

การกำ่าจ้ดน้ำมันในน้ำเสี้ยส้งเคราะห์ของสถาน้บริการน้ำมันโดยใช้วัสดุจากพีชในท้องถื่นเป็นตัวดูดซับ



นาย ธีญ์ลักษณะณ์ ราชภู่ร้ภักดี

สถาบันวิทย์บริการ

จุฬาลงกรณ์มหาวิทยาลัย

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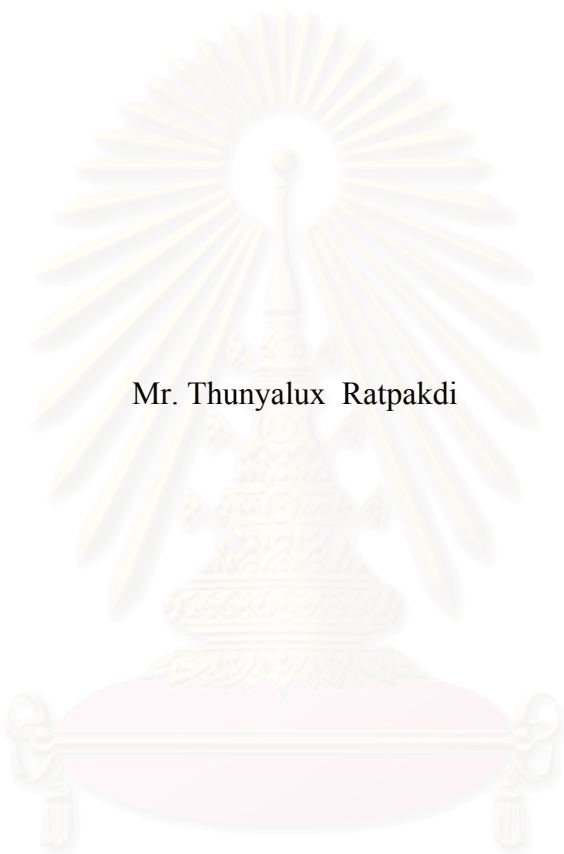
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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

REMOVAL OF OIL AND GREASE FROM SYNTHETIC GAS STATION
RUNOFF USING LOCAL SORBENTS FROM PLANT MATERIALS



Mr. Thunyalux Ratpakdi

สถาบันวิทยบริการ

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Thesis Advisor Associate Professor Wanpen Wirojanagud, Ph.D.
Thesis Co-advisor Assistant Professor Eakalak Khan, Ph.D.

Accepted by the Graduate School, Chulalongkorn University in Partial Fulfillment of
the Requirements for the Master 's Degree

..... Dean of Graduate School
(Professor Suchada Kiranandana, Ph.D.)

THESIS COMMITTEE

..... Chairman
(Assistant Professor Sutha Khaodhiar, Ph.D.)

..... Thesis Advisor
(Associate Professor Wanpen Wirojanagud, Ph.D.)

..... Thesis Co-advisor
(Assistant Professor Eakalak Khan, Ph.D.)

..... Member
(Assistant Professor Nurak Grisdanurak, Ph.D.)

..... Member
(Saroach Boonyakitsombut, Ph.D.)

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Gas station runoff is one of the major sources that contribute oil and grease to receiving waters. Inserts are the devices installed at the inlet of the stormwater catch basins to reduce pollutants including oil and grease. Several commercially available inserts depend on sorbents for the removal of contaminants. However, most of the insert sorbents are synthetic and costly. In this study, the uses of fourteen types of local natural sorbents, specifically plant biomass, which are less expensive and more biodegradable than synthetic sorbents, as insert materials for oil removal from gas station runoff were investigated. Bench scale batch, column, and flume experiments were conducted to evaluate the oil removal capability of biomass sorbents and synthetic sorbents (for comparison). For the batch experiment, with mechanical emulsified oil samples, the results showed that oil would rather be attached to the wall of sample containers than sorbents. In case of chemically emulsified oil samples, only small amounts of oil were adsorbed to the sorbents. The results of the column experiment also confirmed that chemically emulsified oil could not be removed by either biomass or synthetic sorbent. The flume experiment included oil sorption and desorption tests. The sorbents from the sorption test were employed in the desorption test. The results of the oil sorption test showed that *Salvinia* sp. and polyester fiber were the sorbents that provided the least effluent oil concentrations. For the desorption test, however, the polyester fiber exhibited the highest amount of oil desorbed. The results from this study provide valuable information on the use of local plant materials as alternative sorbents to remove oil from water runoff.

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น้ำระบายจากสถานีบริการน้ำมันเป็นแหล่งกำเนิดมลพิษแห่งหนึ่งที่ปล่อยน้ำมันและไขมันลง
 สู່แหล่งน้ำตามธรรมชาติ ซึ่งปัญหานี้สามารถจัดการได้โดยติดตั้งอุปกรณ์ดูดซับน้ำมันในระบบระบาย
 น้ำในสถานีบริการน้ำมัน ในปัจจุบันอุปกรณ์เหล่านี้ได้ถูกผลิตเป็นเชิงการค้าและวัสดุส่วนใหญ่ที่ใช้
 ดูดซับน้ำมันเป็นวัสดุสังเคราะห์ย่อยสลายได้ยากและมีราคาสูง งานวิจัยนี้ได้ศึกษาการใช้วัสดุดูดซับที่
 เป็นวัสดุธรรมชาติจากพืช 14 ชนิด ซึ่งมีราคาถูกและย่อยสลายได้ง่ายกว่าวัสดุสังเคราะห์สำหรับ
 ดูดซับน้ำมันในน้ำระบายจากสถานีบริการน้ำมัน งานวิจัยนี้ได้ทำการศึกษาในระดับห้องปฏิบัติการ
 โดยแบ่งการทดลองออกเป็น 3 ขั้นตอน ได้แก่ การทดลองแบบแบตช์ แบบคอลัมน์ และ แบบวาง
 ระบายน้ำ เพื่อหาประสิทธิภาพในการดูดซับน้ำมันของวัสดุจากพืชเปรียบเทียบกับวัสดุสังเคราะห์
 จากการทดลองแบบแบตช์โดยใช้น้ำตัวอย่างที่มีน้ำมันในรูปของอิมัลชันเชิงกลพบว่า น้ำมันส่วนใหญ่
 ติดอยู่ที่ผนังขวดที่ทำการทดลองมากกว่าจะถูกดูดซับโดยวัสดุดูดซับ สำหรับน้ำตัวอย่างที่มีน้ำมันใน
 รูปอิมัลชันเชิงเคมีพบว่าน้ำมันถูกดูดซับได้น้อยมาก นอกจากนั้นผลการทดลองแบบคอลัมน์ยืนยันว่า
 น้ำมันที่อยู่ในรูปอิมัลชันเชิงเคมีไม่สามารถที่จะกำจัดได้แม้ว่าเป็นวัสดุจากพืชหรือวัสดุสังเคราะห์
 สำหรับการทดลองแบบวางระบายน้ำสามารถแบ่งย่อยได้เป็น 2 ขั้นตอนได้แก่ ขั้นตอนการดูดซับ
 น้ำมัน และขั้นตอนการชะน้ำมันออกจากวัสดุที่ดูดซับแล้ว ผลการทดลองในขั้นตอนการดูดซับน้ำมัน
 พบว่าจอกหนู (*Salvinia sp.*) และเส้นใยโพลีเอสเตอร์มีความสามารถในการดูดซับน้ำมันได้ดีกว่าวัสดุ
 ดูดซับชนิดอื่น โดยมีค่าความเข้มข้นของน้ำมันในน้ำทิ้งต่ำที่สุด สำหรับในขั้นตอนการชะน้ำมันพบว่า
 เส้นใยโพลีเอสเตอร์เป็นวัสดุที่น้ำมันถูกชะออกมากที่สุด ผลจากการวิจัยครั้งนี้ให้ข้อมูลที่เป็ประโยชน์
 ในการเลือกใช้วัสดุจากพืชในการดูดซับน้ำมันที่ปนเปื้อนในน้ำ

สหสาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่ออาจารย์ที่ปรึกษา.....

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NOMENCLATURES

BMPs	=	best management practices
BOD	=	biochemical oxygen demand
COD	=	chemical oxygen demand
EMC	=	event mean concentration
HCl	=	hydrochloric acid
IPA	=	isopropanol alcohol
OGS	=	oil grit separator
PAHs	=	polycyclic aromatic hydrocarbons
SPE	=	solid phase extraction
TEO	=	total extractable organic carbon
THC	=	total hydrocarbons
TOC	=	total organic carbon
TSS	=	total suspended solid
VSS	=	volatile suspended solid

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CHAPTER I

INTRODUCTION

1.1 Background

In the past decade, major environmental problems of concern in Thailand have been water and wastewater because the problems are visible and daily life of Thai people is closely connected to waterways. Because of this, the government has legislated the regulation to improve water quality, which forced the facilities to construct or install a wastewater treatment system. In the case of gas stations, owners are only required to install an oil/water separator and to treat domestic wastewater. However, they have no liability for stormwater discharged, in which most of pollutants are released. In addition, stormwater runoff qualities have not been a major concern in Thailand although they have been recognized in the US since early 1970s (Moffa, ed., 1996).

Gas stations (or petrol stations) are one of the major contributors of the pollutants to sewer systems and/or water bodies. Activities at gas stations are not only fueling but also vehicle services, which generate a variety of discharged wastes such as aliphatic hydrocarbons, heavy metals, polycyclic aromatic hydrocarbons (PAHs), sediment, and detergent (WEF, 1995). Smith *et al.* (2000) also found that gas stations contributed the highest total PAHs loading in urban areas.

Runoff from gas stations is one of the main problems resulting from various activities (floor cleaning, car washing, and raining) and consists of a variety of petroleum products. These petroleum products are from used motor oil, fuel oil spill, and also dry deposition of auto exhaust (Stenstrom *et al.*, 1984; Fam *et al.*, 1987; Lopes *et al.*, 2000). They are flushed to storm drain and are trapped by oil/water separator. Nevertheless, hydrocarbons may escape from the system and contaminate receiving waters due to instantaneous peak flow during storm event. These contaminants affect aquatic lives, accumulate in the food chain, and may cause adversary health effects to human. In addition, US.EPA found that oil and grease concentration as low as 10-100 µg/L cause disruption of physiological processes such

as feeding and reproduction in a variety of aquatic organisms (EPA, 1986 cited in Hrachovec and Minton, 2001).

In place where space is limited like gas station, retrofitting existing drainage structures to act as treatment structures may be a practical technique. Catch basin insert is one of the best management practice alternatives that require less space and can be used to reduce pollutant discharge due to water runoff to receiving waters. The system does not need electricity and has no moving part, so there is nothing to break. The device is installed to capture pollutants in existing drainage system by physical and/or chemical and/or biological processes.

In Thailand, the gas station effluent standard has been enforced since May 29 2002 (PCD Thailand, 2002). As a result, using catch basin insert to remove oil and grease may be alternative technologies to improve effluent quality to comply with the regulation.

1.2 Motivation

Nowadays, there are numbers of commercial catch basin inserts or stormwater treatment devices that could be used to remove oil and grease from stormwater runoff (Stenstrom *et al.*, 2000). Most of them rely the use of synthetic sorbents as the insert materials. Examples of these sorbents are such as rubber, polypropylene sorbents, and other material derived from petroleum products. Although the oil and grease removal performance of these sorbents are promising but their costs are expensive (Lau and Stenstrom, 1995). Therefore, the search for less expensive sorbents, but as effective as synthetic sorbents, is needed. In this research, the uses of local materials derived from plants as insert sorbents were experimented. The materials are less expensive than the commercial synthetic sorbents. The costs are only for their collection and preparation because the sorbents are available in local areas and can be obtained for free. In addition, some of them are aquatic weeds (such as *Salvinia* sp.), which decrease aesthetics and interfere the waterway navigation. Utilizing these materials as oil sorbents will provide a side benefit on the removal of these undesirable materials from water environment. Furthermore, wastes from agriculture and wood industries, such as rice husk and wood chip, that have no value and are burdens to environment were experimented in this study.

Many researches studied the uses of plant materials as sorbents for cleaning up oil spill which was relatively high in oil concentration, from 800 mg/L to pure oil (Choi and Cloud, 1992; Choi, 1996; Lee *et al.*, 1999; Ribeiro and Rubio, 1999; Ribeiro *et al.*, 2000). In addition, the studies focused on the oil sorption capacity of sorbents rather than oil concentration remaining in water. In contrast, oil concentration found in runoff was generally low (approximately 25 mg/L) (Stenstrom, et al. 1984; Fam, et al.1987). Moreover, effluent water quality of the treatment systems is one of performance criteria. A limited number of the studies on the application of plant materials to remove oil and grease in stormwater runoff have been conducted (Stenstrom *et al.*, 2000). Therefore, the feasibility of using the local material to remove oil in runoff should be studied to provide more information for field scale application.

1.3 Objective

The main objective of this study is to investigate the possibility of using local materials (biomass), which are cheaper and more biodegradable than commercial products as catch basin insert sorbents to reduce oil from stormwater runoff. The specific objectives are:

1. To determine oil sorption capability of selected biomass sorbents using a batch experiment.
2. To evaluate the effectiveness of the biomass sorbents, selected from the batch experiment, in a bench scale continuous system (flume experiment) at different operation time, hydraulic conditions, and oil effluent concentrations.
3. To compare the results provided by biomass sorbents with those obtained from commercial oil sorbent (polyester fiber) through the flume experiment.

CHAPTER II

LITERATURE REVIEW

2.1 Gas Station Runoff Characteristics

Gas stations (or petrol stations) are one of the major contributors of pollutants to sewer system and/ or water bodies. The pollutants discharged are generated by various service activities at gas station. Table 2.1 describes vehicle-service-related materials and wastes. Because of improper management and disposal of the wastes, they come into contact with water, consequently create runoff pollution.

In the case of dry weather flow, the pollutants are flushed to storm drains by car washing or floor cleaning. These pollutants are inorganic and organic contaminants that are present in both soluble and particulate forms. The results from previous studies on contaminant concentrations, from gas station or related service facilities, are summarized in Table 2.2.

2.1.1 Organic Contaminants

2.1.1.1 Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD)

Sources of organic contaminants in gas station run-off are cleaning chemicals, vehicle fluids, fuel and vehicle exhaust. Vehicle fluid such as antifreeze can enter runoff systems through radiator leakage, spill, and illegal disposal. Engine coolant containing ethylene glycol and propylene glycol can contribute BOD and COD to receiving waters. Moreover, it contains PAHs that are known to be the carcinogen (WEF, 1995; Bay Area Open Space Council, 2001).

Table 2.1 Typical vehicle service wastes (WEF, 1995)

Activity	Waste	Hydrocarbons	Heavy metals	PAHs	CFCs	Sediment	Oil & grease	Acid	Alkalis	Petroleum distillates	Chlorinated compounds	Lead	Asbestos	Solvents	Ethylene/propylene glycol
Fluid replacement	Motor oil and filter, transmission fluid, and lubricants	X	X	X											
	Engine coolant		X	X											X
	Refrigerant				X										
Fueling	Leaks and spill of gasoline and diesel	X	X	X											
Washing	Wastewater with surfactants/cleaners		X			X	X	X							
Body repair and painting	Solvents and thinners		X	X			X			X	X				
	Paints and primers		X												
	Wet sanding wastewater		X												
Dismantling	Motor oil and filters, transmission fluid, and lubricants	X	X	X											
	Engine coolant		X	X											X

Table 2.1 Typical vehicle service wastes (continued) (WEF, 1995)

Activity	Waste	Hydrocarbons	Heavy metals	PAHs	CFCs	Sediment	Oil & grease	Acid	Alkalis	Petroleum distillates	Chlorinated compounds	Lead	Asbestos	Solvents	Ethylene/propylene glycol
Dismantling (continued)	Refrigerant				X										
	Leaks and spills of gasoline and diesel	X	X	X											
	Corrosion		X			X									
Non repairable equipment replacement	Belts and hoses	X													
	Tires		X	X											
	Batteries							X				X			
	Brake pads and shoes		X										X		
	Pumps/engine parts		X				X								
Flexible equipment repair															
Parts cleaning	Solvents		X	X			X			X	X				
	Aqueous cleaners and wastewater		X				X	X	X						
Brake and clutch cleaning	Brake pads and shoes		X										X		
	Brake dust		X										X		
Shop cleanup	Dirty rags and absorbents		X				X							X	
	Floor cleaning wastewater		X				X		X						
	Oil water separator sludge		X				X								

Table 2.2 Wastewater characteristic of gas station and related facilities

Parameter	Gas station (DC, USA) ^a		Commercial parking lot (LA, USA) ^b	Radiator repair shop (VA, USA) ^c	Gas station (BKK, Thailand) ^d
	Water	Sediment (mg/Kg)	Mean (SD)	Pretreated ^e	Mean (SD)
pH	-	-	6.4 (0.4)	-	7.5 (0.4)
BOD (mg/L)	-	-	-	192	112 (90)
COD (mg/L)	-	-	171.7 (205.0)	-	239 (153)
DOC (mg/L)	-	-	40.1 (57.1)	-	-
TOC (mg/L)	95.51	98071	-	-	-
Hydrocarbons (mg/L)	22.0	18155	-	-	-
Oil & Grease (mg/L)	-	-	7.4 (10.3)	17	36 (34)
TSS (mg/L)	-	-	55.1 (71.6)	160	176 (189)
VSS (mg/L)	-	-	38.6 (60.5)	-	-
Total P (mg/L)	0.53	1056	-	-	-
NO ₃ ⁻ (as NO ₃ ⁻ -N) (mg/L)	-	-	0.1 (0.2)	-	-
Metal in (µg/l)					
Aluminium	-	-	2235	-	-
Cadmium	15.3	35.6	-	-	-
Chromium	17.6	350	-	-	-
Copper	112.6	788	103	192	-
Lead	162.4	1183	45	287	-
Nickel	-	-	75	-	-
Zinc	554	6785	2601	232	-

“-”: no data,

a: adapted from Schueler and Shepp (1993) cited in Schueler (1994)

b: adapted from Stenstrom *et al.* (2000)

c: adapted from WEF (1995),

d: adapted from Srikeaw *et al.* (1997)

e: pretreated water after metal precipitation.

2.1.1.2 Oil and grease

Oil and grease or hydrocarbons concentrations in runoff depend on land use. According to Schueler (1994), gas stations were defined as hydrocarbon hotspots in urban areas. They had much higher level of hydrocarbons both in water and sediment than street and residential parking lots. Stenstorm *et al.* (1984) reported that runoff from commercial and parking areas contained oil and grease concentration almost three times higher than runoff from residential areas; however, the statistical relationship between oil and grease and all storm characteristics was not found. In addition, it was found that commercial/industrial areas emitted aliphatic hydrocarbons much greater than non-commercial areas (Fam *et al.*, 1987).

Oil and grease is a gross term of substance or material that is extractable by solvent. It can present in wastewater many different forms including mechanically emulsified oil, chemically emulsified oil, oil wet solid, dissolved oil, and free oil (Yves, 1985; Alther, 2001). In fact, sheen/film oil is the form that can be obviously seen in the storm drain and oil/water separator at gas stations. These contaminants, which come from used motor oil, fuel oil and vehicle exhaust, contain many different compounds.

Motor oil contains varieties of organic matter such as additive chemicals, aliphatic and aromatic compounds (Gourgouillon *et al.*, 2000). Based on a gas chromatographic result, the chemical components of most oil and grease found in urban runoff are similar to those of used automobile crankcase oil (Stenstorm, 1984). Eganhouse and Kaplan (1981a) characterized the organic matter from urban stormwater run-off as both particulated and dissolved phases and divided each phase into five compounds: total hydrocarbon (THC), fatty acid (FA), ketones (KET), polars (PLR), and nonelutable polar compounds (NEP), respectively. They found that the major amount of total extractable organic (TEO), particularly THC was associated with the particulate matter. These components seem to be mostly anthropogenic, which are from petroleum residues (Eganhouse and Kaplan, 1981b). A study of runoff from San Francisco Bay area (Fam *et al.*, 1987) confirmed the results of Eganhouse and Kaplan (1981a) that concentrations of particulate TEO were higher than soluble TEO.

Recently, stormwater samples from 46 different sampling sites in North Carolina were collected to analyze fuel oxygenates (organic compound containing oxygen) and aromatic hydrocarbons (Borden *et al.*, 2002). It was found that all locations with higher contaminant concentrations were connected with direct runoff from gas station or discharge of contaminated ground water from previous leaking underground storage tank (Table 2.3).

Table 2.3 Fuel oxygenates and aromatic hydrocarbons in stormwater runoff for different land used.

Contaminants ($\mu\text{g/L}$)	Gas Station		Industrial		Commercial	
	Max	Median	Max	Median	Max	Median
MTBE	13.47	1.29	0.77	0.17	0.24	0.07
DIPE	ND	ND	ND	ND	0.55	0.10
Benzene	0.12	0.09	0.08	0.08	0.06	0.06
TAME	0.23	0.06	ND	ND	ND	ND
Toluene	0.40	0.15	32.84	0.13	0.36	0.10
Ethyl-benzene	0.08	0.06	0.08	0.07	0.19	0.08
<i>m,p</i> -Xylene	0.34	0.13	0.12	0.07	0.30	0.09
<i>o</i> -Xylene	0.21	0.08	0.11	0.08	0.29	0.10
1,2,4-TBA	0.15	0.10	0.12	0.11	0.32	0.11
1,3,5- TBA	0.53	0.10	0.14	0.07	0.37	0.08
1,2,3- TBA	0.24	0.11	ND	ND	0.10	0.08

ND: Not detected in any sample

MTBE: Methyl tert-butyl ether

DIPE: Di-isopropyl ether

TAME: Tert-amyl methyl ether

TBA: Tert-butyl alcohol

2.1.2 Inorganic contaminants

2.1.2.1 Heavy Metals

The vehicle service facilities, such as gas stations and repair shop, play an important role in contributing the heavy metal to wastewater treatment plant (WWTP) and/or water bodies. These can not be controlled easily because these facilities are

small in areas but large in number. A study of the vehicle maintenance facility (Hampton Road, VA) found that although the combined flow from these facilities was minute (0.3% of the District's daily flow), the percentage of pollutants loading was greater (as high as 10 to 12%) for chromium and lead (WEF, 1995).

Heavy metals are mostly released by motor vehicles. Automobile fluid, deterioration parts and vehicle exhaust are the sources of heavy metals found in gas station runoff. Antifreeze contains copper, lead, nickel, and zinc (Bay Area Open Space Council, 2001). Motor oil also contains the same heavy metals as antifreeze, especially high levels of zinc, and other metals such as cobalt, iron, boron, and tin (Bay Area Open Space Council, 2001; Gourgouillon *et al.*, 2000; Harper, 1998)

The investigations of Schueler and Shepp (1993) showed that zinc and lead provided the majority of heavy metals in both sediment and pool water of oil and grit separators (OGS) in gas stations (6,785 and 1,183 mg/kg sediment and 557 and 162.4 µg/L, respectively). Stenstorm *et al.* (2000) also found that zinc was the highest heavy metal in stormwater runoff from parking lots, commercial and residential areas and the percent adsorbed to suspended solid was approximately 70 percent. These indicated that heavy metals in stormwater run-off tend to be in sorb phases.

2.1.2.2 Nutrients

Sources of nutrients in gas station runoff come from phosphates containing soap or detergent which are used in car washing and others cleaning processes. Vehicle exhaust also contains nutrients, nitrogen and phosphorus (Bay Area Open Space Council, 2001). This exhaust may be the residue of used motor oil since 806 ppm of phosphorus were found in used motor oil (Gourgouillon *et al.*, 2000). The review in Table 2.2 showed that amount of phosphorus present in sediment is higher than water column (Schueler and Shepp, 1993 cited in Schueler, 1994)

2.1.3 Gas Station Effluent Standard

In Thailand, a gas station effluent standard has been enforced since May 29, 2002 (Table 2.4). However, the regulation was exempted for old gas stations in Bangkok and Pattaya municipality for 2 years and for old gas stations in other areas for 5 years.

Table 2.4 Gas station effluent standard of Thailand.

Parameters	Standard
pH	5.5-9.0
COD (mg/L)	200
Suspended Solid (mg/L)	60
Oil and grease (mg/L)	15

Source: Pollution Control Department (PCD), Thailand (2002), www.pcd.go.th

2.2 Treatment Technologies for Oil and Grease Removal in Water Runoff

Treatment technologies or best management practices (BMPs) to address oil and grease problems in runoff have been numerously commercialized throughout the United States. Gas stations are required to treat their runoff before discharged. Because most gas stations are on relatively small and impervious areas, the stormwater treatment system should be underground and use less space as much as possible. By these limitations, the systems that require large areas such as detention ponds and constructed wetlands are not feasible. The stormwater treatment technologies for land limited areas can be categorized into three groups: oil/water separators, vault type stormwater treatment systems, and catch basin inserts.

2.2.1 Oil/Water Separators

Oil/water separators or oil-grit separators (OGS) are common practices that are used to trap pollutants at gas stations. The systems consist of three chambers (Figure 2.1). The first chamber is designed to trap grit, coarse sediment, trash and debris. The second one is designed to trap oil and grease floating on the water surface. Also, oil and grease and other pollutants tend to be adsorbed with suspended particles

(Fam *et al.*, 1987; Schueler, 1994), which eventually settle to the bottom of the chamber. The water then flows out of OGS from the last chamber.

The advantages of the systems are low construction and maintenance costs. However, they require intensive maintenance. Moreover, OGS were found occasionally not to be effective in removing pollutants. Because of the short detention time, the sediment is resuspended and flushed out of the system during storm events. Dye tests indicated that OGS had less detention time of less than less than 30 minutes during small storms (Shepp, 1997). It was also found that the average of accumulated sediment was 2 inches (from 109 OGS sites). The depth of sediment frequently changed within the OGS, but rarely accumulated over time.

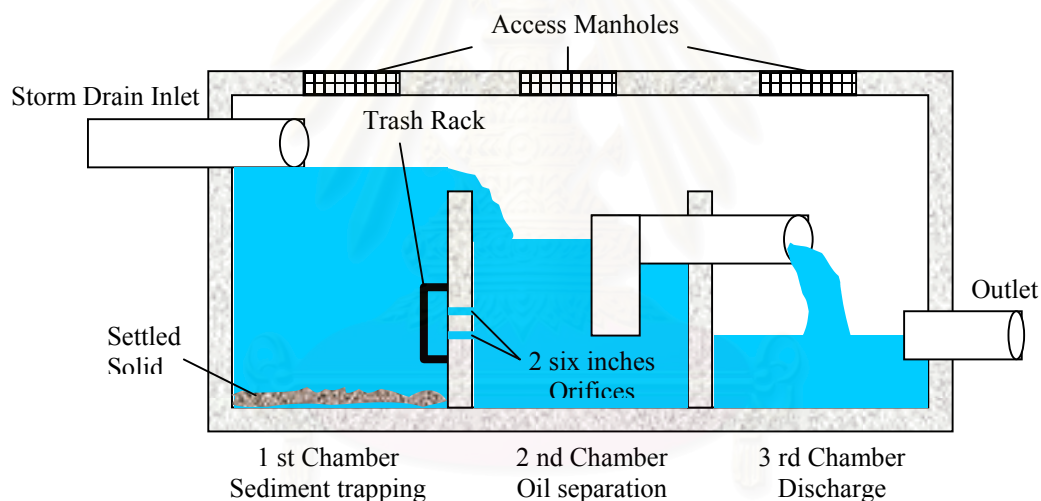


Figure 2.1 Schematic diagram of oil-grit separator (Shepp, 1997).

2.2.2 Vault Type Stormwater Treatment Systems

These systems consist of pre-cast underground vault type structures, which houses filter cartridges or consist of series of baffles and settling tank. They have been developed in a unique design. The sizes and cost of systems are variable depending on model of manufactures. The performances of these systems in the field also vary from site to site due to many factors such as amount of rainfall, influent concentration, and maintenance frequency. The following short list is the examples of vault type stormwater treatment systems (Figure 2.2).

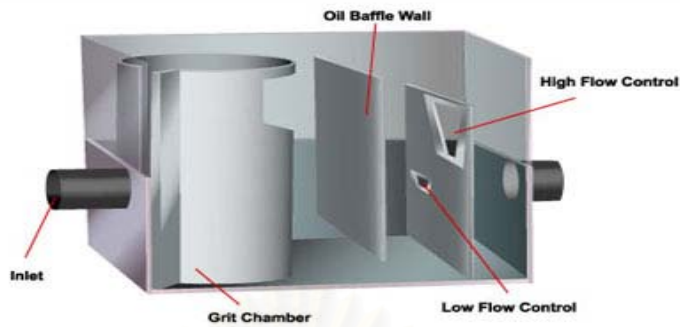
- VortechsTM (Vortechtechnics, Inc.)
- StormfilterTM (Stormwatermanagement, Inc.)
- CDSTM (CDS Technologies, Inc.)
- Baysaver[®] (Baysaver, Inc.)

A disadvantage of these kinds of BMPs is that they are high cost. In addition, the systems are not appropriate for old facilities because concrete pavement and soil must be excavated. Because their structures are reinforced concrete; coupled with the weight of water, improving bearing capacity of soil may be an additional cost.

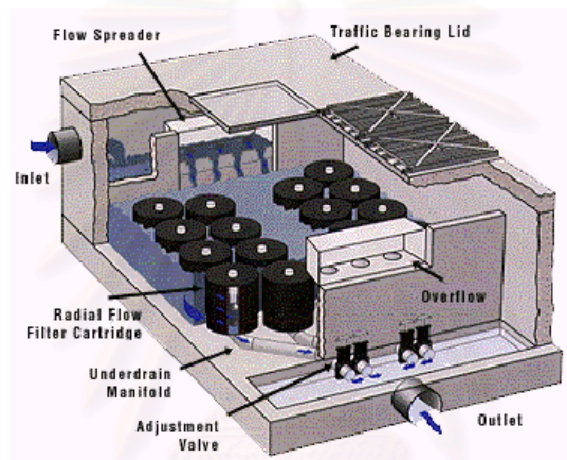
2.2.3 Catch Basin Inserts

Catch basin inserts are any devices that can be inserted into existing catch basins to provide some level of contaminant removal. The water runoff flows into the inlet, through the insert in which contaminants were captured. Figure 2.3 shows various types of manufactured products. The types of inserts depend on target pollutants to be removed. For example, wide-screen is for trash and debris, filter bag for sediment, and oil sorbent for oil and hydrocarbons removal. As a result, costs of the units vary widely, increasing from simple screen bag to more engineered designs.

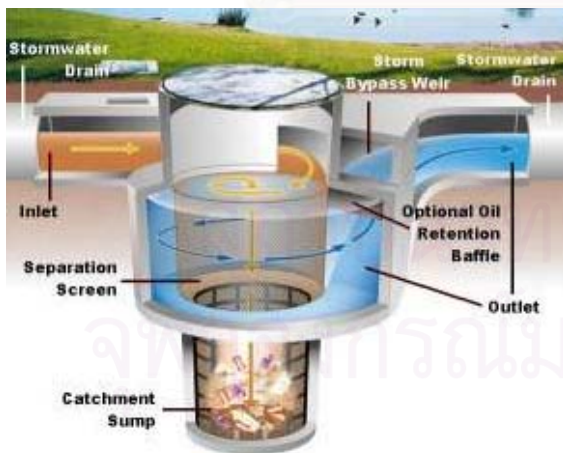
The systems are suitable for treating runoff in small impervious areas such as gas stations, parking lots, convenient stores because they do not need more space and can be retrofitted in existing drainage structure. Since the systems normally do not require construction as for vault type units, the costs of catch basin inserts are relatively low compared to large treatment systems. However, the major drawback to all of the catch basin inserts is that they are maintenance intensive. The filter media rapidly clog when it is exposed to high sediment loading. A study of AquaShiedTM (installed at solid waste transfer station, Knoxville, Tennessee) found that the system became clogged with suspended material and was rendered non-functional in very short time (Figure 2.4) (Wagner, 1999).



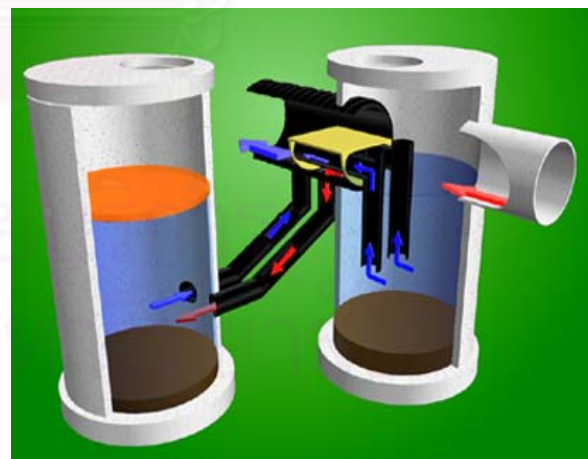
a) Vortechs™, Source: www.vortechnich.com



b) Stormfilter™, Source: www.stormwatermgt.com

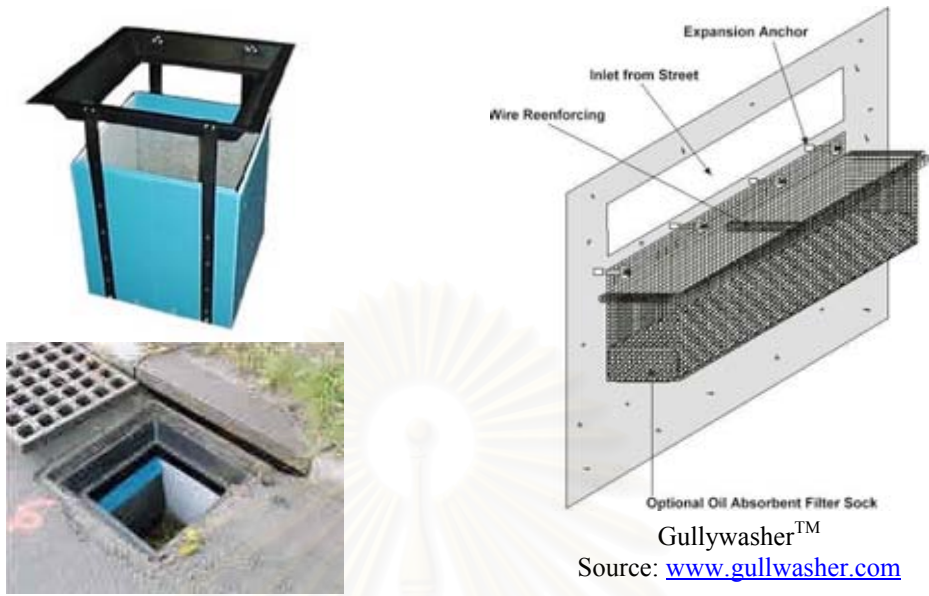


c) CDS™, Source: www.cdtech.com



d) Baysaver®, Source: www.basaver.com

Figure 2.2 Schematic drawing of vault type structures BMPs: a) Vortechs™, b) Stormfilter™, c) CDS™, and d) Baysaver®.



Ultra-Urban® filter
Source: www.abtechindustries.com

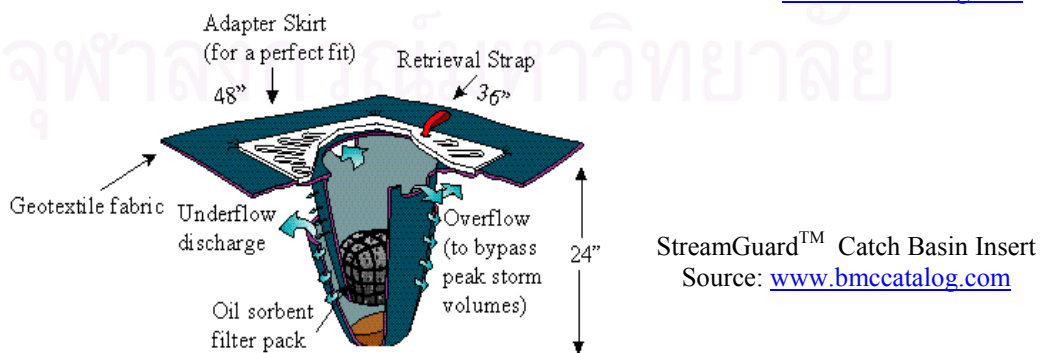
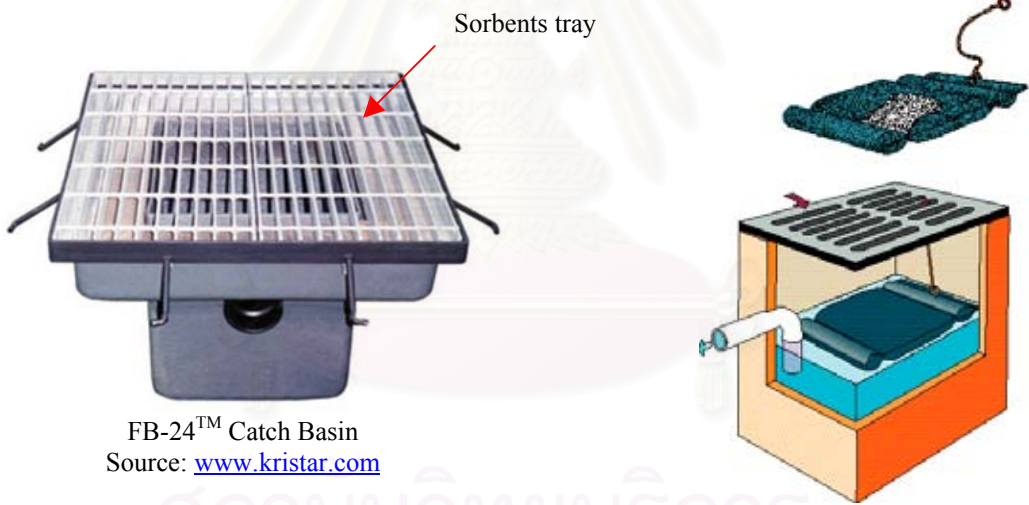


Figure 2.3 Commercial products of catch basin inserts.



Figure 2.4 AquaShield™ at solid waste transfer station, Knoxville, Tennessee, before and after (Wagner, 1999)

2.3 Evaluation of BMPs Removal Efficiency

Generally, the removal efficiency of treatment units was determined from influent and effluent concentrations of the systems. However, this concept may not be applied to stormwater treatment systems because the amounts of rainfall are different from storm to storm and the water flow rate also varies in the same event. Because of these variations, event mean concentration (EMC) should be used for represent the concentration of constituents per each storm event (Sansalone *et. al*, 1997).

$$EMC = C^* = \frac{M}{V} = \frac{\int_0^t c(t)q(t)dt}{\int_0^t q(t)dt} \quad (2.1)$$

where

M = total mass of constituents over entire event duration (M)

V = total volume of flow over entire event duration (L³)

C* = flow weight average concentration for entire event (M/L³)

c(t) = time variable concentration (M/L³)

q(t) = time variable flow (L³/T)

t = time (T)

For discrete sampling equation 2.1 can be modified to equation 2.2:

$$EMC = C^* = \frac{M}{V} = \frac{\sum_{i=1}^n C_i Q_i \Delta t_i}{\sum_{i=1}^n Q_i \Delta t_i} \quad (2.2)$$

where

C_i = concentration of constituent for each time interval (M/L^3)

Q_i = flow rate for each time interval (L^3/T)

Δt_i = interval time of sampling (T)

Therefore removal efficiency per storm event can be calculated by

$$Efficiency = \left(1 - \frac{EMC_{influent}}{EMC_{effluent}} \right) \times 100 \quad (2.3)$$

Since EMC is derived from total mass and total volume, so this removal efficiency is equal to percent of mass reduction of contaminants as follows

$$Efficiency = \left(1 - \frac{\frac{M_{output}}{V}}{\frac{M_{input}}{V}} \right) \times 100 \quad (2.4)$$

$$Efficiency = \left(1 - \frac{M_{output}}{M_{input}} \right) \times 100 \quad (2.5)$$

2.4 Oil Sorbents and Their Applications

Media and/or sorbents are the most important parts of some catch basin inserts and other storm filtration treatment systems. These materials have been developed by several manufactures to capture specific contaminants such as oil and grease or petroleum hydrocarbons in urban runoff.

2.4.1 Commercial Sorbents

Stormwater management, Inc. is one of the manufactures that develop many types of sorbents (media) to use in StormFilter™ systems (Table 2.5). Generally, most commercial sorbents are organic synthetic materials but there are some sorbents that derived from natural material such as compost and perlite.

Table 2.5 Sorbents for StormFilter™ (Stormwater management, Inc, 2000)

<i>Pollutant</i>	PERLITE	CSF©	ZEOLITE	GAC	IRON INFUSED	PLEATED FABRIC
<i>Sediments</i>	Excellent	Good	-	-	-	Excellent
<i>Oil & Grease</i>	Excellent	Excellent	-	-	-	-
<i>Soluble Metals</i>	-	Excellent	Good	-	Good	-
<i>Organics</i>	-	Varies	-	Good	-	-
<i>Total Phosphorous</i>	Good	Good	-	-	Good	Good
<i>Dissolved Phosphorous</i>	-	-	-	-	Excellent	-
<i>Total Nitrogen</i>	Good	Good	-	-	-	Good

CSF® leaf media is a commercial compost sorbent manufactured by Stormwater Management Inc. A feedstock of pure deciduous leaves is collected by the City of Portland, Oregon and composted into mature stable humus. The finished compost is processed into an organic granular media for use to remove TSS, oil and grease, and soluble metals from stormwater run-off.

Perlite (aluminum silicate) is an inorganic material. It is a popular sorbent for oil and grease and also effective for TSS removal. This material is light and hydrophobic. It is also used to increase soil bulky. Its highly porous nature, multicellular structure, and rough edges make it very effective for removing fine particles. This material is brittle; therefore easily abrade to create a fine powder. Examples of this sorbent in the markets are such as XsorbTM (Impact Absorbent Technologies, CA) and Sponge RokTM type 23 (Paramount Perlite Co., Paramount, CA). Stormwater Management Inc. also uses perlite as a stand-alone media or combines with other media to capture pollutants in StormfilterTM system.

OARSTM sorbent is produced by AbTech Industries, AZ. It is a "rubber" type of sorbent. It can be manufactured in any desired size fraction. Bulk density of this sorbents was about 0.26 g/mL (Stenstrom and Lau, 1998). The manufacturer generally believes that the removal mechanism is absorption.

RubberizerTM is a sorbent that is marketed by Haz-Mat Response Technologies, Inc., CA. It is used as a clean up sorbent for various types of solvents, oils and fuels. It is composed of a mixture of hydrocarbon polymers and additives. Its physical shape is similar to the OARS sorbent.

Lau and Stenstrom (1995) conducted continuous flow oil sorption experiments using 2.27 kg of polypropylene oil sorbents (Spill TechTM, Type 210TM Oil Sorbent, and Alisorb[®] II) packed in a basket. The tests were performed at a flow rate of 3 gallon/min and an oil influent concentration of approximately 20 mg/L. Based on 82 hours of operation, the removal efficiencies among the sorbents ranged from 55 to 66 percent and there was no sign of saturation. These results indicated the feasibility of installation polypropylene sorbents in existing drainage systems such as catch basins to remove oil and grease from water runoff.

Stenstrom and Lau (1998) augmented commercial sorbents (XsorbTM, Sponge RokTM type 23, OARSTM, RubberizerTM, and NonofiberTM) in a CDSTM unit to adsorb oil and grease. The augmentation did not improve the oil removal efficiencies.

Stenstrom et al. (2000) studied the oil and grease sorption abilities of OARSTM, activated carbon, aluminum silicate, straw, compost, and polypropylene (PP) under both laboratory and field conditions. They found that all of the sorbents tested were not effective in removing mechanically emulsified oil (Table 2.6). OARSTM and polypropylene sorbents were tested as insert materials to adsorb free oil using a laboratory scale catch basin simulator. Their oil and grease removal efficiencies ranged from 40 to more than 90%, depending on sorbent condition and influent concentration. Particles larger than 100 micron were also significantly removed. Moreover, 16% to 88% of spiked PAHs were removed when an initial concentration was 50 µg/L. The results from the field tests showed that an average removal efficiency of the OARSTM insert was 21% of TSS, 9% of VSS and 12% of turbidity, while the polypropylene insert was able to remove 21% of TSS, 36% of VSS and 34% of turbidity. Oil and grease removal rates varied tremendously that it is not possible to draw any meaningful conclusion.

Table 2.6 Removal Efficiencies of Various Sorbents (Stenstrom *et al.*, 2000)

Sorbent Type	Oil and Grease Type	Removal Efficiency (%)
OARS Polymer	Emulsified	3
Activated Carbon	Emulsified	11
Aluminum Silicate (e.g., Perlite, Xsorb TM)	Emulsified	~0
Straw	Emulsified	~0
Compost	Emulsified	~0
OARS Polymer	Free	88, 91
Aluminum Silicate (e.g., Perlite, Xsorb TM)	Free	88,91,94,89
Compost	Free	28,49
Polypropylene (type 1)	Free	86,92
Polypropylene (type 2)	Free	78,85

2.4.2 Non-Commercial Sorbents

Non-commercial sorbents are mostly natural organic materials. The uses of this type of sorbents depend on their availability in each area. The examples of non-commercial sorbents derived from plants are such as kapok fiber and *Salvinia* sp.

Kapok fiber is a silky cotton-like substance that surrounds the seeds in the pods of the ceiba tree. The silky fiber, or floss, is actually a tiny cellulose tube with air sealed inside. This yellowish cotton contains lignin, a woody plant substance, and cellulose. The fiber is usually removed by hand, dried, separated from the seeds.

Salvinia species are free floating water ferns that grow rapidly, often choking waterways. In many parts of the world, such as Australia, Papua, New Guinea, and Thailand, the plants are exotic and have damaged native fishes and crowded out native vegetation. They have to be washed to remove dirt and then dried before using as sorbents.

Choi and Cloud (1992) employed milkweed, cotton, kenaf fiber, polypropylene fiber and polypropylene web to adsorb crude oil in a seawater bath. Milkweed and cotton fiber showed the potential to sorb the oil approximately 2.5-3.0 times higher than did polypropylene sorbents. It was also found that kapok fiber, adsorbed oil approximately 1.5 –2.0 times higher than polypropylene mat (Kobayashi *et al.*, 1977 as cited in Choi and Cloud, 1992). The mechanism for oil sorption by cotton fiber is controlled by adsorption on the fiber surface and capillary action through its lumen. On the contrary, oil sorption of polypropylene is through capillary bridges between fibers. The electron microscopy results showed that milkweed and kapok fiber have non-collapsed lumen (Choi, 1996). The lumen is very thin skin and its size is almost 90% of total diameter of the fiber. The lumen plays a more important role in oil sorption than surface waxes of fiber. The oil sorption capacities of fibers after extracting surface waxes by hexane did not significantly decrease (Lee *et al.*, 1999).

Ribeiro *et al.* (2000) studied the sorption of oil onto dry biomass of the aquaphyte *Salvinia* sp. (Figure 2.5) compared with Peat sorb, a commercial sorbent. They found that the amount of oil adsorbed by *Salvinia* sp. was higher than Peat sorb[®] in both batch and continuous filter tests (Ribeiro *et al.* 1999; Ribeiro and Rubio,

1999). Comparing to Peat sorb[®], *Salvinia* sp. has higher hydrophobic property, which can be expressed by capillary rising of hexane (Figure 2.6). In addition, they also found that leaves of *Salvinia* sp. have less pore, but more hydrophobicity and more affinity for oil than roots. The electron microscopy results revealed hair-like structure on leaves surface. It is believed that the hair plays a crucial role in oil sorption.

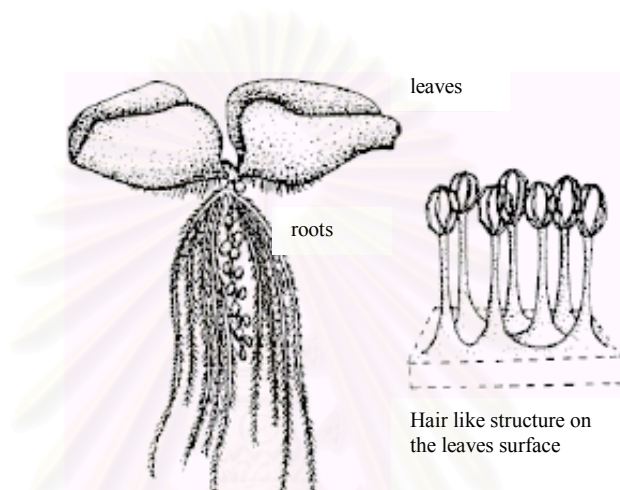


Figure 2.5 Morphological aspects of *Salvinia* sp., hair-like structure of leaf. (Ribeiro *et al.*, 2000)

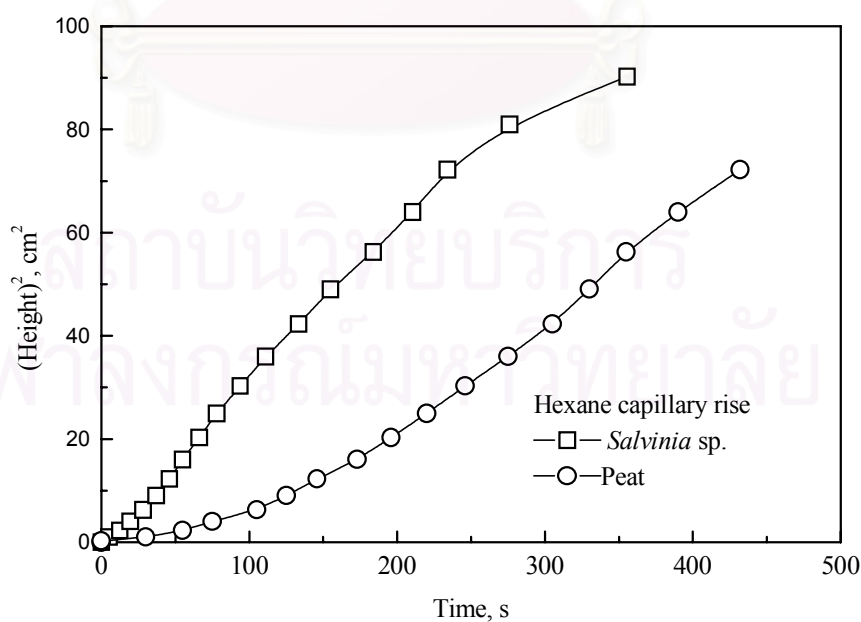


Figure 2.6 Hexane capillary rises in *Salvinia* sp. (Ribeiro *et al.*, 2000)

CHAPTER III

MATERIAL & METHODS

3.1 Oil-Water Samples

Oil-Water samples were synthesized from used motor oil collected from a gas station nearby Khon Kaen University. There were three types of samples used in this study based on the preparation method: mechanically emulsified oil, chemically emulsified oil, and free oil samples.

3.1.1 Mechanically emulsified oil-water samples

Mechanically emulsified oil-water samples were used to screen the sorbents through a batch sorption screening test. They were prepared by mixing 0.1 gram of used-motor oil with 100 mL of tap water in a TeflonTM flask to make a stock solution (Lau and Stenstrom, 1997). The mixture was shaken by hand until emulsion was formed. After shaking, a 20 mL of the solution was then diluted to make up a volume of 500 mL by tap water to achieve an oil and grease concentration of approximately 20 mg/L.

3.1.2 Chemically emulsified oil-water samples

Chemically emulsified oil-water samples were used for the batch sorption screening tests, a batch sorption isotherm test, and a column experiment. These samples were prepared by mixing used-motor oil with two chemicals. First, 2 grams of oil was mixed well with 20 mL of hexane to make the first stock solution. Next, 10 mL of the first stock solution was transferred into a 250 mL volumetric flask and isopropanol (IPA) was added in the flask to make up a volume of 250 mL of the second stock solution. Finally, the second stock solution was diluted with tap water to make up 500 mL of oil-water samples.

3.1.3 Free oil-water samples

Free oil-water samples were employed for a flume experiment. Used-motor oil was injected by a peristaltic pump to mix with tap water in the flume to simulate the actual water runoff in the drain channel. The specific concentration of oil can be adjusted by changing the flow rates of oil and water to represent the values found in gas station runoff in Thailand.

3.2 Sorbents

All of sorbents used in this study are plant materials except NanofiberTM, polyester fiber[®], and RubberizerTM. The fresh plants were washed with water to remove impurities. All sorbents were then dried at 60° C for 24 hours (Ribeiro *et al*, 2000). The sorbents used in each test are listed in Table 3.1. In the batch experiment, the sorbents, except kapok fiber and NanofiberTM, were sieved to obtain sizes of 2.4 to 4.7 mm. In the flume experiment, however, the sorbents were used without sieving because large amounts of sorbents were used and it is more practical when they are applied in the field.

Table 3.1 List of sorbents used in each experiment.

Sorbents	Batch		Column	Flume
	Mech. emulsion	Chem. emulsion		
Bagasse	*			*
Burned rice husk	*			
Cattail fiber				*
Cattail leaf	*	*		
Compost ^a	*			
Coconut husk	*			*
Corn cob	*			
Kapok fiber	*	*	*	*
Nanofiber ^b		*		
Polyester fiber ^b				*
Rice husk	*	*		*
Rubberizer ^b			*	
<i>Salvinia</i> sp.				*
Sawdust	*	*		
Straw	*			
Umbrella plant	*	*		
Water lettuce	*	*		
Wood chip				*

^aCommercial oil sorbent (natural), ^bCommercial oil sorbent (synthetic)

3.3 Experimental Procedures and Set-Ups

3.3.1 Batch Experiment

3.3.1.1 Sorption Screening Test

The sorption screening test was carried out in order to screen the local sorbents (made of plant materials) that have high capability of oil sorption. A known amount of sorbents was added to a 1 L-flask containing 500 mL of oil-water sample and the flask was later capped with aluminum foil. The samples were then shaken by an orbital shaker (Forma Scientific, Inc model 4586) at 25°C 200 rpm for 24 hours. After shaking, the water samples were centrifuged to separate the sorbents from the liquid phase, and then oil concentration in the liquid was measured. After that the best sorbents, which have highest removal efficiency were selected to run the sorption isotherm test to determine the oil sorption capacity.

3.3.1.2 Sorption Isotherm Test

The sorption isotherm test was conducted in order to determine the sorption capacity of oil of the most effective sorbents selected from screening test. The oil concentration was maintained in a range of 20-30 mg/L. However, the mass of sorbent was varied from 0.01 to 2 grams. The shaking was similar to the screening test. The sorption isotherms of oil were obtained by plotting milligram of oil adsorbed per gram of sorbents (q/m) versus the equilibrium concentration of oil and grease (C_e).

3.3.2 Column Experiment

The column experiment was conducted to verify that sorbents could not remove chemically emulsified oil regardless of the types of sorbents (synthetic or natural). RubberizerTM, a commercial oil sorbent, was tested and compared with kapok fiber. Three grams of each sorbent were placed in each column supported with an aluminum screen. Figure 3.1 illustrates schematic diagram of the column experiment. The water sample flowed through the column by gravity. The test was performed for 80 minutes. Three 200 mL influent samples were collected before water flow into the column while a 200 mL effluent sample was collected every 10 minutes.

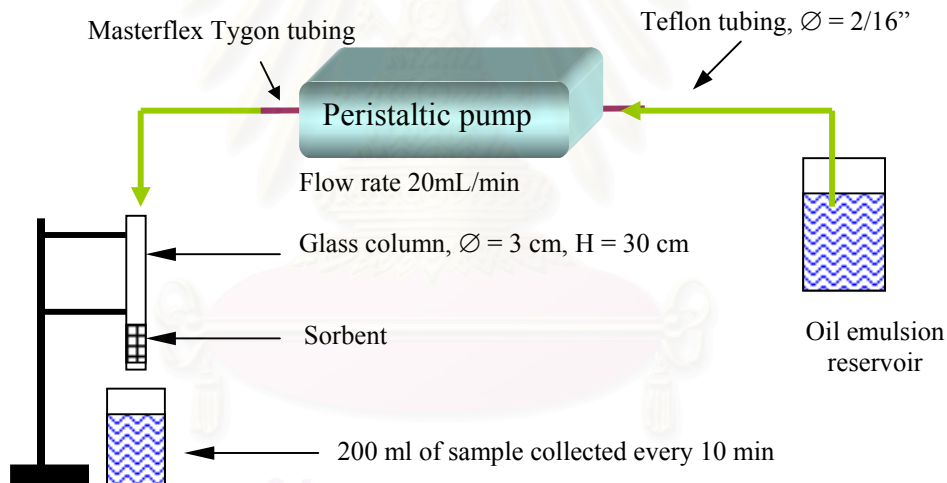


Figure 3.1 Schematic diagram of column test

3.3.3 Flume Experiment

The flume experiment was conducted using a bench scale set-up which was designed to simulate the situation where the sorbents were exposed to the runoff in the catch basin insert. A flume was mocked up as an above ground small scale drain for easy access. A unit of flume test consisted of the glass-flume, a flow meter (Blue White®, model F-40750LN-12, 4-36 L/min), a peristaltic pump (Watson Marlow model 505U), and a galvanized-basket (30 cm high and 25 cm inside diameter). Two hundred fifty grams of sorbent were placed in the galvanized-basket (insert), which was hung from the lower end of flume (Figure 3.2)

The flume experiment was divided into two parts. The first part was the oil sorption test to determine the amount of oil that could be sorbed by the sorbents. The second part was oil desorption test which quantified the amount of oil desorbed from the used sorbents (from sorption experiments) when they were exposed to only water.

3.3.3.1 Oil Sorption Test

The oil sorption test was operated at a water flow rate of 20 L/min and the used motor oil was pumped to the flume at a flow rate of 1 mL/min. A series of runs was conducted for 60 or 120 minutes. During the runs, water samples were collected at the inlet and outlet of the basket at a specific time interval, 200 mL for the influent and 500 mL for the effluent. The runs were terminated when oil and grease concentration of effluent exceeded the standard (15 mg/L) or after 360 minutes. Then the samples were analyzed and the amount of oil adsorbed was determined. The used sorbents were tested for oil desorption. The amount of total oil input and total sorbed can be calculated by equation 3.1 and 3.2

$$\text{Total oil input (mg)} = \sum_{i=1}^n C_{Inf_i} Q_i \Delta t_i \quad (3.1)$$

$$\text{Total oil sorbed (mg)} = \sum_{i=1}^n (C_{Inf_i} - C_{Eff_i}) Q_i \Delta t_i \quad (3.2)$$

where

C_{Inf} = concentration of constituent for each time interval (mg/L)

C_{Eff} = concentration of constituent for each time interval (mg/L)

Q_i = flow rate for each time interval (L/min.)

Δt_i = interval time of sampling (min.)

3.3.3.2 Oil Desorption Test

All of the used sorbents from the sorption test were employed in the desorption test except two sorbents (bagasse and coconut husk) which exhibited low sorption capabilities during the sorption test. The oil desorption test was also operated at a water flow rate of 20 L/min but without the oil injection to the flume. For the desorption test, only 500 mL of effluent samples were collected at 1, 3, 5, 10, and 15 minutes. The amount of total oil desorbed can be calculated by equation 3.3.

$$\text{Total oil sorbed (mg)} = \sum_{i=1}^n C_{Eff_i} Q_i \Delta t_i \quad (3.3)$$

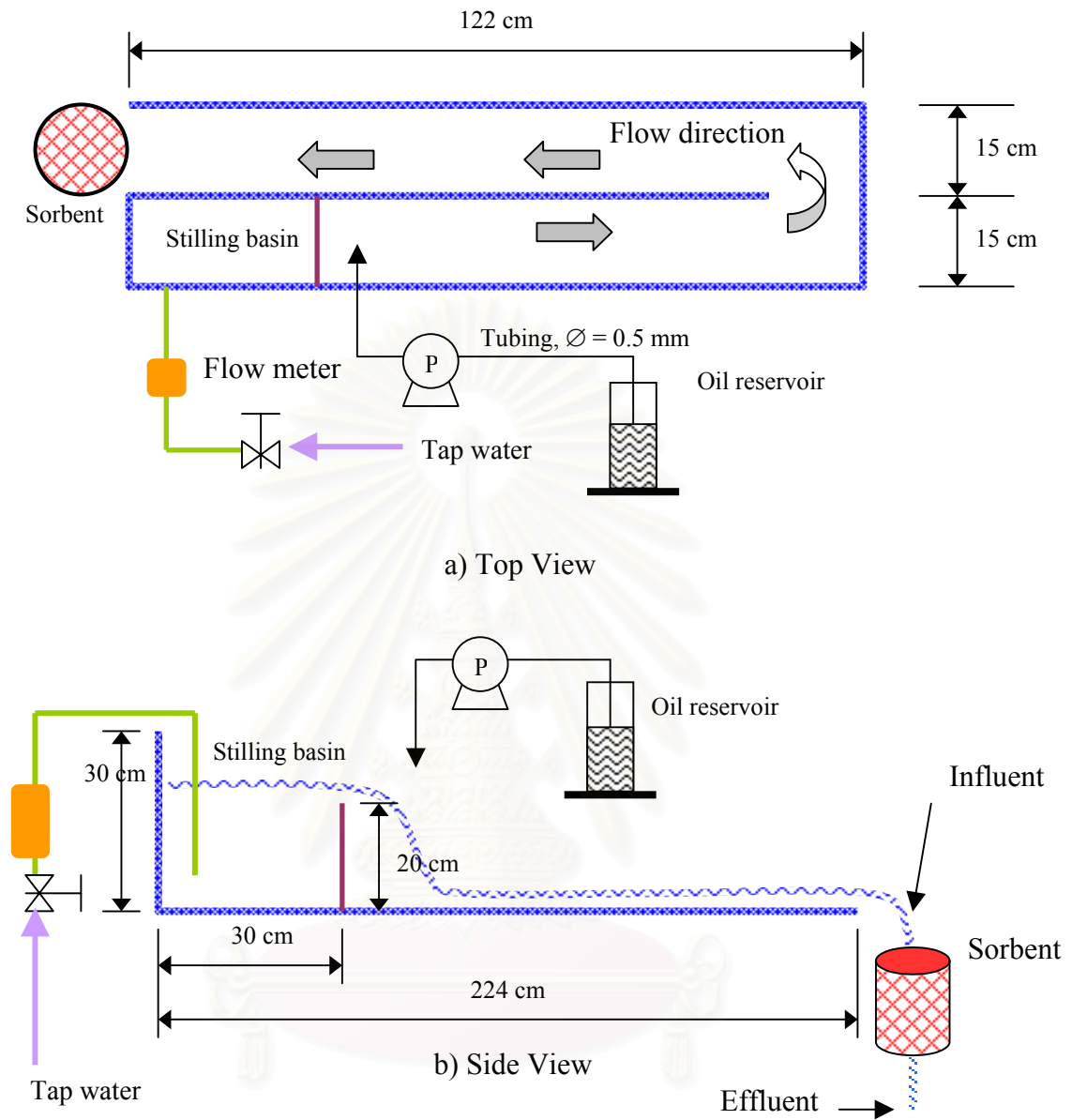


Figure 3.2 Schematic diagram of flume setup experiment: a) top view, b) side view

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3.4 Analyses

All samples generated from the tests were analyzed for pH and oil and grease. pH was measured by a pH meter (sension™ model 51935-00) (Standard method 2310 A and B, APHA *et al.*, 1998). Oil and grease was determined by a solid phase extraction (SPE) technique (Lau and Stenstrom, 1997). The technique was chosen because it requires less amount of solvent than the liquid-liquid phase extraction technique (Lau and Stenstrom, 1997). A 1000-mg of C18 SPE column (Varian, Inc.) was used in this study. First, the SPE column was conditioned with 5 mL of isopropanol (IPA) and 10 mL of deionized (DI) water. The water sample was also pretreated with 5 % v/v of IPA and acidified with 1 mL of hydrochloric acid (HCl). Next, the water sample was transferred to the SPE column under a vacuum pressure (-10 mm. Hg) where the oil was adsorbed to the media (Figure 3.3). After the sample passed through the column, 5 ml of IPA was added to the empty sample bottle to rinse off the oil adhered in the bottle. Then 100 ml of 0.1% v/v concentrated HCl was added to the same bottle and the mixture was again passed through the column. The column was then dried to remove moisture for 30 minutes. After drying, a test tube was placed under the column. Then, 3 mL of methylene chloride and 2 mL of hexane were added to elute oil and grease. The eluted solvent was poured to evaporating disk and later evaporated. Mass of oil and grease was determined gravimetrically. The oil and grease concentration was then calculated by dividing the mass by sample volume.

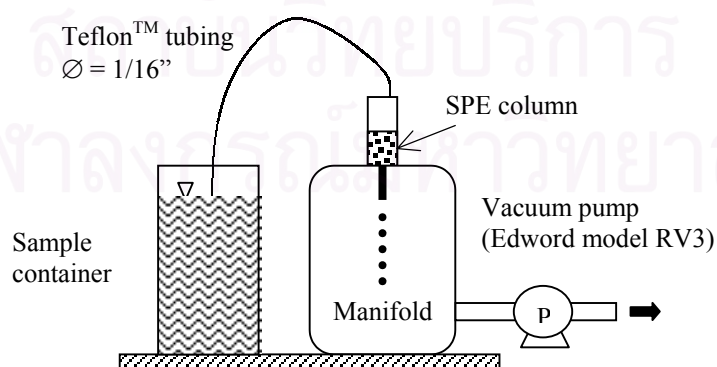


Figure 3.3 SPE diagram for oil and grease analysis.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Batch Experiment

4.1.1 Sorption Screening Test

4.1.1.1 Mechanically Emulsified Oil Samples

The batch oil sorption test with mechanically emulsified oil samples was conducted using various types of sorbents including bagasse, burned rice husk, cattail leaf, compost, coconut husk, corncob, kapok fiber (*Ceiba pentandra*), RubberizerTM, straw, sawdust, umbrella plant (*Cyperus flabelliformis*), water lettuce (*Pistia stratiotes*). The initial oil and grease concentration prepared from the used motor oil was in a range of 18.8 to 26.9 mg/L and mass of sorbent was 0.1 gram. Removal efficiency and amount of oil sorbed to the sorbent (mg/g) are shown in Figure 4.1. It was observed that removal efficiency of the tested sorbents except of corncob and straw were greater than 75 % and amount of oil sorbed ranged from 79.2 mg/g to 119.1 mg/g.

For corncob and straw, less oil sorption might result from both shaking and sorbents characteristics. The shaker provided horizontal motion which caused oil to float. On the contrary, the two ground sorbents, which were denser, tended to sink. These phenomena provided less contact opportunity between oil and sorbents. In addition, straw has lumen structure, which is similar to small tube. Void space inside the lumen provides buoyancy property that oil and grease can penetrate and be trapped inside the lumen. But the grinding of the sorbent destroyed the lumen structure.

For the sorbents that showed high oil removal efficiency, it could not be concluded that oil was really adsorbed by the sorbents. There was some oil residual attached to the wall of the containers and could not be rinsed off by isopropyl alcohol (IPA) after the test. This might be resulted from long sample shaking time which provided more contact opportunity between the oil and the wall of the containers. The

oil adhesion to the containers was not observed when determining the percent recovery, in which the samples were analyzed immediately after the preparation.

To prove that oil removal is rather by adhesion to the containers than sorption, kinetic test was performed. Control samples (no sorbent) and sample containing the burned rice husk were analyzed for oil and grease remaining at 3, 8, and 24 hours after shaking. Oil and grease concentration of the control samples should not change with time if oil did not adhere to the containers. Figure 4.2 shows a similar pattern of oil reduction with time for control samples and burned rice husk.

Based on this result, it could be concluded that oil and grease adhered to the container rather than adsorbed to the sorbents. As a consequence, the results produced from the mechanically emulsified samples could not be used for selecting effective sorbents. To solve this problem, the oil-water sample was prepared in a more water soluble form by mixing the used motor oil with hexane and IPA as described in section 4.1.1.2.

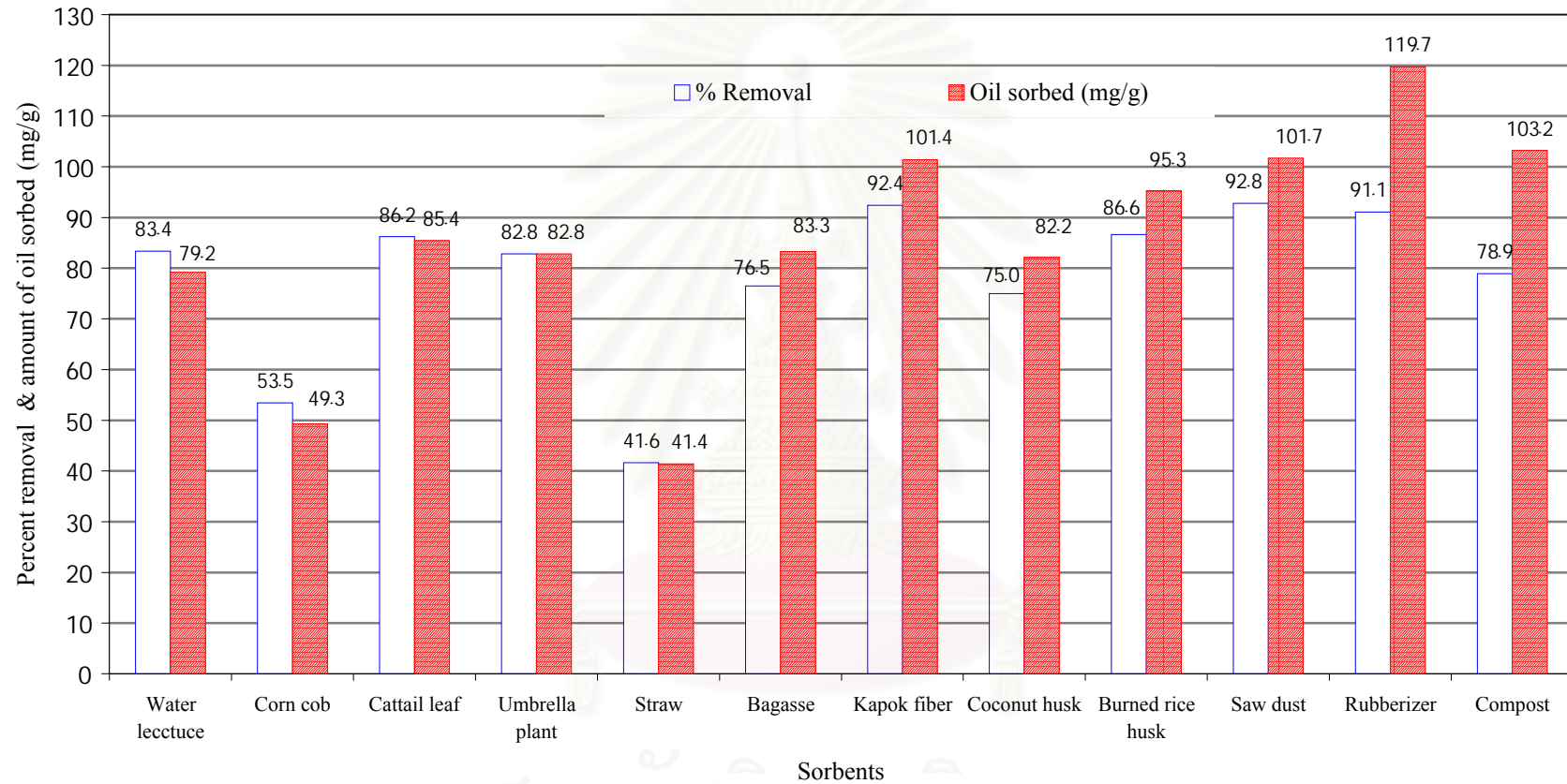


Figure 4.1 Removal efficiency and amount of oil sorbed by various sorbents in sorption screening test using mechanically emulsified oil samples.

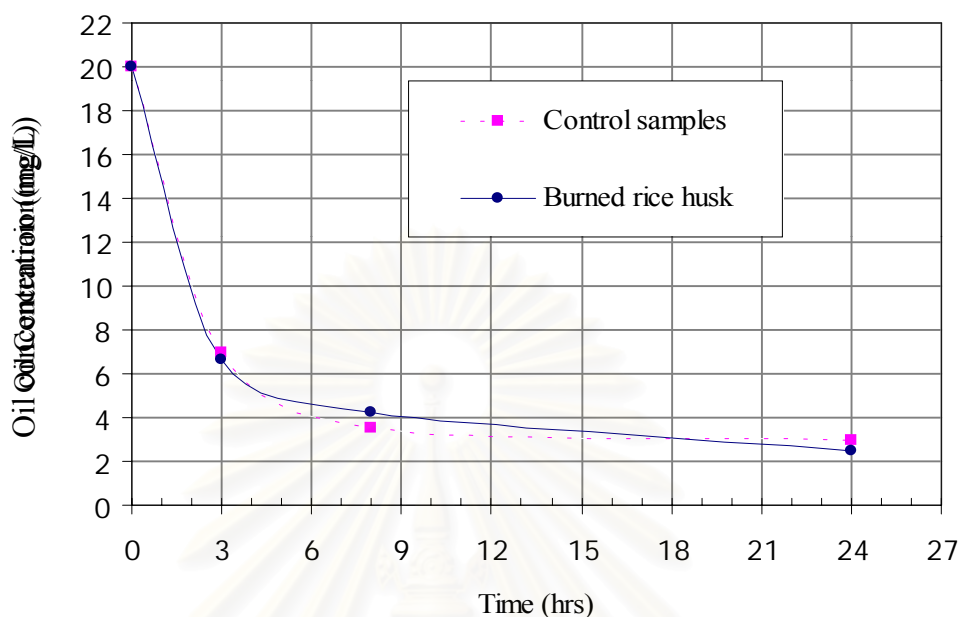


Figure 4.2 Kinetic oil sorption test of burned rice husk (mechanically emulsified oil samples). Change y axis title from Concentration to concentration (small c)

4.1.1.2 Chemically Emulsified Oil Samples

The batch test using chemically emulsified oil samples was developed in order to eliminate problem of oil adhesion encountered when using mechanical emulsion samples. The sorbents explored in this test included burned rice husk, cattail leaf, kapok fiber, NanofiberTM, rice husk, sawdust, umbrella plant, and water lettuce. The test was conducted in a similar manner as the previous batch test but different in mass of sorbents and oil mixture. For all sorbents tested except for NanofiberTM, a 0.5 gram mass was used. Only 0.2 gram of NanofiberTM was utilized because this amount of sorbent was already fill the water surface in the sample container. It was less contact opportunity with adding more amount of NanofiberTM. A synthetic sample was prepared by mixing the used motor oil with hexane, IPA, and tap water. Figure 4.3 presents the removal efficiency and oil influent and effluent concentrations of the tested sorbents. The initial oil and grease concentration was in a range of 15.8 to 26.4 mg/L.

It was visually observed that rice husk, sawdust, and umbrella plant sunk down to the bottom of sample containers after 24 hours of shaking. These sorbents showed lower removal efficiencies (less than 28 %). While water lettuce, cattail leaf, kapok fiber and NanofiberTM had higher removal efficiency (greater than 46 %) than those sinking sorbents. The removal efficiencies of Kapok fiber and NanofiberTM were 84% and 86 % respectively, which were higher than the other sorbents. The high oil removal efficiency of NanofiberTM was expected because it is a commercial oil sorbent made from polypropylene. Oil sorption mechanism occurs by interaction force between hydrocarbon molecules. In case of kapok fiber, favorable sorption of oil could be explained by interaction between the surface waxes of the fiber and the capillary action of oil through hollow lumen of the fiber (Choi, 1996)

Experimentally, kapok fiber was the best sorbent for oil removal compared with other natural sorbents. Therefore, kapok fiber was selected to perform the isotherm test to determine the maximum oil sorption capacity.

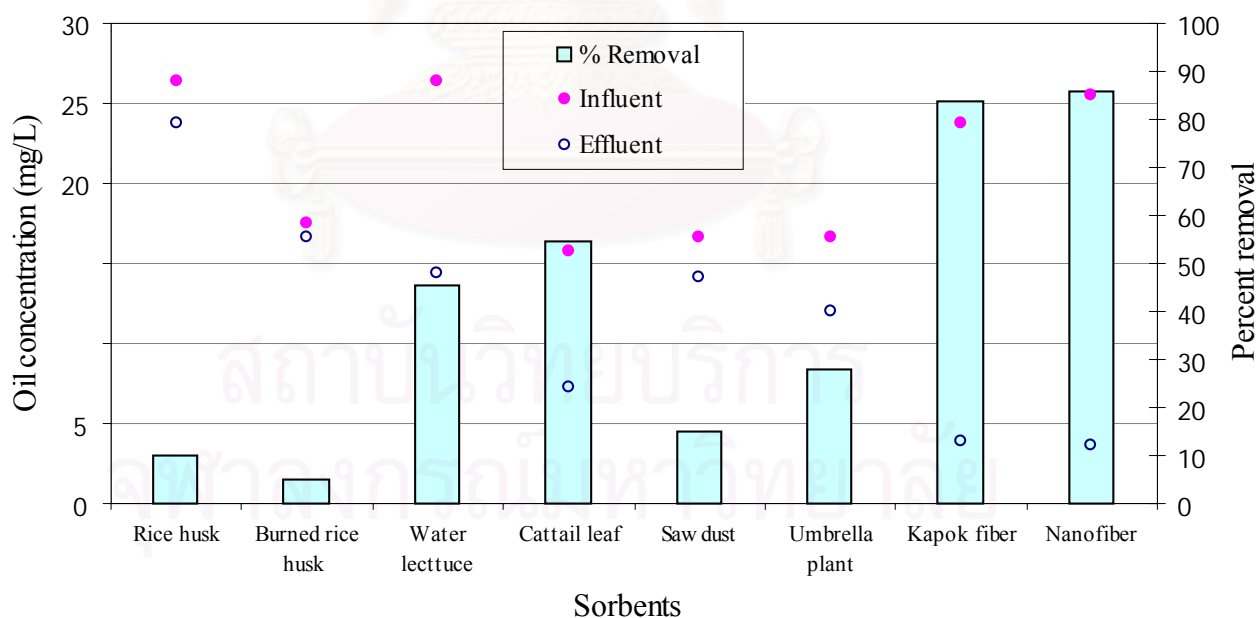


Figure 4.3 Removal efficiencies of various sorbents in batch test (chemically emulsified oil samples).

4.1.2 Sorption Isotherm Test

As previously mentioned, kapok fiber was the only sorbent conducted for the isotherm test. The result is presented in Figure 4.4. The value of R^2 indicated a weak correlation between mass of oil adsorbed (mg/g) and equilibrium concentration of oil and grease (C_e) in water. The weak relationship might be caused by the restricted shaking motion during the test. The sample was only horizontally shaken and therefore was not well mixed. In addition, kapok fiber is bulky and high in buoyancy. When a large amount of sorbent was placed in sample bottles, the upper portion of kapok fiber did not contact with oil but the mass of sorbents was accounted to calculate mass of oil adsorbed (mg/g). These data points were in the low Q and high C_e region.

Lau and Stenstrom (1995) also reported similar results even though in their experiment the water samples were mixed well with the polypropylene sorbents by using a wheel shaker. The oil (captured by kapok fiber) may be free oil because of the volatilization of hexane and IPA, which occurred from horizontal shaking the sample for a long period of time. As shown in Figure 4.5, most part of kapok fiber could not have a contact with oil by this type of shaking. Packing the sorbent in a flow through column may be an effective way to make all part of sorbents contact with oil.

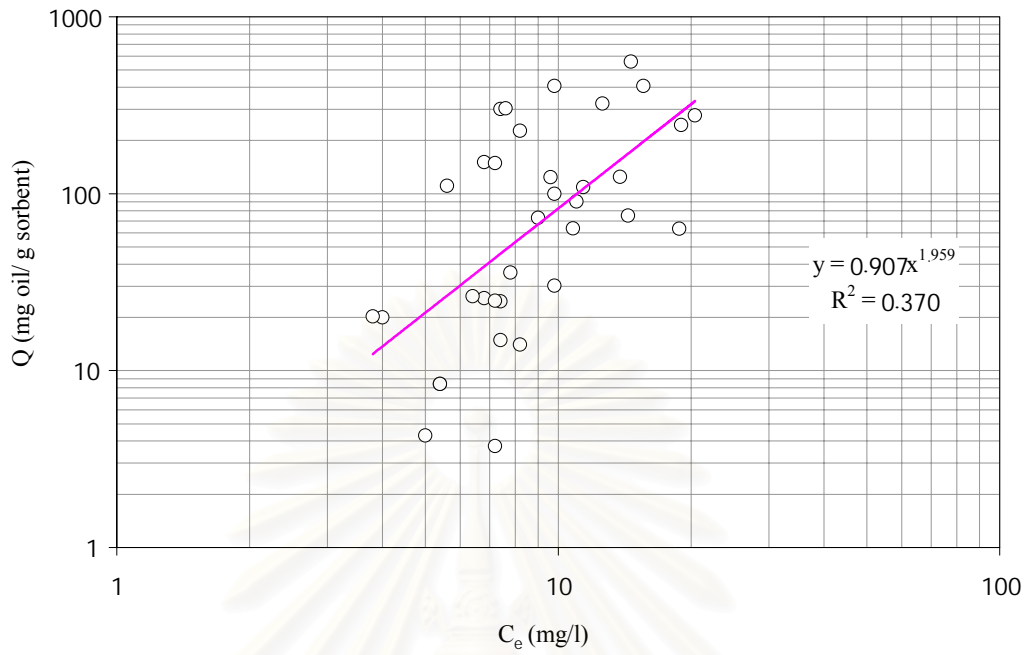


Figure 4.4 Oil sorption isotherm of kapok fiber.



Figure 4.5 Different amounts of kapok fiber placed into sample bottles.

4.2 Column Experiment

Kapok fiber and RubberizerTM were used for the column experiment and chemically emulsified oil-water samples were employed. At first, kapok fiber was tested to determine the removal efficiency versus time. It was found that oil was not well sorbed by kapok fiber (Figure 4.6). Subsequently, RubberizerTM, which is known to adsorb oil very well, was tested to determine whether very little oil sorption was resulted from oil mixture or from the sorbent itself. Like kapok fiber, RubberizerTM could not effectively remove oil from the mixture (Figure 4.7). Therefore, it was concluded that chemically emulsified oil could not be removed by these two sorbents. Stenstrom *et al.* (2000) found the low removal efficiency of commercial sorbents (synthetic material) when using mechanically emulsified oil samples. The results produced by the column experiment demonstrate that using the sorbents to remove chemically emulsified oil may not be a successful approach.

After finding the way to eliminate oil adhesion problem, it was realized that this problem always occurs when working with oil and grease. Moreover, most oil and grease found in stormwater runoff is in a free form. As a result, the direction of the experiments was changed to flume test in which free oil-water samples were employed and sorbents were applied as insert materials in a catch basin insert. This experimental approach is more realistic when comparing to the field conditions.

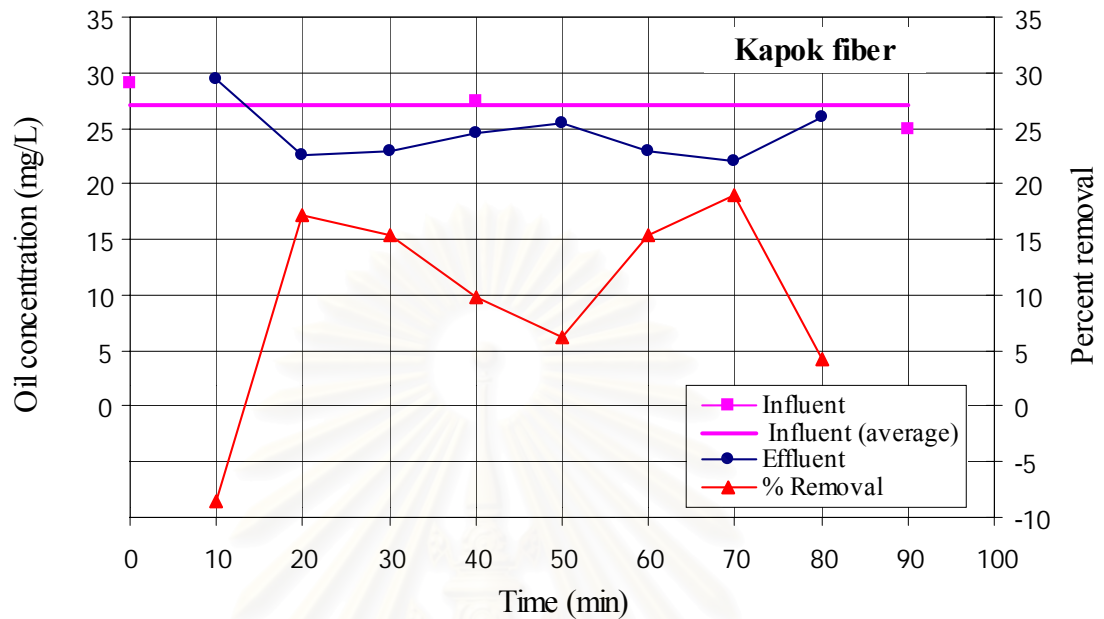


Figure 4.6 Chemically emulsified oil removal by kapok fiber during column experiment.

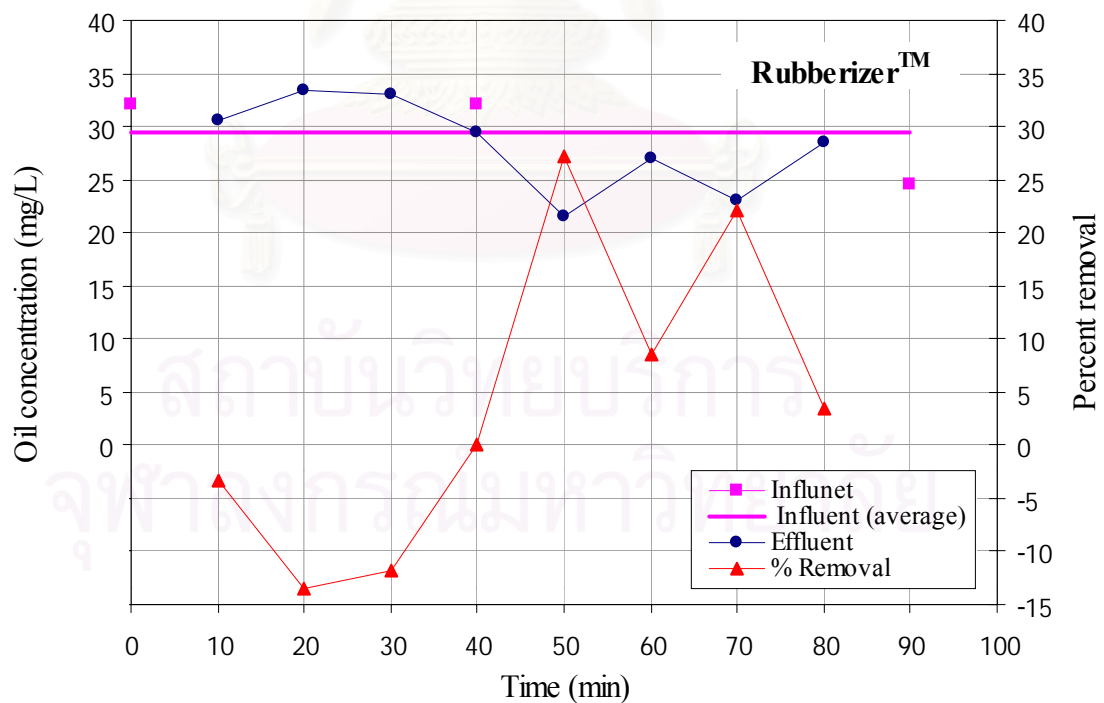


Figure 4.7 Chemically emulsified oil removal by Rubberizer™ during column experiment.

4.3 Flume Experiment

4.3.1 Oil Sorption Test

The sorbents used in the flume oil sorption test included kapok fiber, cattail fiber, *Salvinia* sp., polyester fiber, wood chip, rice husk, coconut husk and bagasse. The results of the tests were illustrated in Figure 4.8 to Figure 4.15. As shown in these figures, the top graphs showed influent and effluent concentrations and the percent removal versus time while the bottom graphs showed the amount of oil adsorbed (mg) versus time and total mass of oil adsorbed (mg). To evaluate oil sorption performance of the sorbents, the results were discussed in terms of operation time, hydraulic conditions, influent and effluent concentrations, and removal efficiency and mass of oil sorbed.

4.3.1.1 Operation Time

By following the protocol described in Section 3.3.3.1, it was found that there was the difference in operation time among the sorbents. Kapok fiber and Cattail fiber were the sorbents that were tested until 360 minutes. For kapok fiber, the effluent oil and grease concentration was close to 15 mg/L (Figure 4.8) during the last 60 minutes of the last run (Run 4). However, the cattail fiber provided the effluent with oil concentration of 10 mg/L or less throughout the entire five runs (Figure 4.9).

For *Salvinia* sp. and polyester fiber, the last run (Run 3) was stopped after 300 minutes of operation (Figures 4.10 and 4.11). The reason that the polyester fiber run was terminated before 360 minutes despite the effluent oil concentration was well below 15 mg/L was that the leaching of oil from the sorbent after Run 3 was observed. This oil leaching by gravity indicated that the polyester fiber could not retain the oil in its structure and was saturated with oil after 300 minutes of operation (Run 3).

In case of wood chip and rice husk, the runs were terminated after 120 minutes. They were stopped because the effluent water no longer met the criteria of oil and grease concentration of 15 mg/L (Figures 4.12 and 4.13). For coconut fiber, the effluent reached 15 mg/L at the first sampling (Figure 4.14) but the run was continued since the oil and grease concentration could not be easily predicted by

visual observation. However, the run of bagasse took place for only 30 minutes (Figure 4.15) because it was experienced that the amount oil sheen was not much different in influent and effluent samples and therefore there was no benefit to continue the run.

Although the operation time can indicate how long the sorbents will function, it should not be used as a sole criteria to evaluate the sorbents for oil and grease removal in runoff.

4.3.1.2 Hydraulic Conditions

For the oil sorption test, the sorbents in the baskets served as filter media to capture oil entering into the baskets. The hydraulic conditions such as head loss and flow pattern in the basket were observed because they can be used to explain the performance of the sorbents. During the tests, it was found that the head loss through the basket was approximately of 1-2 inches in the runs of kapok fiber, cattail fiber, *Salvinia* sp., and polyester fiber, but there was head loss for the wood chip, rice husk, coconut husk, and bagasse runs. The slight head loss may improve the removal efficiency because it increases hydraulic retention time and prevent short circuit flow in the basket. However, high head loss (clogging) may cause an overflow problem (out of the basket).

Moreover, it was found that the patterns of water flow out of the basket were different among the sorbents. This might be due to their physical characteristics. For kapok fiber, the water would rather flow out around the edge of the basket than distribute throughout the cross sectional area of the basket. This occurred because the fiber was further compacted by the inflow water (that fell into the basket) that made the fiber denser and lesser in void space. At this condition, most of the oil was adsorbed to the bulk surface of the fiber especially the channel between the fiber and the inside wall of the basket. Therefore, there was less contact opportunity between the oil and the inside part of the sorbent (Appendix C, Figure C.2). In contrast, for cattail fiber, the effluent flew out uniformly throughout the cross-sectional of the basket. The cattail fiber was used in a spike form; the fiber was not separated from the spike core (Appendix C, Figure C.3). The spike was cut to the size of 2-3 cm long and placed into the basket. Because the core supported the structure of cattail fiber in the

basket, it did not collapse as found for kapok fiber. Moreover, using the cattail fiber with the core provided the void space that promoted the contact opportunity between the oil and sorbent.

Similar to cattail fiber, the effluent water from the other sorbents (*Salvinia* sp., wood chip, rice husk, coconut husk, and bagasse) could also flow throughout the bulk of sorbents and their structures were not collapsed by water. For polyester fiber, the water could also penetrate throughout the sorbent even the sorbent body was compressed like kapok fiber.

4.3.1.3 Oil Influent and Effluent Concentrations

The oil influent concentration was adjusted by changing the flow rate of water and used motor oil. It was found that the values of oil influent concentration fluctuated because of the non-ideal mixing of used motor oil and water and slight oil adhesion to the glass flume (Figures 4.8 to 4.15). To avoid the error, the influent samples were taken from the water that fell from the flume before it got into the sorbent basket.

The oil effluent concentration was one of the parameter that could be used to justify the performance of the sorbents. From Figures 4.8 to 4.15, four distinctive trends of oil effluent concentration were observed among the eight sorbents. The first group was kapok fiber and cattail fiber, which have similar oil effluent trends. There was little fluctuation of effluent oil concentration in both sorbents but not over 10 mg/L (except at saturation for kapok fiber). During the test of kapok fiber and cattail fiber, sorption of used motor oil could be visually observed by dark color of oil attached to the fiber.

According to Choi (1996), oil sorption by kapok fiber was resulted from sorption onto both fiber surface and capillary action through its hollow lumen. Oil can attach to the fiber surface because of high surface wax content (~ 3%). Since, kapok fiber has non-collapsing and large hollow lumens (almost 90% of total diameter of the fiber); oil can penetrate and be trapped inside the lumens. The picture scanning electron microscope (SEM) of kapok fiber can be seen in Figure C.8a (Appendix C).

Likewise, oil sorption by cattail fiber may be attributed to the capillary phenomenon and its hydrophobic properties. The cattail fiber is the pollen of cattail plant, which looks like floss and has lumen inside. The SEM picture of cattail fiber was shown in Figure C.8b (Appendix C). The hydrophobicity of cattail fiber was demonstrated by the non-wetting of water and wetting of hexane on the cattail spike. The hydrophobic properties may originate from the pollen of cattail that was tightly arranged in the spike. It was noticed that water could wet the cattail fiber when it was separated from spike core.

Salvinia sp. and polyester fiber were in the second group, which showed the very low oil effluent concentrations. As illustrated in Figures 4.10 and 4.11, the oil effluent concentrations of both sorbents were relatively low at the first 60 minutes of the tests (compared with the other sorbents). They were in a range of 0.8-2.4 mg/L. Additionally, at this oil effluent concentration range, slight oil sheen in the effluent samples was found but no light reflection was observed.

Like kapok and cattail fiber, the oil sorption onto *Salvinia* sp. and polyester fiber was obviously seen that the dark material associated to the used sorbents (Appendix C, Figures C.4 and C.5). *Salvinia* sp. had shorter service time than polyester fiber; the effluent oil concentration provided by *Salvinia* sp. was over the standard after 210 minutes of operation while that provided by polyester fiber was not exceed the standard during the sorption experiment. The high removal efficiency of polyester fiber was expected because it is a commercial sorbent and has been known as a very olephilic material. In addition, the fiber is petroleum-based material like motor oil. Interaction between hydrocarbon functional groups causes oil sorption to the fiber. *Salvinia* sp. could remove the oil well because of the hydrophobic property of its leaves which was obtained from hair like structure on leaves surfaces (Ribeiro *et al.*, 2000). This hydrophobic property exhibits the water repellence and allows the oil, which has lower surface tension than water, to wet the surface of sorbent (Yves, 1985 and Ribeiro *et al.*, 2000).

The third group of sorbents included wood chip and rice husk. The oil effluent concentrations of both sorbents fluctuated around 10 mg/L and then exceeded the standard (15 mg/L) during the Run 2 (60-120 minutes). The uniform flow throughout the media may promote the oil sorption onto wood chip and rice husk. This condition

increased the contact opportunity between the oil and sorbents. The dark color attached to the sorbent surface (Appendix C, Figures C.6 and C.7) showed that wood chip and rice husk could remove some oil from the influent stream even the obtained effluent oil concentrations were higher than other sorbents.

The fourth group was coconut husk and bagasse. The results showed that the effluent oil concentrations exceeded the standard (15 mg/L) at the beginning of the test (Figures 4.14 and 4.15). From the figures, it was clear that these two sorbents exhibited low oil removal capability. Furthermore, it was found that the amount of sheen oil in the effluent samples was almost the same as obtained in the influent samples. Less oil sorption may be from the unfavorable surface properties of coconut husk and bagasse themselves.

The comparison of oil influent and oil effluent concentrations is illustrated in Figure 4.16. The figure presents the average concentrations of both influent and effluent during the run and the whisker described standard deviation (SD) for each average value. The SD of the effluent oil concentration of *Salvinia* sp. fall below x axis because of the substantial difference in effluent oil concentrations between initial and saturation stages.

All data of influent for each sorbent were averaged. However, the averaged effluent values were calculated by using only data of time at the beginning of the first run to the time that concentration reached standard (15 mg/L). This was except for coconut husk and bagasse. The details are presented in summary of flume test results (Table 4.1).

4.3.1.4 Oil Removal Efficiency and Mass of Oil Adsorbed

As shown in Figures 4.8 through 4.15, the removal efficiencies of all sorbents fluctuated; however, they generally declined over time. It is known that the removal efficiency depends upon the influent and effluent concentrations. Nevertheless, the comparison of the performance of sorbents using average removal efficiency was not appropriate method since the influent oil concentration varied significantly during the test. As a result, the removal efficiency was defined based on the total mass of oil adsorbed over total mass oil input which were calculated using equations 3.1 and 3.2,

respectively. The results are summarized in Figure 4.17 (details are shown in Appendix B, Table B.1). Polyester fiber showed total oil adsorbed of 253,130 mg and the highest total removal efficiency of 93.5%. However, cattail fiber exhibited the highest mass of oil adsorbed of 277,648 mg, which was equal to 86.6 percent of total oil removal efficiency. Kapok fiber could remove 206,862 mg of oil with a removal efficiency of 83.2%. *Salvinia* sp. removed 236,120 mg of oil that was higher than kapok fiber but little lower in removal efficiency (81.7%). It should be noted that the operation time of kapok and cattail fibers was 60 minutes longer than that of polyester fiber.

Although, the total oil removal efficiency of kapok fiber was slightly lower than that of cattail fiber, the mass of oil sorbed should not be much less than that of cattail fiber because they were tested at about the same period of time. This less oil sorbed was because the water flow rate accidentally dropped from 20 L/min to 12 L/min. Therefore, the oil flow rate had to be adjusted to maintain the desirable range of influent oil concentration. Wood chip and rice husk had the total oil removal efficiency of 74% and 73.2%, respectively. But the total oil adsorbed of wood chip and rice husk were much less than kapok fiber, cattail fiber, *Salvinia* sp., and polyester fiber because of shorter operation time. Coconut husk and bagasse were the two least effective sorbents in both total oil removal efficiency and total oil sorbed.

According to the results, kapok fiber, cattail fiber, *Salvinia* sp., and polyester fiber, are the four sorbents that exhibited high oil sorption performance. However, the best sorbent could not be justified without considering the results of oil desorption test.

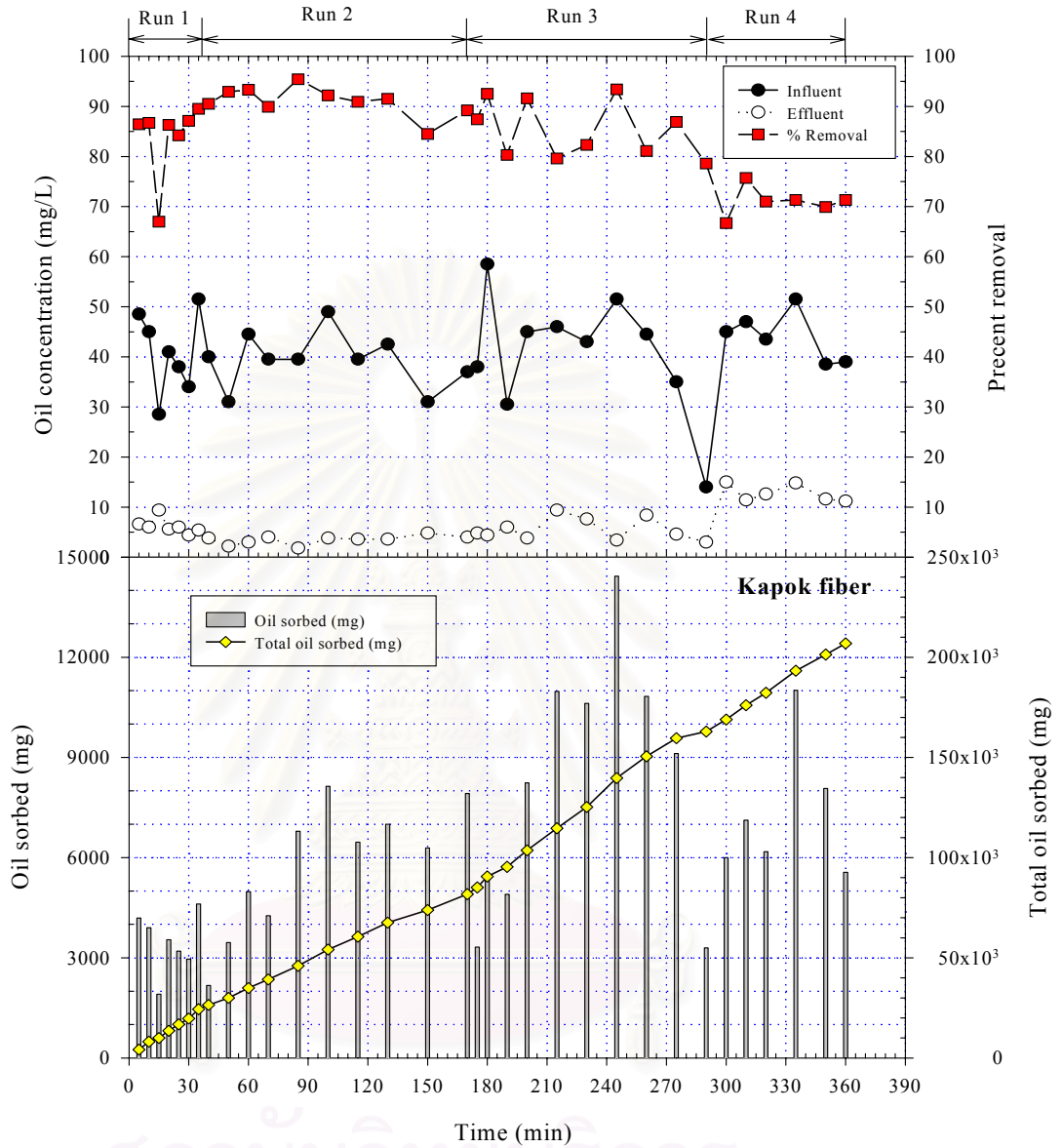


Figure 4.8 Results from the flume oil sorption test of kapok fiber.

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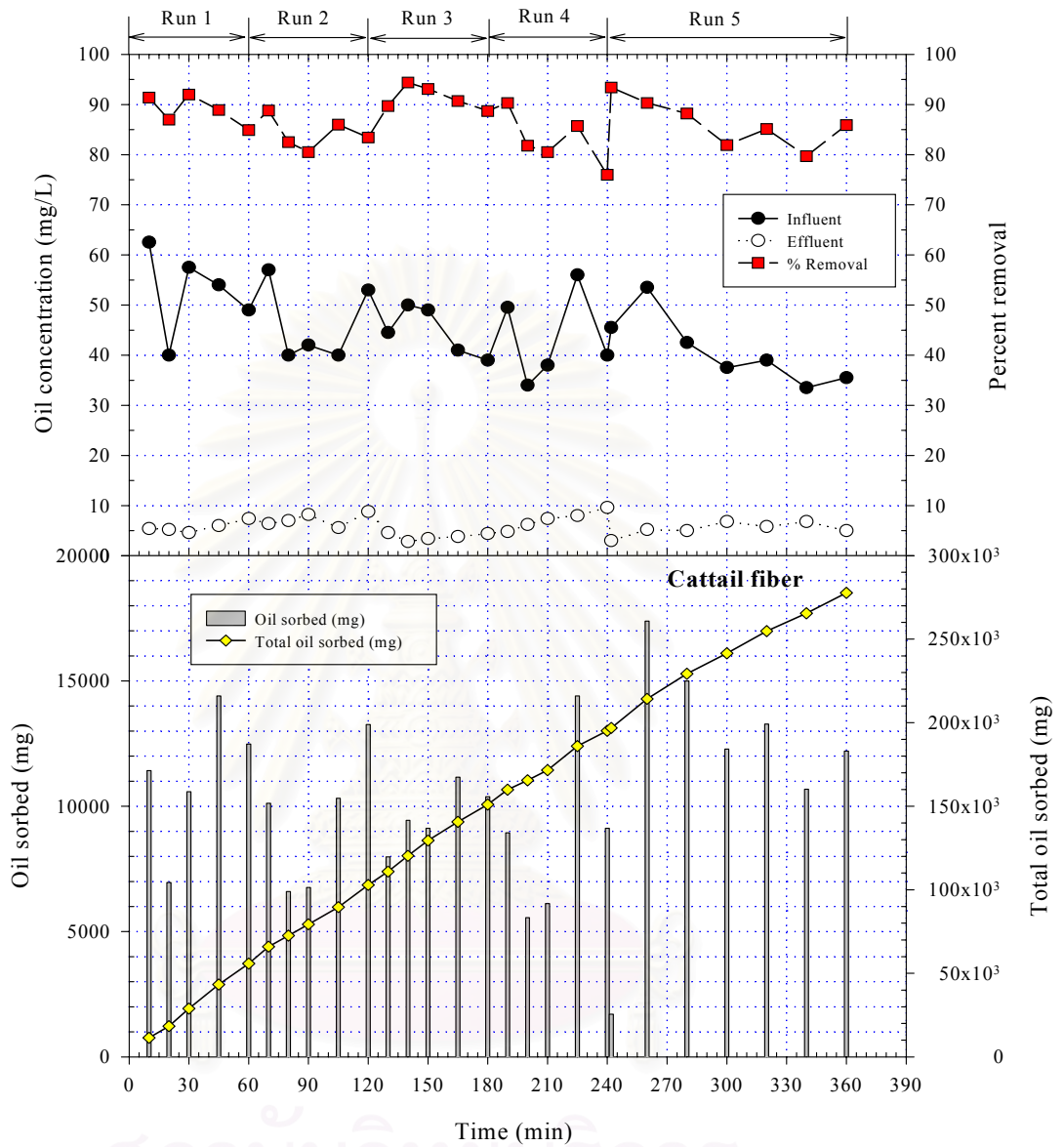


Figure 4.9 Results from the flume oil sorption test of cattail fiber.

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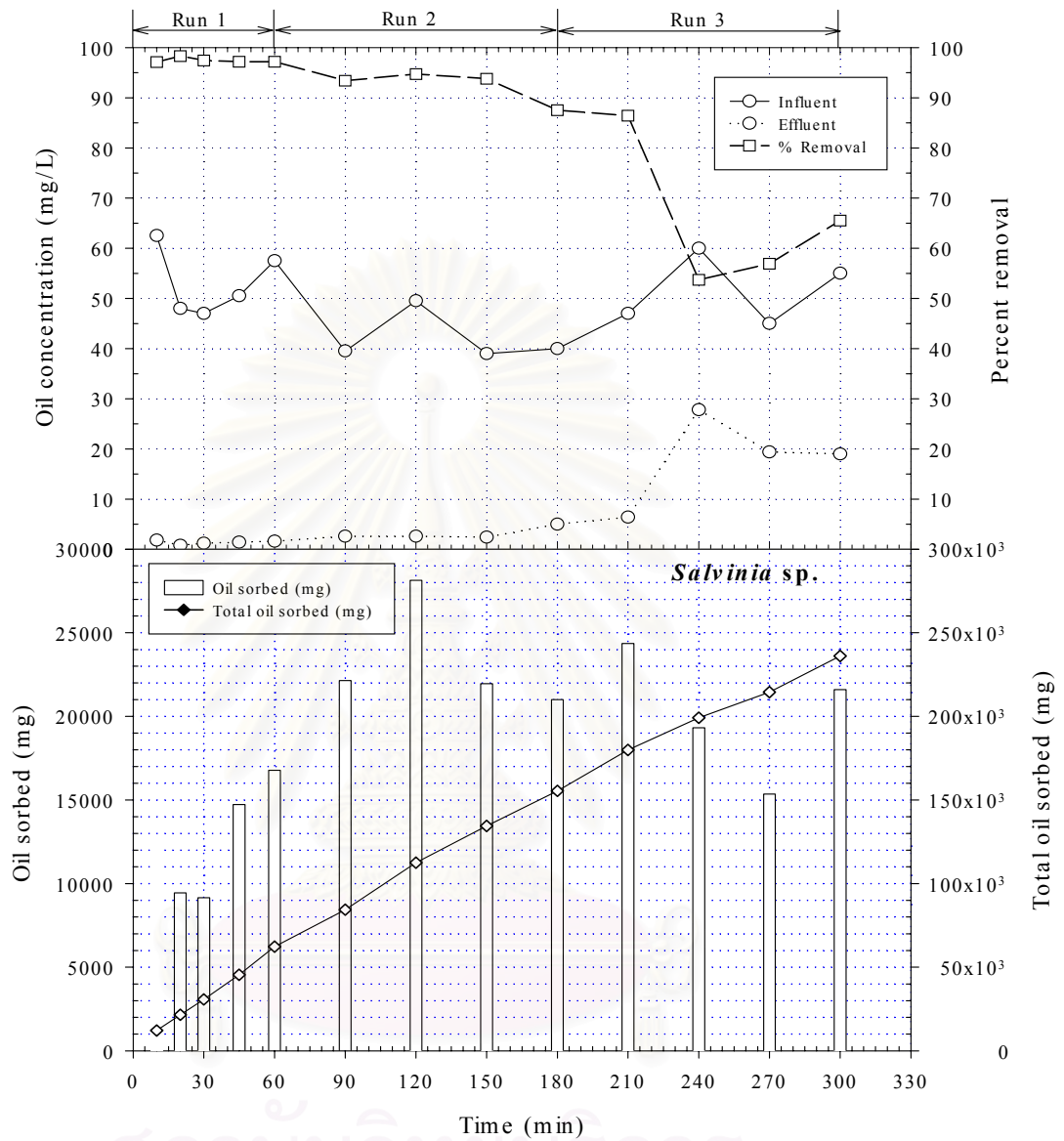


Figure 4.10 Results from the flume oil sorption test of *Salvinia sp.*

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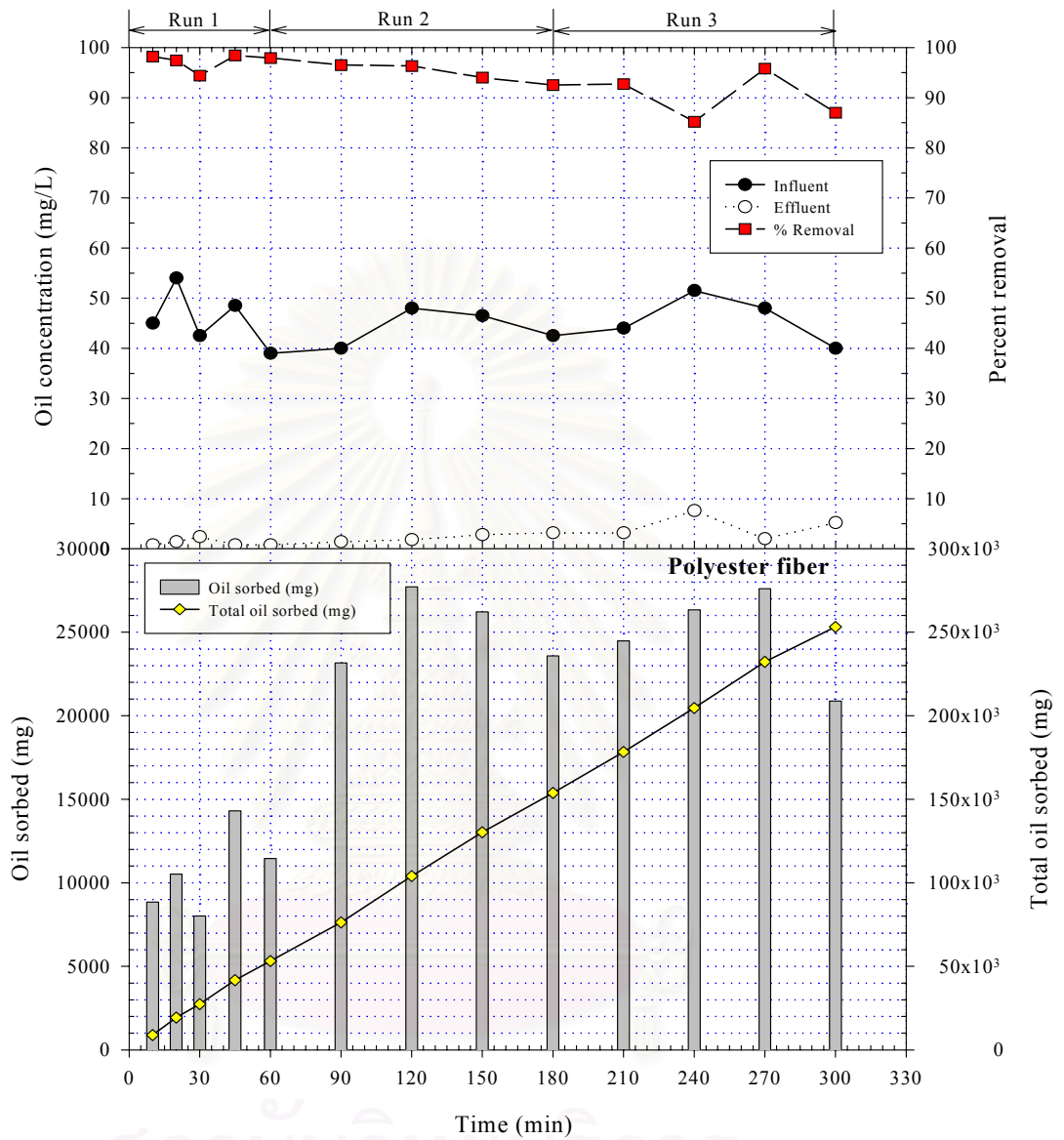


Figure 4.11 Results from the flume oil sorption test of polyester.

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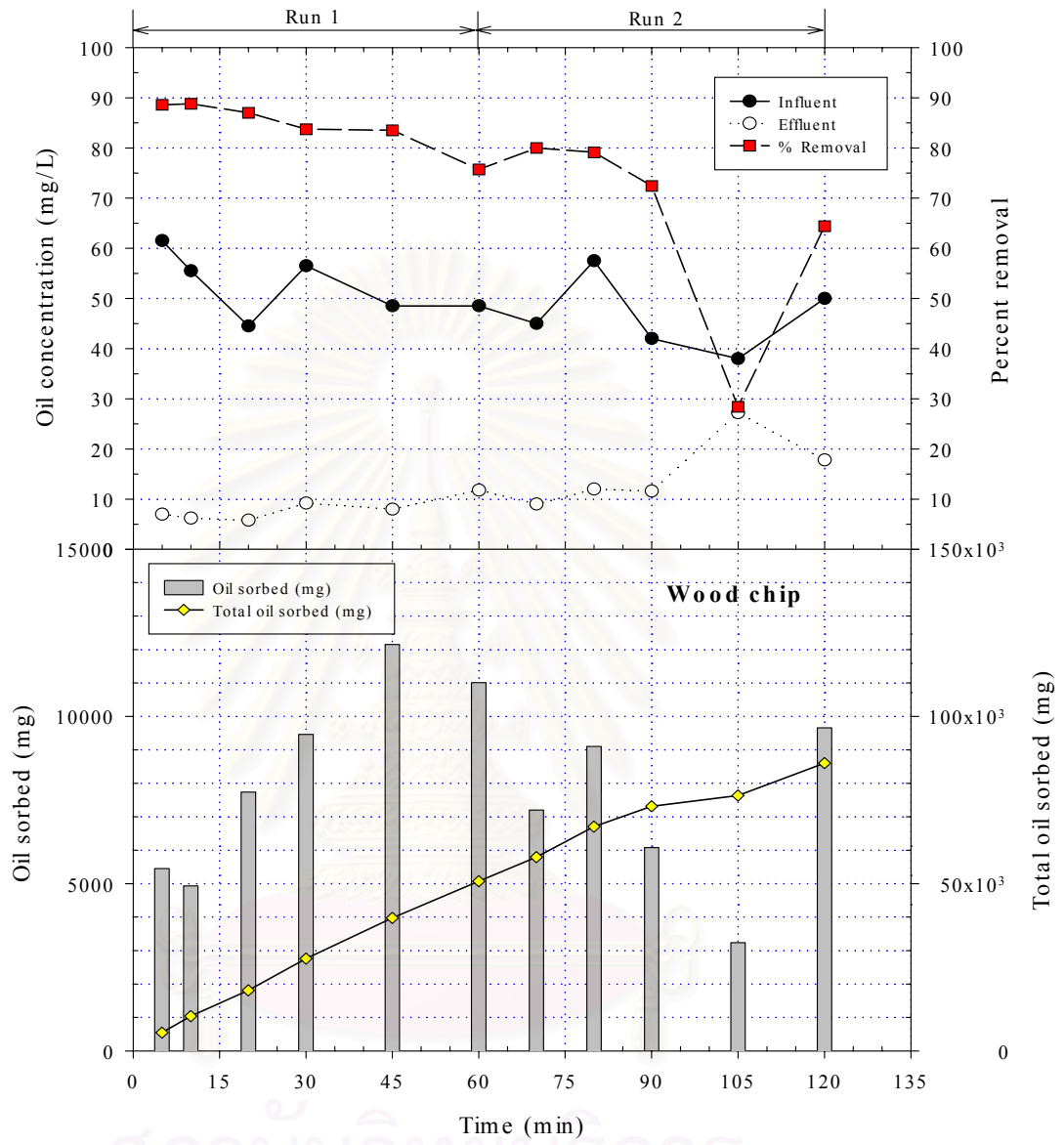


Figure 4.12 Results from the flume oil sorption test of wood chip.

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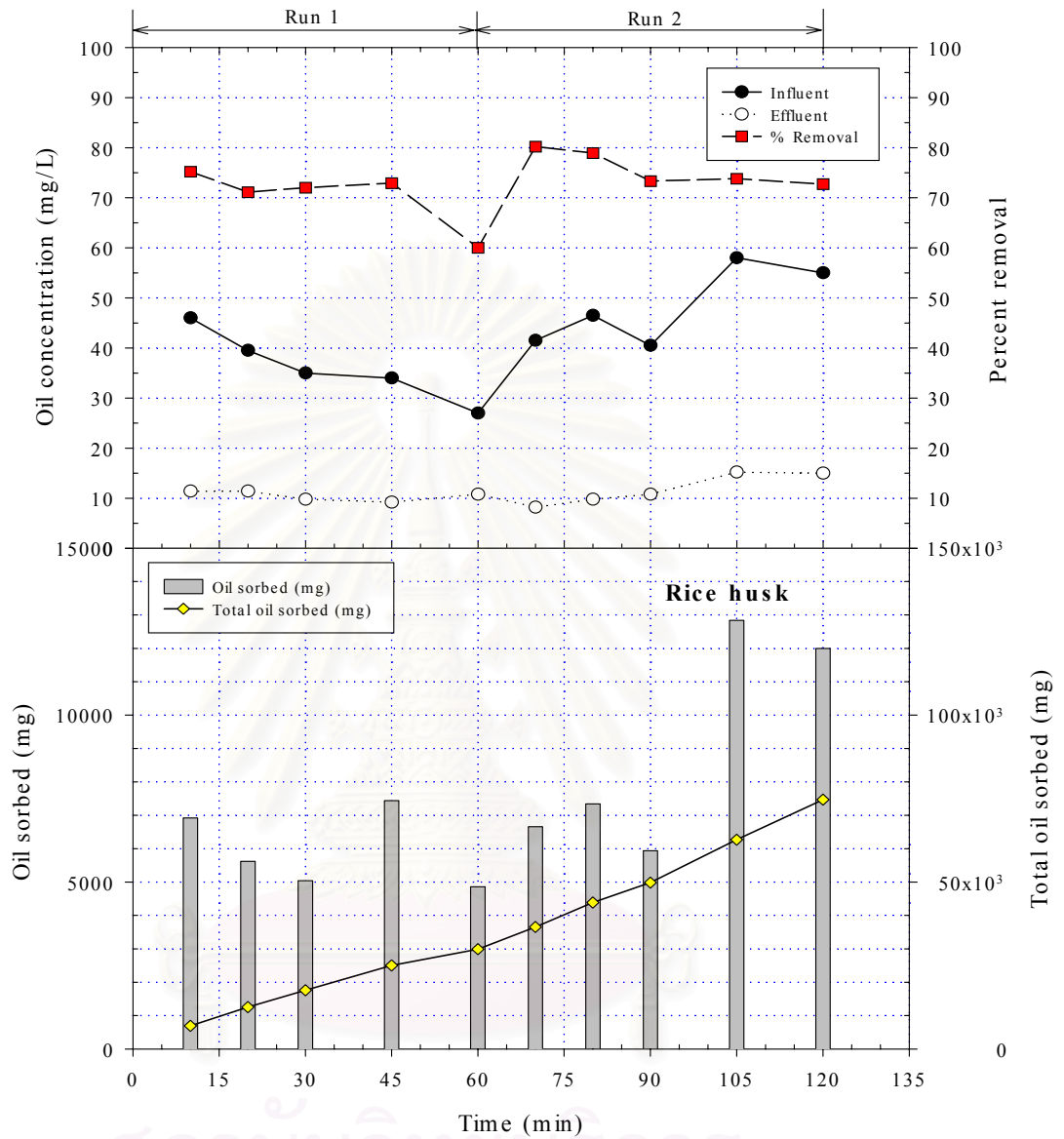


Figure 4.13 Results from the flume oil sorption test rice husk.

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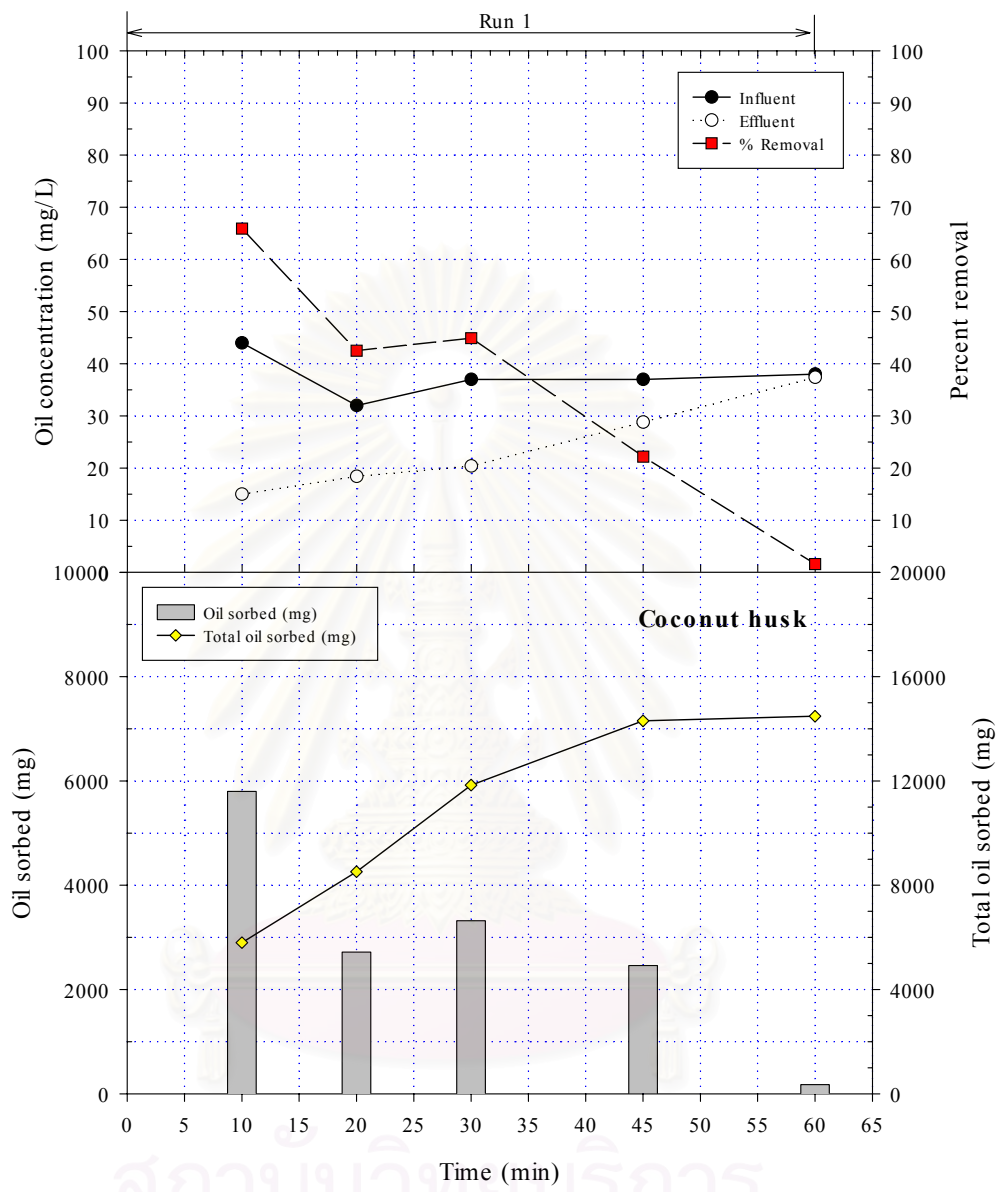


Figure 4.14 Results from the flume oil sorption test of coconut husk.

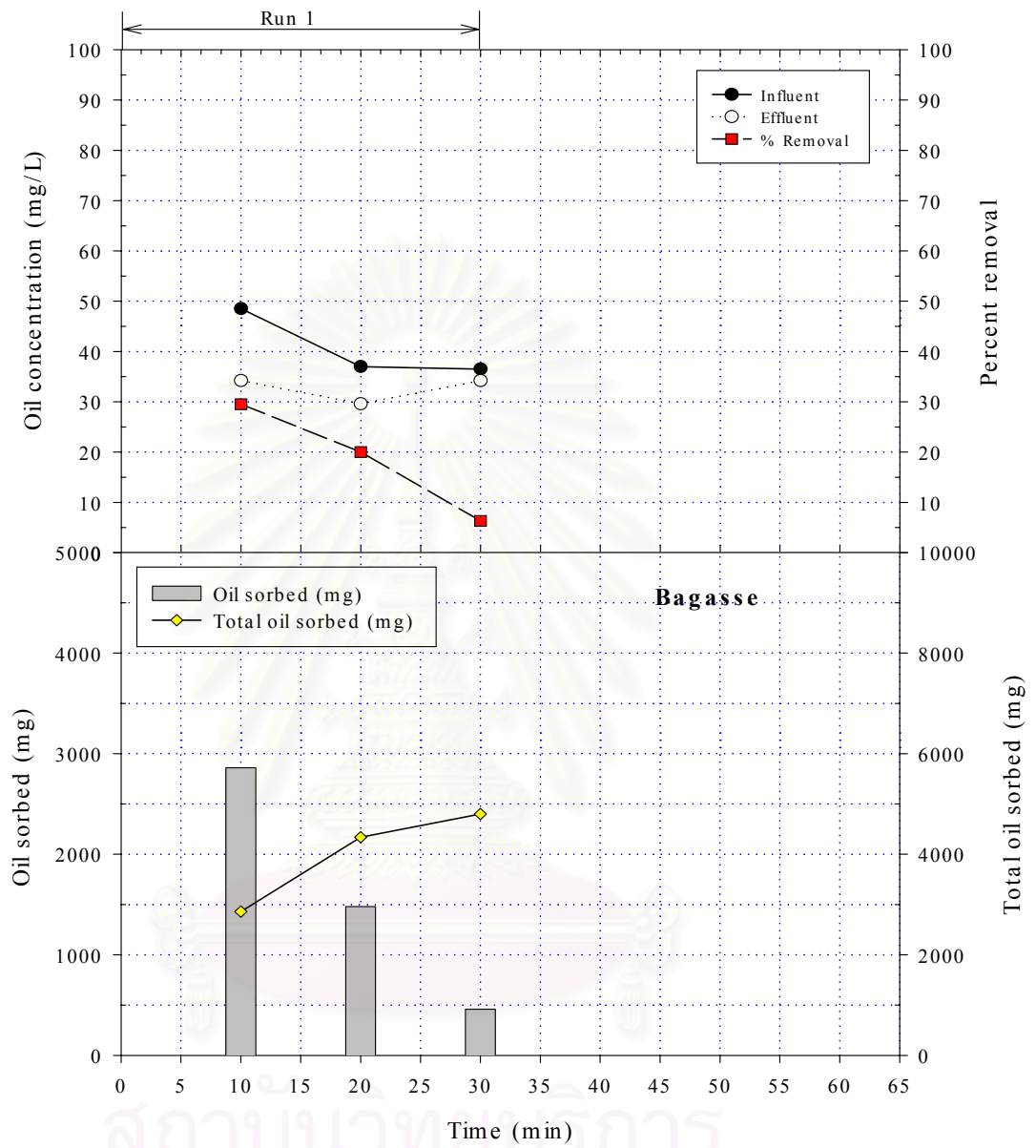


Figure 4.15 Results from the flume oil sorption test of bagasse.

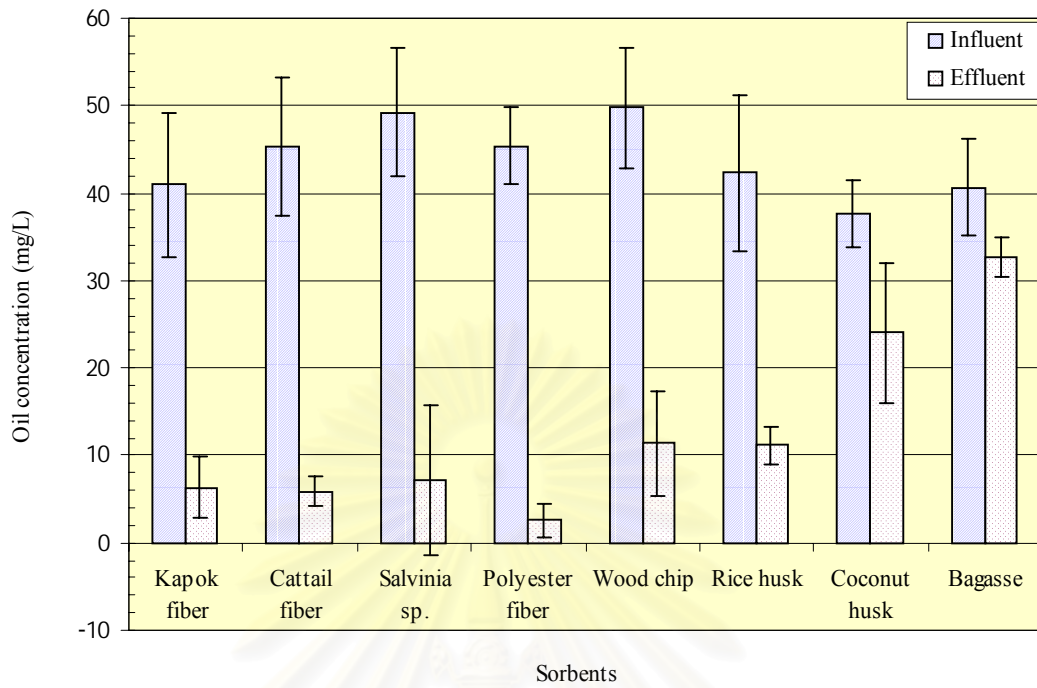


Figure 4.16 Influent and effluent concentrations of the flume oil sorption test (whiskers are standard deviation)

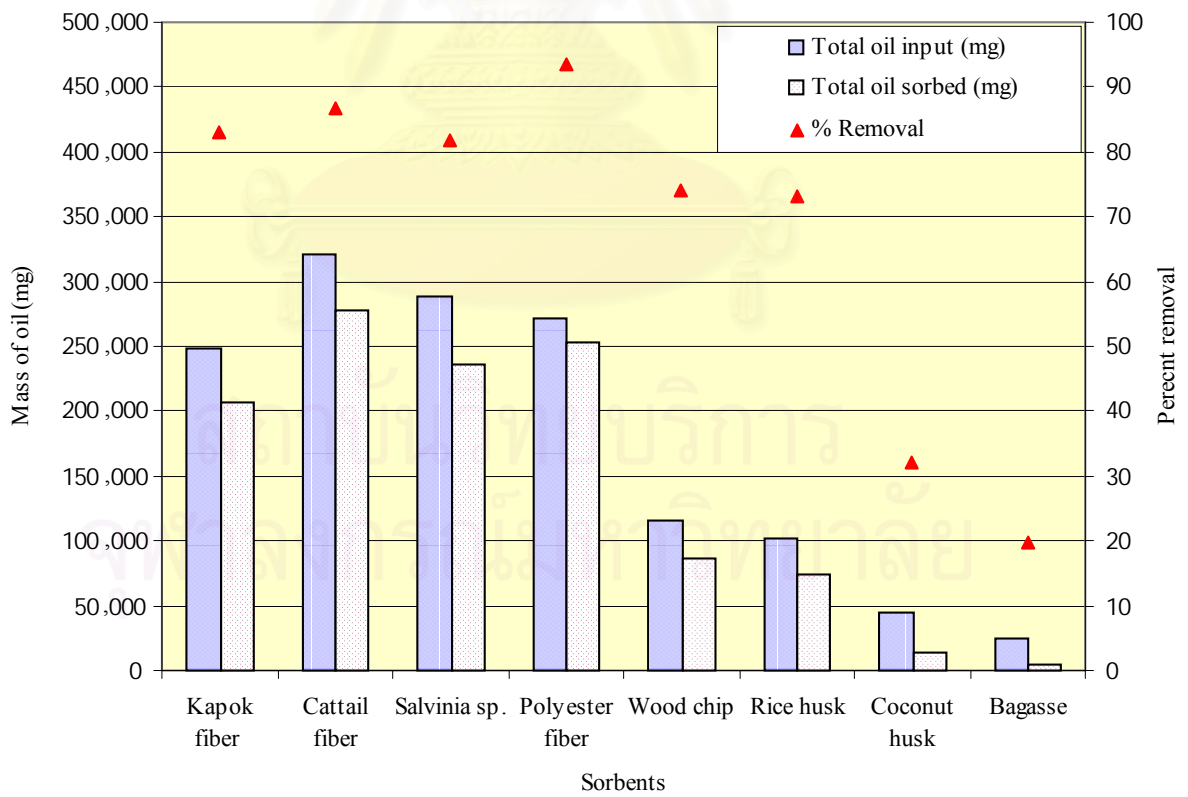


Figure 4.17 Total mass of oil input and sorbed and removal efficiency of various sorbents

4.3.2 Oil Desorption Test

The flume oil desorption test was performed to examine the oil retention capability of the sorbents. There were six types of sorbents from the sorption tests examined in the desorption test: kapok fiber, cattail fiber, *Salvinia* sp., polyester fiber, wood chip, and rice husk. Coconut husk and bagasse were not tested since they showed low oil sorption capacities during the sorption test. As shown in Figures 4.18 to 4.23, the effluent oil concentrations were relatively high at the beginning and then rapidly decreased during the first 5 minutes of the runs. After that, the concentration either slightly fluctuated or gradually decreased until the end of the runs. Polyester fiber released the highest oil concentration (183.4 mg/L) in the first minute of the run. It was interesting that the effluent oil concentrations provided by the desorption test was relatively high in the first flush (1 min.) while the effluent oil concentrations provided by the sorption test were only less than 7.6 mg/L. Because the sampling interval of Run 2 and Run 3 (sorption test) was 30 minutes, the information of effluent concentration during the first flush may be missing. The effluent samples should have been frequently taken in the first period of the run.

On the contrary, wood chip exhibited the lowest effluent concentration (2 mg/L) at the initial stage of the run and also little variation of effluent oil concentration during the run (Figure 4.22). From visual observation, most of oil sorbed by wood chip would rather be trapped inside the wood fiber than accumulated as an oil layer on the surface. Therefore, less amount of oil was scoured out of the wood chip. In addition, the effluent samples of all biomass sorbents (at 1 minute) were turbid and contained brownish tiny particles. However, the turbidity and constituent were not observed in the effluent samples after 3 minutes of the desorption runs.

The oil desorption trends of the sorbents are summarized in Figure 4.24. The amount of oil desorbed and total oil desorbed were calculated based on equation 3.3. For polyester fiber, the desorption increased dramatically in the first five minutes and then steadily increased during the rest of the test period (5 to 15 min.) Desorption from kapok fiber has similar trend as that from polyester fiber; oil rapidly desorbed in first three minutes and later slowly desorbed. However, the other sorbents exhibited gradual increase of oil desorption throughout the run.

To compare the results of desorption run among the sorbents, the percent oil desorption was determined from the ratio of total mass of oil desorbed per total mass of oil sorbed (Figure 4.25). The result indicated that the polyester fiber exhibited the highest percent desorption (4.05%) and also the highest mass of oil desorbed (10244 mg). The scouring of oil out of polyester fiber was because the oil in/on soaked fiber could not resist the shear force of water.



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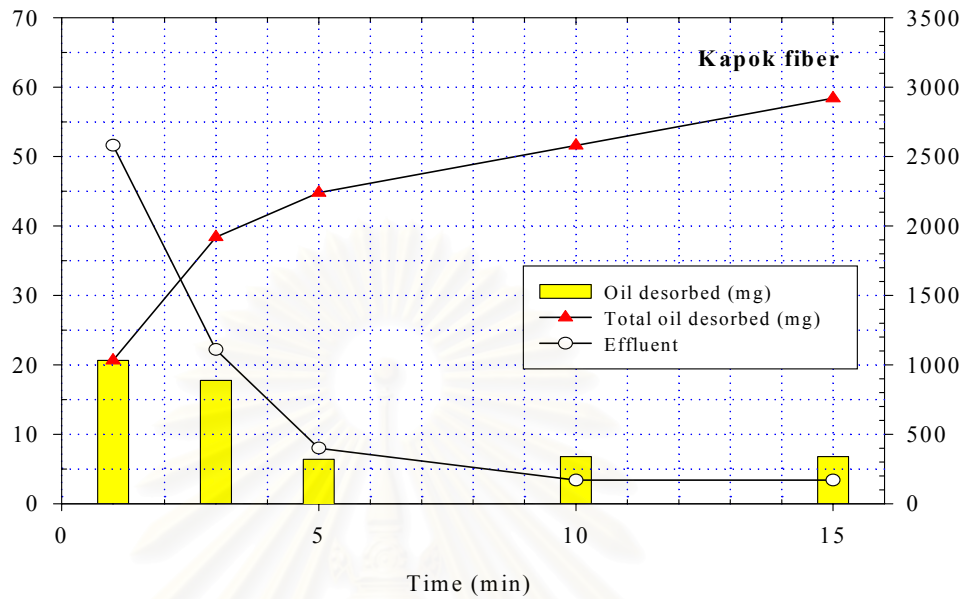


Figure 4.18 Results from the flume oil desorption test of kapok fiber.

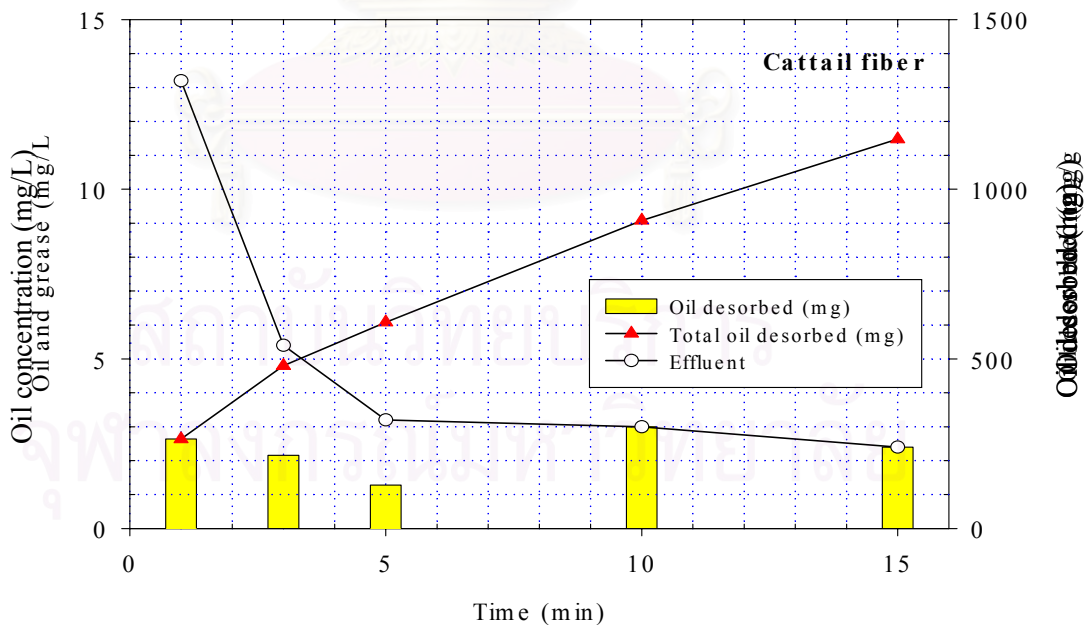


Figure 4.19 Results from the flume oil desorption test of cattail fiber.

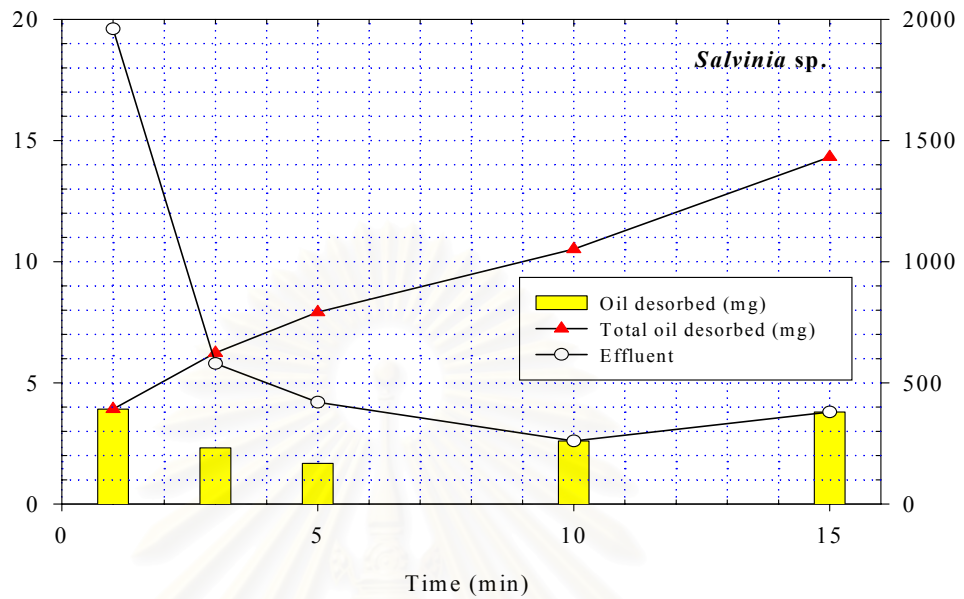


Figure 4.20 Results from the flume oil desorption test of *Salvinia* sp.

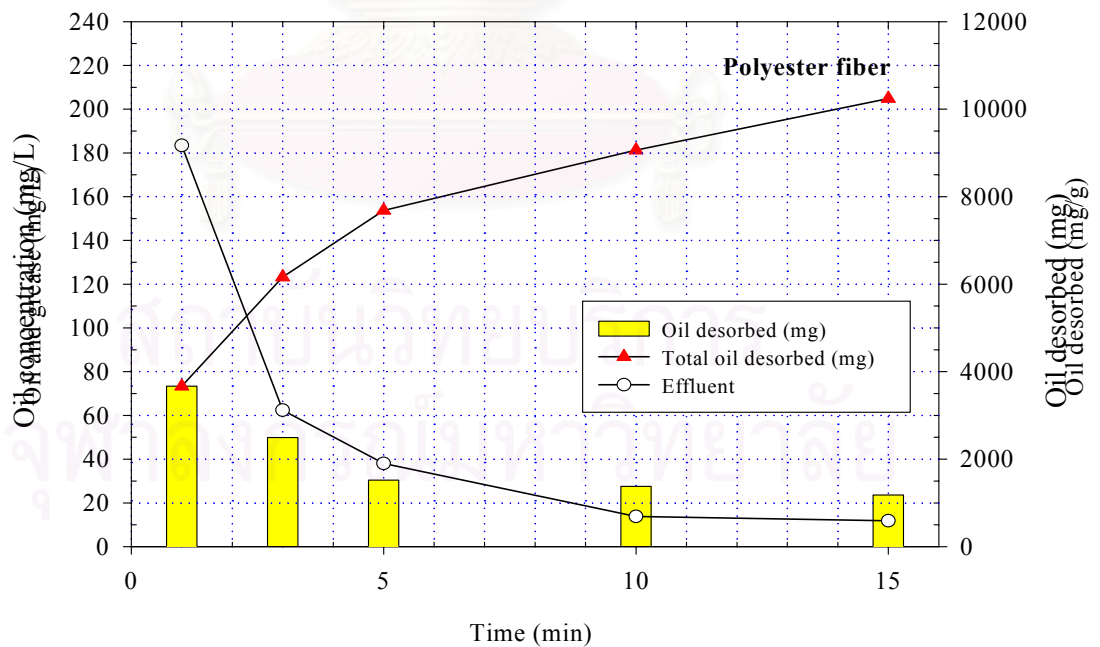


Figure 4.21 Results from the flume oil desorption test of polyester fiber.

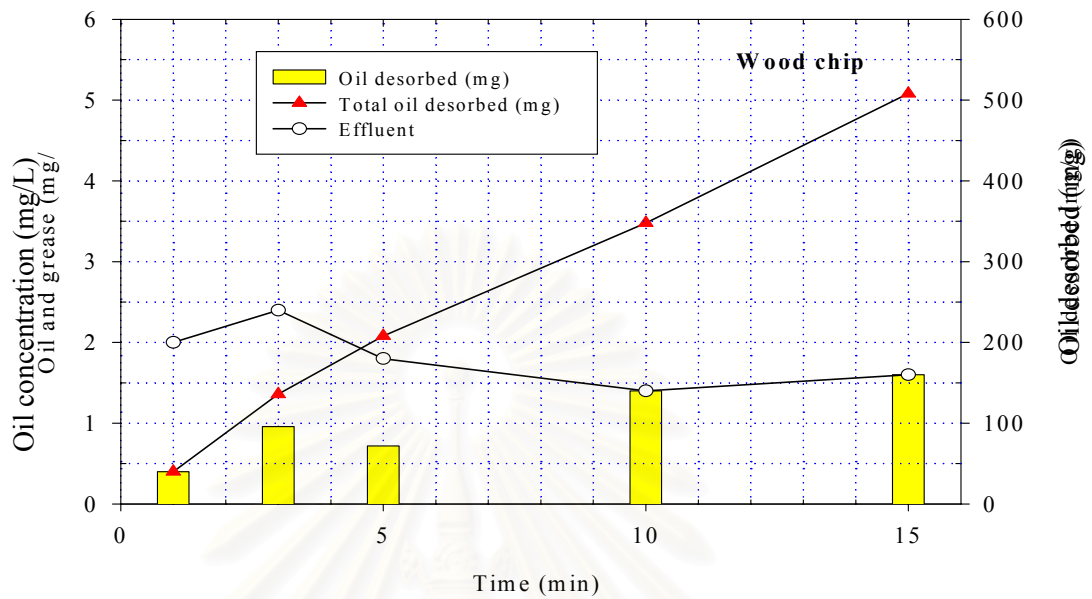


Figure 4.22 Results from the flume oil desorption test of wood chip.

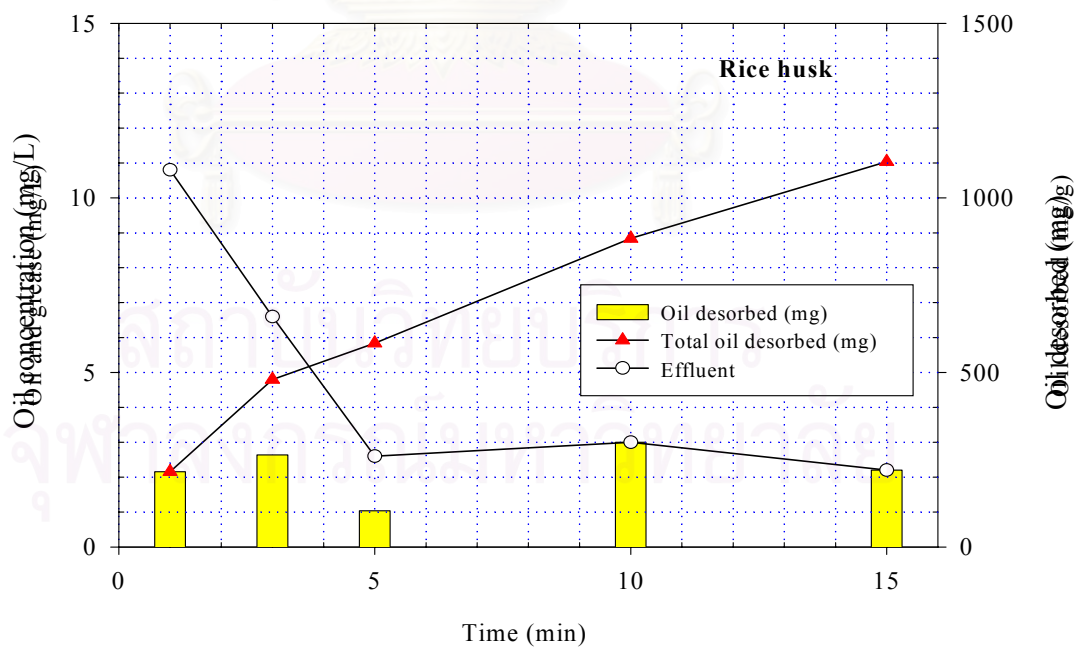


Figure 4.23 Results from the flume oil desorption test of burned rice husk.

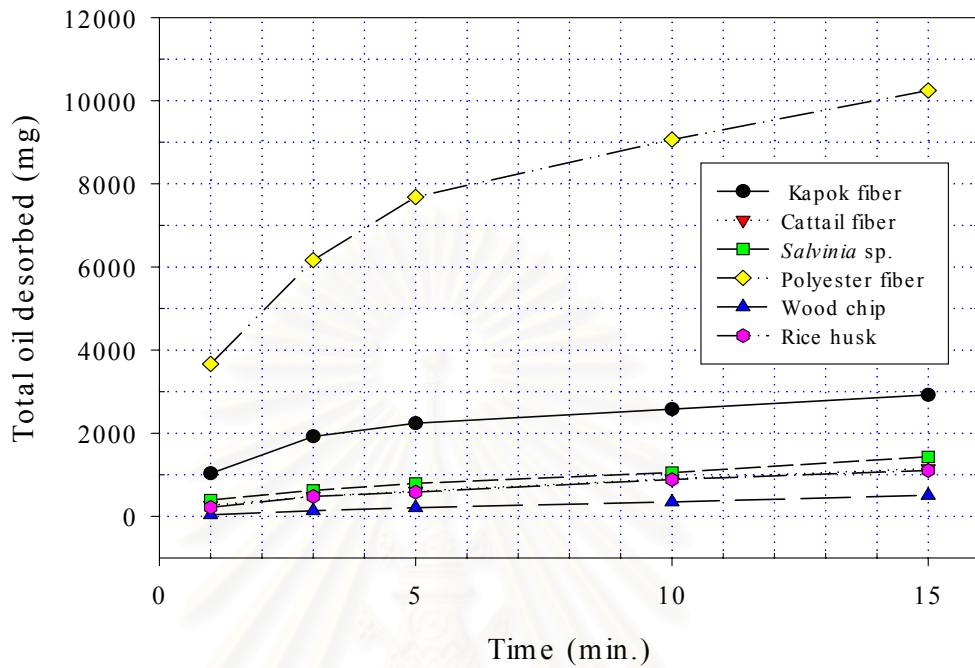


Figure 4.24 Total oil desorption trend of various sorbents

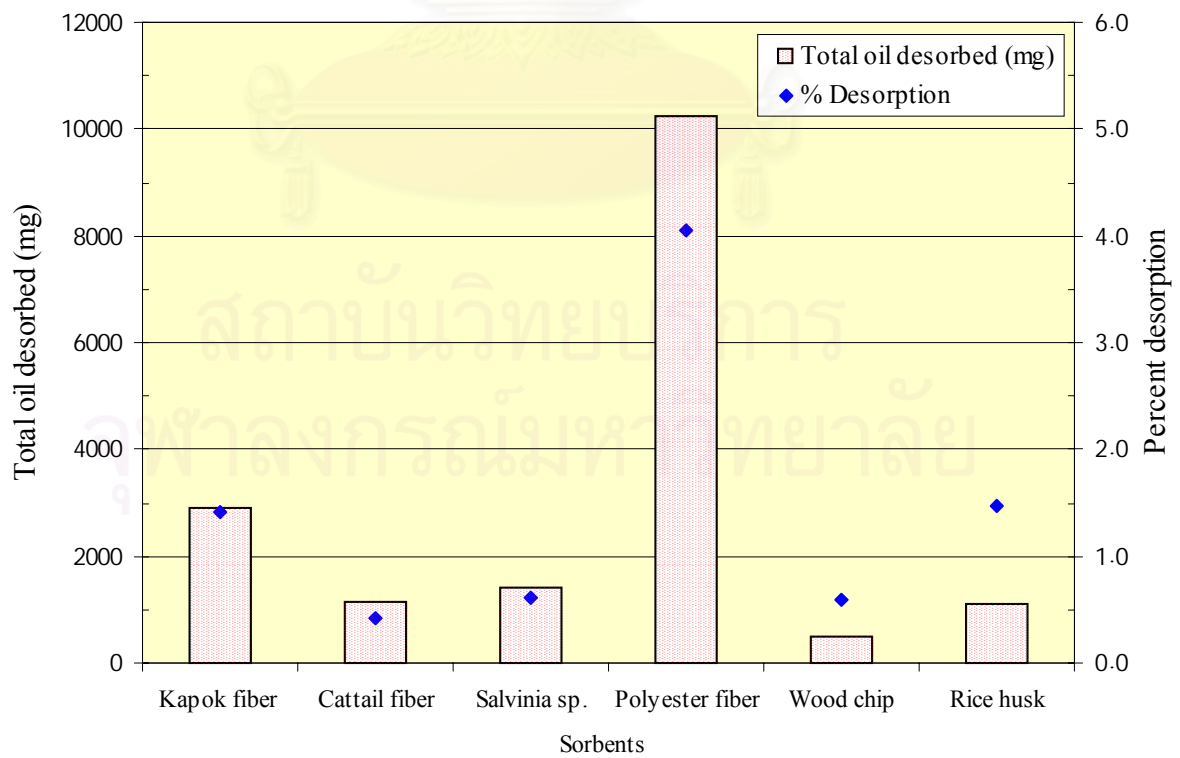


Figure 4.25 Total mass of oil desorbed and percent desorption of various sorbents.

4.4.1 Comparison of Sorbents in The Flume Experiment

All of the results from the flume experiment were summarized in Table 4.1 to compare the sorbents. The results showed that some sorbents were excellent for some criterion but were poor for other criteria. For example, polyester fiber exhibited the highest total oil removal efficiency and also provided low oil effluent concentrations but it was the worst sorbent for oil retention. The selection of sorbents is criteria dependent. However, this research focused on the effluent quality; therefore, *Salvinia* sp. was considered to be the best biomass sorbent for oil removal.

For actual applications, the cost, ease of preparation, and availability of the sorbents may need to be considered. Kapok fiber, cattail fiber, and *Salvinia* sp. require intensive labor for harvesting and preparation. For example, kapok fiber has to be separated from seed and *Salvinia* sp. has to be collected from surface water, washed with water to remove silt and clay, and finally dried. Polyester fiber and wood chip are the waste from industries while rice husk is the agricultural waste. These sorbents will have to be collected from storage or disposal sites but usually are ready for use with minimal preparation.

Table 4.1 Summary of the flume experiment results

Sorbents	Oil sorption test											Oil desorption test	
	Operation time (min)	Influent (mg/L)			Effluent (mg/L)			Total oil input (mg)	Total oil sorbed		Percent removal	Total oil desorbed (mg)	Percent desorption
		Max.	Mean	Min.	Max.	Mean	Min.		mg	mg/g			
Kapok fiber	360	58.5	40.9	14.0	15.0	6.4	1.8	248710	206862	827	83.2	2920	1.41
Cattail fiber	360	62.5	45.3	33.5	9.6	5.8	2.8	320680	277648	1107	86.6	1148	0.41
<i>Salvinia</i> sp.	300	62.5	49.3	39.0	27.8	7.1	0.8	288900	236120	944	81.7	1432	0.61
Polyester fiber	300	54.0	45.3	39.0	7.6	2.6	0.8	270850	253130	1008	93.5	10244	4.05
Wood chip	120	61.5	49.8	38.0	27.2	11.4	5.8	116300	86020	343	74.0	508	0.59
Rice husk	120	58.0	42.3	27.0	15.2	11.2	8.2	102000	74660	298	73.2	1104	1.48
Coconut husk	60	44.0	37.6	32.0	37.4	24.0	15.0	45100	14480	58	32.1	-	-
Bagasse	30	48.5	40.7	36.5	34.2	32.7	29.6	24400	4800	19	19.7	-	-

CHAPTER V

CONCLUSIONS

The main objective of this research is to determine the feasibility of using the biomass sorbents (derived from plants) to remove oil from water runoff. Fifteen biomass sorbents and three synthetic sorbents were investigated for oil sorption performance. Synthetic oil-water samples used in this study include mechanically emulsified oil, chemically emulsified oil, and free oil samples. The study consists of batch, column, and flume experiments. The batch and column experiments were performed to screen the effective biomass. The flume experiment conducted to investigate to oil sorption and retention capability of selected sorbents from the batch experiments.

The batch experiment is composed of two tests: sorption screening test and sorption isotherm test. The screening test was performed using two types of oil-water samples: mechanically emulsified oil and chemically emulsified oil. With mechanically emulsified oil samples, the experiments were not successful because of oil attachment to glassware. Chemically emulsified oil samples were employed to solve this problem. By using chemically emulsified oil samples, the oil adhesion problem was insignificant and negligible and kapok fiber was the only selected sorbents to perform the isotherm test because the fiber exhibited the highest oil removal efficiency among the biomass sorbents tested. However, in the isotherm test, kapok fiber presented a weak correlation between mg oil/g sorbents and large amounts of oil concentration remained in the solution. The weak relationship was a result of the low contact opportunity, provided by an orbital shaking procedure, between oil and kapok fiber. It was later found that the oil removed by kapok fiber was not in emulsified form but free form. This was due to the volatilization of the emulsifiers (hexane and IPA). Based on these unsuccessful results, it was learned that the information obtained from the batch experiment using both mechanically and chemically emulsified oil samples could not be used for pre-identifying effective sorbents.

Chemically emulsified oil samples were used in the column experiment. The results of column experiment also confirmed the results of the batch tests that the chemically emulsified oil could not be removed by the biomass sorbents. Similar result was observed when a commercial oil sorbent (Rubberizer™) was tested for its oil removal ability from a chemically emulsified solution.

For the flume experiment, free oil samples were employed. The sorbents were tested in the simulated conditions that would happen in the field. The experiments included oil sorption and desorption tests.

The results of the sorption test showed that removal efficiencies of all sorbents, except coconut husk and bagasse, were greater than 70%. Moreover, *Salvinia* sp. and polyester fiber (synthetic commercial sorbent) were the sorbents that provided the least effluent oil concentrations. It was found that the sorbents that are hydrophobic such as kapok fiber, cattail fiber, *Salvinia* sp., and polyester fiber, could remove more oil than the other sorbents. Hydrophobic property (water repulsion) of sorbents plays an important role in oil sorption capability. In addition, the oil sorption capability of sorbents can be indicated by their physical characteristic. Kapok fiber, cattail fiber, *Salvinia* sp. (roots), polyester are loose fibers containing ample void spaces that can be used for oil retention. In contrast, the other sorbents are dense and therefore only allows oil coating on their surfaces. The results also showed that the oil sorption performance of some biomass sorbents (kapok fiber, cattail fiber, *Salvinia* sp.) was not much different from the commercial sorbent (polyester fiber). Therefore, the use of biomass sorbent to effectively remove oil in water runoff is possible.

During the desorption test, oil leached out of the all six sorbents tested. Polyester fiber was the sorbent that released the highest amount of oil to effluent stream (4% of total oil sorbed). This poor oil retention capability of polyester fiber was probably because it does not have interior lumen available for oil entrapment as some of the biomass sorbents tested. Furthermore, it was observed that oil started to drain out of the fiber due to gravity during the period between the sorption and desorption tests. This suggests that the use of polyester fiber as an oil sorbent must be practiced with care; frequent inspection to avoid the oil saturation will be needed.

CHAPTER VI

RECOMMENDATIONS FOR FUTURE STUDIES

Since utilizing the biomass sorbents, especially *Salvinia* sp., to remove free oil in runoff was successful; it would be interesting to study the plants, which have similar properties as *Salvinia* sp. Another sorbent that should be evaluated is the fiber waste (petroleum based) from some garment industries, because it has high oil selectivity and does not require any pretreatment before use. The application of the sorbents in the field should also be investigated especially on the lifetime of the sorbents. The biomass sorbents are degradable. Possible release of constituents from the sorbents such as suspended solid, color, nutrients, and BOD should be evaluated. Finally, the cost of the entire process starting from the acquisition to the disposal of the sorbents should be estimated.



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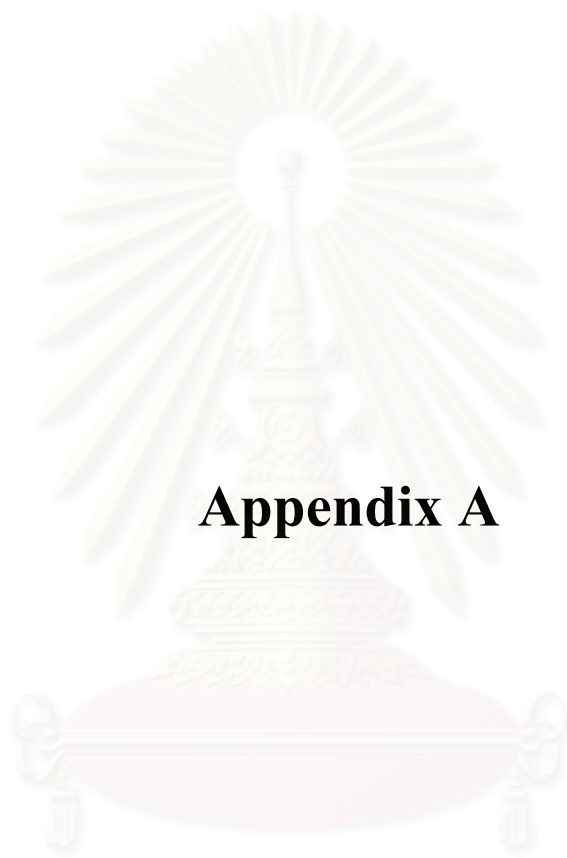
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Appendix A

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Table A.1 Batch oil adsorption test (mechanically emulsified oil)

Sorbents	Mass (g)	Vol. (mL)	Inf. (mg/L)	Eff. (mg/L)	% Removal		Oil adsorbed (mg/g)		pH
						average		average	
water lettuce	0.1020	-	-	-	-	-	-	-	-
	0.0968	500	18.80	3.50	81.4	83.4	79.03	79.2	7.91
	0.1011	500	18.80	2.75	85.4		79.38		7.88
Corncob	0.1030	500	18.80	7.25	61.4		56.07		7.68
	0.1015	500	18.80	9.50	49.5	53.5	45.81	49.3	7.73
	0.1009	500	18.80	9.50	49.5		46.09		7.71
Cattail leaf	0.0996	500	19.92	2.00	90.0		89.96		7.70
	0.1009	500	19.92	3.00	84.9	86.2	83.85	85.4	7.70
	0.1011	500	19.92	3.25	83.7		82.44		7.71
Umbrella plant	0.0994	500	19.92	3.50	82.4		82.60		7.64
	0.0998	500	19.92	3.50	82.4	82.8	82.26	82.8	7.53
	0.0997	500	19.92	3.25	83.7		83.60		7.78
Straw	0.1005	-	-	-	-	-	-	-	-
	0.0991	500	19.92	11.75	41.0	41.6	41.22	41.4	7.78
	0.1013	500	19.92	11.50	42.3		41.56		7.75
Bagasse	0.1005	500	21.98	5.25	76.1		83.23		7.94
	0.1018	500	21.98	6.50	70.4	76.5	76.03	83.3	7.89
	0.1005	500	21.98	3.75	82.9		90.70		7.95
Kapok fiber	0.0996	500	21.98	1.75	92.0		101.56		8.15
	0.0995	500	21.98	1.50	93.2	92.4	102.91	101.4	8.10
	0.1014	500	21.98	1.75	92.0		99.75		8.00
Coconut husk	0.1004	500	21.98	5.75	73.8		80.83		8.10
	0.0996	500	21.98	4.50	79.5	75.0	87.75	82.2	8.12
	0.1009	500	21.98	6.25	71.6		77.95		8.05
Burned rice husk	0.0996	500	21.96	2.00	90.9		100.20		7.95
	0.0997	500	21.96	2.20	90.0	86.6	99.10	95.3	-
	0.1003	500	21.96	4.60	79.1		86.54		-
Saw dust	0.1003	500	21.96	1.50	93.2		101.99		7.62
	0.1004	500	21.96	1.75	92.0	92.8	100.65	101.7	7.58
	0.0998	500	21.96	1.50	93.2		102.51		7.54
Rubberizer*	0.1033	500	26.90	2.00	92.6		120.52		7.95
	0.1047	500	26.90	2.80	89.6	91.1	115.09	119.7	-
	0.0991	500	26.90	2.40	91.1		123.61		-
Compost*	0.1042	500	26.90	7.50	72.1		93.09		7.62
	0.1027	500	26.90	4.50	83.3	78.9	109.06	103.2	7.58
	0.1018	500	26.90	5.00	81.4		107.56		7.54

(-): No data

(*): Commercial sorbents

Table A.2 Oil and grease concentration (mg/L) of kinetic test of burned rice husk (mechanically emulsified oil)

Time (hrs)	Burned rice Husk	Burned rice husk	Burned rice husk (average)	Control samples
0	19.98	19.98	19.98	19.98
3	5.75	7.50	6.63	7.00
8	4.50	4.00	4.25	3.50
24	2.50	2.50	2.50	3.00

Table A.3 Batch oil adsorption test (chemically emulsified oil)

Sorbents	Mass (g)	Inf. (mg/L)	Eff. (mg/L)	% Removal	pH	Sorbents condition
Rice husk	0.5010	26.4	23.8	10	7.98	Sink
Burend rice husk	0.5001	17.5	16.6	5	8.03	Sink
Water lecttuce	0.5004	26.4	14.4	46	7.62	Float
Cattail leaf	0.5008	15.8	7.2	54	7.90	Float
Saw dust	0.5004	16.65	14.1	15	7.62	Sink
Umbrella plant	0.5007	16.65	12.0	28	7.50	Sink
Kapok fiber	0.4998	23.8	3.9	84	7.96	Float
Nanofiber	0.2022	25.5	3.6	86	7.81	Float

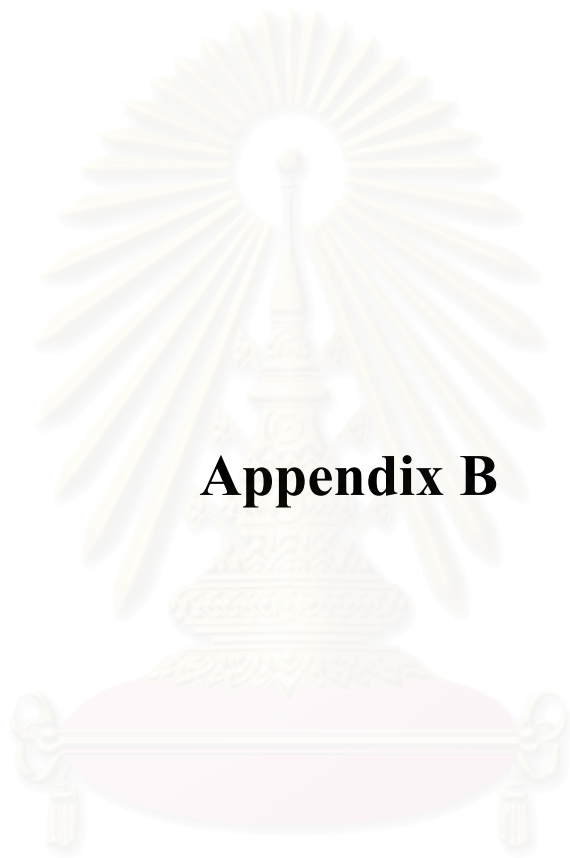
Table A.4 Batch oil sorption isotherm of kapok fiber (chemically emulsified oil)

No	mass (g)	Vol. (mL)	C _{initial} (mg/L)	C _{final} (mg/L)	Oil adsorbed (mg/g)
1	0.0510	500	22.20	6.80	150.98
2	0.0504	500	22.20	7.20	148.81
3	0.3004	500	22.20	6.80	25.63
4	0.3001	500	22.20	6.40	26.32
5	1.0008	500	22.20	5.40	8.39
6	1.0004	500	22.20	5.40	8.40
7	2.0004	500	22.20	7.20	3.75
8	2.0011	500	22.20	5.00	4.30
9	0.4993	500	24.00	4.00	20.03
10	0.4998	500	24.00	3.80	20.21
11	0.1076	500	29.40	5.60	110.59
12	0.0999	500	29.40	14.40	75.08
13	0.0102	500	26.00	14.60	558.82
14	0.0101	500	26.00	20.40	277.23
15	0.0207	500	26.00	12.60	323.67
16	0.0199	500	26.00	9.80	407.04
17	0.0309	500	26.00	7.40	300.97
18	0.0303	500	26.00	7.60	303.63
19	0.0392	500	26.00	8.20	227.04
20	0.0098	500	23.80	19.00	244.90
21	0.0101	500	23.80	15.60	405.94
22	0.0401	500	23.80	13.80	124.69
23	0.0394	500	23.80	18.80	63.45
24	0.0702	500	23.80	9.80	99.72
25	0.0709	500	23.80	11.00	90.27
26	0.1013	500	23.80	9.00	73.05
27	0.1020	500	23.80	10.80	63.73
28	0.0500	500	22.30	11.40	109
29	0.0513	500	22.30	9.60	123.8
30	0.2067	500	22.30	9.80	30.2
31	0.2021	500	22.30	7.80	35.9
32	0.3022	500	22.30	7.40	24.7
33	0.3040	500	22.30	7.20	24.8
34	0.5010	500	22.30	7.40	14.9
35	0.5027	500	22.30	8.20	14.0

Table A.5 Results of column tests (chemically emulsified oil)

Time (min)	Kapok fiber			Rubberizer™		
	Influent (mg/L)	Effluent (mg/l)	% Removal	Influent (mg/L)	Effluent (mg/l)	% Removal
0	29.0	-	-	32.0	-	-
10	-	29.5	-8.6	-	30.5	-3.4
20	-	22.5	17.2	-	33.5	-13.6
30	-	23.0	15.3	-	33.0	-11.9
40	27.5	24.5	9.8	32.0	29.5	0.0
50	-	25.5	6.1	-	21.5	27.1
60	-	23.0	15.3	-	27.0	8.5
70	-	22.0	19.0	-	23.0	22.0
80	-	26.0	4.3	-	28.5	3.4
90	25.0	-	-	24.5	-	-

Remark: Removal efficiencies were calculated from average influent concentration.



Appendix B

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Table B.1 Results of flume oil sorption test

Sorbent :Kapok fiber 250.24g											
Test	Time (min)		Flow rate (L/min)	Inf (mg/L)	Eff (mg/L)	% Removal	Oil input (mg)		Oil sorbed (mg)		
		Total					M_i	ΣM_i	M_s	ΣM_s	mg/g
1 Apr, 4 (2002)	0	0	20								
	5	5	20	48.5	6.6	86.4	4850	4850	4190	4190	16.7
	10	10	20	45.0	6.0	86.7	4500	9350	3900	8090	32.3
	15	15	20	28.5	9.4	67.0	2850	12200	1910	10000	40.0
	20	20	20	41.0	5.6	86.3	4100	16300	3540	13540	54.1
	25	25	20	38.0	6.0	84.2	3800	20100	3200	16740	66.9
	30	30	20	34.0	4.4	87.1	3400	23500	2960	19700	78.7
	35	35	20	51.5	5.4	89.5	5150	28650	4610	24310	97.1
2 Apr, 9 (2002)	5	40	12	40.0	3.8	90.5	2400	31050	2172	26482	105.8
	15	50	12	31.0	2.2	92.9	3720	34770	3456	29938	119.6
	25	60	12	44.5	3.0	93.3	5340	40110	4980	34918	139.5
	35	70	12	39.5	4.0	89.9	4740	44850	4260	39178	156.6
	50	85	12	39.5	1.8	95.4	7110	51960	6786	45964	183.7
	65	100	12	49.0	3.8	92.2	8820	60780	8136	54100	216.2
	80	115	12	39.5	3.6	90.9	7110	67890	6462	60562	242.0
	95	130	12	42.5	3.6	91.5	7650	75540	7002	67564	270.0
3 May, 13 (2002)	115	150	12	31.0	4.8	84.5	7440	82980	6288	73852	295.1
	135	170	12	37.0	4.0	89.2	8880	91860	7920	81772	326.8
	5	175	20	38.0	4.8	87.4	3800	95660	3320	85092	340.0
	10	180	20	58.5	4.4	92.5	5850	101510	5410	90502	361.7
	20	190	20	30.5	6.0	80.3	6100	107610	4900	95402	381.2
	30	200	20	45.0	3.8	91.6	9000	116610	8240	103642	414.2
	45	215	20	46.0	9.4	79.6	13800	130410	10980	114622	458.0
	60	230	20	43.0	7.6	82.3	12900	143310	10620	125242	500.5
4 Jun, 18 (2002)	75	245	20	51.5	3.4	93.4	15450	158760	14430	139672	558.2
	90	260	20	44.5	8.4	81.1	13350	172110	10830	150502	601.4
	105	275	20	35.0	4.6	86.9	10500	182610	9120	159622	637.9
	120	290	20	14.0	3.0	78.6	4200	186810	3300	162922	651.1
	10	300	20	45.0	15.0	66.7	9000	195810	6000	168922	675.0
	20	310	20	47.0	11.4	75.7	9400	205210	7120	176042	703.5
	30	320	20	43.5	12.6	71.0	8700	213910	6180	182222	728.2
	45	335	20	51.5	14.8	71.3	15450	229360	11010	193232	772.2
60	350	20	38.5	11.6	69.9	11550	240910	8070	201302	804.4	
70	360	20	39.0	11.2	71.3	7800	248710	5560	206862	826.7	

Table B.1 Results of flume oil sorption test (cont.)

Sorbent :Cattail fiber 250.82g											
Test	Time (min)		Flow rate (L/min)	Inf (mg/L)	Eff (mg/L)	% Removal	Oil input (mg)		Oil sorbed (mg)		
		Total					M_i	ΣM_i	M_s	ΣM_s	mg/g
1 Jun, 2 (2002)	0	0	20								
	10	10	20	62.5	5.4	91.4	12500	12500	11420	11420	45.6
	20	20	20	40.0	5.2	87.0	8000	20500	6960	18380	73.4
	30	30	20	57.5	4.6	92.0	11500	32000	10580	28960	115.7
	45	45	20	54.0	6.0	88.9	16200	48200	14400	43360	173.3
2 Jun, 4 (2002)	60	60	20	49.0	7.4	84.9	14700	62900	12480	55840	223.1
	10	70	20	57.0	6.4	88.8	11400	74300	10120	65960	263.6
	20	80	20	40.0	7.0	82.5	8000	82300	6600	72560	290.0
	30	90	20	42.0	8.2	80.5	8400	90700	6760	79320	317.0
	45	105	20	40.0	5.6	86.0	12000	102700	10320	89640	358.2
3 Jun, 13 (2002)	60	120	20	53.0	8.8	83.4	15900	118600	13260	102900	411.2
	10	130	20	44.5	4.6	89.7	8900	127500	7980	110880	443.1
	20	140	20	50.0	2.8	94.4	10000	137500	9440	120320	480.8
	30	150	20	49.0	3.4	93.1	9800	147300	9120	129440	517.3
	45	165	20	41.0	3.8	90.7	12300	159600	11160	140600	561.9
4 Jun, 15 (2002)	60	180	20	39.0	4.4	88.7	11700	171300	10380	150980	603.3
	10	190	20	49.5	4.8	90.3	9900	181200	8940	159920	639.1
	20	200	20	34.0	6.2	81.8	6800	188000	5560	165480	661.3
	30	210	20	38.0	7.4	80.5	7600	195600	6120	171600	685.7
	45	225	20	56.0	8.0	85.7	16800	212400	14400	186000	743.3
5 Jul, 1 (2002)	60	240	20	40.0	9.6	76.0	12000	224400	9120	195120	779.7
	2	242	20	45.5	3.0	93.4	1820	226220	1700	196820	786.5
	20	260	20	53.5	5.2	90.3	19260	245480	17388	214208	856.0
	40	280	20	42.5	5.0	88.2	17000	262480	15000	229208	916.0
	60	300	20	37.5	6.8	81.9	15000	277480	12280	241488	965.0
	80	320	20	39.0	5.8	85.1	15600	293080	13280	254768	1018.1
1 Jul, 5 (2002)	100	340	20	33.5	6.8	79.7	13400	306480	10680	265448	1060.8
	120	360	20	35.5	5.0	85.9	14200	320680	12200	277648	1109.5
	0	0	20								
	10	10	20	62.5	1.8	97.1	12500	12500	12140	12140	48.6
	20	20	20	48.0	0.8	98.3	9600	22100	9440	21580	86.3
2 Jul, 7 (2002)	30	30	20	47.0	1.2	97.4	9400	31500	9160	30740	122.9
	45	45	20	50.5	1.4	97.2	15150	46650	14730	45470	181.9
	60	60	20	57.5	1.6	97.2	17250	63900	16770	62240	248.9
	30	90	20	39.5	2.6	93.4	23700	87600	22140	84380	337.5
3 Jul, 9 (2002)	60	120	20	49.5	2.6	94.7	29700	117300	28140	112520	450.0
	90	150	20	39.0	2.4	93.8	23400	140700	21960	134480	537.8
	120	180	20	40.0	5.0	87.5	24000	164700	21000	155480	621.8
1 Jul, 9 (2002)	30	210	20	47.0	6.4	86.4	28200	192900	24360	179840	719.2
	60	240	20	60.0	27.8	53.7	36000	228900	19320	199160	796.5
	90	270	20	45.0	19.4	56.9	27000	255900	15360	214520	857.9
	120	300	20	55.0	19.0	65.5	33000	288900	21600	236120	944.3

Sorbent :*Salvinia* sp. 250.04g

Table B.1 Results of flume oil sorption test (cont.)

Sorbent :Polyester 251.12g											
Test	Time (min)		Flow rate (L/min)	Inf (mg/L)	Eff (mg/L)	% Removal	Oil input (mg)		Oil sorbed (mg)		
		Total					M _i	Σ M _i	M _s	Σ M _s	mg/g
1 Jul, 5 (2002)	0	0	20								
	10	10	20	45.0	0.8	98.2	9000	9000	8840	8840	35.2
	20	20	20	54.0	1.4	97.4	10800	19800	10520	19360	77.1
	30	30	20	42.5	2.4	94.4	8500	28300	8020	27380	109.0
	45	45	20	48.5	0.8	98.4	14550	42850	14310	41690	166.0
	60	60	20	39.0	0.8	97.9	11700	54550	11460	53150	211.7
2 Jul, 7 (2002)	30	90	20	40.0	1.4	96.5	24000	78550	23160	76310	303.9
	60	120	20	48.0	1.8	96.3	28800	107350	27720	104030	414.3
	90	150	20	46.5	2.8	94.0	27900	135250	26220	130250	518.7
	120	180	20	42.5	3.2	92.5	25500	160750	23580	153830	612.6
3 Jul, 9 (2002)	30	210	20	44.0	3.2	92.7	26400	187150	24480	178310	710.1
	60	240	20	51.5	7.6	85.2	30900	218050	26340	204650	814.9
	90	270	20	48.0	2.0	95.8	28800	246850	27600	232250	924.9
	120	300	20	40.0	5.2	87.0	24000	270850	20880	253130	1008.0
Sorbent :Wood chip 250.75g											
1 May, 16 (2002)	0	0	20								
	5	5	20	61.5	7.0	88.6	6150	6150	5450	5450	21.7
	10	10	20	55.5	6.2	88.8	5550	11700	4930	10380	41.4
	20	20	20	44.5	5.8	87.0	8900	20600	7740	18120	72.3
	30	30	20	56.5	9.2	83.7	11300	31900	9460	27580	110.0
	45	45	20	48.5	8.0	83.5	14550	46450	12150	39730	158.4
	60	60	20	48.5	11.8	75.7	14550	61000	11010	50740	202.4
2 May, 22 (2002)	10	70	20	45.0	9.0	80.0	9000	70000	7200	57940	231.1
	20	80	20	57.5	12.0	79.1	11500	81500	9100	67040	267.4
	30	90	20	42.0	11.6	72.4	8400	89900	6080	73120	291.6
	45	105	20	38.0	27.2	28.4	11400	101300	3240	76360	304.5
	60	120	20	50.0	17.8	64.4	15000	116300	9660	86020	343.1
Sorbent :Rice husk 250.26g											
1 May, 18 (2002)	0	0	20.0								
	10	10	20.0	46.0	11.4	75.2	9200	9200	6920	6920	27.7
	20	20	20.0	39.5	11.4	71.1	7900	17100	5620	12540	50.1
	30	30	20.0	35.0	9.8	72.0	7000	24100	5040	17580	70.2
	45	45	20.0	34.0	9.2	72.9	10200	34300	7440	25020	100.0
	60	60	20.0	27.0	10.8	60.0	8100	42400	4860	29880	119.4
2 May, 28 (2002)	10	70	20.0	41.5	8.2	80.2	8300	50700	6660	36540	146.0
	20	80	20.0	46.5	9.8	78.9	9300	60000	7340	43880	175.3
	30	90	20.0	40.5	10.8	73.3	8100	68100	5940	49820	199.1
	45	105	20.0	58.0	15.2	73.8	17400	85500	12840	62660	250.4
	60	120	20.0	55.0	15.0	72.7	16500	102000	12000	74660	298.3

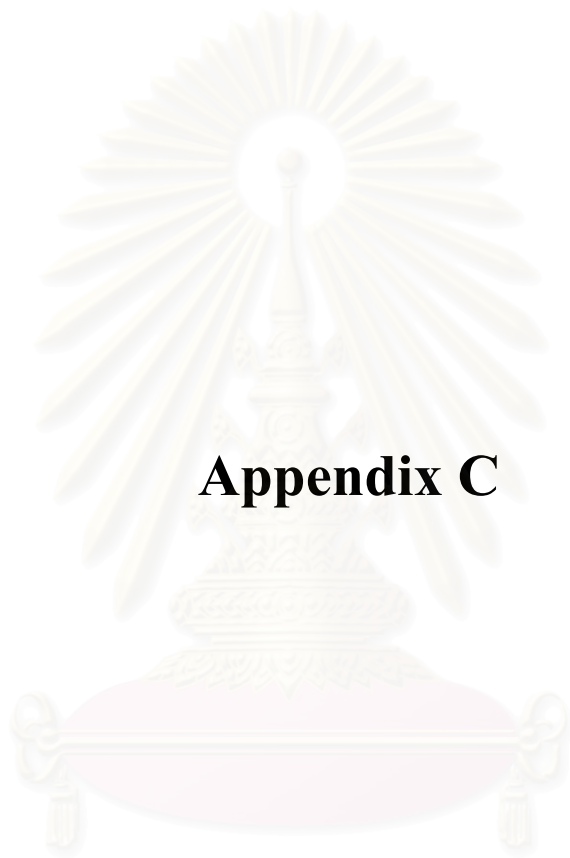
Table B.1 Results of flume oil sorption test (cont.)

Sorbent :Coconut husk 250.23 g											
Test	Time (min)		Flow rate (L/min)	Inf (mg/L)	Eff (mg/L)	% Removal	Oil input (mg)		Oil sorbed (mg)		
		Total					M _i	Σ M _i	M _s	Σ M _s	mg/g
1 May, 18 (2002)	0	0	20								
	10	10	20	44.0	15.0	65.9	8800	8800	5800	5800	23.2
	20	20	20	32.0	18.4	42.5	6400	15200	2720	8520	34.0
	30	30	20	37.0	20.4	44.9	7400	22600	3320	11840	47.3
	45	45	20	37.0	28.8	22.2	11100	33700	2460	14300	57.1
	60	60	20	38.0	37.4	1.6	11400	45100	180	14480	57.9
Sorbent :Baggase 250.15 g											
1 June, 13 (2002)	0	0	20								
	10	10	20	48.5	34.2	29.5	9700	9700	2860	2860	11.4
	20	20	20	37.0	29.6	20.0	7400	17100	1480	4340	17.3
	30	30	20	36.5	34.2	6.3	7300	24400	460	4800	19.2

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Table B.2 Results of flume oil desorption test

Sorbents	Time	Water flow rate (L/min)	Effluent (mg/L)	Oil desorbed (mg)	
					Total
Kapok fiber Jul, 8 2002	0				
	1	20	51.6	1032	1032
	3	20	22.2	888	1920
	5	20	8.0	320	2240
	10	20	3.4	340	2580
	15	20	3.4	340	2920
Cattail fiber Jul, 8 2002	0				
	1	20	13.2	264	264
	3	20	5.4	216	480
	5	20	3.2	128	608
	10	20	3.0	300	908
	15	20	2.4	240	1148
<i>Salvinia</i> sp. Jul, 10 2002	0				
	1	20	19.6	392	392
	3	20	5.8	232	624
	5	20	4.2	168	792
	10	20	2.6	260	1052
	15	20	3.8	380	1432
Polyester fiber Jul, 10 2002	0				
	1	20	183.4	3668	3668
	3	20	62.4	2496	6164
	5	20	38	1520	7684
	10	20	13.8	1380	9064
	15	20	11.8	1180	10244
Wood chip Jun, 11 2002	0				
	1	20	2.0	40	40
	3	20	2.4	96	136
	5	20	1.8	72	208
	10	20	1.4	140	348
	15	20	1.6	160	508
Rice husk Jun, 11 2002	0				
	1	20	183.4	216	216
	3	20	62.4	264	480
	5	20	38	104	584
	10	20	13.8	300	884
	15	20	11.8	220	1104



Appendix C

สถาบันวิทยบริการ
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a) Side view



b) Front view

Figure C.1 Flume setup: a) Side view, b) Front view



Figure C.2 Kapok fiber: Before and after



Figure C.3 Cattail fiber: Before and after

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a) Before



b) After



c) Fresh plant.

Source:

http://www.protectyourwaters.net/images/salvinia_th.gif

Figure C.4 *Salvinia* sp.; a) Before, b) After, c) Fresh plant



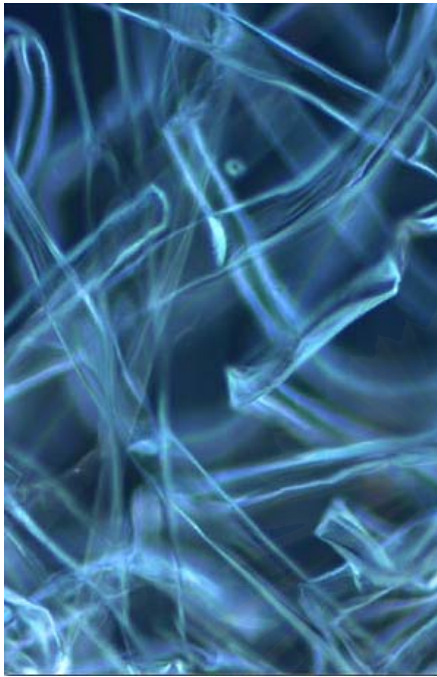
Figure C.5 Polyester fiber: before and after



Figure C.6 Rice husk: before and after

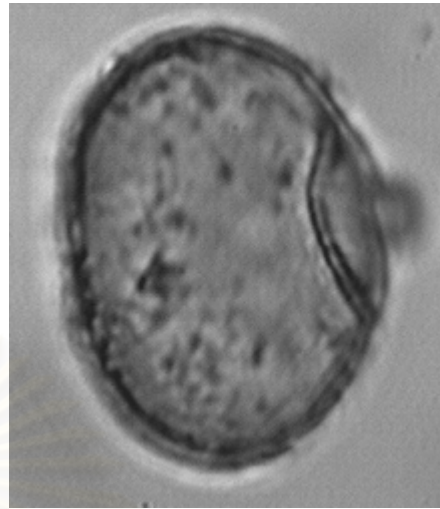


Figure C.7 Wood chip: before and after



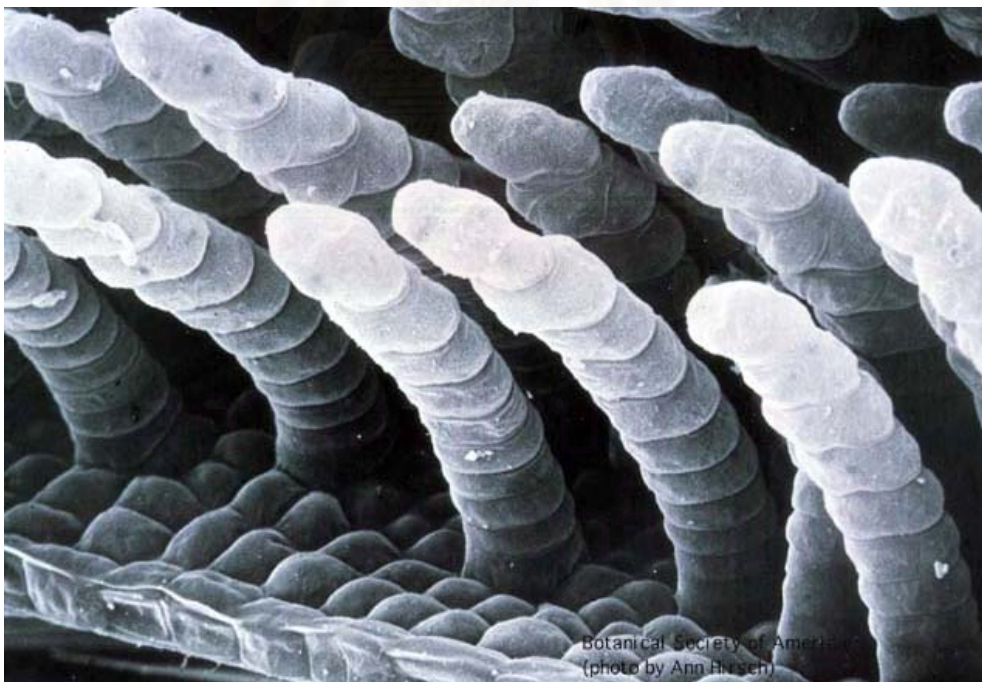
a) Kapok fiber

Source: <http://www.microscopy.fsu.edu/primer/techniques/fluorescence/gallery/images/kapok.jpg>



b) Cattail fiber

Source: <http://geography.berkeley.edu/ProjectsResources/PollenKey/images/Sequoia-semp2.jpg>



c) Leaf surface of *Salvinia* sp. Source: <http://images.botany.org/set-09/09-023v.jpg>

Figure C.8 Scanning Electron Microscope (SEM) of sorbents; a) kapok fiber, b) Cattail fiber, c) Leaf surface of *Salvinia* sp.

BIOGRAPHY

Mr. Thunyalux Ratpakdi was born in Khon Kaen, Thailand, on November 20, 1978. He received Bachelor degree of Environmental Engineering from King Mongkut's University of Technology Thonburi in 1999. He started as a graduate student in International Programs in Environmental Management, Chulalongkorn University in May 2000 and completed the program in October 2002.



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