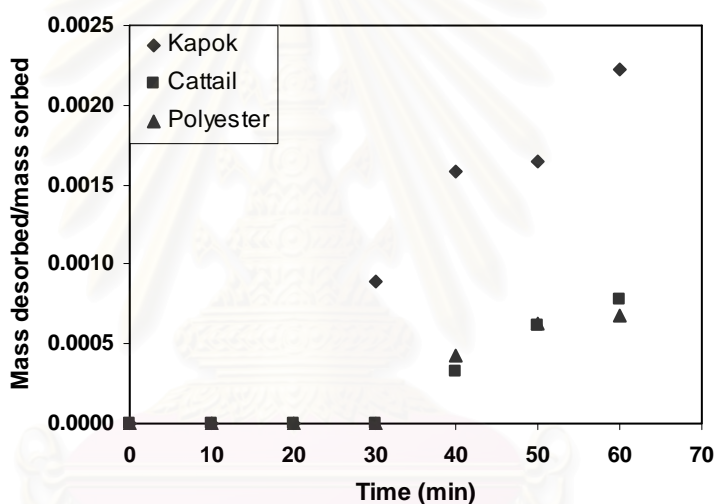


Figure 4.23 Desorption of phenanthrene

4.2 Column Experiment

4.2.1 Non-competitive experiment

The noncompetitive column experiment was conducted for all of PAHs in group 1. For group 2 PAHs, only fluoranthene was studied because the sorption characteristics of fluoranthene and anthracene were not much different according the batch sorption and desorption results. Figures 4.24 – 4.29 show the results for naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, and fluoranthene, respectively. Based on the shape of the breakthrough curves, which was

generated by plotting between treated volumes of PAH solution and relative effluent concentrations, most compounds exhibited similar sorption and desorption characteristics. The results showed that one gram of the sorbents removed 0.08 – 10.82 mg of PAHs. For naphthalene, cattail and kapok fibers showed similar sorption capacities, which were slightly higher than that of polyester fiber. The breakthrough for polyester column occurred right from the beginning of the experiment. Thus, polyester cannot completely remove naphthalene from the solution. The result of acenaphthene showed that the sorption capacities of polyester and cattail fibers were similar and were higher than that of kapok fiber. Desorption of acenaphthene from the three sorbents were not much different. For acenaphthylene, polyester exhibited the highest sorption capacity while kapok fiber showed the lowest sorption capacity. The breakthrough of polyester column occurred from the beginning, 100% removal of acenaphthylene could not be achieved by using polyester fiber. Similar to the results for acenaphthene, desorption of acenaphthylene from the three sorbents were not much different. For fluorene, the sorption capacity of polyester fiber was similar to that of cattail fiber and slightly higher than that of kapok fiber. However, all sorbents were similar in their fluorene desorption. One gram of polyester, cattail, and kapok fibers removed 421 μg , 395 μg , and 343 μg of fluorene, respectively. These sorbents have higher fluorene sorption capacities than that of aspen wood, which is 25.5 $\mu\text{g/g}$ (Boving and Zhang, 2004). The sorption result of phenanthrene showed that the sorption capacity of polyester fiber was the highest among the three sorbents. Kapok and cattail were not much different in their sorption capacities. Phenanthrene desorption of the three sorbents were similar. The sorption result of fluoranthene was similar to that of naphthalene; the polyester fiber had the lowest sorption capacity. However, desorption of fluoranthene for all three sorbents was alike.

Kapok fiber tended to provide the lowest sorption capacity in the column test, which agreed with the results from batch test. For acenaphthene and fluorene, cattail and polyester fibers showed similar sorption capacities. For acenaphthylene and phenanthrene, polyester fiber had higher sorption capacities than cattail fiber but for naphthalene and fluoranthene cattail fiber was better. The sorption capacities of the three sorbents tested in the column were higher than those observed in the batch test. For the column tests, one gram of cattail, kapok, and polyester fibers removed 0.124 - 10.821 mg, 0.126 - 9.492 mg, and 0.083 - 5.277 mg of PAHs, respectively. For the

batch tests, one gram of cattail, kapok, and polyester fibers removed 0.019 – 7.488 mg, 0.010 - 4.205 mg, and 0.013 – 3.025 mg of PAHs, respectively. Note that the amounts of PAHs removal in the batch test were calculated using the Freundlich model using the Freundlich constants in Table 4.2.

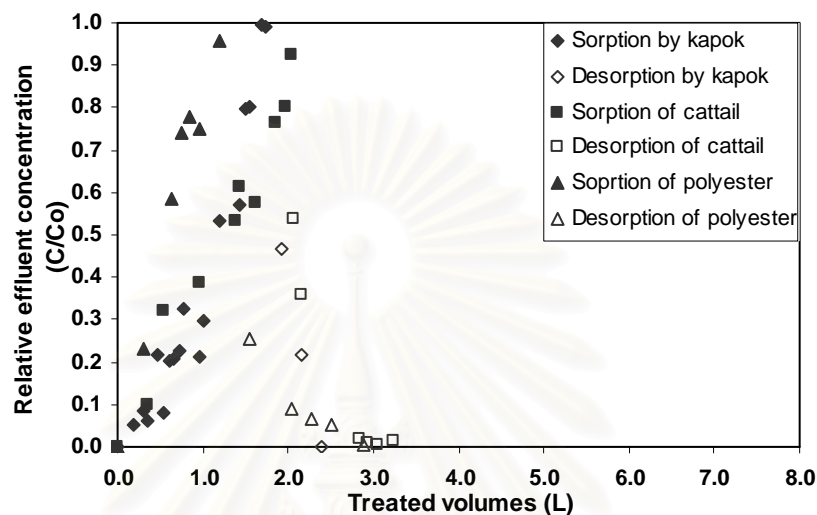


Figure 4.24 Sorption and desorption results for naphthalene in the non-competitive column test

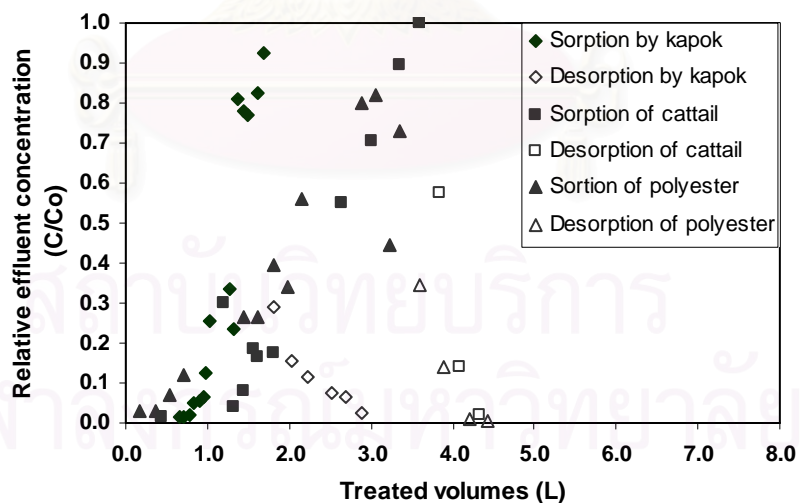


Figure 4.25 Sorption and desorption results for acenaphthene in the non-competitive column test

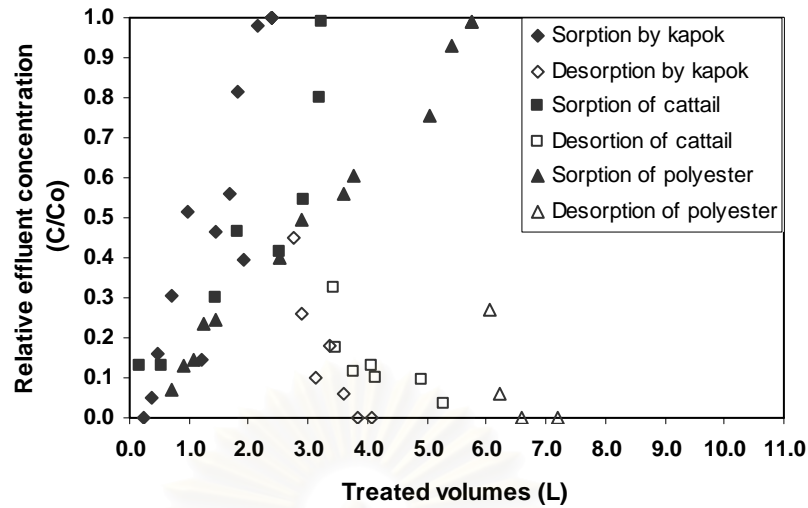


Figure 4.26 Sorption and desorption results for acenaphthylene in the non-competitive column test

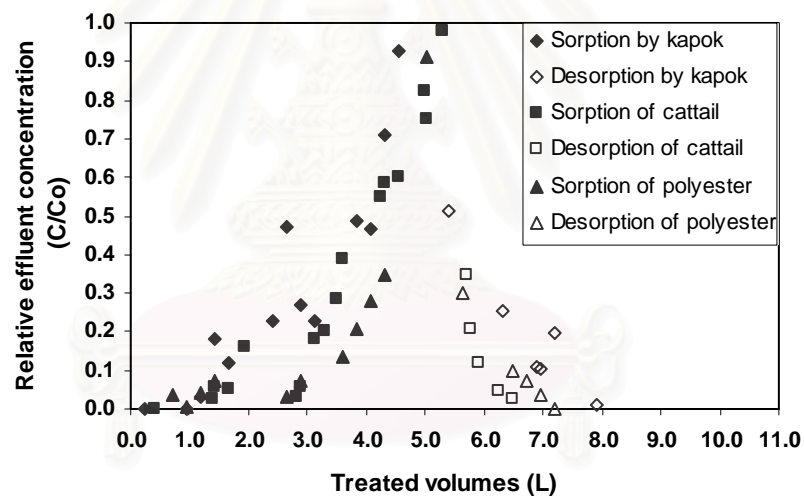


Figure 4.27 Sorption and desorption results for fluorene in the non-competitive column test

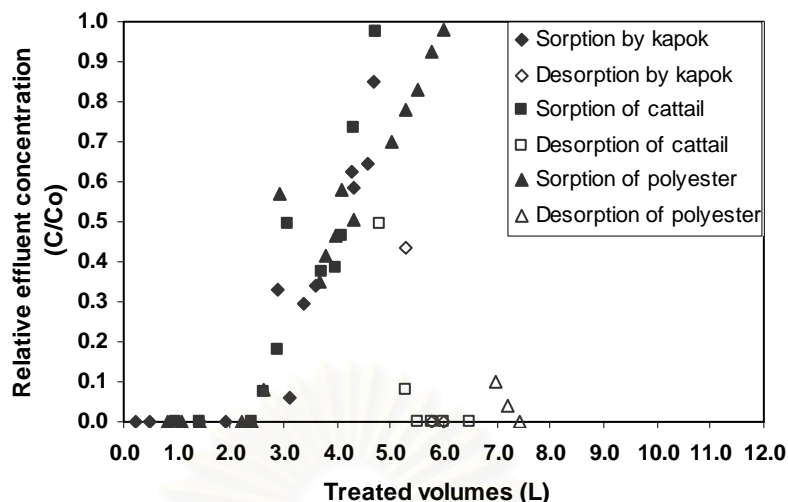


Figure 4.28 Sorption and desorption results for phenanthrene in the non-competitive column test

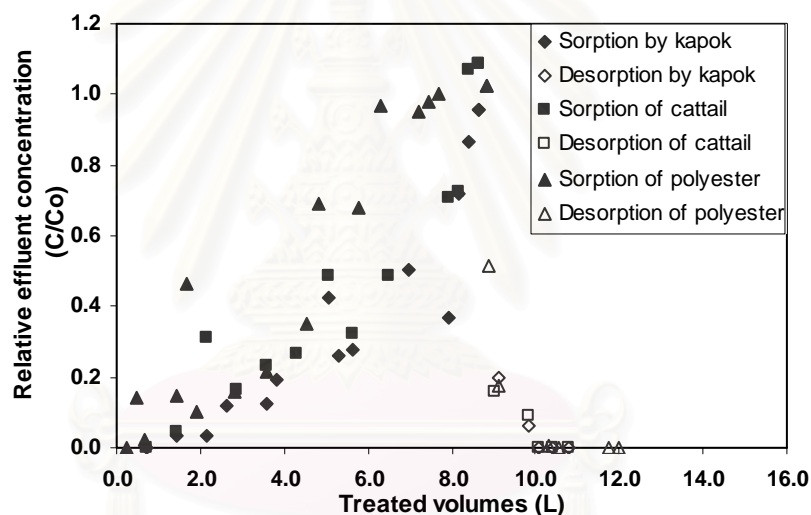


Figure 4.29 Sorption and desorption results for fluoranthene in the non-competitive column test

Table 4.5 summarizes the mass desorbed and mass desorbed/mass sorbed (%) of PAHs from the sorbents. Percent of mass desorbed/mass sorbed of PAHs tended to be less for PAHs with higher hydrophobicity. This was similar to the desorption results from the batch tests except for the desorption of naphthalene. Similar results to the batch test, the PAH retention ability of kapok fiber was the lowest. Polyester fiber had slightly higher retention abilities than cattail fiber for most PAHs excluding naphthalene and fluoranthene.

Table 4.5 Desorption amounts of PAHs from the column experiment

Sorbents	PAHs	Mass desorbed (ug/g of sorbent)	Mass desorbed/mass sorbed (%)
Cattail	Naphthalene	1,570.49	14.51
	Acenaphthene	312.58	12.99
	Acenaphthylene	298.98	10.44
	Fluorene	27.70	7.01
	Phenanthrene	8.34	4.32
	Fluoranthene	3.37	2.73
Polyester	Naphthalene	1,673.79	31.72
	Acenaphthene	204.65	8.58
	Acenaphthylene	146.19	3.96
	Fluorene	23.72	5.63
	Phenanthrene	2.60	1.26
	Fluoranthene	4.41	5.29
Kapok	Naphthalene	1,827.94	18.99
	Acenaphthene	221.30	15.06
	Acenaphthylene	418.38	24.25
	Fluorene	60.69	17.71
	Phenanthrene	21.08	11.13
	Fluoranthene	4.37	3.46

4.2.2 Competitive Experiment

Figures 4.30 – 4.32 show the sorption and desorption of the acenaphthylene and acenaphthene mixture in the competitive column tests for cattail, kapok, and polyester fibers, respectively. The same type of data for the naphthalene and acenaphthene mixture is presented in Figures 4.33 – 4.35. In order to compare the desorption characteristics between the two PAHs of the mixtures, the desorption test was started after the C/C_0 values of both compounds in the system were equal to 1. In the acenaphthylene–acenaphthene system, cattail and kapok fibers showed similar sorption capacities, which were slightly lower than polyester fiber. Both acenaphthylene and acenaphthene had similar sorption and desorption characteristics. They exhausted at the same time. The explanation is that the chemical properties: configuration and hydrophobicity, of both two compounds are similar. Both acenaphthylene and acenaphthene in a mixed-solute system were exhausted more rapidly than when they were tested in the single-solute system. The difference was not substantial indicating that competition was weak. For the desorption test, both compounds showed similar desorption trend. At the beginning, the C/C_0 values

rapidly decreased indicating that little amount of PAHs was desorbed from the sorbents. However, when the C/C_0 values were close to zero, they tended to decrease slowly.

The breakthroughs of acenaphthene were slower than those of naphthalene resulting in the exhaustion at later times. Acenaphthene is more hydrophobic than naphthalene and therefore has a higher affinity to the sorbents. However, the desorption behaviors of the two compounds were not much different. Their C/C_0 decreased less rapidly compared to the acenaphthylene-acenaphthene system indicating slightly more desorption. Similar to the results from the acenaphthylene-acenaphthene system, the sorbents were completely impotent earlier in this test compared to the noncompetitive test. Therefore, in the naphthalene-acenaphthene system, there was some degree of competitiveness. Among the three sorbents, cattail fiber showed the highest sorption capacities for both naphthalene and acenaphthene whereas kapok fiber was the lowest capacity sorbent.

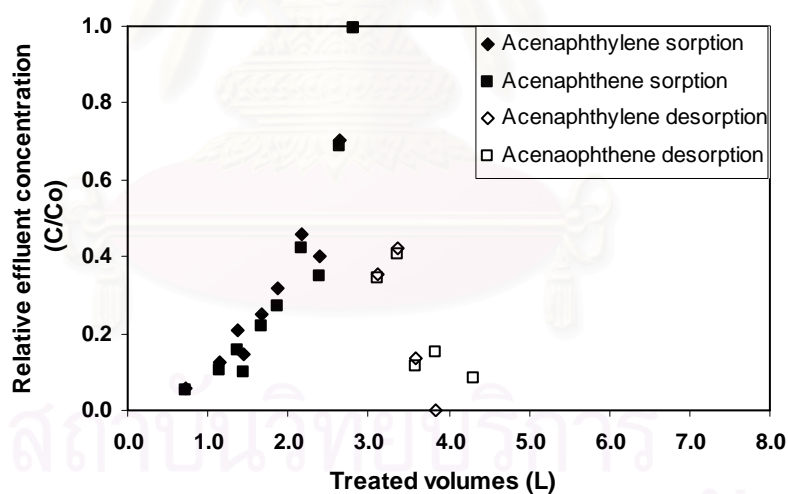


Figure 4.30 Sorption and desorption of acenaphthylene and acenaphthene by cattail in the competitive column test

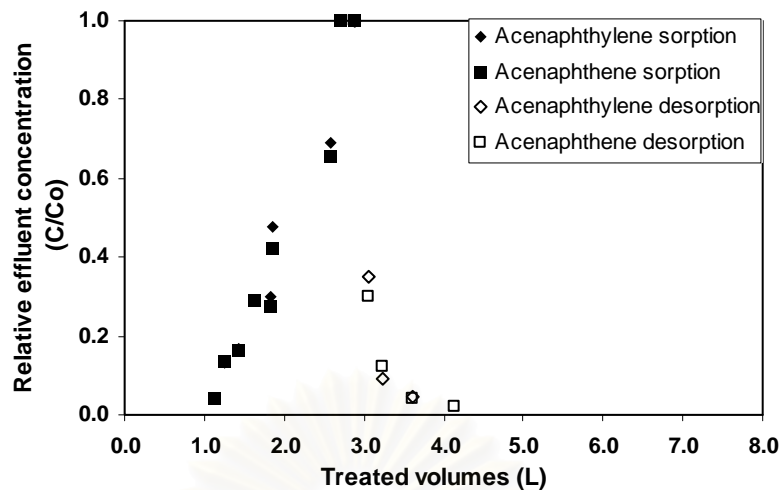


Figure 4.31 Sorption and desorption of acenaphthylene and acenaphthene by kapok in the competitive column test

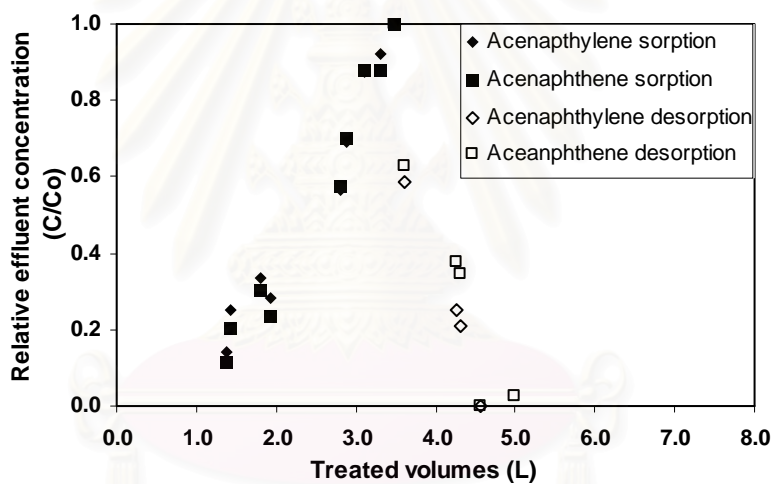


Figure 4.32 Sorption and desorption of acenaphthylene and acenaphthene by polyester in the competitive column test

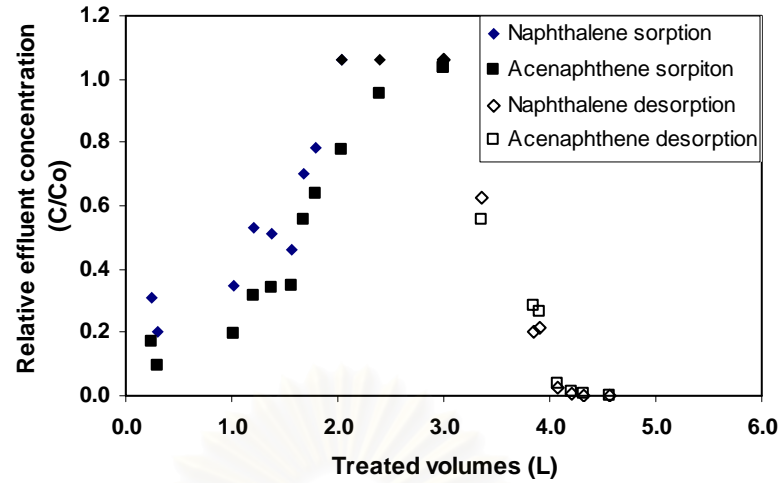


Figure 4.33 Sorption and desorption of naphthalene and acenaphthene by cattail in the competitive column test

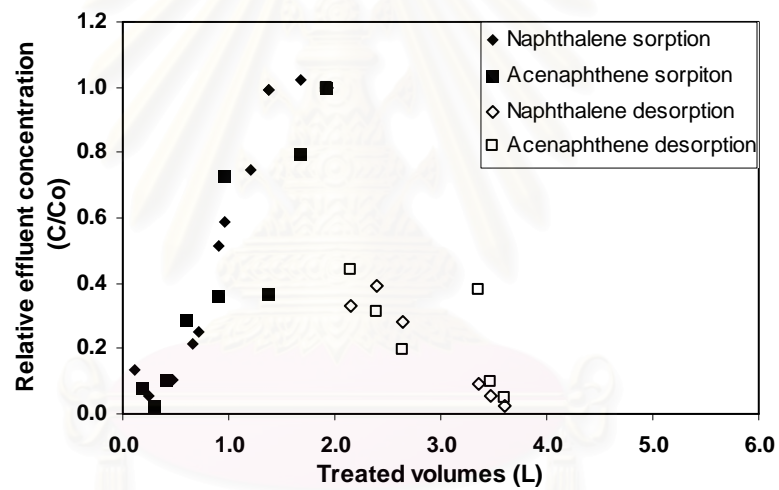


Figure 4.34 Sorption and desorption of naphthalene and acenaphthene by kapok in the competitive column test

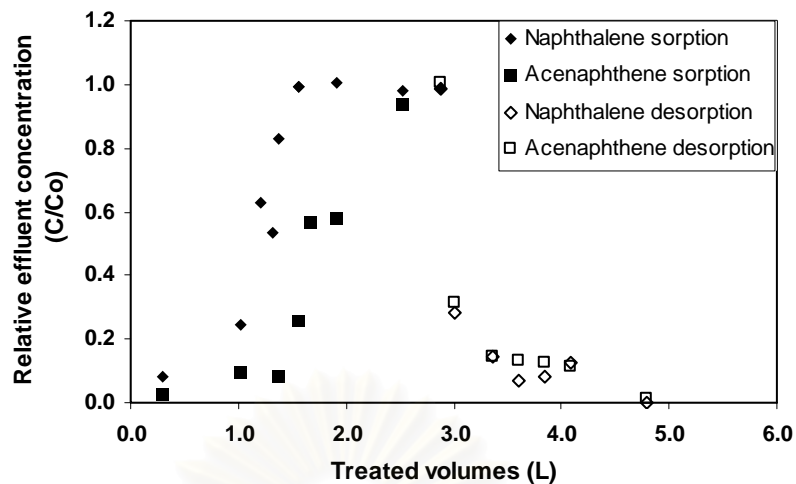


Figure 4.35 Sorption and desorption of naphthalene and acenaphthene by polyester in the competitive column test

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

This study investigated the PAH sorption and retention capacities of two natural fibers, cattail and kapok, and a commercial polyester fiber. The study consisted of batch and column experiments on both noncompetitive and competitive sorption. For the non-competitive sorption batch test, the results demonstrated that the natural fibers and commercial fiber can efficiently remove PAHs from water. Cattail fiber had the highest PAH sorption capacity among the three sorbents. The removal tended to increase with increasing molecular weight and hydrophobicity of the PAHs studied. The sorption could be described well by the Freundlich model. For the competitive batch sorption, the IAST model underestimated the sorption capacity of all three sorbents. The IAST model assumes that all sorptive sites are available to any components in the mixture. The underestimation was probably because there were some surface sites of the sorbents on which there were no competitive effect. In the batch desorption test, cattail fiber had slightly higher PAH desorption than polyester fiber, which provided highest PAH retention. Kapok fiber had lowest PAH retention among the three sorbents. The desorption tended to be less for PAHs with higher hydrophobicity.

For the non-competitive sorption column test, the results indicated that one gram of the sorbents could remove 0.08 – 10.82 mg of PAHs. Kapok fiber tended to have the lowest sorption capacity for most PAHs which agreed with the results from batch test. The sorption capacities of the three sorbents in the column test showed higher value than those in the batch test. For the competitive sorption column test, PAH configuration and hydrophobicity had an effect on PAH sorption and desorption characteristics. In the acenaphthylene–acenaphthene system, two compounds revealed similar sorption and desorption characteristics because they are similar in their configuration and hydrophobicity. On the other hand, the naphthalene–acenaphthene system showed a different result. The breakthrough of acenaphthene progressed

slower than that of naphthalene. It may be due to a higher hydrophobicity of acenaphthene. Both systems showed that PAHs in the bi-solute systems were exhausted more rapidly than in the single-solute systems suggesting some degree of competitive sorption.

Cattail fiber can potentially be used as a catch basin insert sorbent for removing PAHs from runoff. There are many advantages for using cattail fiber to remove PAHs. Cattail is generally found in the environment, easily degraded, and inexpensive. Proper incineration can be a safe way to dispose of PAH loaded fiber. Kapok fiber also showed high PAH sorption capacity but its retention capability was low for some PAHs and therefore is not as suitable as cattail fiber. Comparison of the PAH removal performances between cattail and commercial polyester fibers showed that the performance of cattail fiber was as good as polyester fiber. Cattail fiber exhibited higher sorption capacity and its retention capability was not much lower than polyester fiber. One gram of cattail fiber can remove PAHs up to 10 mg while PAH concentration in runoff is in nanogram or microgram units. Therefore, using of cattail fiber will not require frequent replacement of the virgin fiber. The sorption capacities of cattail fiber were not significantly affected under the competitive sorption conditions, which are better represents of real runoff.

It is recommended that characteristics of the tested fibers, such as surface area, functional groups, or pore sizes, should be studied. These characteristics may be used to explain the experimental results. According to the high PAH sorption capacities of cattail fiber in the laboratory scale tests, pilot and field tests of cattail fiber with real runoff are recommended. The efficiencies of the fibers in the field may be different from the experiments. The degradation and lifetime of the natural sorbents should also be studied. The total costs of using natural sorbents, starting from acquisition to the disposal step, should be evaluated and compared with the commercial sorbents. Moreover, removal of other contaminants by these sorbents may be an interesting research topic.

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