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ABSTRACT

REMOVAL AND RECOVERY OF VOCs AND OILs FROM SURFACTANT-FLUSHED RECOVERED WATER BY MEMBRANE PERMEATION

by

Ashish Nagnath Saraf

Surfactant-enhanced subsurface remediation appears to be capable of removing efficiently contaminants from the source area as well as the concentrated plume. Initial research was conducted on separate removal of trichloroethylene (TCE) and an oil. It was found that oil permeation and modified pervaporation are effective techniques of removing oil and TCE respectively from the simulated feed. It was found that the oil permeation technique can effectively remove 98-99% of oil from an oil-in-water emulsion. The subsurface-entrapped organic pollutants often have high boiling components along with the VOCs. A combined permeation technique is applied here to simultaneously remove TCE and n-dodecane (a model oil) from a model surfactant-flushed aqueous solution in a hollow fiber membrane device. The oil-in-water emulsion containing TCE and oil flows through the bore of microporous hydrophobic hollow fibers. The shell is subjected to vacuum for the modified pervaporation-based removal of TCE which diffuses through the pores and the nonporous silicone skin on the outer surface of fibers. The oil wets the pores and is removed by permeation through the nonporous silicone rubber skin by applying a positive feed pressure. The presence of oil affected the flux of TCE but the water flux was cut down by almost 90%. It was observed that the presence of surfactant adversely affected the removal of oil. It was found that removal of TCE decreases with increased flow rate whereas the removal of oil increases with increased flow rate. Removal of TCE was constant at a low concentration of oil but at higher concentrations, the removal of TCE showed a decline with time.

**REMOVAL AND RECOVERY OF VOCs AND OILs FROM SURFACTANT-
FLUSHED RECOVERED WATER BY MEMBRANE PERMEATION**

by
Ashish Nagnath Saraf

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APPROVAL PAGE

**REMOVAL AND RECOVERY OF VOCs AND OILs FROM SURFACTANT-
FLUSHED RECOVERED WATER BY MEMBRANE PERMEATION**

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NOMENCLATURE

A_M	= Mass transfer area, cm^2
C	= Concentration, mg/L
C_{in}	= Concentration of TCE at the module inlet, mg/L
C_{final}	= Final concentration of n-dodecane in feed reservoir, mg/L
C_o	= Initial concentration of n-dodecane in feed reservoir, mg/L
C_{out}	= Concentration of TCE at the module outlet, mg/L
ΔC	= Concentration difference between the feed and retentate, mg/L
C_t	= Concentration of n-dodecane at any time t , mg/L
$C_{t+\Delta t}$	= Concentration of n-dodecane at any time $t+\Delta t$, mg/L
D_o, D_i	= Diameter of hollow fiber outside and inside respectively, μm
J_{TCE}	= TCE flux, mol/hr.cm^2
J_{WATER}	= Water flux, mol/hr.cm^2
K	= lumped model parameter.
L	= Length of the module, cm
M_{TCE}	= Molecular weight of TCE, gm/gmol
M_{WATER}	= Molecular weight of water, gm/gmol
N	= Number of fibers
P	= Adjustable constant
R	= Mass of n-dodecane permeating per unit time, mg/hr

NOMENCLATURE
(continued)

t, t_{total} = Duration of experiment, total duration of experiment, hrs.

V = Volume of feed reservoir, L

v = Feed flow rate, mL/min

V_w = Volume of water collected, mL

CHAPTER 1

INTRODUCTION

1.1 The Problem Genesis

Oil-in-water emulsions are one of the major pollutants of the aquatic environments. This is due to a variety of industrial oily wastes from sources such as petrochemical, metallurgical industries, transportation, rolling mills, chemical processing plants, machine and vehicle maintenance shops and even domestic sewage (Koltuniewicz et al, 1995). Many different types of oils may be present in oily wastewater such as diesel oil, cutting and grinding oils, lubricating oils, water soluble coolants, natural animal or vegetable fats or any other organic immiscible in water. Before discharging these streams to sewers, the oil must be demulsified and separated from the water phase along with any other objectionable substances such as solids. The pollution of groundwater also directly affects more people than the more visible marine spills as the pollution commonly affects public water supplies. The removal of these oily wastes from wastewater is of importance in preventing pollution and meeting environmental standards. The EU (European Union) maximum admissible concentration for dissolved or emulsified hydrocarbons in potable water is $10\mu\text{l/L}$. For discharge to the municipal sewer system the "oil and grease" content may have to be on the order of mg/L. This means that the fuel tank of an average car holding say 40 of gasoline, can render 4 million cubic meter of water unsafe for drinking (Clark ,1990).

Oily waste removal may also be beneficial for water or oil recovery or reuse. The degree of difficulty in separating oil from oily wastewater is strongly affected by the

form(s) of oil that are present. Other wastewater characteristics that affect the separation process include the suspended solids concentration and particle size distribution, oil and bulk fluid densities, viscosity, surface tension and interfacial tension, the presence or absence of various chemicals, pH and temperature. Demulsification and water removal is a critical requirement before downstream processing of oil (Tirmizi et al, 1996).

The emulsions used in liquid membrane processes are formulated to remain stable under the process operating conditions and are therefore difficult to break. Typical demulsification methods found in literature are additions of demulsifying agents, pH adjustments, gravity or centrifugal settling, filter coalescers and membranes. There are advantages and disadvantages to each of these demulsification techniques. Table 1.1 indicates some of the polymeric membranes which are suitable for separating oil from water.

1.2 Conventional Treatments

Oily wastewater treatment techniques may be physical, chemical, physiochemical, electrical, mechanical or biological in nature, and they may be used singly or in combination depending upon the wastestream characteristics and the objectives of wastewater treatment. Oily wastewaters to which chemical emulsifying agents have been added are more difficult to treat because of the electrical and mechanical barriers that prevent the oil droplets from agglomerating.

Gravity separation is the most widely used wastewater treatment technique. The main objective is to separate free oil and suspended solids from the wastewater by utilizing differences in specific gravity. Effluent oil concentrations that can be achieved

with gravity separators typically range from 20-100 mg/L. More recently, the limitations of this approach have been recognized. This is due to the fact that it cannot remove emulsified or soluble oil. Secondly it occupies fairly large space and lastly is affected by temperature fluctuations.

Table 1.1. Some polymeric membranes potentially suitable for oil/water separation*

Manufacturer	Type	Configuration	Pore Size	Material
Amicon	UF MF	plate & frame, spiral wound hollow fibre	3-100K MWCO 0.1 μ m	PS PS copolymer
Aqua Air Environmental	UF	spiral wound		polymeric organic
Dow/DDS	MF	plate & frame	0.1-5 μ m	PS, fluoropolymer
Desal	UF MF	spiral wound	1-15K MWCO 0.02-3 μ m	thin film composite PTFE fluorocarbon
Enka	MF	capillary, tubular	0.2 μ m	PP
Epoc/Exxflow	MF	tubular	0.5-5 μ m	polyester
Hoescht Celanese	UF	spiral wound tubular	4-200K MWCO 10-400K MWCO	PES modified PAN
Koch/Abcor	MF	spiral wound, tubular	0.1-4 μ m	PVDF, PES
Memtec	MF	hollow fibre	0.2 μ m	PP
Millipore	MF	plate & frame	0.1-0.5 μ m	fluoropolymer
Nitto/Denko	UF	spiral wound, tubular	20 K MWCO	PO, PS, composite
Osmonics	UF	spiral wound	100 μ m-0.1 μ m	modified PS, fluoropolymer
Patterson Candy International	UF	tubular, plate & frame	4-200 K MWCO	PS, PES, PVDF, PAN
Romicon	UF	hollow fibre	0.005 μ m	PP, PS, PAN
Sartorius	UF	plate & frame	20 K MWCO	cellulose triacetate
Separation Dynamics Inc.	UF	hollow fibre	40 K MWCO	cellulosic
Stock Priceland	MF/UF	tubular		PS, PES, PAN, PVDF
Tech Sep/Rhone-Poulenc	MF	plate & frame	0.1-1 μ m	fluoropolymer
X-Flow	MF	hollow fibre plate & frame	0.1-0.2 μ m 0.05-1 μ m	PS
Zenon	UF	tubular	5-20K MWCO	PS

Note: PAN- polyacrylonitrile; PES- polyether sulfone; PO-polyolefine; PP-polypropylene; PS- polysulfone; PVC- polyvinylchloride; PVDF-polyvinylidene fluoride.

* Source: Zaidi et al., (1992)

Another conventional technology for oil separation is coalescence. Coalescence is used primarily to remove free and mechanically dispersed oil from water; chemically emulsified oil droplets are normally too stable to be forced together. Effluent oil concentrations that can be achieved with coalescence typically range from 1-50 mg/L. Coalescence has the disadvantage of requiring pretreatment. Secondly the surface-active chemicals may alter the nature of the coalescing media (Magdich and Semmens, 1988).

1.3 Techniques for Removal of Oil from Aqueous Solutions

Dilute oil-in-water emulsions which are frequently encountered as wastestreams have to be demulsified to separate the oil before it can be discharged to the sewers. Chemical demulsification methods are the most widely used and they usually include acidification and/or coagulation followed by flocculation. In this process, the pH is lowered into 2-4 range by the addition of acid which causes most of the oil droplets to destabilize and separate out; the freed oil is subsequently removed by skimming. The disadvantage associated with this method is that chemicals are required in large quantities. The method is not cost effective and also faces various problems like corrosion and sludge. The disadvantages associated with chemical emulsion breaking techniques have led to the development of a non-chemical oil-water emulsion separation method like the electrolytic treatment (Magdich and Semmens, 1988).

More recent efforts have focused on the application of electrochemical techniques to break emulsions and separate destabilized oil without the addition of chemicals. The key process involved in most of these methods is electrocoagulation which can be

considered as a two step process: (1) aluminum or iron ions are introduced electrolytically to reduce the repulsive forces on the negatively charged oil droplets and break the emulsion; (2) a DC voltage is applied across the emulsion to cause the charged droplets to migrate and coalesce. The method has the disadvantages of not being able to handle shock loads and high solids. The applicability of this process on the industrial level remains questionable.

Ultrafiltration is another method of dewatering the waste emulsified oils. It is a pressure driven membrane technique for the separation of material in the 1nm to 10 μm size range. "Clean" water (permeate) is forced through the microporous membrane while the oil retained by the membrane becomes more concentrated. UF reduces the volume of a waste-cutting oil emulsion by 95 to 98% and concentrates oil and solids to as much as 60%. Ultrafiltration is an efficient way of dewatering the emulsified oil but has several disadvantages. The performance of UF system is adversely affected by suspended solids and free oil. The short-term permeate flux is reduced by one or two orders of magnitude due to membrane fouling over long periods of time (Zaidi et al., 1988). The decrease in permeate flux is attributed to the following phenomena.

Concentration polarization is defined as the generation of a concentration gradient of rejected particles at the membrane surface. A gel layer is formed at the membrane surface as a result of increase in concentration of contaminant at the surface. The contaminant may adsorb on the membrane surface and within the membrane pores. The adsorption process is often an irreversible process and hence results in permanent decrease in permeate flux.

1.4 Proposed Removal Technology

This thesis is concerned with a membrane permeation technique to remove volatile organic compounds (VOCs) and oils simultaneously. Initial research was conducted on the removal of VOCs from a feed containing VOCs. A modified pervaporation technique was used to separate the VOCs from simulated contaminated ground water obtained in surfactant flushing processes (Chandra, 1996). Chandra (1996) briefly explored the phenomenon of separating the oil from an oil-in-water emulsion using the hollow fiber membrane modules. The surfactant-flushed water in site remediation process also has nonvolatile organic compounds for which the pervaporation technique is not suitable as the nonvolatile compounds have low vapor pressures. Tirmizi et al. (1996) studied the demulsification of water/oil/solid emulsions using hollow fiber membranes. Experiments were carried out by them using porous hydrophobic polypropylene membranes at a low oil concentration of 1%; they obtained a purified aqueous stream containing 25 ppm oil content. The permeate was oil. Their system did not have any surfactants. Magdich and Semmens (1988) at the University of Minnesota and Tirmizi et al. (1995) at Rutgers employed porous hydrophobic hollow fibers to separate oil from the oil-in-water or water-in-oil emulsion by preferential pore wetting and pressure driven flow through the pore. The phenomenon of breakthrough of water within minutes of starting the experiment was observed by Magdich and Semmens (pages 81-82, 1988) when surfactants were present.

Lipp et al. (1987) at the University of New South Wales, Australia, used the ultrafiltration technique to permeate the water and was able to collect water having less

than 20 ppm oil in the permeate. The ultrafiltration membranes used for the research were the microporous polyamide membranes, CJT 35. They also used regenerated cellulose and polysulfone membranes, Amicon YM5 and Amicon PM30 respectively. Zaidi et al. (1992) reported that the oil content of several oilfield brines was reduced to less than 20 mg/L and the short term permeate flux of water was about 80 gal/ft².d. Bodzek et al. (1992) at the Technical University of Silesia, Poland reported oil reductions of about 95 to 99% in the UF permeate from a metal industry emulsion.

Oil permeation technique was employed here to separate the oil from the recovered water. In this technique, a oil-in-water microemulsion is brought to the substrate side of a silicone-coated porous hydrophobic fiber. The experiment was carried out in the batch recirculation mode. The shell side was maintained at atmospheric pressure. The oil-in-water emulsion was allowed to flow under pressure through the fiber bore. The feed pressure was maintained at a certain level. Dodecane was chosen in this research to be the model oil. A positive feed pressure was applied to drive the permeation of oil and the oil was collected in a vessel. Magdich and Semmens (1988) also studied oil removal from an oil-in-water emulsion by using porous hydrophobic hollow fibers having a nonporous silicone skin on the outside surface; in their case the emulsion flowed in a crossflow manner at a higher pressure over the silicone skin surface; However the porous hydrophobic surface was not properly utilized.

Often the surfactant-flushed water has a combination of volatiles and nonvolatiles. An alternative method, the combined permeation (CP) technique, which is carried out in once through mode in this research is proposed to remove both VOCs and the oil

simultaneously from the recovered water obtained from surfactant-enhanced subsurface remediation. In the combined permeation process, the recovered water to be treated flows on one side and vacuum is pulled on the other side of the membrane. A positive feed pressure is applied to provide additional driving force for the oil contaminant. The membrane is highly selective to the VOC over water. The VOCs dissolve in the membrane, diffuse through it and are evaporated on the other side of the membrane. The nonvolatile component passes through the membrane by diffusion and is collected as oil drops in a oil trap connected in series with the condenser for collecting the VOCs. The vapor collected and highly enriched in VOCs is condensed and the condensate separates into two layers of organic and aqueous phases. A schematic diagram of the hollow fiber is shown in Figure 1.1. A considerable reduction of volume of waste is obtained as the oil and the VOCs are collected separately in relatively pure form by the process of combined permeation. The aqueous phase collected in the condenser can be recycled back to the feed reservoir. Such a process can reduce the VOC and the oil concentrations to a level of low ppms and also reduce the water flux considerably due to the presence of oil in the pores.

In the oil permeation experiments the feed was allowed to flow through the bore of a hydrophobic microporous hollow fiber with a nonporous hydrophobic coating on the outer diameter. Dodecane was chosen as a model oil in this research. The oil-in-water emulsion with or without the surfactant flowed through the fiber bore. The shell side was maintained at atmospheric pressure.

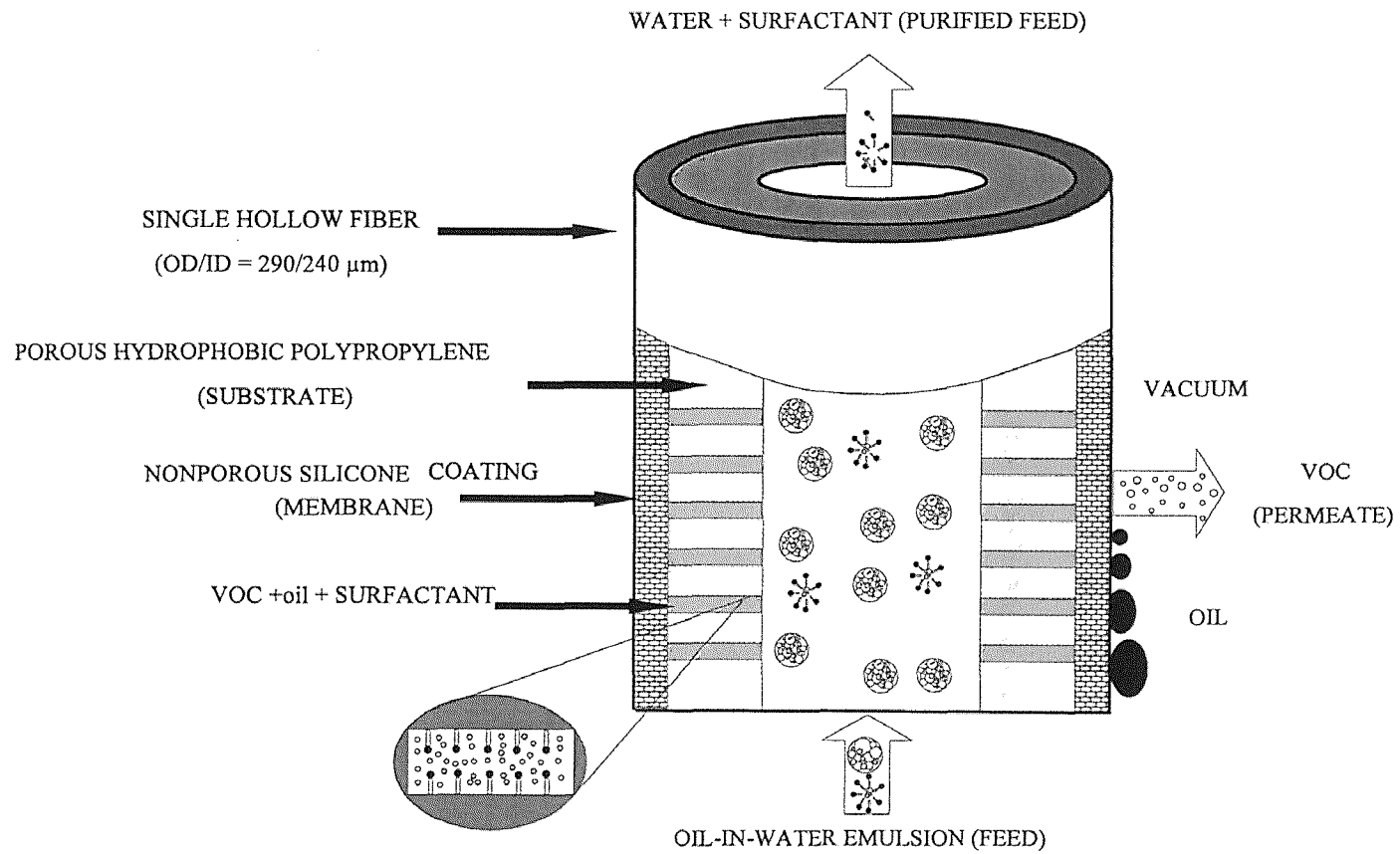


Figure 1.1. Separation of a micellar solution of VOC and oil fed into the coated hollow fiber bore by permeation and modified pervaporation

Some experiments were also carried out with the emulsion flowing on the shell side and the tube side was maintained at atmospheric pressure.

1.5 Research Objectives

A) Devise a hollow fiber membrane-based demulsification process to remove and recover oil from an oil-in-water emulsion with or without surfactant by permeation through the substrate-side of silicone-coated hollow fiber. This research will focus primarily on the removal of oil, n-dodecane ($C_{12}H_{26}$). Dodecane is one the priority pollutants declared by EPA.

B) Explore simultaneously the possibility of removal and recovery of trichloroethylene from a dodecane-based oil-in-water emulsion by hollow fiber membrane-based combined permeation process.

1.6 Research Approach

The approach adopted consists of the following steps:

- 1) Fabricate hydrophobic hollow fiber membrane module using appropriate hollow fibers.
- 2) Study the removal of dodecane from a synthetic microemulsion of oil-in-water flowing under pressure by demulsification using a hollow fiber membrane module.
- 3) Study the effects of hydrodynamics on dodecane removal and the flux of dodecane.
- 4) Study the removal of dodecane by varying the concentrations of dodecane and surfactant in the micellar or saturated solution.

- 5) Compare the tube-side and shell-side performances of the modules made of silicone coated hollow fibers.
- 6) Carry out experiments keeping the surfactant concentration above the critical micelle concentration (cmc) level to ascertain the extended term performance.
- 7) Explore the removal of TCE from a dodecane-based oil-in-water microemulsion by combined permeation.
- 8) Study the effect of concentration of TCE on TCE and water fluxes using combined permeation process.
- 9) Study the effect of n-dodecane concentration on TCE and water fluxes keeping the TCE concentration constant.
- 10) Study the effects of hydrodynamics on the TCE removal in the presence of oil.

CHAPTER 2

MATERIALS AND METHODS

2.1 Chemicals and Gases Used

n-Dodecane (purity 99%, FW 170.34) from Acros Organics (Springfield, NJ); n-Hexane (purity 99%) from Sigma (St. Louis, MO); sodium dodecyl sulfate (SDS, purity 99%, FW 288.4), isopropyl alcohol (IPA, HPLC grade, FW 60.1) from Fisher Scientific (Springfield, NJ); trichloroethylene (TCE, purity 99.9%, FW 131.39, density 1.456 gm/cc), methanol (purity 99.9%, FW 32.04) from Fisher Scientific (Springfield, NJ); ultrapure nitrogen, helium, air and liquid carbon dioxide from Matheson (E.Rutherford, NJ); liquid nitrogen from GCI Medical and Laboratory Gases (Lodi, NJ).

2.2 Hollow Fiber Membrane Module and Fabrication

The membrane module contained hydrophobic polypropylene microporous hollow fibers (Celgard X-10, I.D 240 μ m, O.D 290 μ m, Hoechst Celanese, Charlotte, NC). The fibers provided by AMT Inc. (Minnetonka, MN) were coated with a thin layer of non-porous plasma polymerized PDMS (polydimethyl siloxane) skin on the outer surface. The fabrication of the module involved the following major steps. At the outset, a polyethylene sheet was spread over a table and three fibers were taken at a time from the spool. They were cut to appropriate lengths and the process was repeated until there were 75 fibers arranged on the polyethylene sheet. To avoid any entanglement of the fibers, scotch tape was used to attach them to the polyethylene at both ends. After the cutting was complete, the scotch

tapes were removed by trimming the edges of the polyethylene sheet. The fibers were rolled into a bundle and the ends of the bundle were tied with cotton threads.

The next step involved putting this fiber bundle inside a 1/4" OD seamless stainless steel tube (McMaster-Carr, New Brunswick, NJ). Prior to placing the fiber bundle inside, the tube was cut to the desired length and one end was connected to a 1/4" stainless steel male run tee (Swagelok, R.S.Crum, Mountainside, NJ). To avoid any friction between the fiber and the metal, the tube was filled with water. Once the fibers were in place inside the tube, the membrane module was dried by passing prefiltered oil-free air through it for 48 hours.

The third and last stage of the module fabrication was potting of the tube sheet with a mixture of epoxy resin and silicone rubber. Two layers of potting were done – external and internal. The external layer was potted at the end of the male tee connector using a mixture of A-2 resin and Activator A (Armstrong products, Easton, MA); for the internal layer, C-4 resin and D-activator (Beacon Chemicals, MT. Vernon, NY) were mixed in a plastic cup (4:1 proportion by weight) and then deaerated in a vacuum desiccator. Using a disposable plastic pipette the resin mixture was carefully and slowly poured into the shell side. The module was kept for a day at room temperature so that the epoxy was adequately hardened. The module was not used for two weeks so that the tube sheet had sufficient time for curing. Table 2.1 provides the geometrical characteristics of the hollow fiber module so prepared.

Table 2.1. Characteristics of the module for permeation experiments

Hollow fiber	Celgard (X-10)
Membrane Coating*	Silicone
Fiber Number (N)	75
O.D., μm (D_o)	290
I.D., μm (D_i)	240
Active Length, cm (L)	32.8
A_M , Mass Transfer area based on I.D. (cm^2)	185.5

* source of coated fibers: AMT Inc., Minnetonka, MN

2.3 Experimental Setup

2.3.1 Oil Permeation Experiments

The experimental setup for oil permeation is shown schematically in Figure 2.1. The feed was pumped into the module by a peristaltic Masterflex pump, model 7518-60 (Cole Palmer, Vernon Hills, IL). The feed solution of dodecane was made in a 2 liter high density polyethylene (HDPE) Erlenmeyer flask (Cole Palmer, Vernon Hills, IL) and was kept under continuous stirring during the experiments. Two pressure gages (Cole Palmer, Vernon Hills, IL) were connected before and after the module to monitor the pressure drop along the module length. A bypass valve was connected to the feed inlet to the module to regulate the flow into the module, and hence, the inlet pressure. A pressure regulating metering valve (R.S.Crum, New Brunswick, NJ) was connected at the outlet of the module to maintain the desired back pressure. The outlet liquid was recycled to the feed reservoir; the operation was thus in the batch recirculation mode. The shell side was maintained at atmospheric pressure. The permeate was collected in a 15mL measuring cylinder.

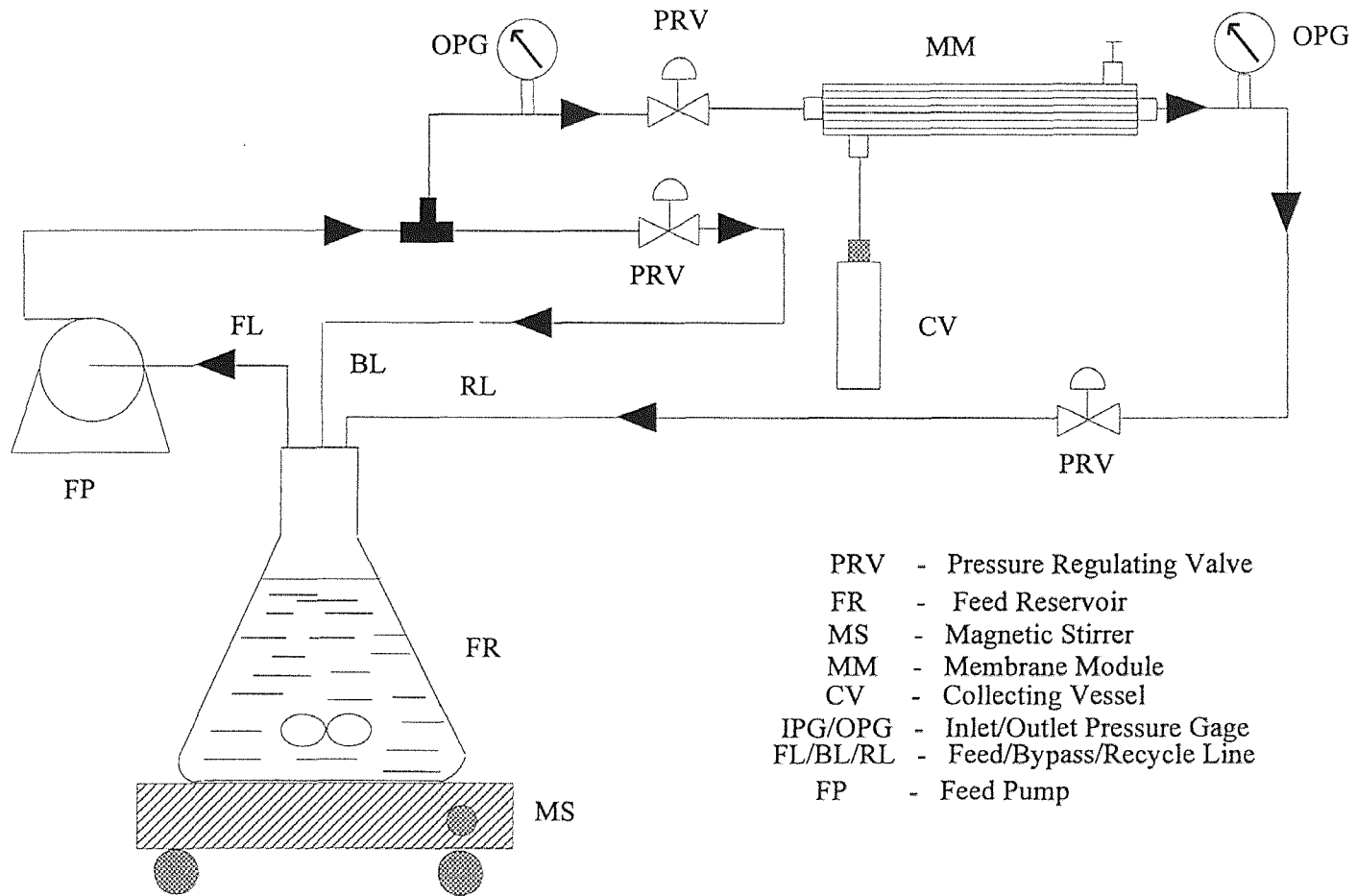


Figure 2.1. Experimental Setup for Oil Permeation Experiments

2.3.2 Combined Permeation Experiments for Oil and TCE

The experimental setup is shown in Figure 2.2. Feed was pumped into the module by a peristaltic Masterflex pump, model 7518-60 (Cole Palmer, Vernon Hills, IL) from a collapsible Teflon bag (Cole Palmer, Vernon Hills, IL). A Teflon bag of capacity 4.8 liters with one on-off valve was used as the experiments were carried out in the once through mode. Transparent 1/4" ID Teflon tubing (Cole Palmer, Vernon Hills, IL) and stainless steel fittings (Swagelok, R.S. Crum, New Brunswick, NJ) were used for the feed and all the connecting lines to and from the membrane module. A three-way valve (Swagelok, R.S. Crum, New Brunswick, NJ) was installed in the feed line to collect samples for measuring the drop in concentration in the Teflon bag. Micrometering valves (Swagelok, R.S. Crum, New Brunswick, NJ) were connected to the feed line and the outlet line to the module to regulate the feed and the back pressure. An oilless vacuum pump (KNF Neuberger, Trenton, NJ, Model UN 726.1.2 FTP, S/N 245177) was used to maintain a vacuum of -28/28.5 inch Hg. Convuluted Teflon tubes (Cole Palmer, Vernon Hills, IL) were used for the vacuum line connections to the condensers and for the oil trap connections. The module was installed in an inclined position to favor the permeation of oil by gravity from the shell side. An oil trap was connected in series with the condenser (Labglass, Vineland, NJ) with graduated tip to the vacuum line before the vacuum pump. Dry ice and methanol were used as cooling medium in a Dewar flask (Labglass, Vineland, NJ), inside which the condenser was kept to trap the permeate vapor from the module outlet.

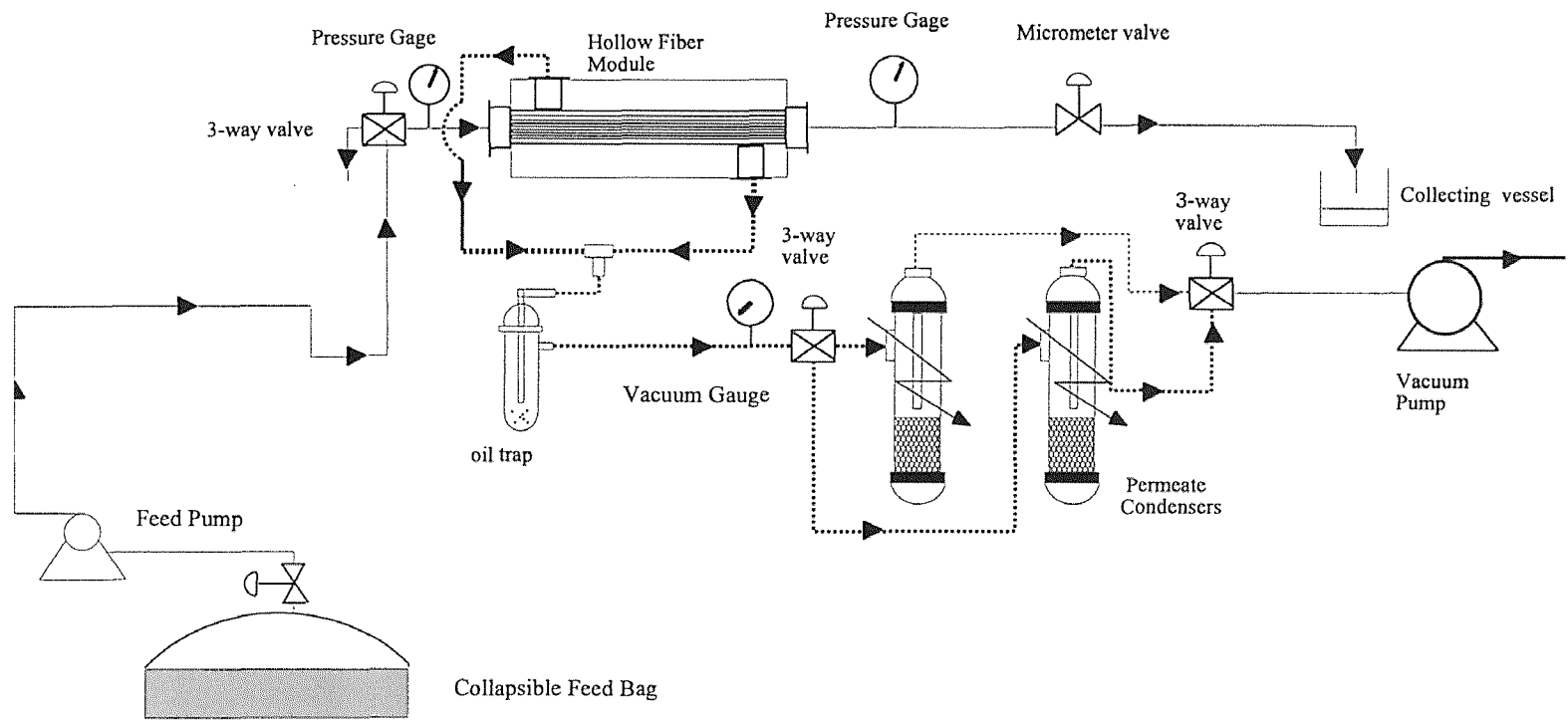


Figure 2.2. Experimental setup for combined permeation of VOC/Oil

2.4 Experimental Procedure

2.4.1 Preparation of Feed

Fresh feed for the oil permeation experiments was prepared by adding dodecane to a specific volume of water in the reservoir. The feed was kept under vigorous stirring, using a magnetic stirrer overnight to achieve an oil-in-water (O/W) emulsion. The reservoir used for the experiment was a High Density Polyethylene (HDPE) Erlenmeyer flask.

Fresh feed for experiments on combined permeation of oil and VOCs was prepared before each experiment to avoid volatilization of TCE. The feed was prepared in a glass flask with minimum headspace to avoid volatilization of TCE. TCE and oil (dodecane) were added to a specific amount of deionized water in the glass reservoir. The feed was kept under rapid stirring, using magnetic stirrer overnight.

For runs containing surfactants, a stock solution of the desired surfactant concentration was prepared at least 48 hours before the experiment for proper micelle formation. To prepare a desired concentration of surfactant (w/v), deionized water was heated just above the Krafft point of SDS (18-20°C) before adding the surfactant. This led to instant solubilization of the surfactant and micelle formation instead of dissociation into ions. This surfactant solution was kept in slow stirring for a minimum of 48 hours before adding dodecane.

2.4.2 Experiment

For oil permeation experiments, oil-in-water microemulsion was fed into the module by a Masterflex pump. The outlet from the module was recirculated back to the feed reservoir.

The feed in the reservoir was kept under constant stirring during the experimental run to maintain a homogeneous emulsion. A bypass valve was connected at the inlet to regulate the flow. The flow rate and the pressure drop along the module was noted every ½ hour; simultaneously, the drop in concentration of oil in the reservoir was noted. The experiment was generally carried out for 30 hours. The permeate was collected during the experimental run in a graduated cylinder.

In experiments with SDS, the surfactant solution was prepared first before adding dodecane. Although the emulsion was much more stable in the presence of surfactant, the reservoir was kept under constant stirring during the experimental runs. After every set of runs, the permeate side was flushed with 30mL of hexane to remove any traces of dodecane in the permeate side. Next, the module was washed with deionized water and 40% isopropyl alcohol (IPA) solution and dried overnight by passing oil-free prefiltered air.

The oil permeation experiments were carried out using dodecane as a model oil. Experiments were done by passing the feed both from the tube side and the shell side to determine the performance of the module. The main focus of experiments was on the effect of the flow rate and the surfactant on the oil flux. Experiments were also carried out to find out the effect of initial concentration of oil. The shell side was flushed with hexane to remove any traces of dodecane which did not go into the collecting vessel.

In combined permeation experiments using both TCE and the oil, the feed solution was pumped from the glass flask to the collapsible Teflon bag which prevented formation of headspace during an experimental run. Two magnetic stirrers were kept in the Teflon bag for continuous stirring of the feed so that a homogeneous solution could be pumped. The

experiment was carried out in once-through mode. The feed pressure was kept in the range of 4-5 psig by using a micrometering flow control valve (Swagelok, R.S. Crum, New Brunswick, NJ) at the outlet of module. Two dial pressure gages (Cole Palmer, Vernon Hills, IL) were used to monitor the pressure at the inlet and outlet of the module so as to maintain a certain a transmembrane pressure. Vacuum was tested at -28"-28.5" Hg before starting the system. Dry ice was prepared in a dry ice machine (Insta-Ice™, Model 3716-10, Cole Palmer, Chicago, IL) using liquid carbon dioxide. Dewar flasks were filled with dry ice and methanol after putting in the condenser to achieve a low cooling temperature. Samples were taken from the zero hour every half hour and analyzed. The experiment usually reached steady state after 3 hours, experiments were carried out for at least 7-8 hours. The weight of the empty condenser was noted before the start of the every experiment and the weight of the condenser after the experiment was measured. The volume of the permeate was observed and noted from the collection in the condenser. The volume of water and the VOC could be easily noted as the permeate separated into two distinct organic and aqueous phases. The mass of water collected was measured by multiplying the specific gravity by the volume of water collected; the mass of VOC collected was calculated by subtracting the mass of water from the total mass. The oil drops collected from the permeate were collected in the oil trap and measured. After every experiment the module was flushed in the same manner used for simple oil permeation experiments. Experiments were done by varying the concentrations of VOC and oil respectively one at a time. The effect of the flow rate was tested on the removal of TCE and oil. The effect of SDS on the removal of TCE and oil with feed flowing from tube and shell side was also tested.

2.5 Analytical Procedure

2.5.1 Gas Chromatography

Dodecane and TCE concentrations were measured in a HP 6890 series gas chromatograph (GC) using a HP 7694 Headspace Sampler and a HP 6890 integrator (Hewlett Packard, Wilmington, DE). Dodecane and TCE were analyzed by a Flame Ionization Detector (FID) using a HP-5 capillary column (cross-linked 5% PH ME Siloxane) of 30 m length, 320 μm diameter and 0.25 μm film thickness (Hewlett Packard, Wilmington, DE). Ultrahigh purity nitrogen (Matheson Gas Products, E.Rutherford, NJ) was used as the carrier gas. Headspace technique was used for the analysis of TCE. Separate analytical procedures were developed for dodecane with and without TCE.

2.5.1.1 Analysis of Dodecane: The volume of sample collected from the feed reservoir of dodecane-water mixture was 2 mL. A 2:1 dilution factor was employed for the complete extraction of dodecane into hexane. Dodecane was extracted into the hexane phase by using a centrifuge (Model no. IEC 438, International Equipment, Needham Heights, MA). The hexane phase was next analyzed by headspace GC. Reproducible results were obtained by using 3 μL of sample in a 22.5 mL headspace vial. The optimum headspace oven temperature (70°C), the sample volume (3 μL) and the sample equilibration time (12 min) were determined after an extensive study by varying each parameter one at a time.

A sample volume of 3 μL was used to prevent column flooding by hexane. Figure 2.3 shows the effect of equilibration time on dodecane output signal. The curve reached a plateau after 12 minutes indicating that the peak area became independent of the

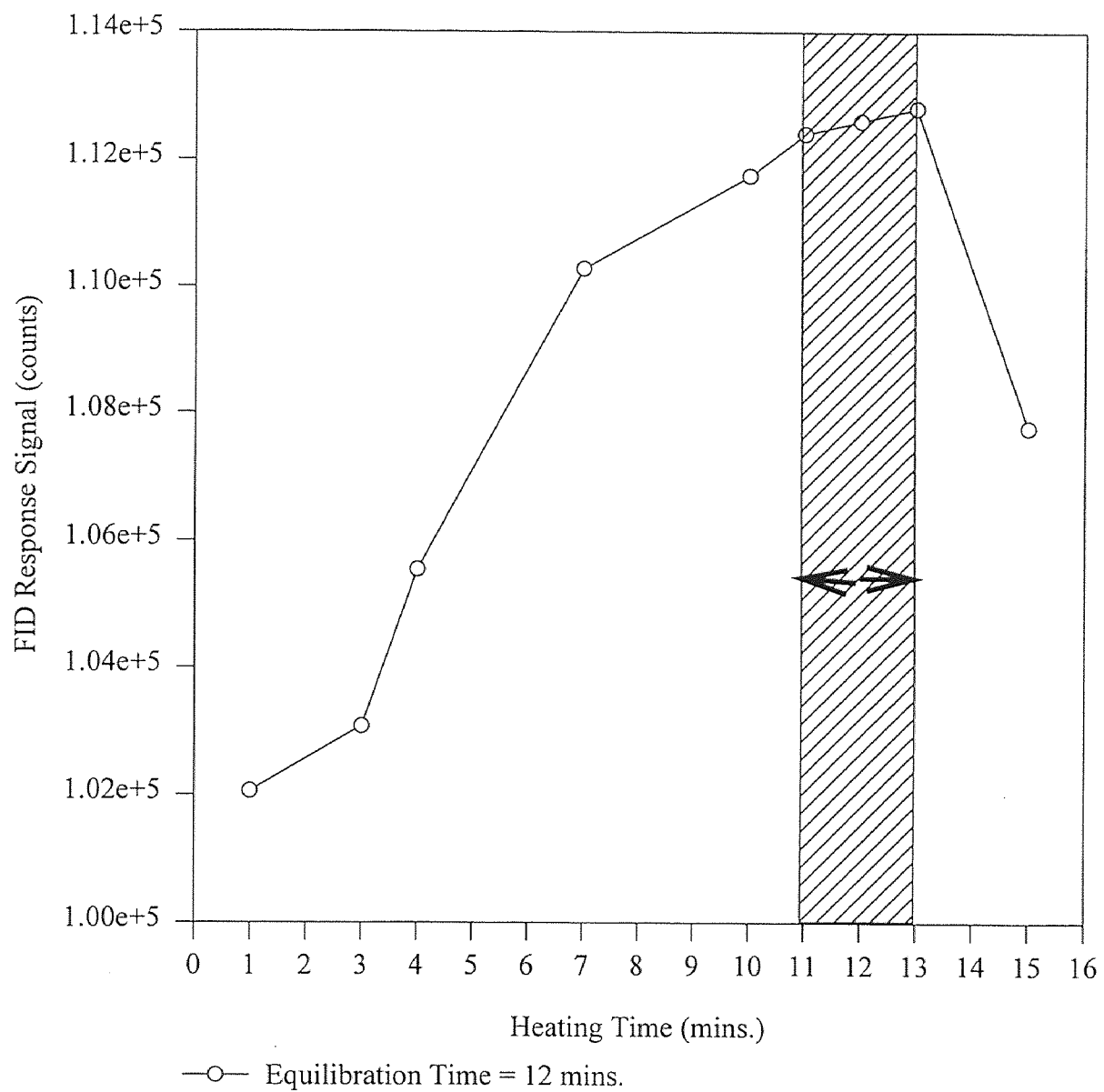


Figure 2.3. Effect of equilibration time on n-dodecane output signal

equilibration time. Longer time led to cracking of dodecane. Sample vials were thermostated and shaken in the headspace oven for 12 minutes at 70°C. Headspace vapors were analyzed by pressurizing the vials for 0.15 minute for sample introduction into the gas chromatograph column. A temperature program was fixed for the GC and was set at 40°C for 1.5 minute. In the next step, temperature was ramped at 25°C per minute until it reached 75°C, where it was kept for 1 minute. In the final step, the temperature was ramped at 40°C per min. until it reached the final temperature of 220°C, which was maintained for 3 minute. The final temperature was kept at 220°C as the boiling point of dodecane is 215°C. Figure 2.4 shows the dodecane calibration curve.

2.5.1.2 Analytical Procedure for Analyzing n-Dodecane with TCE: A similar procedure was used for analyzing dodecane and TCE in the GC headspace device. A 3 μL sample for analysis was taken from the hexane phase and analyzed in the GC-Headspace. The optimum headspace oven temperature (80°C) and sample equilibration time (6 min) were determined after an extensive study by varying each parameter one at a time. Figure 2.5 shows the effect of equilibration time on TCE/Dodecane output signal. The curve reached a plateau after 5 minutes indicating that the peak area became independent of equilibration time. Sample vials were thermostated in the headspace analyzer for 6 minutes at 80°C. The temperature program was modified for the GC to get clear separation of TCE from others. The initial oven temperature of the GC was set at 25°C for 10 minutes for separating the hexane and TCE peaks. To attain the initial temperature the oven was precooled down to 25°C using liquid nitrogen.

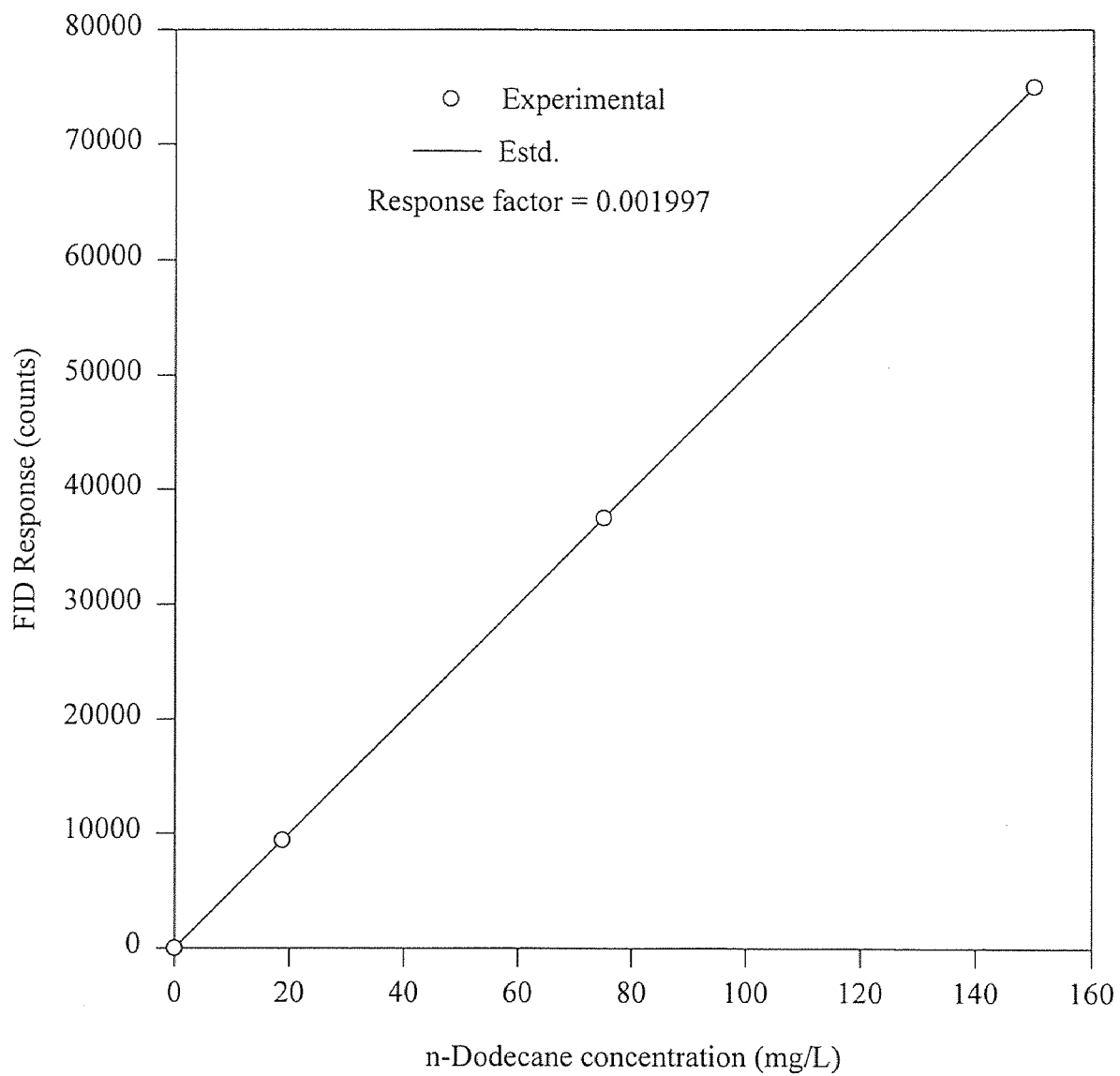


Figure 2.4. Calibration of n-dodecane FID response

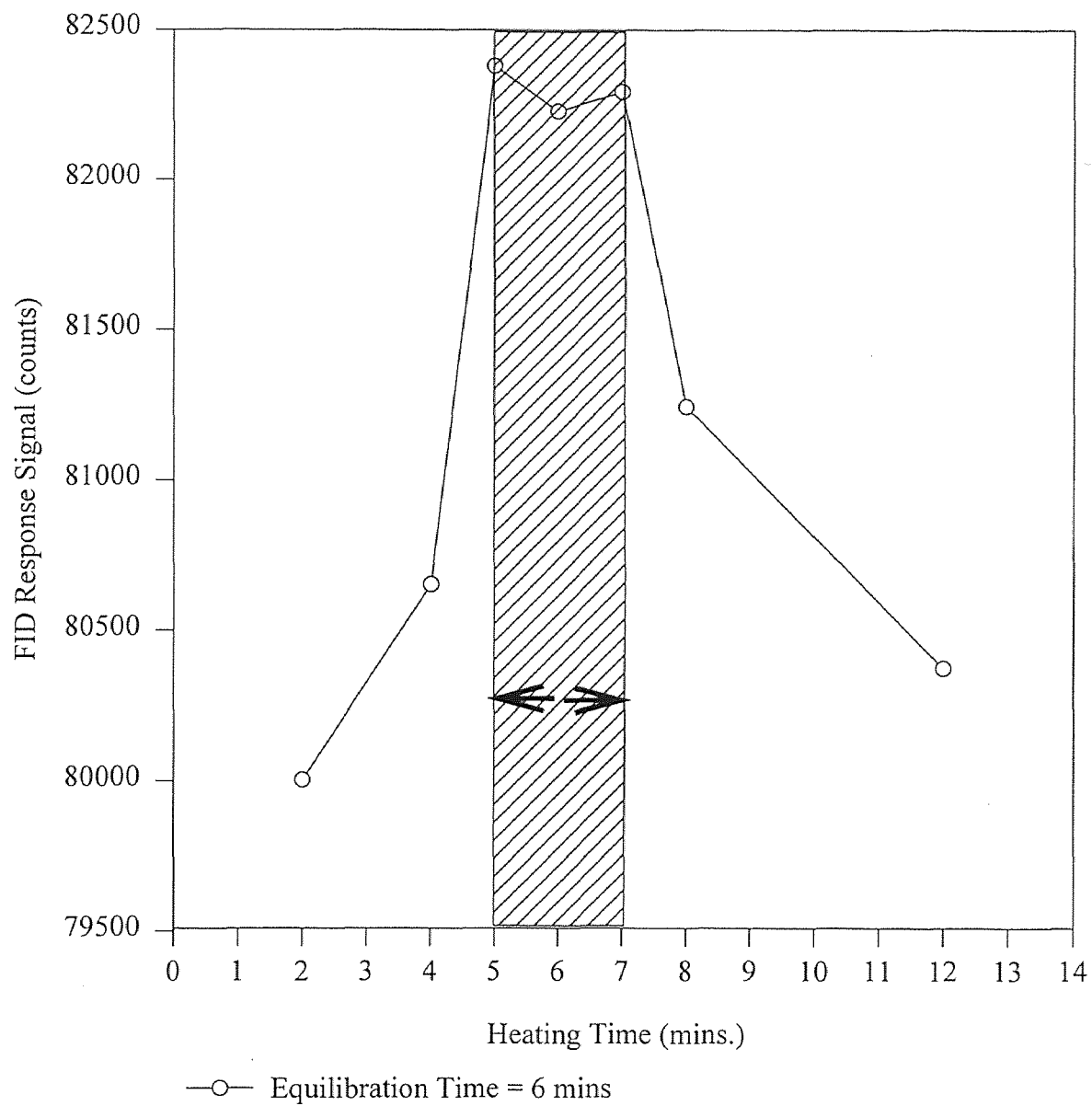


Figure 2.5. Effect of equilibration time on TCE/n-dodecane output signal

In the final step the temperature ramp was changed from 40°C per minute to 10°C per minute to prevent cracking of dodecane. The properties of sodium dodecyl sulfate (SDS), trichloroethylene (TCE) and n-dodecane are provided in Tables 2.2, 2.3 and 2.4 respectively.

Table 2.2. Properties of surfactant*

Property	SDS (Sodium Dodecyl Sulfate)
Chemical name	Sodium Dodecyl Sulfate
Source	Sigma Chemicals
Type	Anionic
Formula Weight	288.4
Formula	$C_{12}H_{25}O_4SNa$
Active component	99%
CMC, 0.1 M electrolytes	0.28
Free energy of micellization	ΔG°
DDI water (KJ/mole)	-22.27
0.1 M electrolyte	-28.77
Area per molecule (Å^2)	43.70

* source: Rosen (1989), Dow Chemical Company (Midland, Michigan)

Table 2.3. Physical and chemical properties of TCE*

molecular weight (g/mol)	131.39		
melting point (° C)	-87.10		
boiling point (° C)	86.70		
density (g/cc), liquid (20 ° C)	1.456		
viscosity, mPa.s 20 ° C 60 ° C	0.58 0.42		
critical properties temperature (° C) pressure (MPa)	271.0 5.02		
heat capacity, (J/kg.K) liquid vapor at boiling point	941.0 653.0		
dipole moment, debye	0.77		
dielectric constant ϵ	3.43		
vapor pressure (kPa) ^b Antoine constants	A 5.94606	B 1187.51	C 214.474
solubility (mg/L)	1100.0		

$$^b \log_{10} P = A - [B / (T + C)]$$

* source: Kirk-Othmer (1983)
Lyman et al. (1990)

Table 2.4. Physical and chemical properties of dodecane*

Trade name	n-dodecane (C ₁₂ H ₂₆)
boiling point (° C)	216.11
melting point (° C)	- 9.4444
vapor pressure (mm Hg/ 21C)	0.3
vapor density (Air=1)	5.9
specific gravity	0.749
chemical solubility ^b solubility constants	A 23.755 B -15607.170 C 2325.47E+03
molecular weight	170.337
solubility in wt. ppm	3700E-06

$$^b \log S = A + B/T + C/T^2$$

where S = solubility in water, wt. ppm

A, B, C = correlation constants

T= temperature constants, K

* source: Fisher Scientific Company. (Fairlawn, NJ);

Yaws (1993).

2.6 Calculation Methods

The percent removal or drop in the concentration of n-dodecane of reservoir was calculated from

$$\%Removal = \frac{(C_o - C_{final})}{C_o} * 100 \quad (2.1)$$

The average flux of n-dodecane over the total duration of experiment (t_{total}) was calculated from

$$J = \frac{V}{A_M} * \frac{(C_o - C_{final})}{t_{total}} \quad (2.2)$$

The flux for TCE was calculated in terms of mol/hr.cm² as

$$J_{TCE} = \frac{v * (C_{in} - C_{out}) * 60}{M_{TCE} * A_M * 10^6} \quad (2.3)$$

The water flux was calculated in terms of mol/hr.cm² over the whole duration of experiment (t_{total}) as

$$J_{WATER} = \frac{V_{WATER} * 60}{t_{total} * A_M * M_{WATER}} \quad (2.4)$$

The local flux of n-dodecane at any time t was given as

$$J = -\frac{V}{A_M} * \frac{dC}{dt} \quad (2.5)$$

where C is the n-dodecane concentration.

The percent removal of the concentration of TCE was calculated from

$$\%Removal = \frac{(C_{in} - C_{out})}{C_{in}} * 100 \quad (2.6)$$

where C_{in} = Concentration of TCE at the module inlet,

C_{out} = Concentration of TCE at the module outlet.

The membrane area A_M is based on the fiber inside diameter D_i :

$$A_M = \pi * N * D_i * L \quad (2.7)$$

CHAPTER 3

RESULTS AND DISCUSSION

The objectives of the chapter are to discuss the effects of various parameters on the removal of n-dodecane and TCE from an oil-in-water emulsion. Four parameters that were studied in depth were the effect of flow rate, surfactant concentration, initial concentration and feed flow side. The results will be presented first for the oil-permeation experiments and then for combined permeation experiments. The data for oil permeation experiments will be discussed in terms of % removal of n-dodecane and n-dodecane fluxes. The data for the combined permeation will be discussed in terms of % removal of TCE, TCE fluxes and water fluxes. Data will be compared for the combined permeation experiments with the modified pervaporation experiments to judge the effect of n-dodecane.

3.1 Oil Permeation Experiments

The effects of various parameters on the removal of n-dodecane from an oil-in-water emulsion with or without a surfactant are considered here. The experiments were conducted at 25°C. An oil-in-water emulsion was fed to the hollow fiber module and the oil fluxes were calculated on the basis of a drop in the concentration of oil in the feed reservoir. All experiments were carried out in the batch recirculation mode. The experiments were usually carried out for 28-32 hours.

3.1.1 Effect of Flow Rate

Figures 3.1 and 3.2 show the effect of flow rate on the removal and instantaneous flux of n-dodecane respectively for the oil-in-water emulsion flowing on the tube side. Table 3.1 provides the experimental results for the effect of flow rate. It was observed that increasing the flow rate from 21mL/min to 48mL/min increased the averaged flux of n-dodecane marginally from 1.92×10^{-5} to 2.03×10^{-5} mol/hr.cm². The removal of oil from the oil-in-water emulsion increased with an increase in the flow rate. When the flow rate was increased from 21mL/min to 48mL/min, the oil removal increased from 84% to 88% and with a further increase in flow rate to 64mL/min the removal increased further to 91% for the initial 10 hours. This may be due to the fact that increasing the flow rate from 21mL/min to 64mL/min not only increases the rate of oil transport to the membrane but it also enhances the attachment and coalescence step as n-dodecane droplets are brought into increasing contact with fibers which allows more of n-dodecane molecules to permeate through the membrane. The overall removal over a 32-hour period remained almost unchanged at 97-98% when the flow rate was increased from 21mL/min to 64mL/min. The transport of oil through the membrane, therefore, is not strongly enhanced at higher feed flow rates. The removal and the flux of n-dodecane did not change much after ten hours of experiment.

3.1.2 Effect of Concentration of n-Dodecane

Figures 3.3 and 3.4 show the effect of initial concentration on the removal and instantaneous flux of n-dodecane respectively for the oil-in-water emulsion flowing on the tube side. It was observed that increasing the oil concentration from 1563 ppm to 14220 ppm increased the

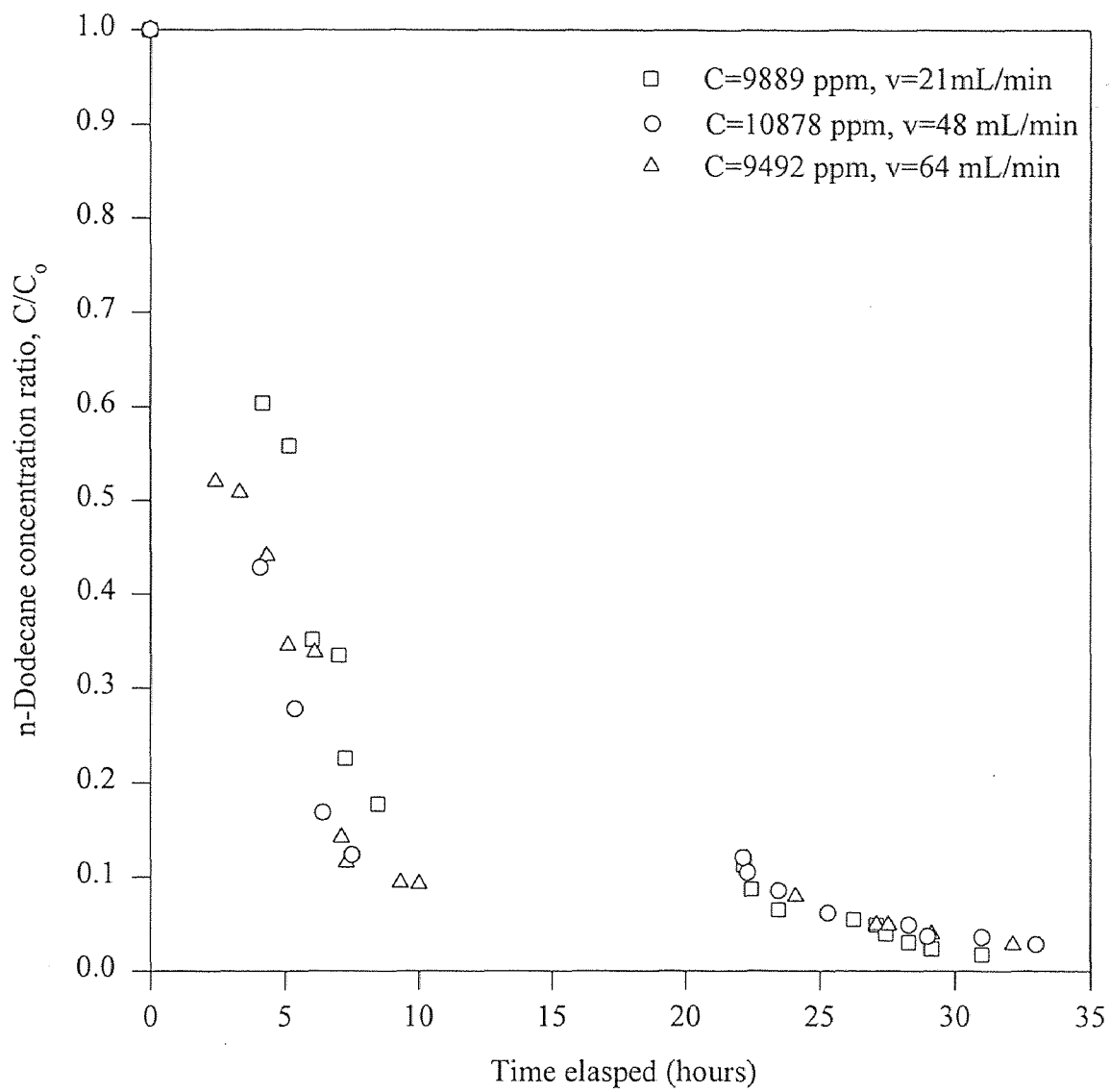


Figure 3.1. Effect of flow rate on the removal of n-dodecane

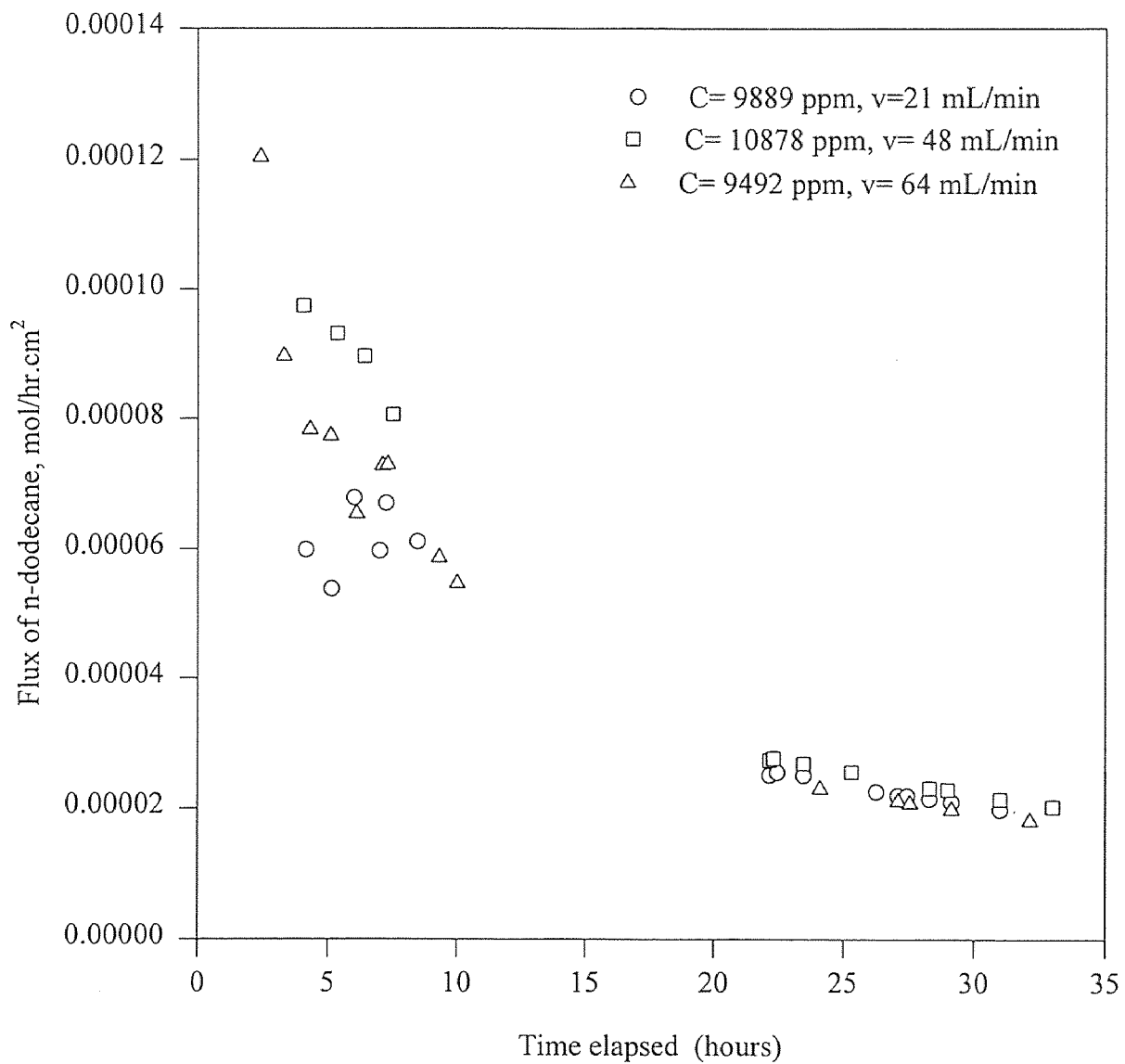


Figure 3.2. Effect of flow rate on the flux of n-dodecane

Table 3.1. Effect of feed flow rate on removal and the flux of n-dodecane

$C_{t=0}$ (ppm)	C_{final} (ppm)	Time (hours)	Flow rate (mL/min)	Pressure (psi)	% Removal	*Flux of n-dodecane $\times 10^6$ (mol/hr.cm ²)
9889	176	32	21	23/10	98	19.2
10878	310	33	48	24/8	97	20.3
9492	273	32.15	64	25/7	97	18.2

* Averaged flux over the whole experiment, equation (2.2)

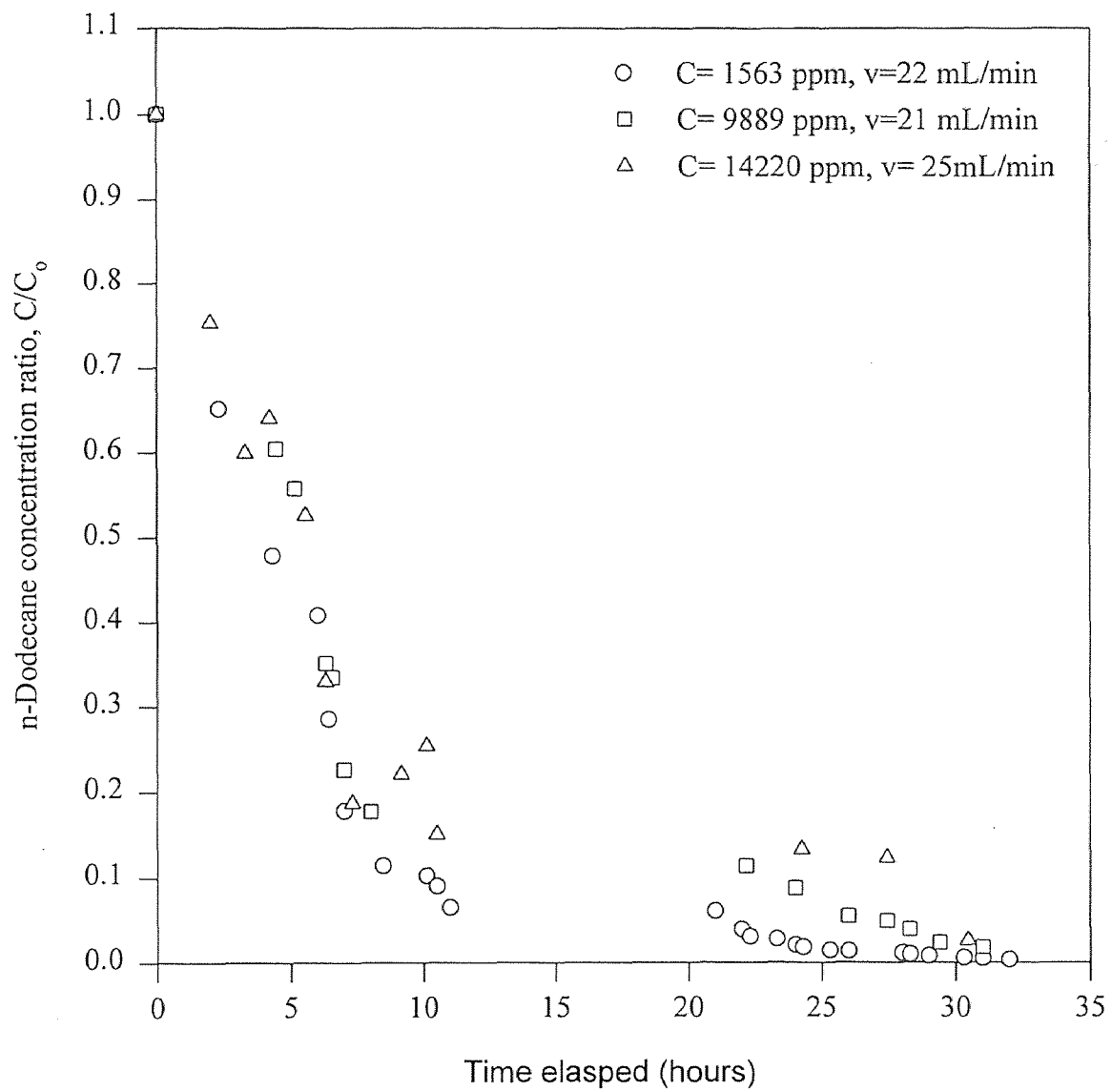


Figure 3.3. Effect of n-dodecane initial concentration on removal

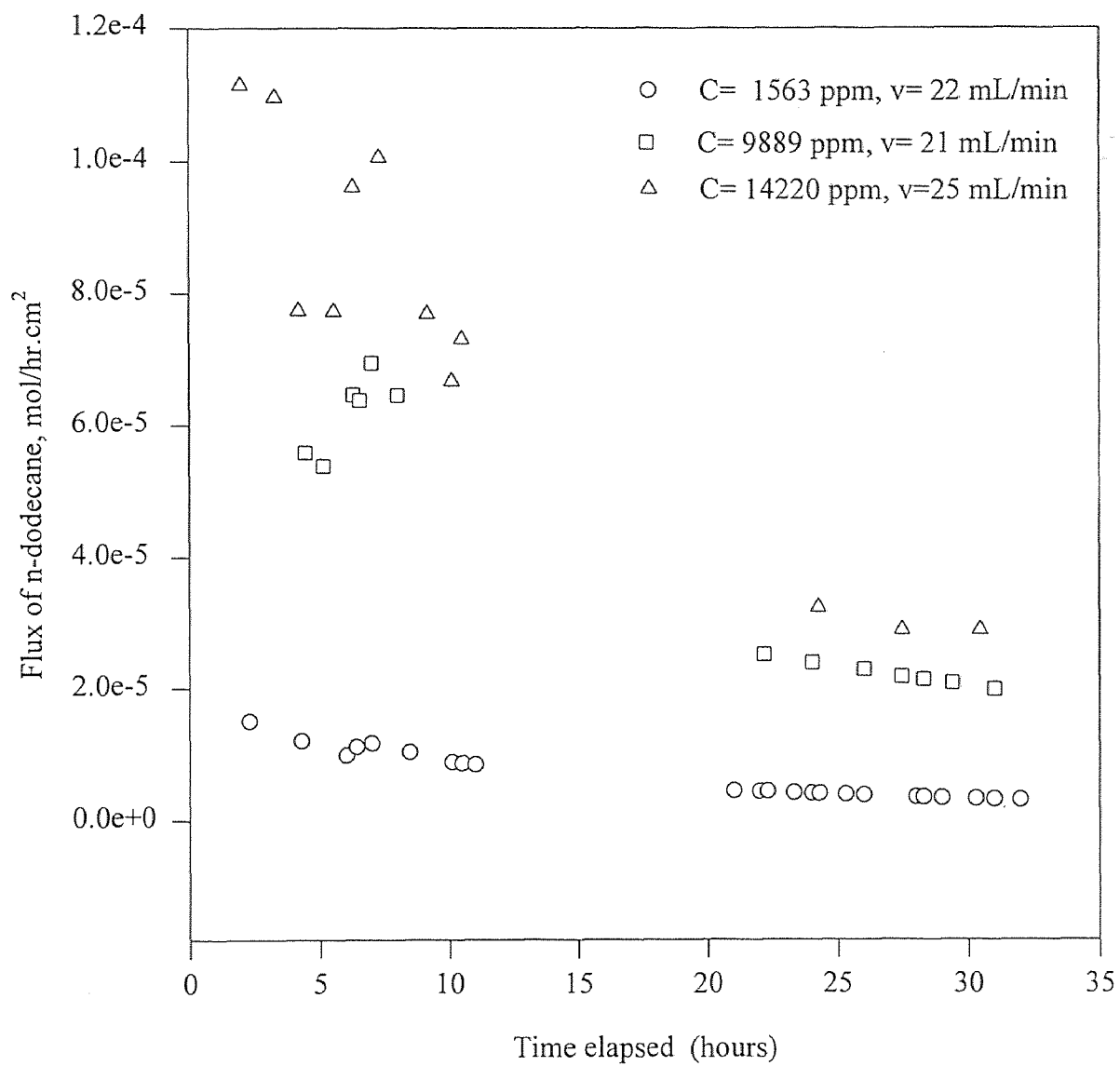


Figure 3.4. Effect of n-dodecane initial concentration on the flux behavior

averaged flux of n-dodecane from 0.31×10^{-5} mol/hr.cm² to 2.9×10^{-5} mol/hr.cm². A nine-fold increase in averaged flux was observed by an approximate nine-fold increase in the initial concentration of n-dodecane. In the concentration range of 9889 ppm to 14220 ppm, a two-fold increase in the flux was observed. The effect of oil concentration was more marked at low concentrations than at higher concentrations. The experiments were carried out in a flow rate range of 21-25 mL/min. The results are provided in Table 3.2. A removal of 97-99.7% was achieved by changing the initial concentration of n-dodecane. The increase in flux with concentration may be due to fact that more of n-dodecane molecules were available for a given flow rate for transport through the membrane pores which increased the permeation of n-dodecane. This phenomenon was also observed at low concentrations of oil by Magdich and Semmens (1988) and Tirmizi et al.(1996).

3.1.3 The Role of Feed Flow Side

The next set of experiments were conducted to compare the performance of the module w.r.t the effect of a tube-side feed versus shell-side feed in terms of the flux and the removal performance of n-dodecane. Figures 3.5 and 3.6 illustrate the role of feed-flow side on the removal and instantaneous flux of n-dodecane respectively for the oil-in-water emulsion flowing on either the shell or the tube side. Two feed composition ranges were used: 1025-1095ppm and 444-498 ppm. At the higher concentration range, a flow rate of 50-54 mL/min was used; for the lower concentration range, a flow rate of 32-34 mL/min was utilized. The shell side had a higher flow area so there was less pressure drop along the module and less resistance for flow which was not the case for tube-side feed. Table 3.3 shows the effect of

Table 3.2. Effect of n-dodecane initial concentration on its removal and flux

$C_{t=0}$ (ppm)	C_{final} (ppm)	Time (hours)	Flow rate (mL/min)	Pressure (psi)	% Removal	*Flux of n-dodecane* 10^6 (mol/hr.cm ²)
1563	5	32	22	24/15	99.7	3.1
9889	176	32	21	23/10	98	19.2
14220	366	30.45	25	25/16	97	29.0

* Averaged flux over the whole experiment, equation (2.2)

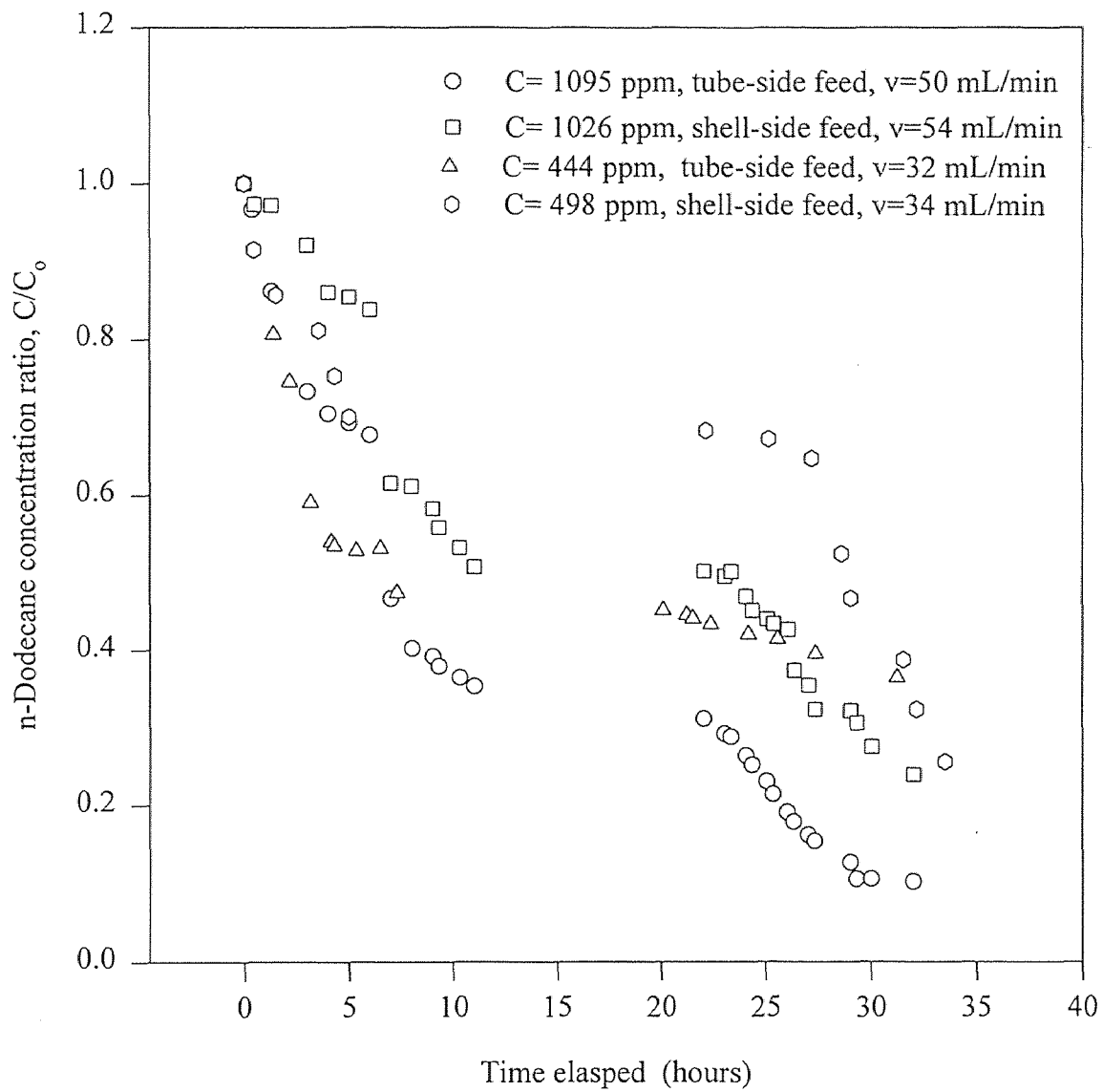


Figure 3.5. Effect of shell side and tube side on the removal of n-dodecane

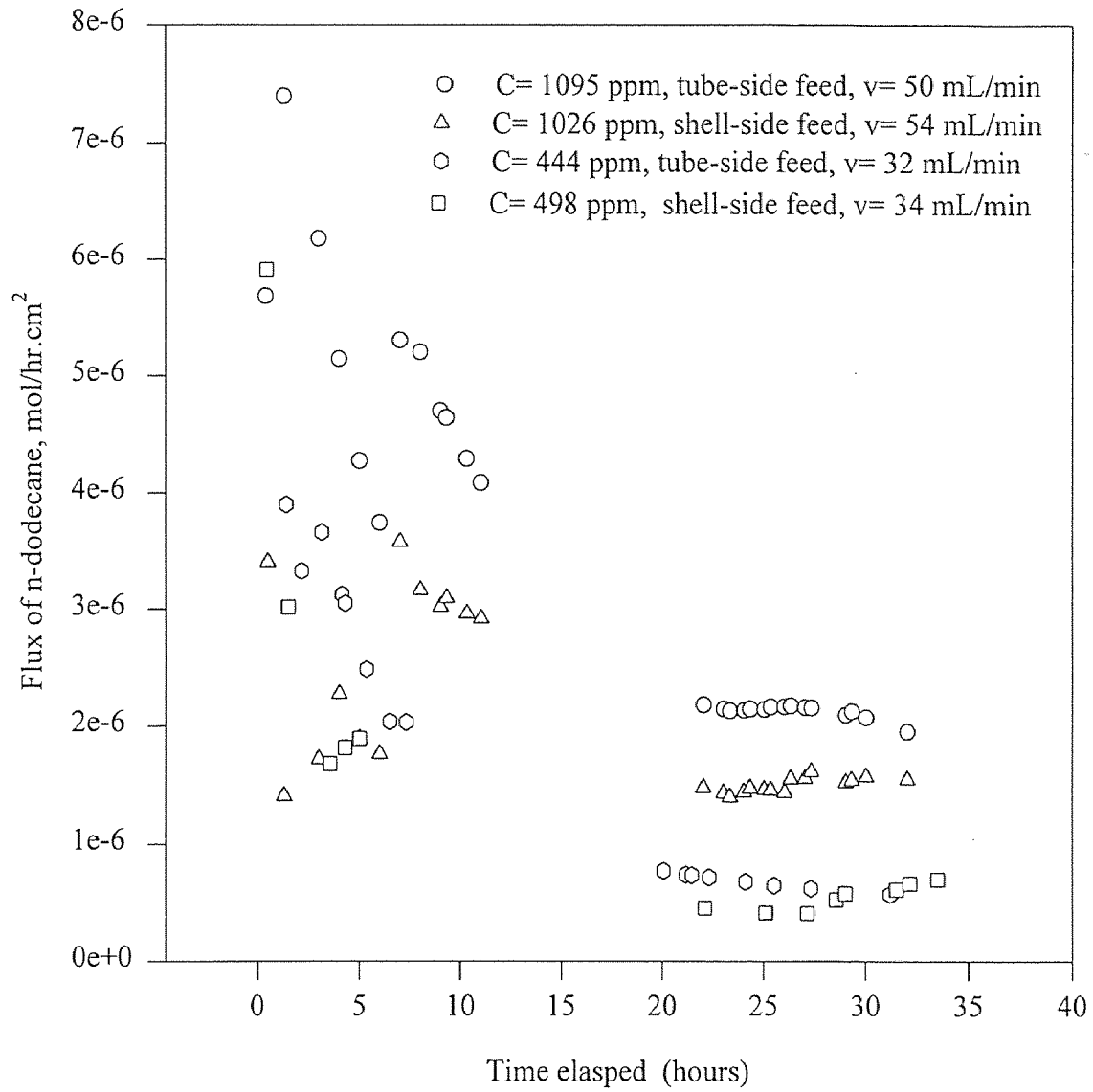


Figure 3.6. Effect of shell side and tube side on the flux of n-dodecane

Table 3.3. Effect of shell-side and tube-side performances on removal and flux of n-dodecane

Feed side	$C_{t=0}$ (ppm)	C_{final} (ppm)	Time (hours)	Flow rate (mL/min)	Pressure (psi)	% Removal	SDS conc.	*Flux of n-dodecane *10 ⁶ (mol/hr.cm ²)
tube	1095	111	32	50	25/7	90	1	1.94
shell	1026	246	32	54	15/12	76	1	1.54
tube	444	127	31.2	32	24/7	71	1	0.64
shell	498	162	33.5	34	22/19	68	1	0.635

* Averaged flux over the whole experiment, equation (2.2)

feed flow side on the removal and flux of n-dodecane. The surfactant concentration was maintained at 1% for all experiments. The average removal of n-dodecane dropped by 14-16% when the feed was flowing through the shell side. However there was a significant difference in the overall flux for the higher concentration feed. In the first eleven hours of the experiment, the removal of n-dodecane was 15% higher when fed from the tube side. A feed of 1026-1095 ppm fed from the shell and tube side showed respectively averaged fluxes of magnitude of 1.54×10^{-6} mol/hr.cm² and 1.94×10^{-6} mol/hr.cm². Similar performance was observed when the feed concentration was changed to 444-498 ppm. The emulsified feed fed to the module was in micellar form with no free n-dodecane in the feed. The free n-dodecane was separated using a separating funnel. Higher concentrations of n-dodecane were not used as it was observed that a large pressure drop was created and difficulties occurred in maintaining the flow rate.

3.1.4 Effect of Surfactant

Figures 3.7 and 3.8 show the effect of flow rate on the removal and flux of n-dodecane respectively for the oil-in-water emulsion flowing on the shell side for different surfactant concentrations. Experiments were conducted at n-dodecane concentrations of 5000-5300 ppm while the surfactant concentration was varied from 0-3%. The flow rate was maintained at essentially 39-41 mL/min. The purpose of passing the feed through the shell side was to avoid the accumulation of the oil at the feed inlet and to avoid higher pressure drop over the module. The results for the removal and fluxes are presented in Table 3.4. It was seen that by increasing the concentration of SDS from 0% to 3% the removal dropped by 17%

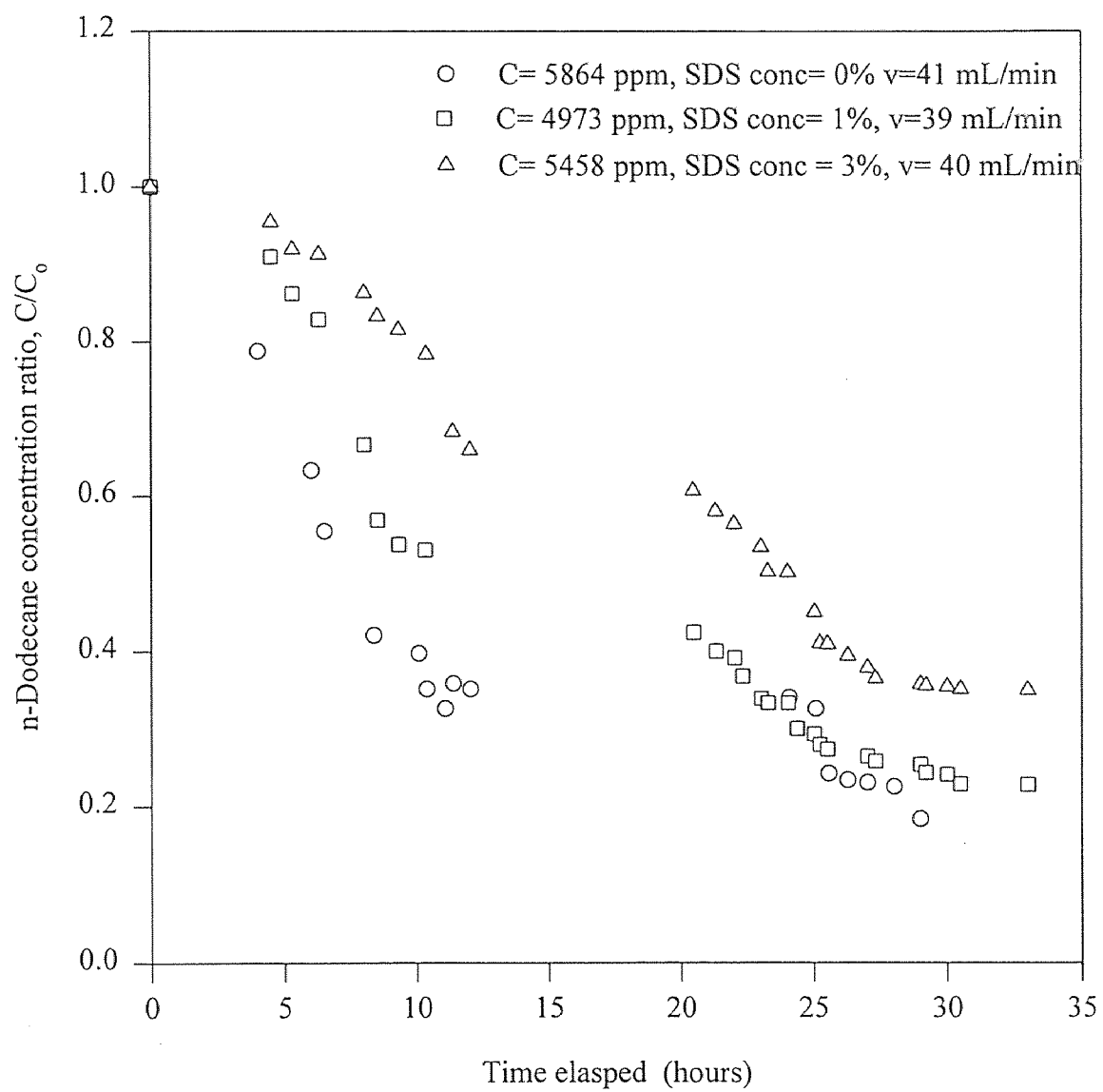


Figure 3.7. Effect of SDS on removal of n-dodecane with feed from shell side

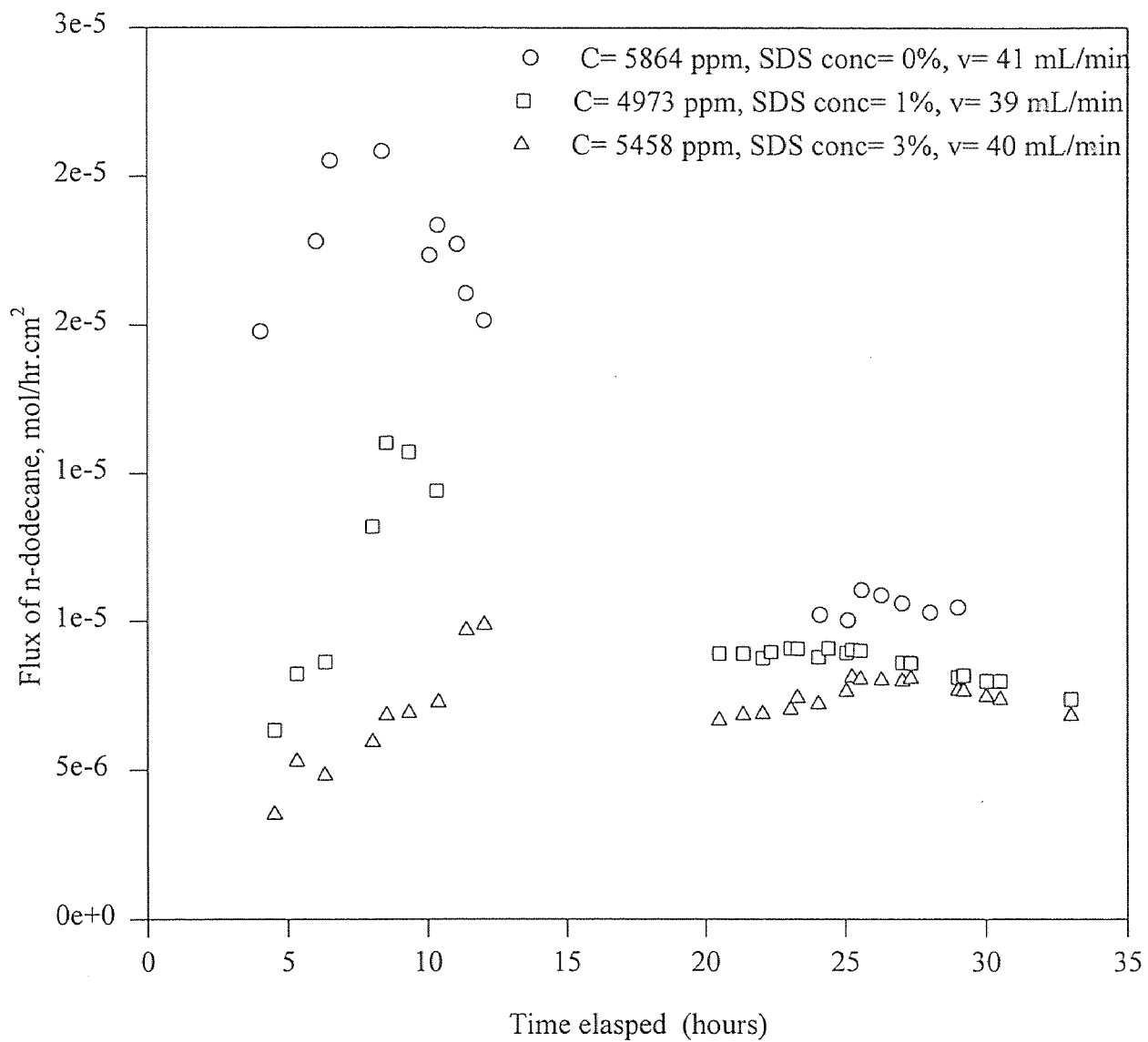


Figure 3.8. Effect of SDS on flux of n-dodecane with feed from shell side

Table 3.4. Effect of surfactant on shell-side performance

$C_{t=0}$ (ppm)	C_{final} (ppm)	Time (hours)	Flow rate (mL/min)	Pressure (psi)	% Removal	SDS conc.	*Flux of n-dodecane *10 ⁶ (mol/hr.cm ²)
5864	1080	29	41	24/20	82	0	10.4
4973	1135	33	39	25/22	77	1	7.37
5458	1911	33	40	26/23	65	3	6.81

* Averaged flux over the whole experiment, equation (2.2)

and the flux dropped by almost half. The removal dropped from 82% to 65% as the SDS concentration was increased from 0% to 3%. The averaged flux dropped from 10.4×10^{-6} mol/hr.cm² to 6.81×10^{-6} mol/hr.cm². The drop in flux was not significant as the surfactant concentration increased from 1% to 3%; the corresponding drop in flux was 7%: the averaged flux dropped from 7.37×10^{-5} mol/hr.cm² to 6.81×10^{-5} mol/hr.cm². A similar phenomenon was observed by Magdich and Semmens (1988) when the surfactant concentration was increased. The decrease in flux with increasing SDS concentration may be due to an increase in emulsion stability with increasing surfactant concentration. Alternatively the decrease may be due to the buildup of surfactant at the surface which presents a mechanical and/or electrical barrier to the membrane transport.

Magdich and Semmens (1988) observed a flux of 0.249 mL/min.ft² (7.085×10^{-5} mol/hr.cm²) at a pressure of 10 psi, surfactant concentration of 500 mg/L, n-dodecane concentration of 5%, temperature of 37°C, flow rate of 300 mL/min. Table 3.2 here shows that the flux increases proportionally to the oil concentration. Therefore extrapolating the results for Table 3.4, we can assume that in this study, at 5% n-dodecane concentration, a flux in the range 10×10^{-5} mol/hr.cm² is quite likely at 25°C. Obviously it will go up significantly at 37°C. Further, a higher flow rate will increase it even further.

3.2 Combined Permeation Experiments

In the combined permeation experiments, both the VOC and the oil were removed from the emulsified oil-in-water feed. The results are presented and discussed with respect to three parameters, namely the n-dodecane concentration, TCE concentration and the flow rate. The experiments were carried out in an once-through mode.

3.2.1 Effect of TCE Concentration on Removal of TCE at a n-Dodecane Concentration of 200 ppm

The experiments were carried out at a flow rate of 2.5 mL/min to get a baseline idea of the process behavior for the combined removal of TCE and n-dodecane. n-Dodecane concentration was kept constant at 200 ppm and the TCE concentration was varied in the range of 425-636-842 ppm. The transmembrane pressure was maintained at 4 psi. The shell side was maintained under vacuum at -28"Hg. Figures 3.9 and 3.10 show the effect of n-dodecane on the removal and flux of TCE respectively for the oil-in-water emulsion flowing on the tube side. Tables 3.5 to 3.7 provide the results from the experiments carried out at three different TCE concentrations. It was observed that the TCE removal dropped with time. It was also observed that the drop in removal decreased with an increase in concentration of TCE. At a TCE concentration of 425 ppm it was observed that over the length of the experiment (~6.5 hours) the removal of TCE dropped from 67% to 26% and the TCE flux dropped from $1.7 * 10^{-6}$ mol/hr.cm² to $7.7 * 10^{-7}$ mol/hr.cm². Similar behavior was observed for TCE concentrations of 636 ppm and 842 ppm but the rate of decline of TCE removal decreased with increasing TCE concentrations. The results in Tables 3.5 to 3.8 show that the presence of n-dodecane decreases the water flux by approximately 90% when compared to the flux values obtained from modified pervaporation experiments (Table 3.8). Modified pervaporation is defined as a process wherein the liquid feed flows on the tube side, and is not in direct contact with the VOC-selective silicone membrane layer. The VOC will permeate through the silicone skin subjected to vacuum on the shell side via vapor permeation. An averaged water flux of $4.3 * 10^{-5}$ mol/hr.cm² was observed with n-dodecane in comparison with an averaged flux of $1.45 * 10^{-4}$ mol/hr.cm² without

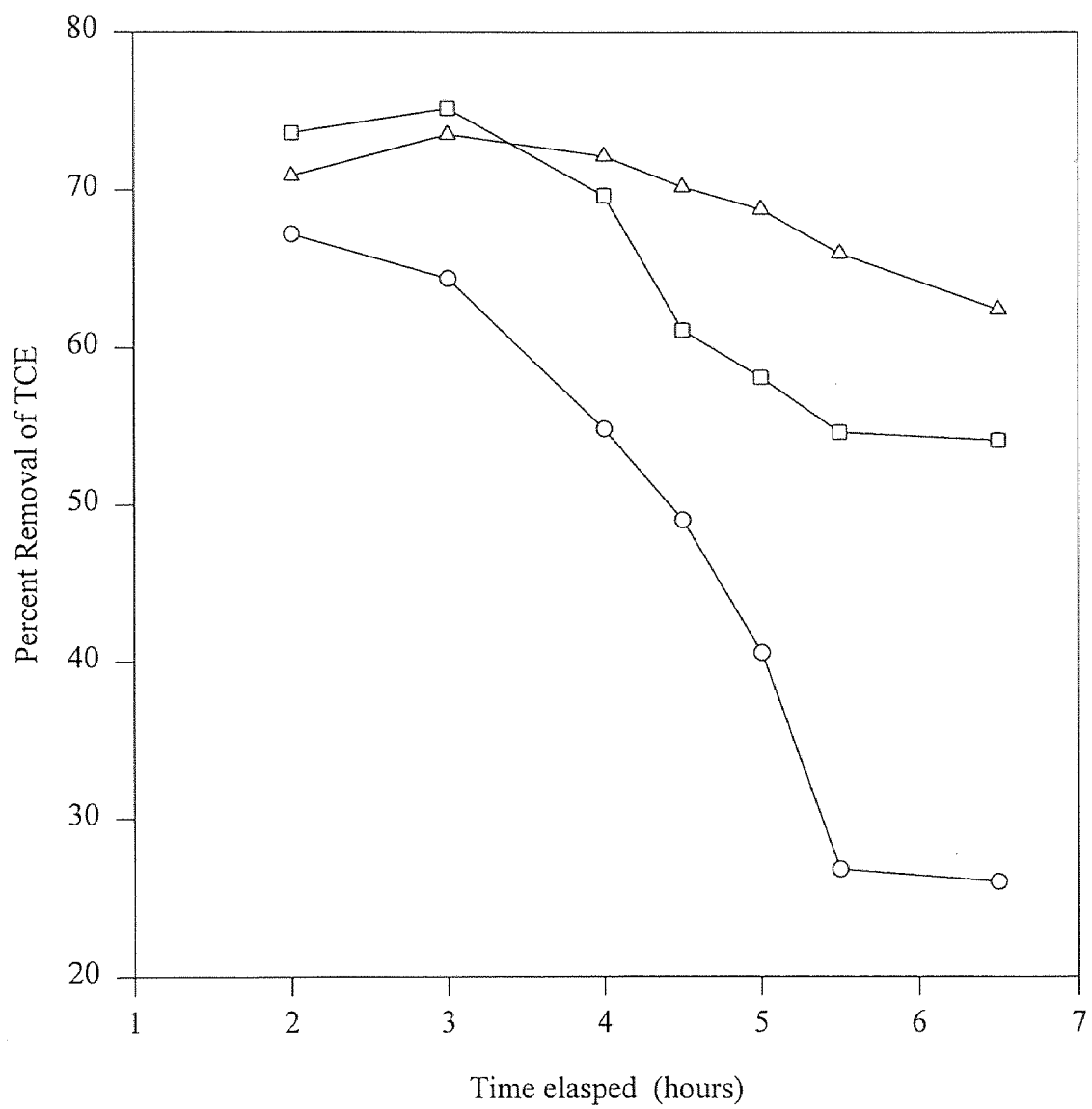


Figure 3.9. Variation of TCE removal with time at different TCE concentrations and a constant n-dodecane concentration of 200 ppm

○ C = 426 ppm □ C = 636 ppm △ C = 842 ppm

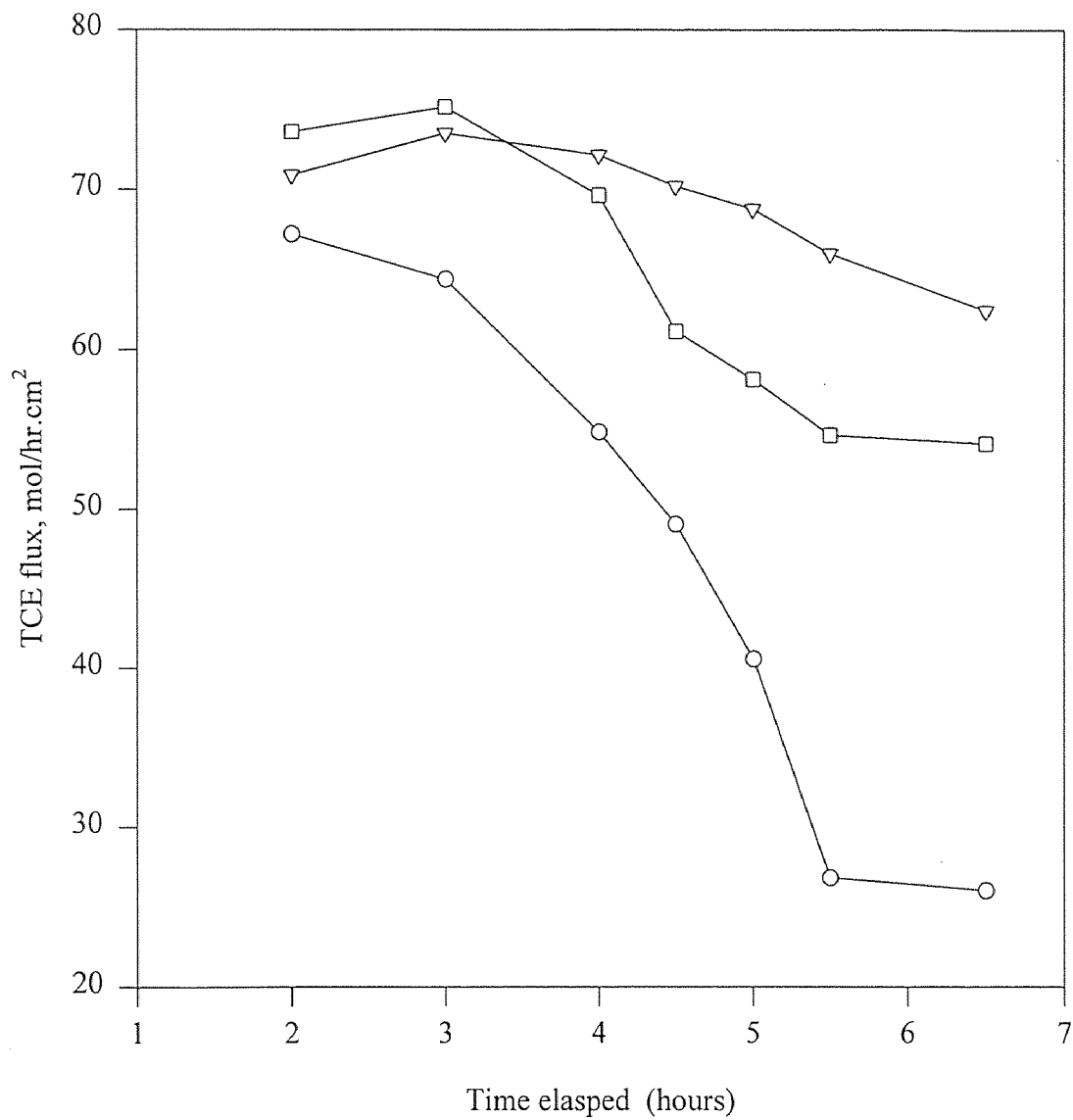


Figure 3.10. Variation of TCE flux with time at different TCE concentrations and a constant n-dodecane concentration of 200 ppm

○ C = 426 ppm □ C = 636 ppm ▽ C = 842 ppm

Table 3.5. Effect of n-dodecane on the removal of TCE with n-dodecane concentration remaining constant at 200 ppm for 425 ppm of TCE feed
 Conditions: flow rate= 2.5 mL/min, pressure= 6/2 psi,
 n-dodecane collected= 7-8 drops

Time (hours)	C _{in} ppm	C _{out} ppm	% Removal	TCE flux mol/hr.cm ²	Water flux mol/hr.cm ²
2	425	140	67	1.7e-06	
3	425	152	64	1.6e-06	
4	425	192	55	1.4e-06	
4.5	425	217	49	1.4e-06	
5	425	253	41	9.9e-07	
5.5	425	312	27	6.9e-07	
6.5	425	315	26	7.7e-07	4.61e-05

Table 3.6. Effect of n-dodecane on the removal of TCE with n-dodecane concentration remaining constant at 200 ppm for 636 ppm of TCE feed
 Conditions: flow rate= 2.5 mL/min, pressure= 6/2 psi,
 n-dodecane collected=7-9 drops

Time (hours)	C _{in} ppm	C _{out} ppm	% Removal	TCE flux mol/hr.cm ²	Water flux mol/hr.cm ²
2	636	168	74	2.9e-06	
3	636	158	75	3.0e-06	
4	636	193	69	3.0e-06	
4.5	636	247	61	2.4e-06	
5	636	266	58	2.3e-06	
5.5	636	289	54	2.0e-06	
6.5	636	292	54	1.9e-06	4.14e-05

Table 3.7. Effect of n-dodecane on the removal of TCE with n-dodecane concentration remaining constant at 200 ppm for 842 ppm of TCE feed
 Conditions: flow rate= 2.5 mL/min, pressure= 6/2 psi,
 n-dodecane collected=9-11 drops

Time (hours)	C _{in} ppm	C _{out} ppm	% Removal	TCE flux mol/hr.cm ²	Water flux mol/hr.cm ²
2	842	245	70.8	3.6e-06	
3	842	223	74	3.8e-06	
4	842	234	72	3.6e-06	
4.5	842	250	70	3.4e-06	
5	842	263	69	3.8e-06	
5.5	842	286	66	3.6e-06	
6.5	842	316	62	3.3e-06	4.15e-05

Table 3.8. Effect on the removal of TCE without n-dodecane
 Conditions: flow rate= 2.5 mL/min, pressure= 6/2 psi

Time (hours)	Flow rate mL/min	C _{in} ppm	C _{out} ppm	% Removal	TCE flux* mol/hr.cm ²	Water flux* mol/hr.cm ²
420	2.5	178	26	85	9.3e-07	0.000141
400	2.5	420	28	93	2.4e-06	0.000136
400	2.5	675	60	91	3.8e-06	0.000159
410	2.5	897	29	97	5.3e-06	0.000155
370	5	826	161	81	8.18e-06	9.71e-05
405	10	837	334	60	1.24e-05	9.76e-05

* Water flux and TCE flux were calculated after steady state was reached; the unsteady state period is not considered here.

n-dodecane (Table 3.8). This may be explained due to the fact that the oil present in the pores reduces the water transport. The water flux remained almost constant at 4.15×10^{-6} mol/hr.cm² in the results of Tables 3.5-3.7. 8-12 drops of n-dodecane were collected after each experiment.

3.2.2 Effect of TCE Concentration on Removal of TCE at a n-Dodecane Concentration of 100 ppm

In this set of experiments same experimental conditions were maintained as identified in section 3.2.1 except that n-dodecane concentration was decreased to 100 ppm. Four experiments were carried out at TCE concentrations of 210-324-591-903 ppm. Figures 3.11, 3.12 and 3.13 show the values of TCE removal, TCE flux and water flux respectively. Table 3.9 tabulates the experimental results. It was observed that TCE removal was constant over the whole length of the experiment unlike that with 200 ppm n-dodecane. It was also observed that by increasing the concentration of TCE from 210 ppm to 903 ppm the removal increased from 61% to 91%. Comparing Tables 3.8 and 3.9, the % removal of TCE was lower compared to modified pervaporation experiments. The TCE fluxes increased from 7.88×10^{-7} mol/hr.cm² to 5.04×10^{-6} mol/hr.cm² with an increase in the TCE concentration from 210 ppm to 903 ppm. The water fluxes dropped from 4.61×10^{-5} mol/hr.cm² to 3.42×10^{-5} mol/hr.cm² with an increase in TCE concentration. Comparing the results obtained with those from modified pervaporation experiments (Tables 3.8 and 3.9) we see that the TCE flux is comparable and the water flux is lowered by 90% (a drop from 4.2×10^{-5} mol/hr.cm² to 1.45×10^{-4} mol/hr.cm²). 6-7 drops of n-dodecane were collected after each experiment.

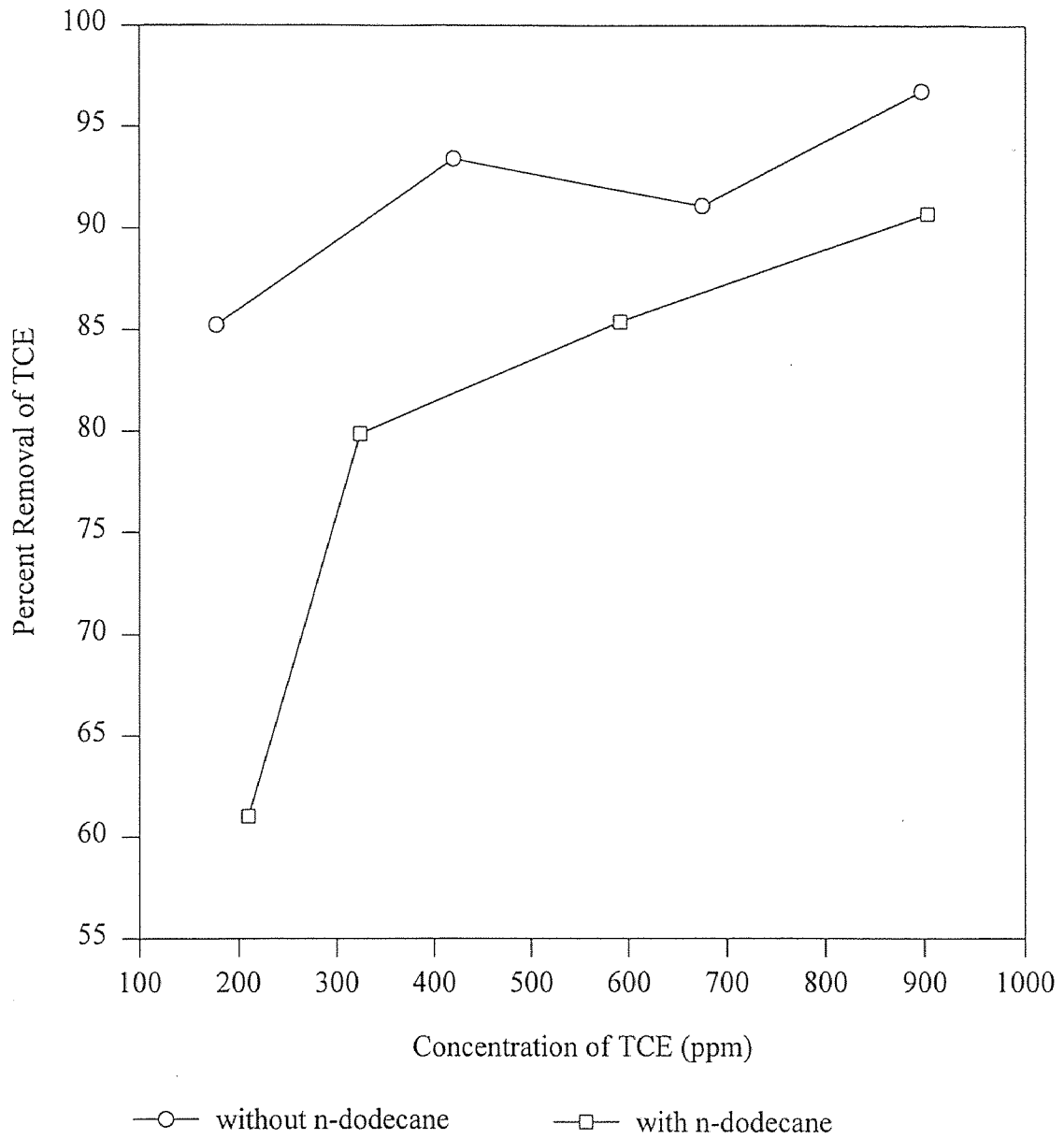


Figure 3.11. Effect of concentration of TCE on the removal of TCE with or without n-dodecane concentration of 100 ppm

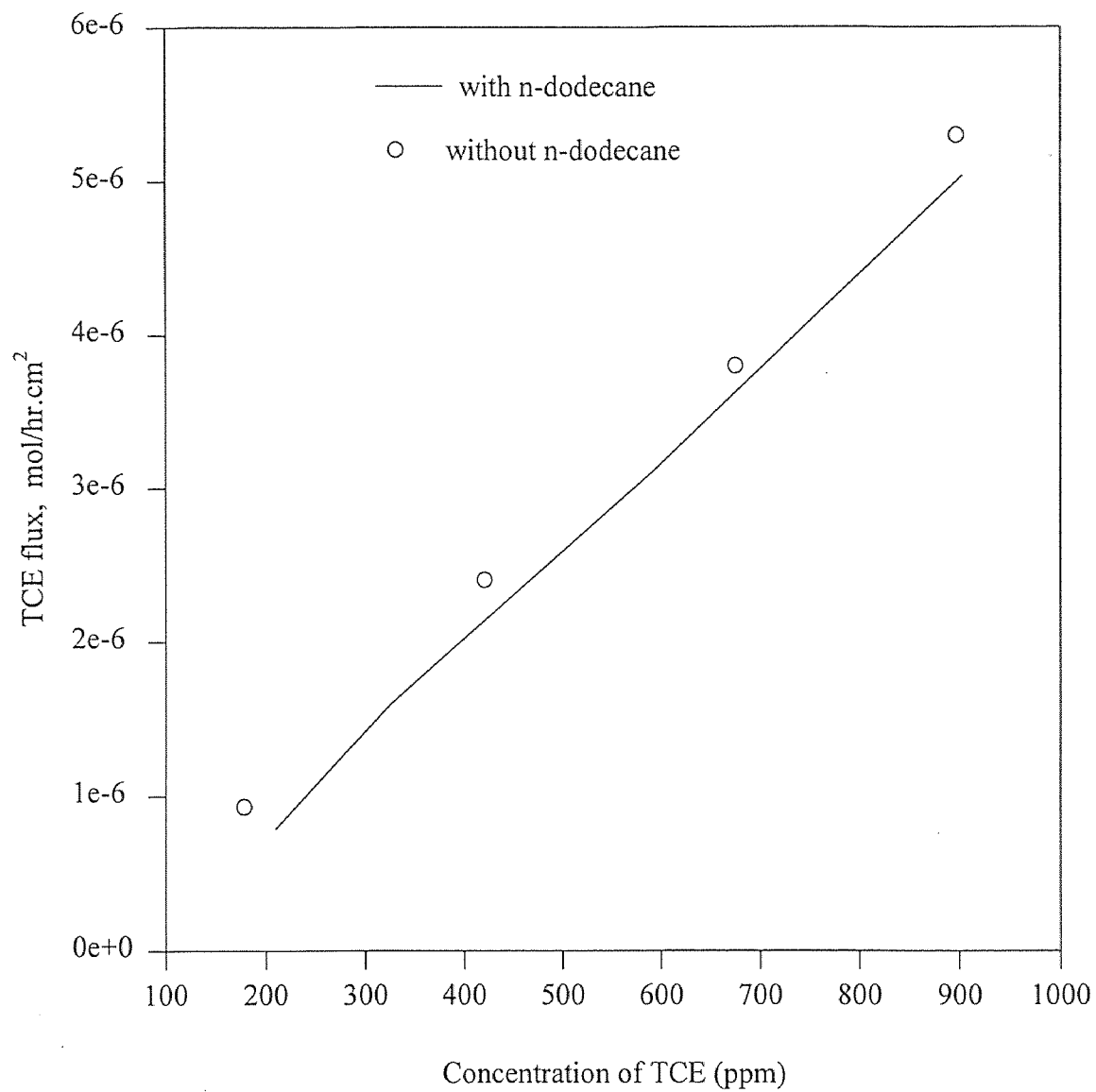


Figure 3.12. Effect of n-dodecane on TCE flux with or without n-dodecane concentration of 100 ppm

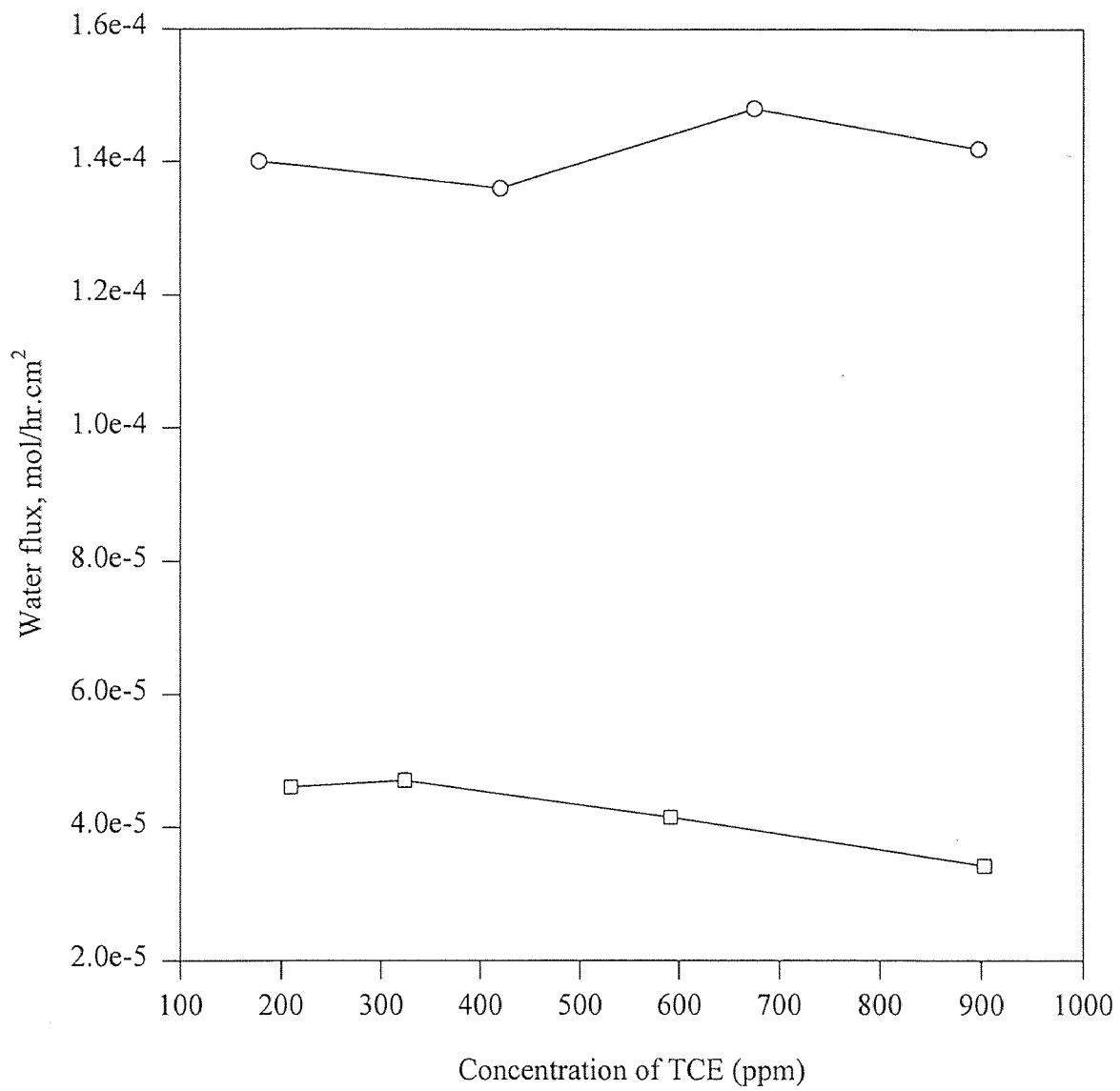


Figure 3.13. Effect of n-dodecane on water flux with or without n-dodecane concentration of 100 ppm

—□— with n-dodecane

—○— without n-dodecane

Table 3.9. Effect of n-dodecane on the removal of TCE with n-dodecane concentration remaining constant at 100 ppm
 Conditions: flow rate = 2.5 mL/min, pressure = 6/2 psi,
 n-dodecane collected = 6-7 drops

Time (hours)	C _{in} ppm	C _{out} ppm	% Removal	TCE flux mol/hr.cm ²	Water flux mol/hr.cm ²
6.5	210	82	61	7.88e-07	4.61e-05
6.5	324	65	80	1.6e-06	4.71e-06
6.5	591	86	85	3.1e-06	4.15e-05
6.5	903	84	91	5.04e-06	3.42e-05

Table 3.10. Effect of flow rate on the removal of TCE with n-dodecane concentration remaining constant at 100 ppm
 Conditions: TCE conc. = 903-1006-971 ppm,
 pressure = 6/2 psi, n-dodecane collected = 7-11 drops

Time (hours)	Flow rate mL/min	C _{in} ppm	C _{out} ppm	% Removal	TCE flux mol/hr.cm ²	Water flux mol/hr.cm ²
6.5	2.5	903	84	91	5.04e-06	4.49e-05
7	5	1006	546	46	5.65e-06	3.42e-06
6.5	7.5	971	658	32	5.79e-06	3.14e-05

3.2.3 Effect of Flow Rate on the Removal of TCE at a n-Dodecane Concentration of 100 ppm

The effect of flow rate was studied by varying the flow rates from 2.5 mL/min to 7.5 mL/min and keeping the TCE and n-dodecane concentrations constant at approximately 1000 ppm and 100 ppm respectively. Figures 3.14, 3.15 and 3.16 show the effect of flow rate on removal, water flux and the TCE flux respectively. Table 3.10 tabulates the experimental results.

It was observed that by increasing the flow rate from 2.5 mL/min to 5 mL/min the removal dropped from 91% to 46%. When the flow rate was increased to 7.5 mL/min the removal dropped to 32%. The TCE flux increased from 5.04×10^{-6} mol/hr.cm² to 5.79×10^{-6} mol/hr.cm². This may be due to an increase in removal of n-dodecane as it was observed that the removal of n-dodecane increased with flow rate in the oil permeation experiments which adversely affected the removal efficiency of TCE. The oil facilitated in cutting down the water flux but it also reduced TCE flux significantly. The water flux dropped from 4.49×10^{-5} mol/hr.cm² to 3.14×10^{-5} mol/hr.cm² as the flow rate was increased from 2.5 to 7.5 mL/min. Comparing Tables 3.8 and 3.9, the % removal of TCE was lower compared to those in modified pervaporation experiments. The oil collected in the collecting vessel increased with an increase in flow rate.

3.2.4 Effect of Surfactant

The effect of surfactant was studied using two different SDS concentrations (0.3% and 1.0%). Experiments were carried out at a flow rate of 2.5 mL/min and the TCE and n-dodecane concentrations were kept constant at approximately 1500 ppm and 1050 ppm

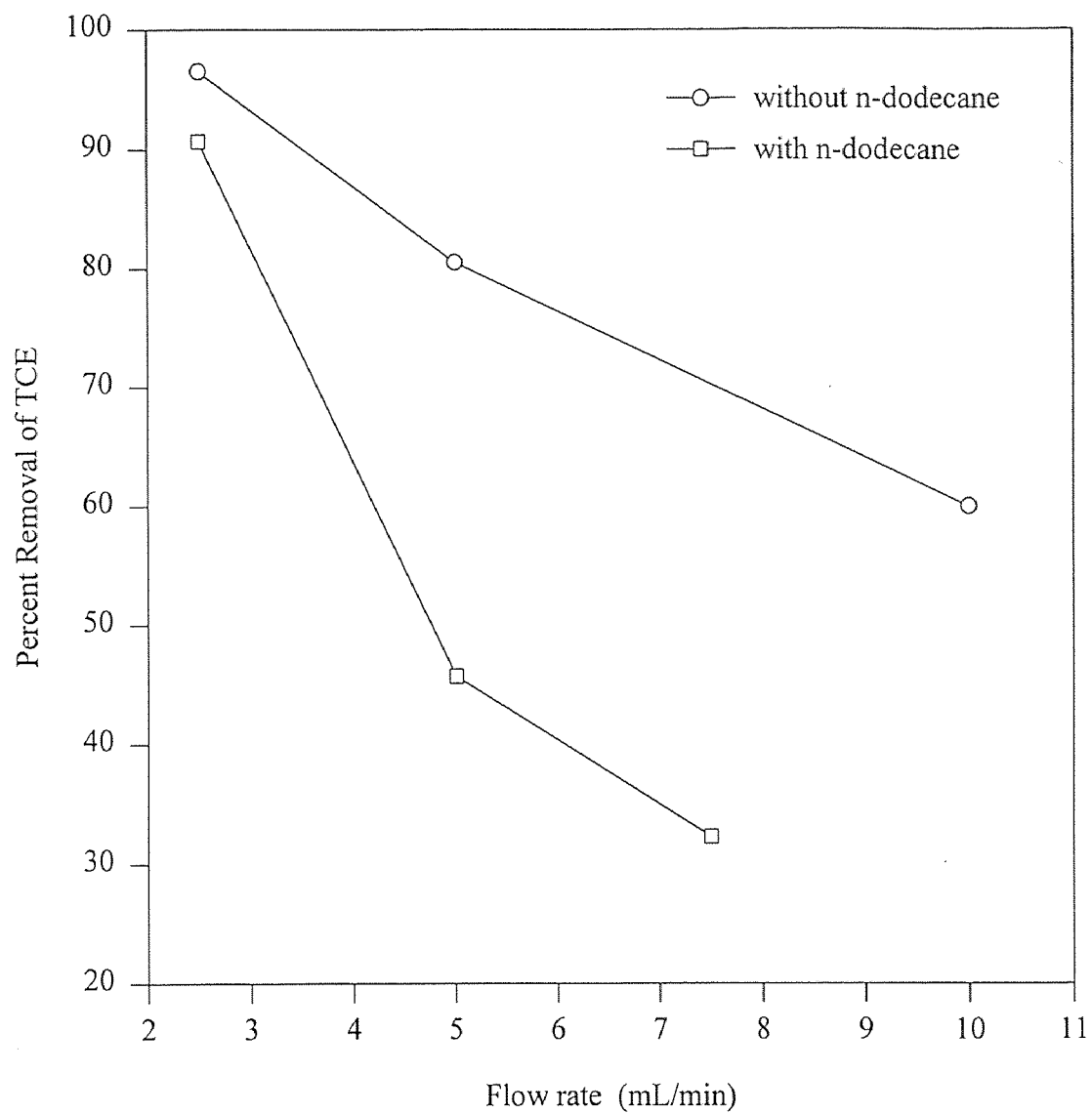


Figure 3.14. Effect of flow rate on removal of TCE with or without n-dodecane concentration of 100 ppm

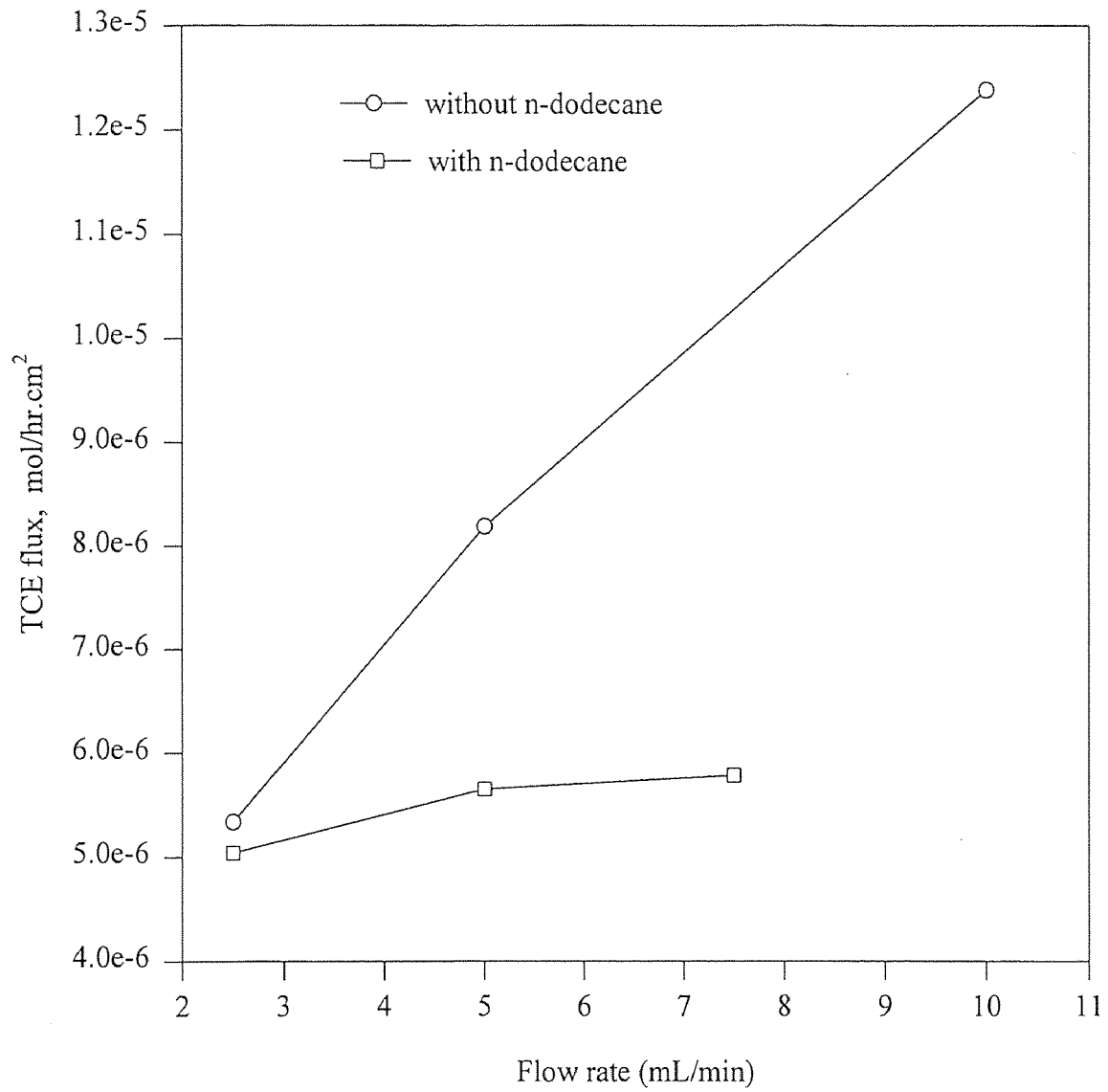


Figure 3.15. Effect of flow rate on TCE flux with or without n-dodecane concentration of 100 ppm

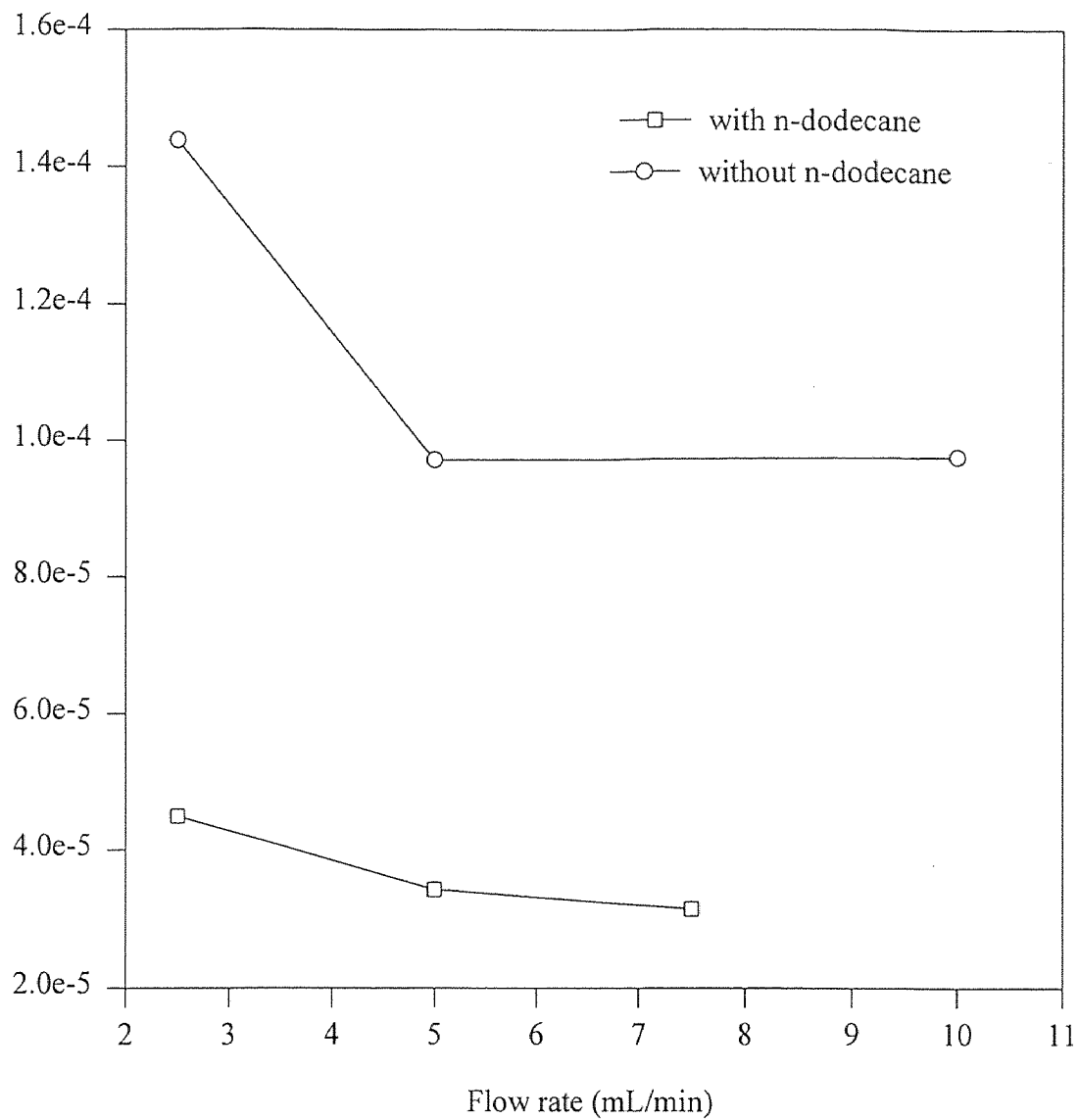


Figure 3.16. Effect of flow rate on water flux with or without n-dodecane concentration of 100 ppm

respectively. Figures 3.17 and 3.18 show the effect of surfactant concentration on TCE removal and flux respectively. Tables 3.11 and 3.12 tabulate the experimental data collected.

It was observed that TCE removal dropped with time. It was also observed that by increasing the surfactant concentration from 0.3 to 1%, the TCE removal was lowered. At a surfactant concentration of 0.3%, the % removal of TCE dropped from 61% to 40% over a period of five hours and the TCE flux was lowered from 6.3×10^{-6} mol/hr.cm² to 3.0×10^{-6} mol/hr.cm². In the case of 1% SDS, the drop over a period of four hours was from 41% to 16% and the TCE flux was decreased from 3.7×10^{-6} mol/hr.cm² to 1.6×10^{-6} mol/hr.cm². The water flux dropped from 3.7×10^{-5} mol/hr.cm² to 2.8×10^{-5} mol/hr.cm² as the SDS concentration increased. Studying Tables 3.7, 3.11 and 3.12 it may be noted that the TCE removal was significantly reduced due to the presence of the surfactant and oil.

3.2.5 Effect of Feed Flow Side

The last set of experiments were conducted to compare the performances of the module with respect to tube-side feed and shell-side feed. The performance was based on the removal and the flux behavior of TCE. The feed composition of TCE was maintained at 1516-1624 ppm and the n-dodecane concentration was maintained at 1100-1140 ppm. The flow rate was maintained at 2.5 mL/min. Tables 3.11 and 3.13 provide the results from the two experiments. Figures 3.17 and 3.18 illustrate the behavior of the removal and the flux of TCE for feed flowing from the tube side and Figures 3.19 and 3.20 illustrate the removal and the flux of TCE for feed flowing from the tube side and shell side. The surfactant concentration was maintained at 1% for both experiments. It was

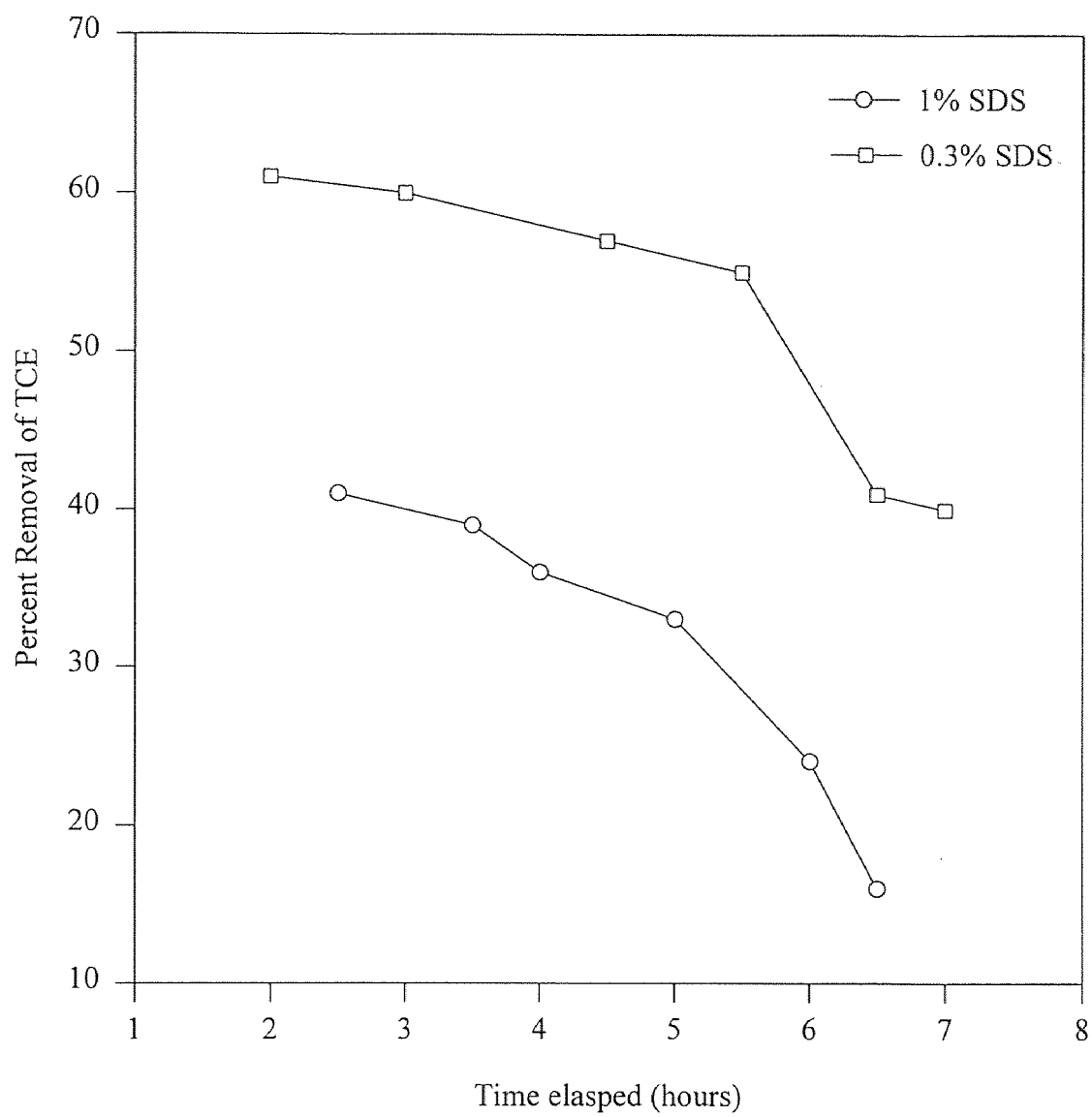


Figure 3.17. Effect of surfactant on the removal of TCE

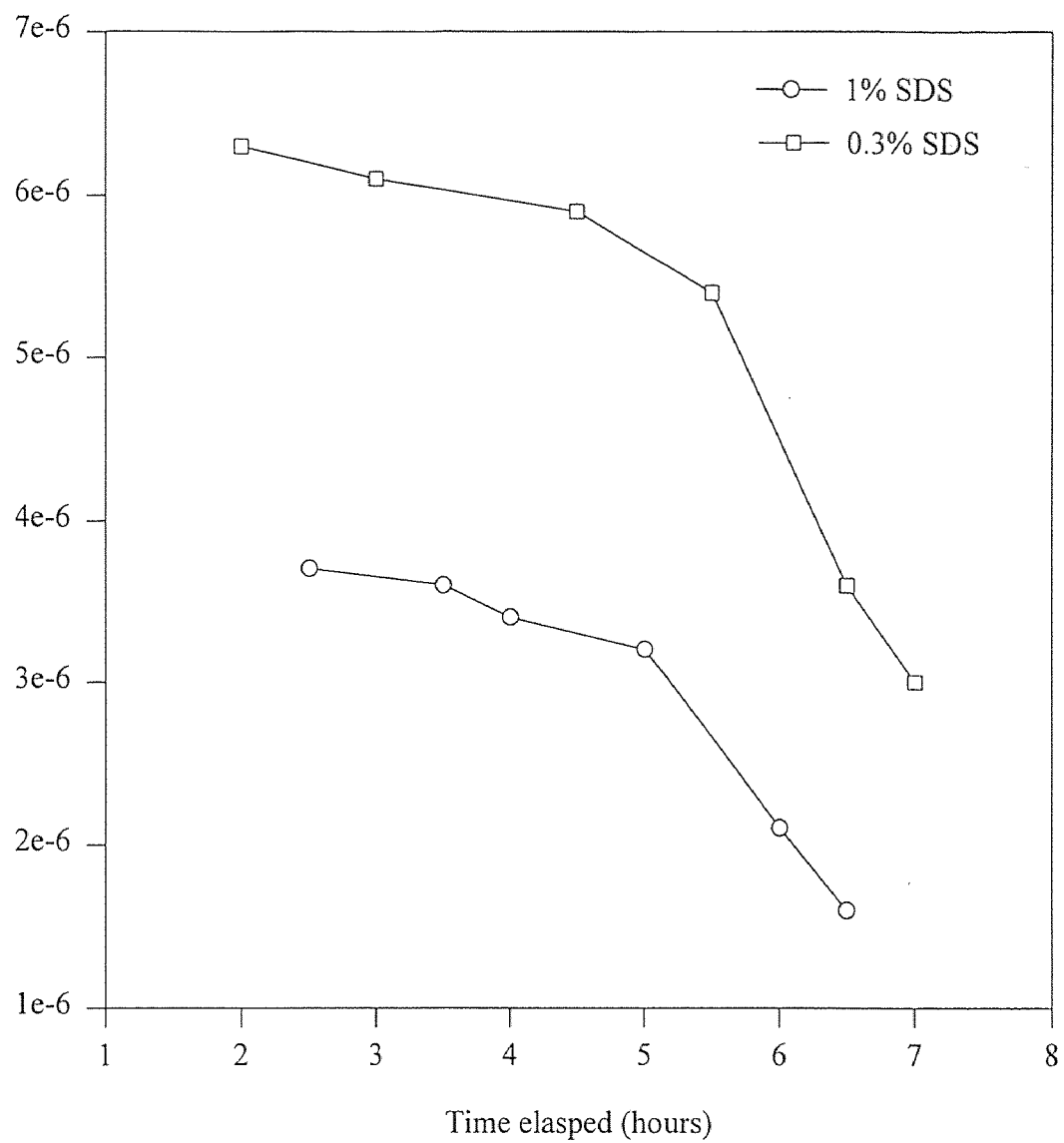


Figure 3.18. Effect of surfactant on the flux of TCE

Table 3.11. Effect of surfactant on the removal of TCE with 1% SDS

Concentration of n-dodecane= 1100 ppm, flow rate= 2.5 mL/min, pressure= 6/2 psi,
water collected=0.6 mL, n-dodecane collected = 10-12 drops, tube-side feed.

C_{in}	C_{out}	Time (hours)	%Removal	TCE flux mol/hr.cm ²	Water flux mol/hr.cm ²
1516	898	2.5	41	3.7e-06	
1516	923	3.5	39	3.6e-06	
1516	974	4	36	3.4e-06	
1516	1017	5	33	3.2e-06	
1516	1150	6	24	2.1e-06	
1516	1281	6.5	16	1.6e-06	2.8e-05

Table 3.12. Effect of surfactant on the removal of TCE with 0.3% SDS

Concentration of n-dodecane= 1050 ppm, flow rate= 2.5 mL/min, pressure= 6/2 psi,
water collected=0.8 mL, n-dodecane collected = 8-9 drops, tube-side feed.

C_{in}	C_{out}	Time (hours)	%Removal	TCE flux mol/hr.cm ²	Water flux mol/hr.cm ²
1567	612	2	61	6.3e-06	
1567	626	3	60	6.1e-06	
1567	666	4.5	57	5.9e-06	
1567	706	5.5	55	5.4e-06	
1567	923	6.5	41	3.6e-06	
1567	941	7	40	3.0e-06	3.7e-05

Table 3.13. Effect of surfactant on the removal of TCE with shell-side feed
 Concentration of n-dodecane= 1140 ppm, SDS concentration= 1%,
 flow rate= 2.5 mL/min, pressure= 4/1 psi, water collected=0.5 mL,
 n-dodecane collected =8-9 drops.

C_{in}	C_{out}	Time (hours)	%Removal	TCE flux mol/hr.cm ²	Water flux mol/hr.cm ²
1624	773	2	52	5.6e-06	
1624	654	3	60	6.2e-06	
1624	690	4	58	5.7e-06	
1624	730	4.5	55	5.0e-06	
1624	884	5.5	46	4.2e-06	
1624	983	6	39	4.0e-06	
1624	1088	7	33	3.3e-06	2.14e-05

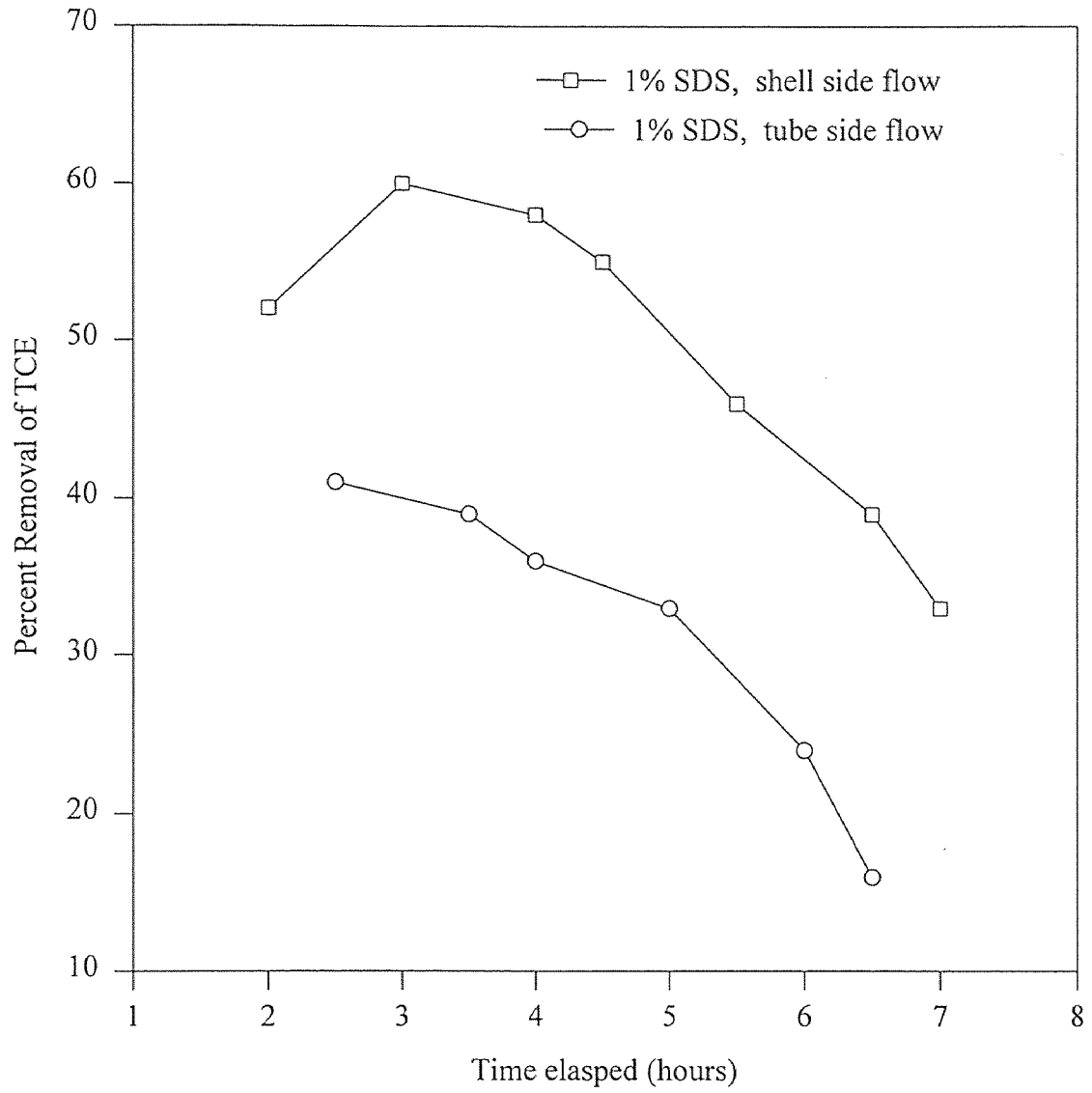


Figure 3.19. Effect of feed flow side on the removal of TCE

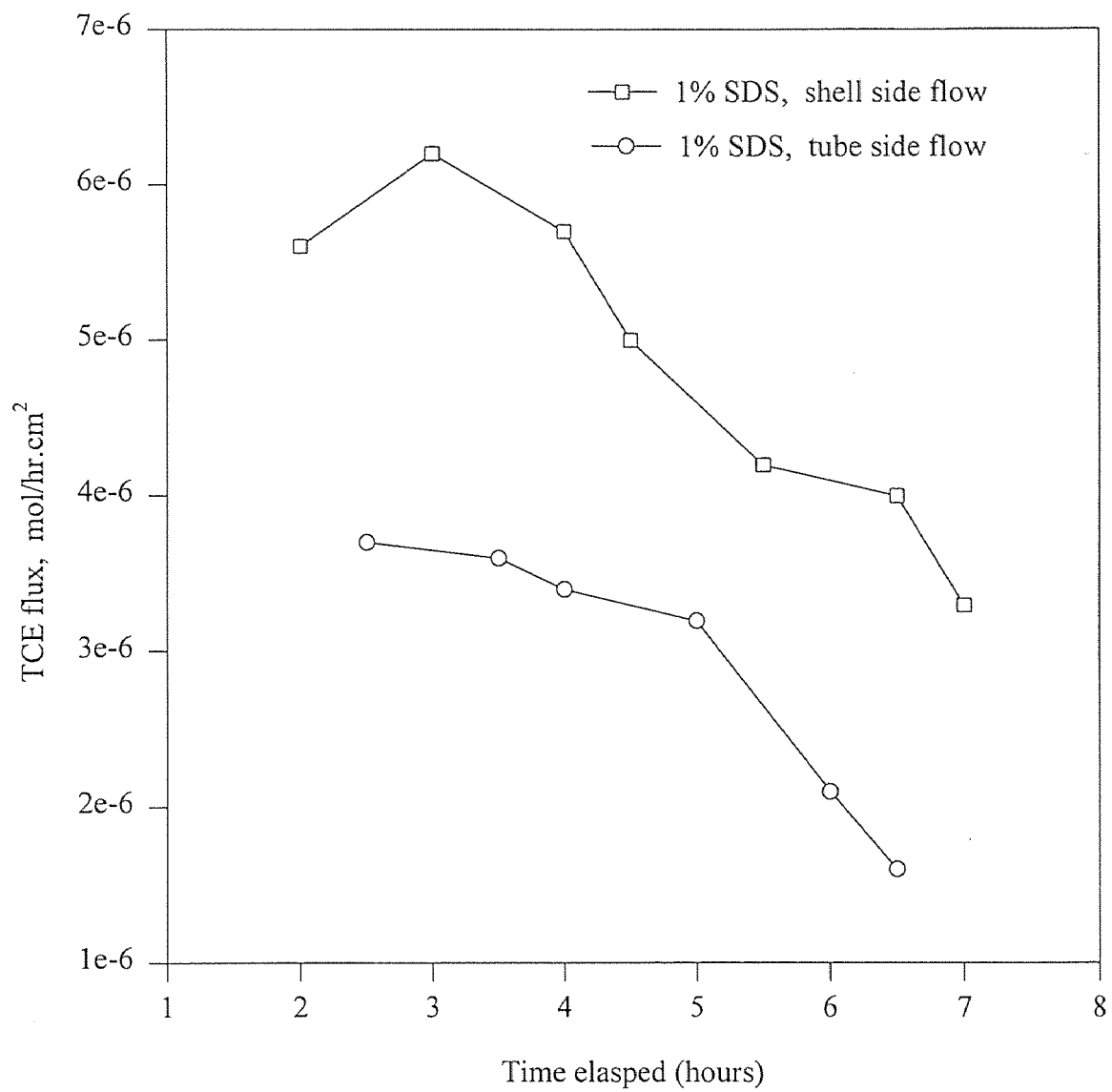


Figure 3.20. Effect of feed flow side on the flux of TCE

observed that for the feed flowing from the shell side the drop in removal of TCE was less as compared to the feed flowing from the tube side. Also the % removal at any point of time was better in the case of shell side. In the case of shell side the flux of TCE dropped from 5.6×10^{-6} mol/hr.cm² to 3.3×10^{-6} mol/hr.cm² whereas the flux of TCE dropped from 3.7×10^{-6} mol/hr.cm² to 1.6×10^{-6} mol/hr.cm² in the case of tube side. The water flux dropped from 2.8×10^{-5} mol/hr.cm² to 2.14×10^{-5} mol/hr.cm² when the feed flow was changed from tube to shell.

Permeation of n-dodecane from the shell-side into the substrate pores and the tube-side is expected to create considerable resistance to the pervaporation process; the collected oil will create difficulties in maintaining the vacuum. In these experiments discussed above, the amount of n-dodecane permeated was quite limited (8-9 drops). Therefore an extended term experiment spanning 1-2 days is needed to find out the long-term behavior of such a system when there is shell-side feed.

CHAPTER 4

CONCLUSIONS

The following conclusions can be drawn from the study of removal and recovery of n-dodecane from an oil-in-water emulsion by permeation experiments and removal and recovery of TCE and n-dodecane from recovered water obtained from surfactant-enhanced subsurface remediation by combined permeation experiments.

- 1) It was observed that n-dodecane can be efficiently removed from an oil-in-water emulsion by using membrane module having hydrophobic hollow fibers with a plasma-polymerized silicone skin on the outer surface.
- 2) It was observed that by increasing the flow rate, both removal and flux of n-dodecane increased during the initial period and thereafter remained constant.
- 3) The oil flux increased significantly when the initial concentration was increased but the overall removal remained constant with an increase in concentration.
- 4) The oil flux of n-dodecane changed significantly when the feed was pumped from either the tube side or shell side. In the case of tube side, the feed side effect was more pronounced during the initial period, wherein the n-dodecane concentration dropped rapidly. A higher flux and overall removal was observed when the feed was pumped from the tube side. This effect was not clear at very low concentrations of n-dodecane.
- 5) At lower concentration range of SDS, an increase in concentration of SDS decreased the oil flux significantly and at higher concentration range of SDS the oil flux did not change drastically when the SDS concentration was increased.

- 6) The oil permeation process was facilitated by higher concentration of n-dodecane and operation at higher flow rates.
- 7) The surfactant flushed groundwater contains both volatile and non-volatile components. Although research was conducted in an exploratory manner for the combined permeation of TCE and n-dodecane, the combined permeation employed for separating the VOC and oil from groundwater was found out to be an efficient technique.
- 8) With an increase in concentration of oil, the TCE removal decreased with time. But with higher TCE concentrations, the rate of decrease in TCE removal was lower. The water flux was reduced by an order of magnitude due to the presence of oil.
- 9) It was observed that when the combined feed was flowing through the shell side the performance of TCE removal was better as compared to tube side. However, these experiments were of limited duration. Only extended-term experiments can provide the correct answer.
- 10) The combined permeation technique was an efficient way of separating both the low boiling components and the high boiling components.

APPENDIX A

THEORY

A.1 Theory of Surfactants

A.1.1 Chemical and Physical Properties of Surfactants

A surfactant or a surface active agent can be defined as a substance which when present in small quantities in a system, has a property of adsorbing onto the surface or interfaces of the system due to which a significant change occurs in the surface or interfacial free energies of those surfaces or interfaces. The term interface here indicates a boundary between two immiscible phases; the term surface indicates an interface where one phase is a gas, usually air.

The interfacial free energy is the minimum amount of work required to create that interface. Surfactants can be expected to play a major role in the system when the phase boundary area is so large relative to the volume of the emulsion system (oil-in-water) that a substantial fraction of the total mass of the system is present at the boundaries.

Surface active agents have a characteristic amphipathic structure. This is due to fact that a surfactant has two groups namely the lyophobic and the lyophilic. The lyophobic group has a lower affinity towards the solvent whereas the lyophilic group has a strong attraction towards the solvent. The lyophobic group creates a distortion of the solvent liquid structure, increasing the free energy of the system. As a result less work is required for bringing the surfactant molecule to the surface than the water molecule, which leads to the increased concentration of the surfactant at the surface. The presence of lyophilic group prevents the surfactant from being completely expelled from the solvent

as a separate phase. The amphipathic structure of the surfactant therefore causes not only concentration of surfactant at the surface and reduction of surface tension of water, but also orients the molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it.

A.1.2 Surfactant Classification

The hydrophilic group of the surfactant is an ionic or a highly polar group. The classification of the surfactant is based on the nature of the hydrophilic group.

a) Anionic - The surface-active portion of the molecule bears a negative charge,

e.g. $C_{12}H_{25}O_4SNa$, (Sodium Dodecyl Sulfate).

b) Cationic - The surface-active agent bears a positive charge, e.g. $RN(CH_3)_3^+Cl^-$

(quaternary ammonium chloride).

c) Zwitterionic - The surface-active portion may carry both a positive as well as

negative charge, e.g. $R^+NH_2 CH_2 COO^-$ (Long chain amino acid).

d) Nonionic - The surface-active agent bears no ionic charge, e.g. $RC_6H_4(OC_2H_4)_xOH$

(polyoxyethylenated alkyl phenol).

A.1.3 Micelle Formation by Surfactants

The property of the surface-active solutes to form colloidal-sized clusters in solution at higher concentration is known as micellization.

A micelle can also be defined as a stable colloidal particle having a self-organizing structure in which the polar groups are exposed to water, while the hydrophobic groups

are in contact. This minimizes the interfacial energy and leaves the maximum number of water molecules in mutual contact. Micellization plays an important role in number of interfacial phenomena such as detergency and solubilization which depends on the existence of micelles. The distortion of the solvent structure can also be decreased by aggregation of the surface-active molecules into clusters (micelles) with their hydrophobic groups directed towards the interior of the cluster and the hydrophilic groups directed towards the solvent. The free energy of the system is reduced as a result of which micellization can be looked upon as an alternative mechanism to adsorption at the interfaces as the hydrophobic groups are separated from water.

The shape of the micelle produced in aqueous media is of importance in determining various properties of the surfactant solution, such as its viscosity, its capacity to solubilize water-insoluble material. The various types of micelle structure may range from small spherical to elongated cylindrical, rod-like micelles to large, flat lamellar micelles and vesicles. The interior region of the micelle, containing the hydrophobic groups, is of radius approximately equal to the length of the extended hydrophobic chain.

A.1.4 Thermodynamic Parameters of Micellization

The determination of the thermodynamic parameters of micellization ΔG°_{mic} , ΔH°_{mic} , ΔS°_{mic} has played an important role in developing a clear understanding of the process of micellization which helps to provide a rationale explanation of the effects of structural and environmental factors on the value of CMC. A standard free energy of micellization ΔG°_{mic} may be calculated by choosing for the standard initial state of the nonmicellar

surfactant species a hypothetical state at unit mole fraction x but with the individual ions or molecules behaving as at infinite dilution, and for the standard final state, the micelle itself.

The negative values of $\Delta G^\circ_{\text{mic}}$ are due mainly to the large positive values of $\Delta S^\circ_{\text{mic}}$. $\Delta H^\circ_{\text{mic}}$ is often positive and even if it is negative is much smaller than the value of $T\Delta G^\circ_{\text{mic}}$.

The process of forming micelles is primarily controlled by the entropy gain associated with it and the driving force for the process is the tendency of the lyophobic group of the surfactant to transfer from the solvent environment to the interior of the micelle. The entropy gain on micellization in aqueous medium is due to structuring of the water molecules around the hydrocarbon chains in aqueous medium which when removed from the aqueous medium to the interior of the micelle results in increase in entropy. Also, the hydrocarbon chain when enter the non-polar interior of micelle have more freedom than in the aqueous environment which helps in entropy gain. Any structural or environmental factors that may affect solvent-lyophobic group interactions or interactions between the lyophobic groups in the interior of micelle will therefore affect $\Delta G^\circ_{\text{mic}}$ and hence the value of CMC.

A.1.5 Wetting Phenomena by Surfactants

Wetting in a general sense is the displacement from a surface of one fluid by another. Wetting is a process involving surfaces and interfaces and the modification of the wetting power of water is a surface property shown to some degree by all surface-active agents.

The area required to be wetted determines the controlling factor. When the surface to be wetted the equilibrium conditions close to it can be attained during the wetting process and the free energy changes involved in the process determine the degree of wetting attained.

Water has a high surface tension, 72 dyne/cm; hence it does not spread over covalent solids that have surface free energies of less than 72 erg/cm². The addition of surface-active agent to water helps in modifying the interfacial tensions of the system. Therefore it is used to enable water wet a solid or liquid surface. The spreading coefficient $S_{w/s} = \gamma_{SA} - (\gamma_{sw} + \gamma_{WA})$ must be positive for the water to wet the surface spontaneously. The addition of surface-active agent to water reduces the surface tension of the water γ_{SA} and perhaps the interfacial tension between water and the substrate γ_{sw} which may cause the spreading coefficient to have a positive value and make spreading spontaneous.

But under certain conditions the addition of surface-active agent to water may make spreading more difficult.

When the substrate is porous and considering that it has a mass of capillaries, the pressure causing the movement of liquid into the capillaries because of the curvature of the liquid surface is given by.

$$\Delta P = (2 \gamma_{LA} \cos \theta) / r = 2(\gamma_{SA} - \gamma_{SL}) / r$$

where r is the equivalent radius of the capillaries and θ the contact angle at the air-liquid substrate interface.

A.2 Theory of Emulsions

Emulsification-the formation of emulsions from two immiscible liquid phases-is probably the most versatile property of surface active agents for practical applications and, as a result, has been extensively studied. Metal cutting oils, metal cleaners, and textile processing oils are all emulsions or are used in emulsified form.

A.2.1 Definition

An emulsion is a significantly stable suspension of particles of liquid of a certain size within a second, immiscible liquid. Emulsions are stable and intimate mixtures of oil or oily material with water.

A.2.2 Types of Emulsions

There are three different types of emulsions, based on size of the dispersed particles: (1) *macroemulsions*, the most well-known type, opaque emulsions with particles with >400 nm easily visible under a microscope; (2) *microemulsions*, transparent dispersions with particles <100 nm in size that have been intensely studied during the past decade or so because of their enhanced oil recovery; (3) *miniemulsions*, a recently suggested type that is blue-white, with particle sizes between the first two types (100-400 nm).

A.2.3 Theory

A proper theory of emulsions can be described by the following characteristics

1. Formation

2. Stability
3. Breaking and inversion
4. The role of emulsifying agents and other chemical factors such as pH and non-surface-active ions.
5. The influence of physical factors.

A.2.4 Formation

Two immiscible, pure liquids cannot form an emulsion. In the formation of emulsions, one of the two immiscible liquids is broken up into particles that are dispersed in the second liquid. Since the interfacial tension between two immiscible pure liquids is always greater than zero, this dispersion of the inner liquid, which produces a tremendous increase in the area of the interface between them, results in a correspondingly large increase in the interfacial free energy of the system. The emulsion produced is consequently highly unstable thermodynamically, relative to the two bulk separated by a minimum area interface. It is for this reason that two immiscible liquids, when pure, cannot form an emulsion. The formation of *O/W* emulsion can be explained on the basis of difference in contact angles at the oil-water-emulsifier boundary. If the water contact angle is less than 90° , then the water surface is concave toward the oil, producing an *O/W* emulsion. If the water contact angle is less than 90° , then $\gamma_{WE} < \gamma_{OE}$ and the emulsifying agent is more hydrophilic than hydrophobic. Thus, emulsifying agents with mainly hydrophilic character produce *O/W* emulsion.

Macroemulsions are of two types, based on the nature of the dispersed phase: oil-

in-water (*O/W*) and water-in-oil (*W/O*). The oil-in-water type is a dispersion of a water-immiscible liquid or solution, always called the “oil”(*O*), regardless of its nature, in an aqueous phase(*W*). The oil is, in this case, the “discontinuous” (inner) phase; the aqueous phase is the “continuous” (outer) phase. The type of emulsion formed by the water and the oil depends primarily on the nature of emulsifying agent and, to a minor extent, on the process used in preparing the emulsion and the relative proportions of the oil and water present. In general, *O/W* emulsions are produced by emulsifying agents that are more soluble in the water than in the oil phase.

A.2.5 Breaking and Inversion

O/W and *W/O* emulsions are not in thermodynamic equilibrium with each other; one type is usually inherently more stable than the other for a particular emulsifying agent at a given concentration under a given set of conditions. However, the one type can be converted to the other by changing conditions. This is called inversion of the emulsion.

A.2.6 Effect of Surface-Active Agent

For a suspension of one liquid in another to be stable enough to be classified as an emulsion, a third component must be present to stabilize the system. The third component is called the emulsifying agent and it is usually a surface-active agent. Thus, emulsifying agents with mainly hydrophilic character produce *O/W* emulsion. The emulsifying agent provides the stability by adsorption at the liquid-liquid interface as an oriented interfacial film. This oriented film reduces the interfacial tension between the two liquids and

consequently the thermodynamic instability of the system resulting from the increase in the interfacial area between the two phases. Also it decreases the rate of coalescence of the dispersed liquid particles by forming mechanical, steric, and/or electrical barriers around them.

A.2.7 Stability

The term *stability*, when applied to emulsions used for practical applications, usually refers to the resistance of emulsions to the coalescence of their dispersed droplets.

APPENDIX B

CALCULATION OF THE FLUX OF N-DODECANE

The experimental data from different experiments in oil permeation showed a decline in concentration C of the reservoir with time (t). The plot (e.g 3.1) of the concentration versus time curve shows somewhat of a first-order decline model. The data were fitted to a first order expression and a lumped parameter for the model was determined.

The lumped parameter (K) was used for the purpose of calculating the flux (J). The lumped parameter may be assumed to be a function of the process conditions (temperature, viscosity, pressure differential etc.).

The mass of n-dodecane permeating per unit time (R) is given by the expression below.

$$R = - \frac{(C_t - C_{t+\Delta t}) V}{(\Delta t)} \quad (\text{B.1})$$

where,

C_t = Concentration of the reservoir at ant time t , mg/L

$C_{t+\Delta t}$ = Concentration of the reservoir at any time $t. +\Delta t$, mg/L

V = Volume of feed reservoir, Liters

t = time interval, hours

R = Mass of n-dodecane permeating per unit time, mg/hr

As $\Delta t \rightarrow 0$ the above expression can be written as

$$R = -V * \frac{dC}{dt} \quad (\text{B.2})$$

The flux (J) can be calculated by dividing the above expression by the area of the hollow fiber module and is given by

$$J = -\frac{V}{A_M} * \frac{dC}{dt} \quad (\text{B.3})$$

It is seen that the concentration $C(t)$ profile follows a first order behavior and therefore one may write

$$C(t) = C_o e^{-Kt} \quad (\text{B.4})$$

where K is the lumped model parameter.

To determine K the experimental data were fitted to the above equation using non-linear regression.

Differentiating equation B.4 w.r.t time gives us

$$\frac{dC(t)}{dt} = -K * C_o * e^{-Kt} \quad (\text{B.5})$$

Substitute equation (B.5) into equation (B.3)

$$J = \frac{V}{A_M} * C_o * K * e^{-Kt} \quad (\text{B.6})$$

K and C_0 are known for a given set of experiments and V and A being constant parameters the flux (J) can be calculated for any time t .

Sample calculation

J (mol/hr.cm²) is calculated using equation (2.5)

J can also be calculated in the following manner as follows

In Table 3.5, $C_0 = 9889$ ppm, $K=0.1538$.

$V = 2$ liters, $A_M = 185.5$ cm², $M_{n\text{-dodecane}} = 170$ gm/gmol

Substituting the values in equation (B.3) we get the flux in terms of time:

$$J = 9.6456 * 10^{-5} * e^{0.1538 * t}$$

Where J can be expressed in terms of mol/cm².hr.

The following tables tabulates the values of K and the corresponding experimental condition the value of K came out to be 0.1538.

C_0 ppm	Flow rate mL/min	Pressure (psi)	K	Standard error
9889	21	23/10	0.1538	0.01
5864	41	24/20	0.0735	0.006
1563	22	24/15	0.1998	0.1998

Three experiments were taken to fit the data to the first order model. The results are shown in the Figures B.1 to B.6 and Tables from B.1 and B.6.

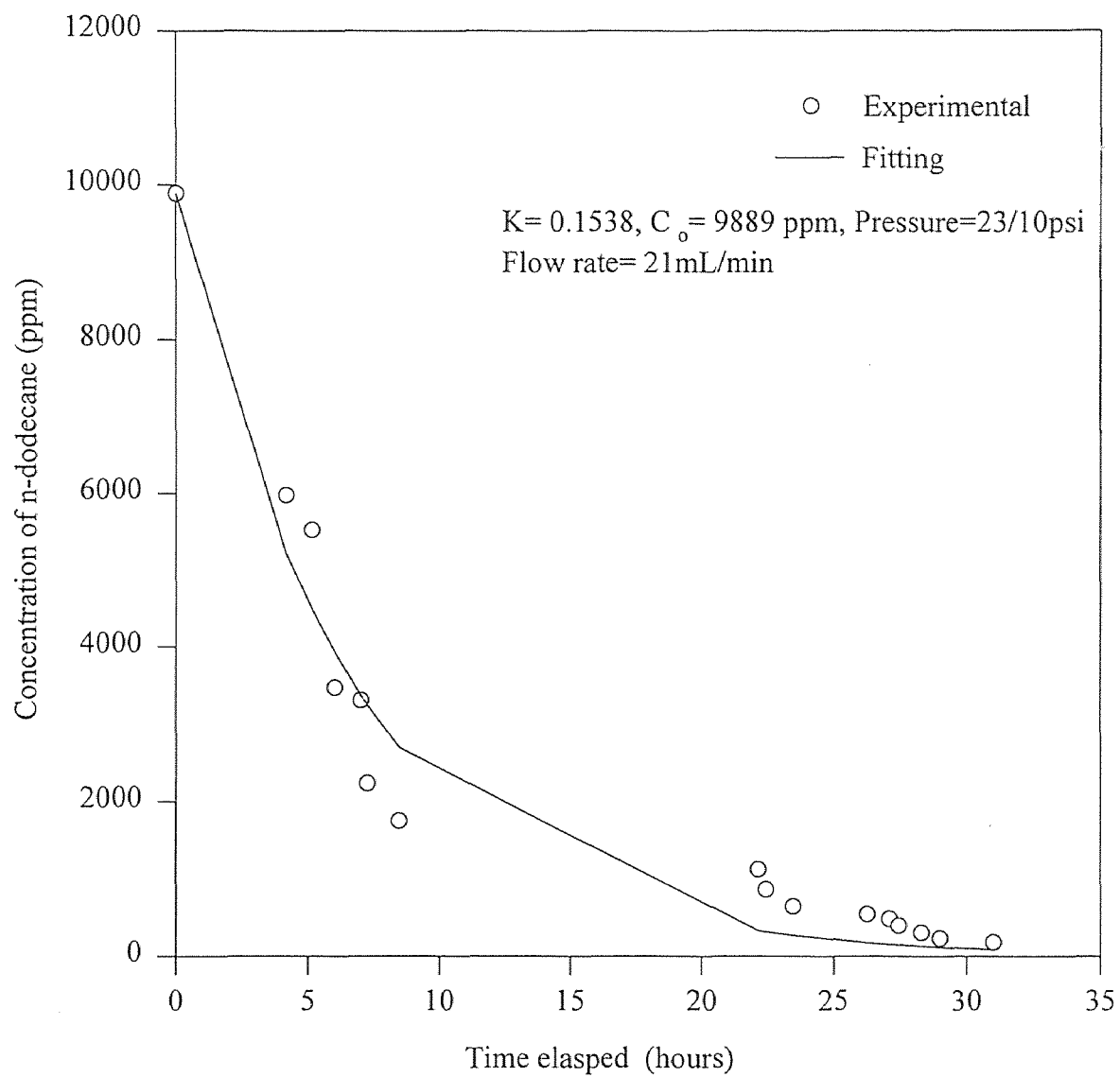


Figure B.1. Fitted concentration profile versus experimental concentration data

Table B.1. Experimental results for $C_0=9889$ ppm, $\Delta P= 13$ psi,
flow rate=21mL/min

Time elapsed (hours)	Concentration of n-dodecane, ppm
0	9889
4.15	5972
5.15	5519
6	3471
7	3306
7.25	2232
8.45	1753
22.15	1121
22.45	863
23.45	642
26.25	541
27.1	483
27.45	392
28.3	302
29	231
31	175

The value of K predicted from the non-linear regression was found out to be 0.1538.

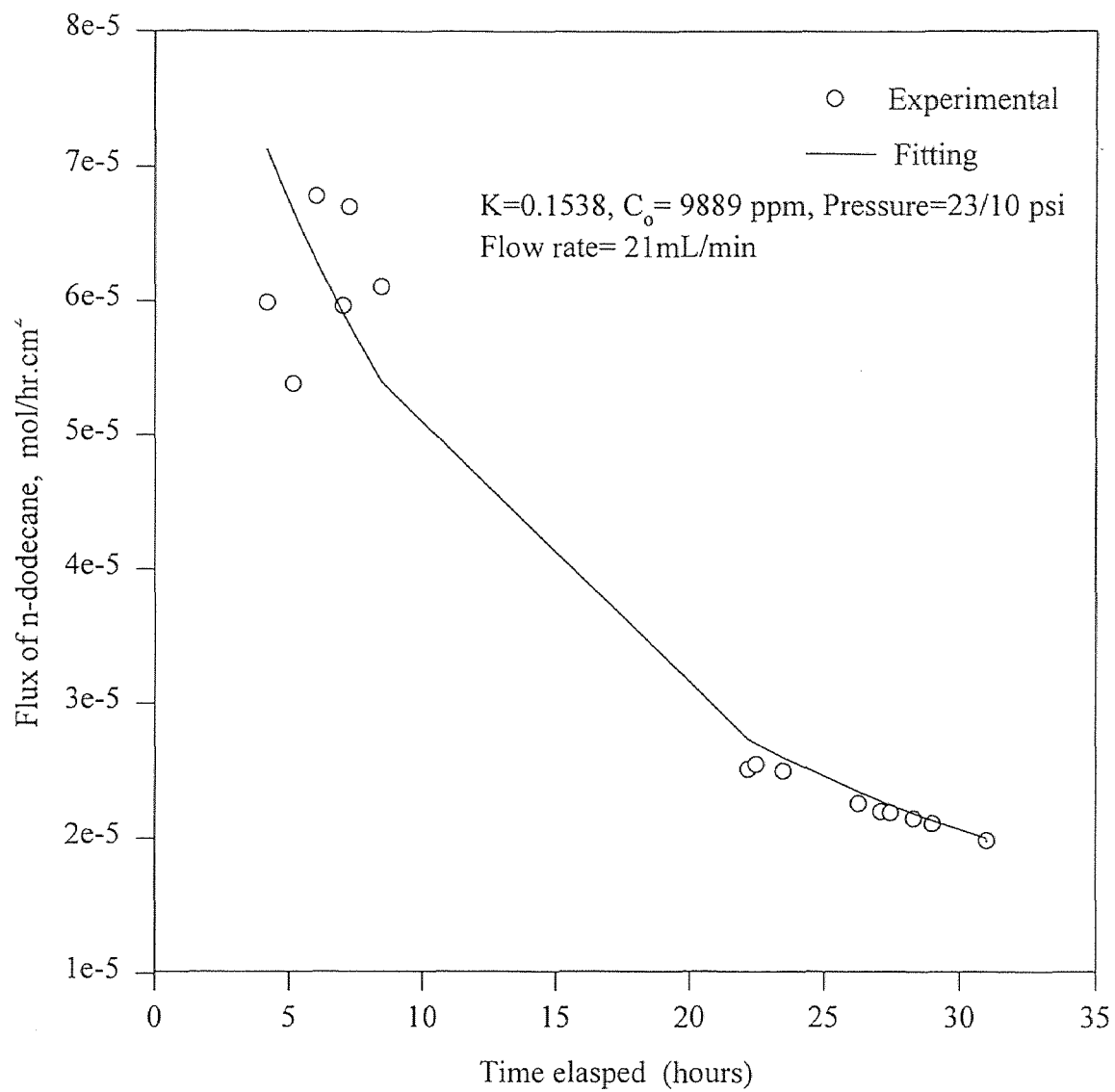


Figure B.2. Fitted flux profile versus experimental flux data

Table B.2. Experimental results for $C_o=9889$ ppm, $\Delta P= 13$ psi,
flow rate=21mL/min

Time elapsed (hours)	Flux of n-dodecane ($1*10^5$), mol/cm ² .hr
4.15	5.986
5.15	5.381
6.0	6.784
7.0	5.964
7.25	6.697
8.45	6.107
22.15	2.510
22.45	2.550
23.45	2.501
26.25	2.258
27.1	2.201
27.45	2.194
28.3	2.148
29.0	2.112
31.0	1.987

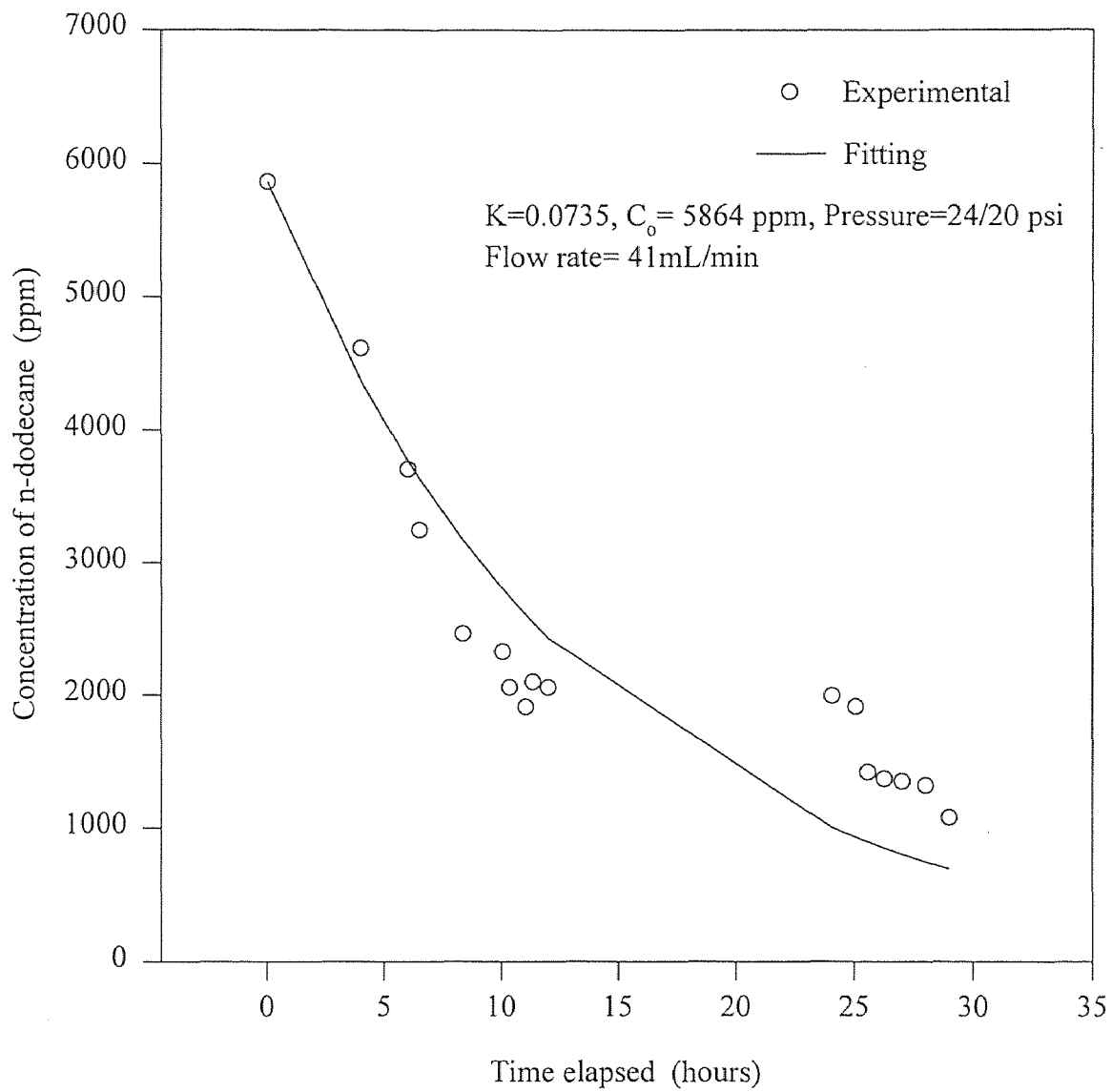


Figure B.3. Fitted concentration profile versus experimental concentration data

Table B.3. Experimental results for $C_0=5864$ ppm, $\Delta P= 4$ psi,
flow rate= 41mL/min

Time elapsed (hours)	Concentration of n-dodecane, ppm
0.00	5864
4	4617
6	3707
6.5	3249
8.35	2463
10.05	2325
10.35	2056
11.05	1909
11.35	2098
12	2056
24.05	1994
25.05	1909
25.55	1419
26.25	1371
27	1353
28	1321
29	1080

The value of K predicted from the non-linear regression was found out to be 0.0735.

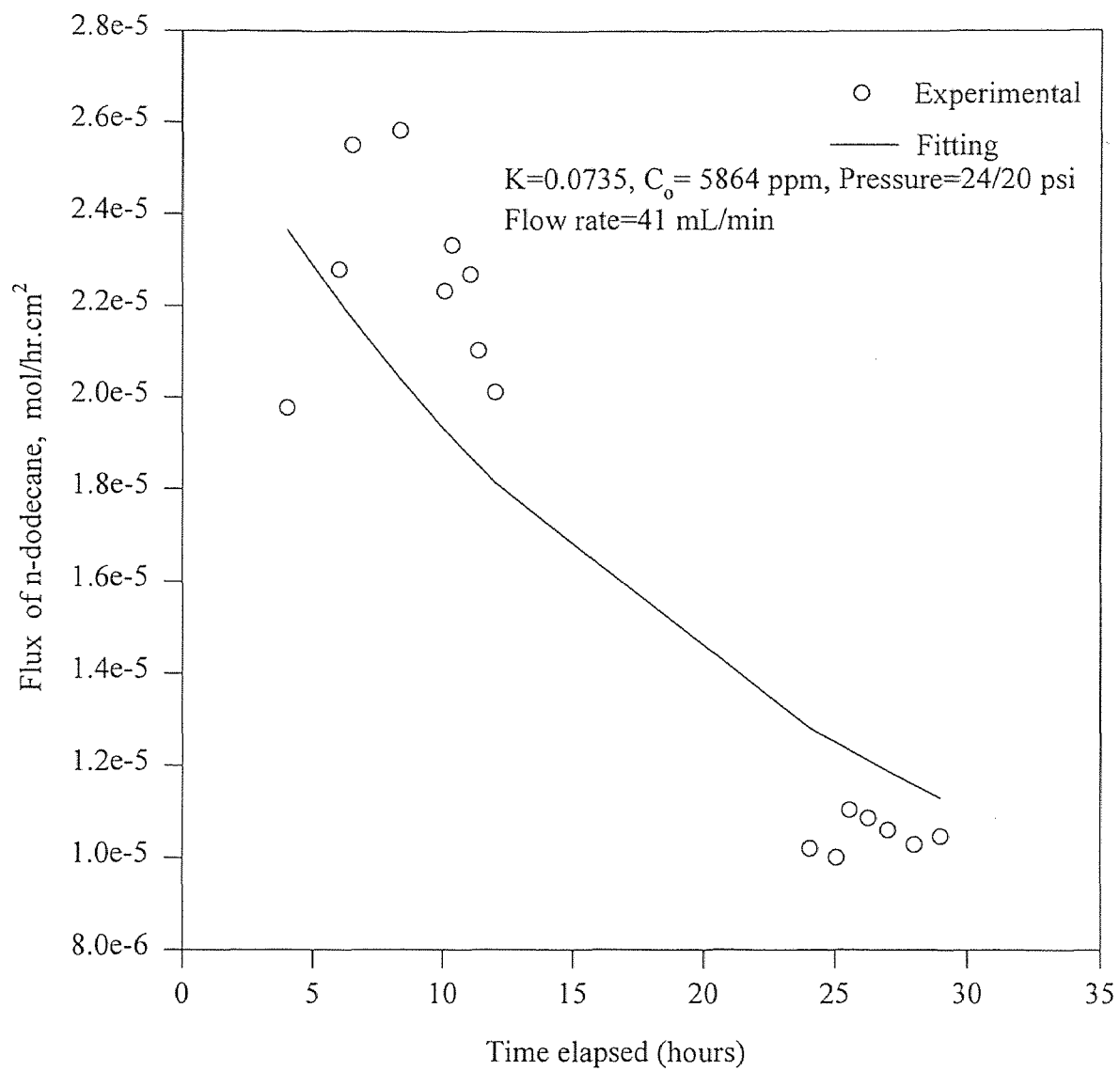


Figure B.4. Fitted flux profile versus experimental flux data

Table B.4. Experimental results for $C_o=5864$ ppm, $\Delta P= 4$ psi,
flow rate = 41mL/min

Time elapsed (hours)	Flux of n-dodecane ($1*10^5$), mol/cm ² .hr
4	1.977
6	2.279
6.5	2.552
8.35	2.583
10.05	2.233
10.35	2.334
11.05	2.270
11.35	2.104
12.0	2.013
24.05	1.021
25.05	1.001
25.55	1.103
26.25	1.086
27.0	1.060
28.0	1.029
29.0	1.046

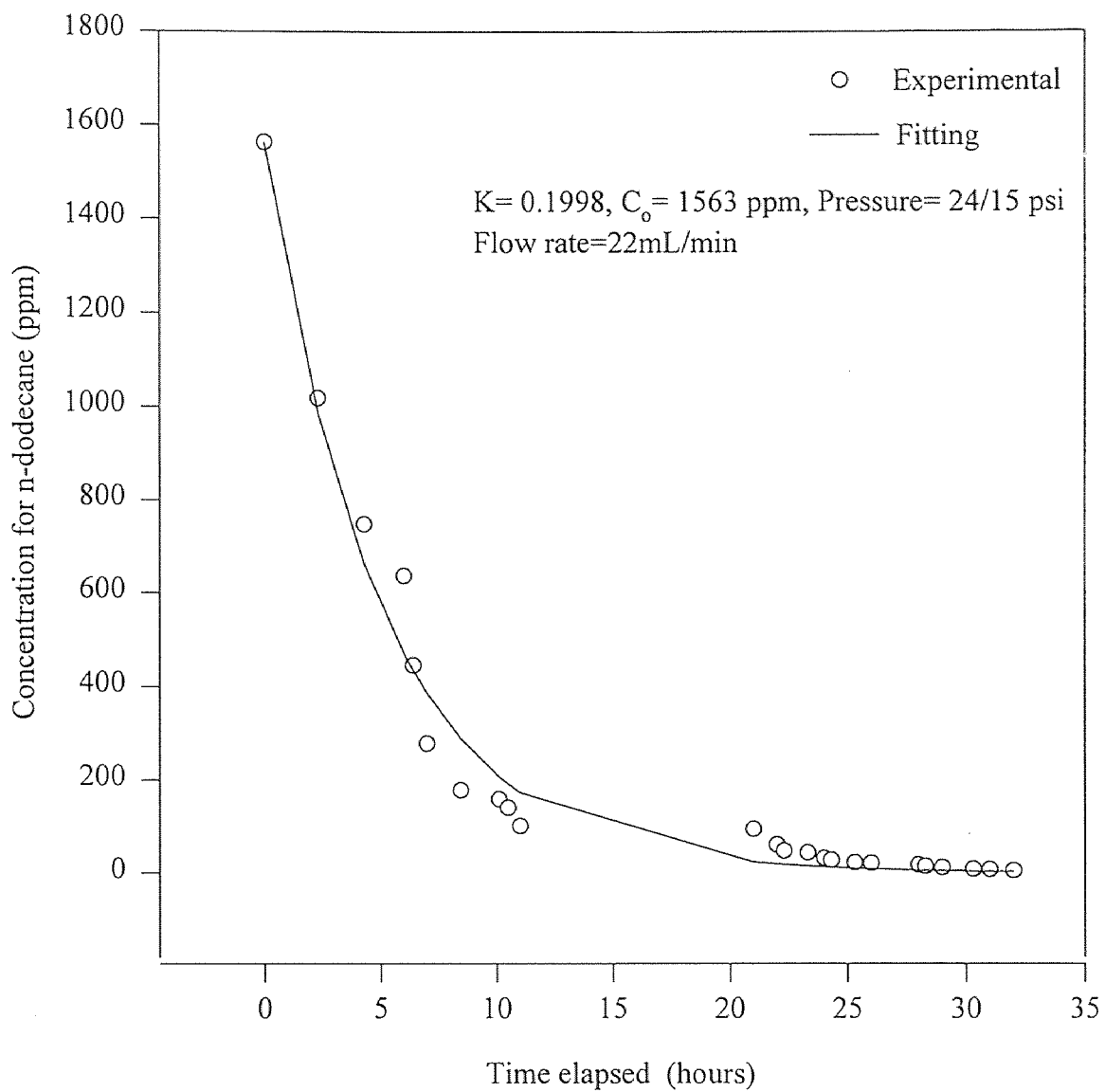


Figure B.5. Fitted concentration profile versus experimental concentration data

Table B.5. Experimental results for $C_0=1563$ ppm, $\Delta P=9$ psi,
flow rate=22 mL/min

Time elapsed (hours)	Concentration of n-dodecane, ppm
0	1563
2.3	1018
4.3	748
6	637
6.4	445
7	278
8.45	178
10.1	159
10.5	140
11	101
21	94
22	60
22.3	47
23.3	43
24	32
24.3	28
25.3	22
26	21
28	18
28.3	15
29	11
30.3	9
31	7
32	5

The value of K predicted from the non-linear regression was found out to be 0.1998

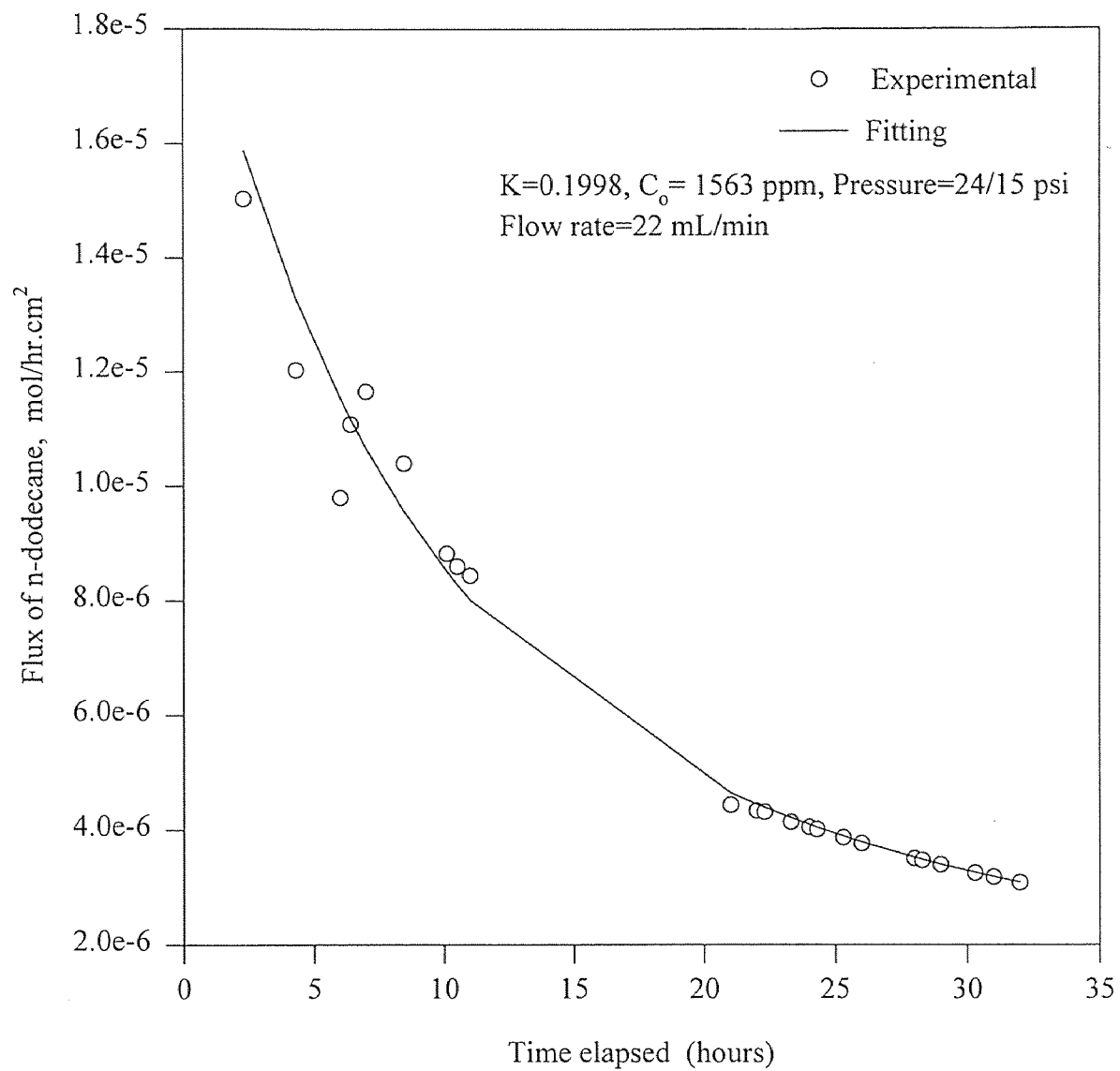


Figure B.6. Fitted flux profile versus experimental flux data

Table B.6. Experimental results for $C_0=1563$ ppm, $\Delta P=9$ psi, flow rate=22 mL/min

Time elapsed (hours)	Flux of n-dodecane ($1 \cdot 10^5$), mol/cm ² .hr
2.3	1.503
4.3	1.202
6.0	0.979
6.4	1.108
7.0	1.165
8.45	1.040
10.1	0.882
10.5	0.860
11.0	0.843
21.0	0.444
22.0	0.433
22.3	0.431
23.3	0.414
24.0	0.405
24.3	0.401
25.3	0.386
26.0	0.376
28.0	0.350
28.3	0.347
29.0	0.339
30.3	0.325
31.0	0.318
32.0	0.309

APPENDIX C

ADDITIONAL SAMPLE CALCULATIONS

C.1 Calculation of TCE flux

TCE flux, J_{TCE} , is proportional to the solute concentration difference ΔC , the feed flow rate v , and the mass-transfer area A_M . The three parameters can be related to the flux by the following expression as

$$J_{TCE} \left(\frac{\text{mol}}{\text{hr.cm}^2} \right) = v \left(\frac{\text{mL}}{\text{min}} \right) * \left(\frac{60 \text{ min}}{\text{hr}} \right) * \Delta C \left(\frac{\text{gm}}{10^6 \text{ cm}^3} \right) * \frac{1}{M_{TCE}} \left(\frac{\text{mol}}{\text{gm}} \right) * \frac{1}{A_M} \left(\frac{1}{\text{cm}^2} \right)$$

$$J_{TCE} = P * v * \frac{\Delta C}{A_M} \quad (\text{C.1})$$

where,

J_{TCE} = TCE flux (mol/hr.cm²),

ΔC = Concentration difference between the feed and retentate (mg/L),

A_M = Mass transfer area (cm²),

v = Feed flow rate (mL/min),

M_{TCE} = Molecular weight of TCE, (gm/mol), and

P = Adjustable constant.

The mass transfer area was calculated as

$$A_M = \pi * N * D_i * L \quad (C.2)$$

C.2 Calculation of Water Flux

The water flux J_{WATER} , was calculated by measuring the volume of water collected in the condenser in the permeate side. The water flux can be calculated as

$$J_{WATER} = \frac{V_w}{M_w * A_M * t_{total}} \quad (C.3)$$

where,

V_w = Volume of water collected in the permeate (mL),

M_w = Molecular weight of water (gm/mol),

A_M = Mass transfer area of the membrane module (cm²),

t_{total} = Duration of experiment (hr).

C.3 Sample calculation

Taking the experimental data from Table 3.9 and substituting in (C.1):

$C_{in} = 903$ ppm, $C_{out} = 84$ ppm, $v = 2.5$ mL/min, $t = 390$ mins, $P = 4.57 * 10^{-7}$,

water collected = 0.8mL, $A_M = 185.5$ cm², $M_{TCE} = 131.4$ gm/gmol.

$$J_{TCE} = \frac{2.5 * (903 - 84) * 60}{(131.4 * 185.5 * 10^6)} \quad (C.4)$$

$$J_{TCE} = 5.04 * 10^{-6}, \frac{mol}{(hr.cm^2)}$$

The water flux can be calculated using the equation (C.3)

$$J_{WATER} = \frac{0.8 * 60}{390 * 185.5 * 18} \quad (C.5)$$

$$J_{WATER} = 3.42 * 10^{-5}, \frac{mol}{hr.cm^2}$$

C.4 Calculation of n-dodecane flux

The average flux of n-dodecane over the total duration of experiment (t) can be calculated using equation (C.6).

$$J = \frac{V}{A_M} * \frac{(C_o - C_{final})}{t * M_{n-dodecane}} \quad (C.6)$$

Taking the experimental data from Table 3.4 and substituting in (C.6), V= 2L,

C_o=5864 ppm, C_{final} = 1080 ppm, v=41 mL/min, t=29 hours, M_{n-dodecane}=170 gm/gmol,

$$J_{n-dodecane} = \frac{2}{185.5} * \frac{(5864 - 1080) * 10^{-3}}{29 * 170} \quad (C.7)$$

$$J_{n-dodecane} = 10.4 * 10^{-6}, \frac{mol}{hr.cm^2}$$

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