ABSTRACT

MASS TRANSFER OF PYRENE BETWEEN A SOLID PHASE AND OIL/WATER SUSPENSIONS

by
Sachin Ashok Purekar

This study dealt with understanding the partitioning of pyrene between water and mineral oil, and the mass transfer of pyrene from solid particles to oil/water suspensions.

It was found that when pyrene is dissolved in mineral oil, the amount transferred to water is negligible even after 10 days of phase contact.

Glass beads and sand were used as model solid phases to simulate soil and PAH (pyrene)-contaminated industrial sludges.

The transfer of pyrene from glass beads to mineral oil when no water phase is present was quantified. Mass transfer coefficients, and their dependence on the rate of environment shaking were determined and show that the transfer of pyrene is fast.

Experiments with oil/water suspensions showed that pyrene transfer depends on the amount of oil, the degree of dispersion of oil in the water phase, the speed of mixing, and the type of solids on which pyrene is attached/adsorbed. It was found that mixing leads to detachment of pyrene from glass beads and sand surfaces, something which did not allow for determination of the mass transfer coefficient per se. It was found however, that mass transfer rates are slow (especially with sand) which suggests that biological treatment of PAH-contaminated soil and industrial sludges in slurry reactors must be mass-transfer limited.

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by
Sachin Ashok Purekar

A Thesis
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Master of Science in Chemical Engineering

Department of Chemical Engineering,
Chemistry, and Environmental Science

May 1996

APPROVAL PAGE

MASS TRANSFER OF PYRENE BETWEEN A SOLID PHASE AND OIL/WATER SUSPENSIONS

Sachin Ashok Purekar

Dr. Basil C. Baltzis, Thesis Advisor — Date
Professor of Chemical Engineering
New Jersey Institute of Technology

Dr. Piero Armenante, Committee Member — Date
Professor of Chemical Engineering
New Jersey Institute of Technology

Dr. Dana Knox, Committee Member — Date
Associate Professor of Chemical Engineering
New Jersey Institute of Technology

BIOGRAPHICAL SKETCH

Author: Sachin Ashok Purekar

Degree: Master of Science

Date: May 1996

Date of Birth:

Place of Birth:

Undergraduate and Graduate Education:

- Master of Science in Chemical Engineering,
  New Jersey Institute of Technology, Newark, NJ, 1996

- Bachelor of Chemical Engineering (B.Chem),
  University of Bombay, Department of Chemical Technology (UDCT),
  Bombay, India, 1994

Major: Chemical Engineering

Publications:

Purekar, Sachin Ashok, Shailendra Bordawekar, and Manav Lahoti. 1992
"The Use of Biofiltration to Decontaminate Gases." *Bombay Technologist* **44** : 88-89.

ACKNOWLEDGMENT

The author would genuinely like to thank his advisor, Professor Basil Baltzis, for his guidance, patience, friendship and moral support throughout this research. Special thanks to Professors Piero Armenante and Dana Knox for serving as members of the committee. The author also acknowledges the useful suggestions of Professor Richard Bartha and his doctoral student, Ilya Jimenez of Rutgers University, New Brunswick.

The author is thankful to the Hazardous Substance Management Research Center (HSMRC) for the initial funding of this project.

The author is also grateful to Mr. Clinton Brockway for his expert assistance and cooperation; and to Ms. Gwendolyn San Augustin who in spite of her illness took extensive interest in the project and also helped in the analytical methodology.

The author appreciates the valuable help, suggestions, and encouragement from his friends including : Dr. K.W. Wang, C. Mpanias, D. Mandal, D.de la Cruz, S. Ioannidis, A. Mora, J. Yi, M. Cohen, P. Stamatiades, S.M. Wojdyla, A. Saraf, M. Kothavale, and T. Deshpande.

The author wishes to express his sincere gratitude to his parents and brother for their incessant encouragement and determination. Finally, the author is extremely grateful to his uncle and his family who were a constant source of inspiration and motivation, and without their support this work would never have been accomplished.

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NOMENCLATURE

C : concentration of pyrene in mineral oil (mg/L)

C^* : saturation concentration of pyrene in mineral oil (mg/L)

f : speed of flask shaking (rpm)

k_L : overall mass transfer coefficient (min^{-1})

k_{Lo} : value of k_L when the flask is not shaken (min^{-1})

t : duration of a run (min, h)

Greek Symbols

α : proportionality constant in equation (5.4)

CHAPTER 1

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants and constitute a class of hazardous organic chemicals consisting of three or more fused benzene rings in linear, angular and cluster arrangements. PAHs mostly occur as a result of fossil fuel combustion and as by-products of industrial processing. They enter the environment from a multiplicity of sources which include : direct aerial fallout, chronic leakage of industrial or sewage effluents, accidental discharges during the transport, use and disposal of petroleum products, or from natural sources such as oil seeps. More specifically, industrial effluents from coal gasification and liquefaction processes, waste incineration, coke, carbon black, and other petroleum-derived products release high quantities of PAHs into the environment (Cerniglia 1993). PAHs are on the United States Environmental Protection Agency's (EPA) priority pollutant list since some are known carcinogens and mutagens (Cerniglia 1993; Keith & Telliard 1979).

PAHs are hydrophobic compounds and their persistence within ecosystems is chiefly due to their low water solubility. The lipophilicity, environmental persistence and genotoxicity increase as the molecular size of PAHs increases with the number of fused benzene rings. As the PAH size increases, toxicological concern shifts towards chronic toxicity, primarily carcinogenesis (Jacob et al. 1986). The possible fates of

PAHs in the environment include photooxidation, chemical oxidation, bioaccumulation, adsorption to soil particles, leaching and microbial degradation.

The Resource Conservation and Recovery Act (RCRA) of 1990 requires that listed hazardous wastes such as PAHs be pretreated prior to land disposal using a technology that meets or exceeds treatment standards established by a best demonstrated available technology (BDAT). Biodegradation tends to be a rather economical method of waste treatment when compared to the other available methods of treatment. Microbial degradation of PAHs with up to 3 rings is well documented and reviewed (Cerniglia 1984), while reports on pathways of bacterial degradation of PAHs with more than 3 rings are relatively rare (Heitkamp et al. 1988; Mahaffey et al. 1988; Weissenfels et al. 1992; Kelley et al. 1991; Walter et al. 1991). Higher PAHs such as pyrene were demonstrated to serve as growth substrates for some microorganisms (Boldrin et al. 1993) whereas in most cases they can be mineralized by cometabolism only. Of particular concern among the higher PAHs are the carcinogenic benzo(a)pyrene (BaP) and benz(a)-anthracene (Cerniglia 1993).

It is generally accepted that biodegradation of PAHs is limited by their bioavailability which is low due to extremely low water solubility and strong adsorption to soil components (Alexander 1973, 1975; Weissenfels et al. 1992). Water solubility of PAHs ranges from 1.29 mg/L (phenanthrene-3 rings) to 0.14 μg/L (coronene-7 rings) (Dzombak & Luthy 1984). Moreover, biodegradation of PAHs in soil typically approaches a limiting value, after which little change in PAH concentration is observed. This indicates that mass transfer limitations have to be overcome in order to develop efficient biological treatment processes for hydrophobic compounds such as PAHs.

The slowness of PAH biodegradation requires a very large reactor capacity, making the biodegradation option capital-intensive. Any rate increase in the biodegradation process would reduce the need for additional capacity and the related capital expenditure. The possibility of enhancing the rates of PAH biodegradation either through the use of physiological/biochemical approaches (addition of trace elements, growth factors, cosubstrates) or by mass transfer-enhancing factors (detergents, dispersants, solvents) has been investigated (Jimenez 1995).

The study of Jimenez used two approaches. One was to test additives such as trace elements, vitamins or cosubstrates that would enhance the growth and activity of PAH-degrading microorganisms. The other approach was directed at increasing the mass transfer of PAHs to the aqueous phase and/or to the degrading microorganisms, since several studies have shown that this transfer rate can limit the rate of the biodegradation process in case of hydrocarbons with low water solubility (Miller & Bartha 1989, Zhang & Bartha 1992). The study was based on the use of a pyrene-degrading *Mycobacterium* isolate, which was found to be capable of utilizing pyrene as its sole carbon and energy source.

A 0.8% (v/v) addition of mineral oil to the mineral medium containing pyrene as sole carbon and energy source for *Mycobacterium* sp., enhanced pyrene mineralization significantly when compared to control experiments (no oil addition) and experiments in which instead of oil, other substances were used as either cosubstrates or potential mass transfer enhancers. Jimenez (1995) explained the results of her study as follows. Mineral oil served as a solvent for pyrene, which has a solubility in water of only 0.14 mg/L (Cerniglia 1993). The pyrene containing mineral oil was emulsified during culture incubation with shaking and formed oil droplets with a wide variety of sizes. The pyrene degrading bacteria with their hydrophobic cell surface made direct contact with the mineral oil droplets and thus, the transfer of pyrene was facilitated, leading to the enhanced biodegradation rates.

The study reported in the present thesis was performed, at least in part, in parallel with the study of Jimenez (1995). The study of Jimenez focused on the determination of substances which could enhance degradation of PAHs and the mechanism of the enhancement. It utilized model systems in which pyrene was coated on the bottom of glass beakers in which the culture was placed. However, in real systems (e.g., refinery sludges) pyrene (and PAHs in general) are adsorbed on solid phases. Hence, it is important to determine the rate of mass transfer of PAHs between solid phases and water/oil suspensions, since oil was determined as an enhancer of the overall process. Determination of these mass transfer rates was the topic of the present thesis. The study was based on pyrene as the model PAH whereas glass beads and sand were used as model solids. During the experiments, the amount of mineral oil added was varied as was the agitation speed of the suspension. For comparison purposes, experiments were also performed in the absence of a solid phase and with the pyrene initially dissolved in mineral oil.

CHAPTER 2

LITERATURE REVIEW

Environmental scientists and engineers are most interested in understanding the fate of hazardous hydrophobic pollutants and optimizing the remediation of soil contaminated with these compounds. Biological treatment is a potential, cost effective, technology for efficient removal of such compounds. Hydrophobic compounds like polycyclic aromatic hydrocarbons (PAHs) may be sorbed to soils and sediments, or present in a separate phase (e.g., oil and coal tar).

2.1 Physical Properties of PAHs

The knowledge of physical properties of PAHs is extremely vital in the study of their biodegradation and mass transfer between different phases. Of these properties, the aqueous solubility is of prime significance. An understanding of solubility of PAHs in aqueous systems is important in designing water pollution control processes, modeling natural water systems, designing toxicity experiments, and developing analytical techniques for PAH monitoring (May et al. 1978). It has been suggested that the natural mechanism that modifies PAH homologue distribution on sediments, following initial distribution, is the differential water solubility of the various alkyl homologues (Hites et al. 1977).

For some PAHs, properties like ring size, molecular weight, aqueous solubility, and vapor pressure are listed in Table 2.1 (Huesemann et al. 1993). The partition coefficient ($\log K_{ow}$) between the organic (octanol) and water phases reflects the solubility in water. In fact, the higher the value of $\log K_{ow}$ is, the lower is the aqueous solubility. The $\log K_{ow}$ value for pyrene is 5.32 and its solubility in water is 0.14 mg/L. Although the vapor pressure of most PAHs is very low, volatilization (especially under intense aeration) may cause abiotic PAH losses. Hence air pollution control devices may be necessary in systems such as slurry reactors.

Table 2.1 Physical Properties of some representative PAHs

Compound Name	Number of Rings	Molecular Weight g/mole	Aqueous Solubility mg/L	Partition Coefficient $\log K_{ow}$	Vapor Pressure mm Hg
Naphthalene	2	128	30.0000	3.37	4.92×10^{-2}
Phenanthrene	3	178	1.2900	4.46	6.80×10^{-4}
Anthracene	3	178	0.0700	4.45	1.96×10^{-4}
Pyrene	**4**	**202**	**0.1400**	**5.32**	$\mathbf{6.85 \times 10^{-7}}$
Chrysene	4	228	0.0020	5.61	6.30×10^{-7}
Benzo(a)pyrene	5	252	0.0038	5.98	5.00×10^{-7}

2.2 Solubilization of PAHs

Hydrophobic organic compounds (such as PAHs) sorbed onto soil or other solid phases can be desorbed by the addition of surfactants (Liu et al. 1991). Solvents and surface active agents (surfactants) promote desorption by modifying the free energy of the surface and by increasing the aqueous solubility. Surfactant solubilization of PAHs involves a number of physicochemical processes, including partitioning of surfactant and the PAHs between soil and solution, micelle formation, and PAH partition between micelles and the aqueous pseudophase. Generally, surfactant solutions in the range of 1 to 4% have been suggested as promising for scrubbing fuel components, PCBs and other chlorinated hydrocarbons from soil. The solubilization of anthracene, phenanthrene and pyrene in soil water systems has been reported to occur at surfactant doses much greater than the clean water surfactant critical micellar concentration (CMC) (Liu et al. 1991). Use of surfactants in soil clean-up operations involves problems related to soil clogging, separation and treatment of surfactant solutions, and recovery of surfactants for reuse.

The use of cosolvents to enhance solubilization of sparingly soluble compounds has also been demonstrated and described in the pharmaceutical literature (Yalkowsky 1981). The applicability of cosolvent theory to sorption and solubilization of non-polar contaminants in soil has also been investigated (Rao et al. 1990; Fu & Luthy 1986).

2.3 Partitioning of PAHs

The partitioning of PAHs between diesel fuel/water and coal tar/water has been studied by Lee et al. (1992a & 1992b). These authors used the measured partition coefficients in evaluating a model derived using Raoult's law convention for activity coefficients and hypothetical supercooled liquid solubilities. The extent of deviations from "ideal" behavior was sufficiently small. The same authors also suggested that several site-specific hydrogeologic factors might lead to significant mass transfer constraints for solute partitioning between diesel fuel and water. However, larger concentrations might be found in groundwater in the presence of surfactants, emulsifiers, or cosolvents. The conclusion was that the concentrations of PAHs in groundwater in equilibrium with diesel fuel, as well as gasoline, estimated by assuming ideal behavior may be considered an upper limit (within a factor of 2) for most field-scale applications.

2.4 Biodegradation of PAHs

The persistence and bioavailability of PAHs in the environment depend on the physical and chemical characteristics of the PAH as well as the composition and chemical characteristics of the sediment (Wang et al. 1990; Sims et al. 1990). The recalcitrance of PAHs for microbial degradation increases directly with the molecular weight and the octanol/water partition coefficient (log K_{ow}) and inversely with water solubility since high molecular weight PAHs are more slowly desorbed and therefore less available for biological uptake (Aronstein et al. 1991). The PAH degradation is influenced by environmental factors, including temperature, pH, nutrients, oxygen and water availability, salinity and soil type (Atlas 1991). Although microbial metabolic pathways for degradation of PAHs containing up to three rings have been proposed (Gibson & Subramaniam 1984), there is little information concerning the ability of microorganisms to metabolize the larger, more recalcitrant, high molecular weight PAHs.

Some information regarding biodegradation of PAHs can be possibly inferred from studies on hydrocarbon fermentation for production of single-cell protein. To understand the hydrocarbon uptake process, systems involving microbial cultures and two liquid phases have been studied by Nakahara et al. (1977). These authors investigated the cell and hydrocarbon concentration distribution in batch systems and showed that some cells attach to the large oil drops whereas others are suspended in the water. The interfacial tension between oil and water and the Sauter mean drop size were found to decrease as cultivation proceeded. The oil drop size was found to be proportional to the 0.6 power of the interfacial tension between the phases involved. The spreading coefficient (measure of the tendency of the oil phase to spread on the air-water interface) was found to increase as the batch cultivation proceeded. The velocity of spreading was directly proportional to the spreading coefficient and inversely proportional to the sum of the viscosities of the two fluids.

2.5 Enhancement of Degradation of PAHs

Enhancement of biodegradation of PAHs has been investigated with the use of mineral oil and surfactants.

2.5.1 Mineral Oil

The study of Jimenez (1995) mentioned in the Introduction, has showed that the mineralization rates of phenanthrene and pyrene by a *Mycobacterium* isolate were found to increase 1.8- and 1.9-fold respectively in the presence of 0.8 % (v/v) mineral oil. The solubility of pyrene in mineral oil was reported as 25 mg/mL. Mineral oil addition did not stimulate the mineralization of ^{14}C-glucose demonstrating that the effect was specific for PAHs. Mineral oil itself did not serve as a growth substrate for the *Mycobacterium* strain. The rate of mineralization was higher in the case of cells attached to the oil than in the case of cells unattached. It was concluded that enhancement in mineralization was due to the increased availability of PAHs directly from the oil to the microbial cells.

2.5.2 Surfactants

There have been several investigations to assess the potential for using surfactants to treat contaminated soil and enhance its treatment via biodegradation (Rickabaugh et al. 1986; Edwards et al. 1994a & 1994b). These studies have shown that concentration of surfactants should be optimized in order to avoid foaming and inhibition of growth which might lead to hindrance or cessation of biodegradation of the contaminants.

Biodegradation of phenanthrene has been reported to be enhanced in both organic and mineral soils in low concentration of non-ionic alcohol ethoxylate surfactants (Aronstein et al. 1991). Mineralization was inhibited at high surfactant concentrations. The effect of non-ionic surfactants on biodegradation of anthracene, pyrene, and perylene in artificially contaminated soils has also been investigated by Christodoulatos et al. (1995). The authors concluded that the enhancement is due to the utilization of the surfactant as a carbon source. This leads to an increase in the biomass concentration and thus, to a higher rate of uptake of hydrocarbons. In this case, due to partial utilization of the surfactant, the initial surfactant concentration needed to exceed the value corresponding to CMC.

2.6 Slurry Reactors

Bioremediation of contaminated soil and sludges is normally done in slurry reactors. The slurry-phase treatment is analogous to conventional suspended biological systems (e.g. activated sludge). Slurry reactors involve three phases, i.e., water, suspended particulate matter, and another liquid phase or air. If a second liquid phase is used, it is dispersed in the water phase. Water is also serving as the phase in which other nutrients, chemical conditioners, and desorbed contaminants are dissolved. The suspended particulate matter consists soil particles and biomass attached to the soil matrix. The air provides the necessary oxygen for bacterial growth.

Due to the various interactions among the phases involved and the physical as well as biological phenomena involved, slurry reactors are highly complicated systems and their modeling is difficult. Some of the processes that might occur in slurry reactors include dissolution/precipitation, adsorption/desorption, oxygen transfer, particle size reduction and biodegradation. These processes can occur simultaneously or in series. For the design of slurry reactors, the rate limiting step of the entire process needs to be determined. Regarding bioavailability, it can be enhanced by increasing agitation speeds, use of additives, or by particle size reduction.

Of the processes listed above, adsorption/desorption is of extreme importance since it mainly affects the bioavailability and the efficiency of the entire process (Aronstein et al. 1991; Christodoulatos et al. 1994; Talimcioglu et al. 1993). Solute adsorption is an interfacial phenomenon resulting in solute accumulation at the solid-liquid interface. The solid molecules are held by electrostatic forces or chemical binding leading to a dynamic equilibrium between the two phases. The large interfaces formed by the tiny particles hinder the release of solute to the aqueous phase. The desorption of contaminants from the soil matrix is a strong function of soil and solution properties.

The recommended soil/water ratio is between 5-50 %. Higher ratios result in mixing problems whereas lower ratios lead to high volumetric requirements causing high costs. The residence time of the slurry in a reactor can range from a few days to several months.

The design and operation of an efficient mixing system for slurry reactors is of paramount importance. It is also a complex issue since it depends on the vessel, impeller geometry/size, baffles, agitation speed and other physical properties of the slurry such as solid density, solid content and particle size distribution. Although mixing and agitation have been investigated extensively over the years, there is very little information available on soil/water systems. For this reason, the design of slurry reactors is based on empirical rules such as those of Walas (1988).

2.7 Mass Transfer Studies

The importance of mass transfer for decontamination of PAH containing solids has been discussed by various authors as mentioned in earlier sections. However no study was found in the literature on the quantification of mass transfer rates and mass transfer coefficients.

CHAPTER 3

OBJECTIVES

The objective of this study was to determine the characteristics of mass transfer of PAHs from soil phases to suspensions of water and mineral oil. In order to examine whether mineral oil plays simply the role of intermediary for the eventual transfer of PAHs to the water phase, experiments were also performed in the absence of a solid phase.

Pyrene was used as the model PAH. Glass beads and sand were used as model solid phases with sand being the most realistic approximation and the glass beads providing what was thought to be a simple system for initial experiments.

Monitoring of pyrene was based on HPLC as in most cases reported in the literature. However, the presence of mineral oil complicated things and made the development of the analytical method almost an objective of the whole study.

More specifically then, the objectives of this study were the following:

I. Development of the Analytical Method.

Due to the presence of mineral oil, reverse phase HPLC could not be employed as oil is immiscible with most of the common polar solvents, e.g., acetonitrile and methanol. Hence normal phase HPLC was adopted with hexane/methylene chloride as the mobile phases.

II. Mass Transfer of Pyrene in Oil/ Water Mixtures.

The objective was to study the mass transfer of pyrene from the oil to the water phase. It was established that the amount transferred to water was negligible, even after 10 days of contact between the two phases. The amounts transferred never approached the (already low) solubility limit of pyrene in water.

III. Mass Transfer of Pyrene from Solid Surfaces to Oil.

The intent was to determine the mass transfer of pyrene coated on solids (glass beads) to mineral oil in the absence of a water phase. Experiments with flasks shaken in an incubator (no mixer used) allowed determination of the mass transfer coefficient quantitatively.

IV. Mass Transfer of Pyrene Between Glass Beads and Oil/Water Suspensions.

The intent here was to investigate the mass transfer of pyrene coated on glass beads to the oil phase which was dispersed in water. An overhead mixer with two propellers was used for this purpose and the amount of pyrene transferred was analyzed at various time intervals. The experiments were performed with varied volumes of oil. The data indicated that glass beads were a poor choice as a model solid phase because flakes of pyrene were found suspended in water. Thus, the amount of pyrene transferred to the oil phase was not because of its direct contact with the beads (solid).

V. Mass Transfer of Pyrene Between Sand and Oil/Water Suspensions.

Sand was used in meeting the same objective as in IV above. Sand was a better solid matrix for pyrene and is closer to systems involving sludges. Experiments were performed with different volumes of oil and different speeds of agitation.

CHAPTER 4

MATERIALS AND METHODS

4.1 Mass Transfer and Partitioning of Pyrene Between Oil and Water

These experiments entailed finding the rate of mass transfer and partitioning of pyrene between water and mineral oil. Pyrene was initially dissolved into mineral oil. The experimental procedure is quite complex as it involves a number of extraction and dilution steps which affect the final accuracy of the measurements. Specifically, this protocol can be divided into the steps discussed in the next three subsections.

4.1.1 Preparation and Experimentation

An amount of pyrene was first dissolved into mineral oil. An amount of this solution (ca. 5 mL) was transferred into volumetric flasks (50 or 100 mL) which contained 25 mL water. The mineral oil transferred into the flasks was measured by weight as its high viscosity prevented accurate measurement of the volume of the quantity added. Knowing the weight of the added solution and the density of the mineral oil (0.8657 mg/mL), the volume could be calculated more precisely. The flasks carrying the two liquid phases (water and mineral oil) were then placed in an incubator shaker (G-24, New Brunswick Scientific Co., Edison, NJ) and shaken over various time spans. It was observed that for the rates of shaking used, the oil phase never dispersed into the water phase as opposed to what was happening in the presence of microorganisms (Jimenez 1995).

Measurements were made as follows: After a particular period of contact of the two phases under shaking, the contents of a flask (ca. 30 mL) were transferred to 50 mL centrifuge tubes and centrifuged for 15 min at 3,500 rpm. The total liquid (two phases) was then transferred into separatory funnels and allowed to separate for a period of 15 min.

After separation of the two phases, a sample was taken from the oil layer, diluted with hexane (4:1) and injected to the HPLC unit for monitoring the amount of pyrene in the oil phase. The water layer could not be submitted to direct analysis for its pyrene content, primarily due to the very low amounts of pyrene present in it and the type of HPLC column used for the analysis. For this reason, the pyrene transferred into the water from the mineral oil was first extracted using solid phase extraction cartridges (Supelclean LC-18, Supelco Co., Bellefonte, PA).

4.1.2 Solid Phase Extraction

The procedure for the solid phase extraction was as follows: The cartridge columns were prewashed with four 10 mL aliquots of methylene chloride followed by four 10 mL aliquots of methanol and then two 10 mL aliquots of water. A thin layer of water was allowed to remain on the packing of the column in order to promote better contact between the aqueous layer to be extracted and the hydrophobic solid phase of the cartridge. The water layer obtained as discussed in the preceding section was then passed through the cartridge which was then allowed to dry for 30 minutes. The water and solvents passing through the cartridge were discarded.

The pyrene retained in the cartridge was eluted with two 5 mL portions of methylene chloride. This extract was then passed through a chromatographic column packed with anhydrous sodium sulfate which was first washed with 10 mL of methylene chloride. After passing the cartridge extract through the chromatographic column, the column was rinsed with an additional amount of 2 mL methylene chloride. The chromatographic column was used to ensure that no water was present in the final eluate which was collected in a concentrator tube. This final eluate was evaporated with a stream of nitrogen gas to a final volume of 0.1 mL. This final sample (0.1 mL) containing the entire amount of pyrene present in the water layer which had been contacted with the mineral oil, was then diluted to 1.0 mL with hexane before it was analyzed with the HPLC unit.

The validity of the method was checked as follows. An amount of 89 μg pyrene was weighed out and dissolved in 100 mL methanol. The expected concentration was 0.89 mg/L (solution A). In order to check this value, 4 mL of solution A was taken and diluted to 10 mL with methylene chloride (solution B). Subsequently, 4 mL of solution B were taken and diluted to 10 mL with hexane. Samples of this final solution were injected into the HPLC and the concentration value found was 0.84 mg/L. This means that the concentration of pyrene in the original solution in methanol was 0.84 mg/L rather than 0.89 mg/L. This difference is probably due to the errors from weighing out pyrene and the dilutions. The value of 0.84 mg/L was taken to be the correct one.

From the original solution in methanol, 5 mL were withdrawn and diluted to 25 mL with water (solution C). From solution C, 3 mL were withdrawn and diluted to 100 mL with water. This volume of 100 mL was divided into five parts of 20 mL each. Based on the concentration of 0.84 mg/L for the original solution, solution C should have a concentration of 0.00504 mg/L. Hence, the amount of pyrene in each one of the 20 mL parts should be 0.1008 µg. Each part of 20 mL was analyzed following the solid phase extraction procedure. The pyrene amounts recovered and the corresponding concentrations of pyrene for solution C are shown in Table 4.1. The percent pyrene recovery was good as shown in the table and thus, the method was proved valid.

Table 4.1 Data from the Experiments Performed to check the Validity of the Solid Phase Extraction Methodology.*

Flask #	A[1] µg	B[2] mg/L	% recovery of pyrene
1	0.093	0.00465	91.9
2	0.104	0.00520	102.8
3	0.101	0.00505	99.8
4	0.102	0.00510	100.8
5	0.095	0.00475	93.9

* For all flasks, the amount of pyrene should be 0.1008 µg and the corresponding concentration 0.00504 mg/L

[1] Amount of pyrene detected

[2] Concentration of pyrene in water (solution C, section 4.1.2) based on the detected amount of pyrene (second column of this table)

4.1.3 HPLC Analysis

As discussed above, pyrene in the oil or water phase was fully monitored through HPLC analysis. A normal phase column (LiChrosorb Si 60; L = 25 cm, 4.0 mm i.d., EM Science, Gibbstown, NJ) was used. The unit had a Waters 600E (Millipore Corporation, Milford, MA) system controller and an autosampler (Series 1050, Hewlett Packard, Piscataway, NJ). The eluent used was a 90/10 (v/v) mixture of hexane/methylene chloride at a flow rate of 1.2 mL/min and the temperature was maintained at 30°C. Peaks were detected by a photodiode array detector (Waters 994) at a wavelength of 241 nm. The retention time for pyrene was 4.9 min. Calibration curves are given in Appendix A.

4.2 Coating of Glass Beads with Pyrene

The beads used had diameters of 3 and 6 mm (Fisher Scientific, Springfield, NJ), and were prepared as follows: An amount of pyrene was dissolved in methylene chloride. A number of beads were then added to the solution and the methylene chloride was evaporated with a stream of nitrogen gas till the beads were completely dry. During the evaporation process, the flask carrying the beads was intermittently shaken to facilitate uniform pyrene coating on the beads. The coated beads were transferred into a clean flask and the flask used during coating was washed three times with 10 mL hexane. The hexane used in the washing was collected and further diluted with hexane to a total volume of 50 mL. Samples of this solution were used in HPLC analysis for determining the amount of pyrene present in the original methylene chloride solution but not on the coated beads (pyrene lost to the surface of the flask).

To check the uniformity of the coating procedure, the coated beads were divided into six equal parts for some control experiments. Each portion of beads was washed four times with 10 mL of hexane and the washings were diluted to 50 mL. Samples of the pyrene-containing hexane were analyzed by HPLC and the percentage of pyrene recovered was determined. Results are shown in Table B-1 of Appendix B and indicate that coating was relatively uniform.

4.3 Mass Transfer of Pyrene Between Oil and Glass Beads

These experiments were performed in shake flasks which received mineral oil and glass beads coated with various amounts of pyrene. Their intent was to study the effects of speed of flask shaking and initial amount of pyrene on the beads on the mass transfer rate. The methodology was as discussed below.

4.3.1 Effect of Speed of Flask Shaking

Initially, 1,400 glass beads of 3 mm diameter were coated with 16,201 μg pyrene. Amounts containing 200 of these beads (coated with 2,314.4 μg pyrene) were placed in shake flasks. Each flask was also charged with 20 mL of mineral oil. The flasks were then placed in an incubator shaker. The following shaking speeds were used: 50, 75, 100, and 200 rpm. All experiments were performed in duplicates. In no case was the shaking speed enough to disperse the beads in the mineral oil. The beads remained at the bottom of the flasks.

In each experiment and at different time intervals, mineral oil samples of 0.18 mL average volume were drawn from the flasks using Pasteur pipettes. For accuracy, the volume of samples was determined through their weight. Each sample was diluted with hexane to 25 mL in a volumetric flask. Samples of these (completely homogenous) oil/hexane solutions were subjected to HPLC analysis.

4.3.2 Effect of Initial Pyrene Amount

These experiments were performed at a constant shaker speed of 90 rpm. Each flask received 200 glass beads of 6 mm diameter and 40 mL mineral oil. Two sets of experiments were performed. In the first, the beads were coated with 2,189.8 μg pyrene whereas in the second, the amount was 586.2 μg. Sampling and analysis followed the steps discussed in section 4.3.1.

4.4 Mass Transfer of Pyrene Between Beads and Oil/Water Suspensions

These experiments were performed in order to determine, as a function of time, the amount of pyrene transferred from the surface of beads to the oil phase which was dispersed in water.

An amount of pyrene was first used for coating a quantity of beads as explained in section 4.2. The coated beads were divided into six equal portions. Each portion of beads was placed in a 1L beaker along with 450 mL water and 1 mL mineral oil. The contents of each beaker were agitated using an overhead mixer equipped with two propellers and a motor. The speed of agitation (389 rpm) was controlled by a variable autotransformer (Staco Energy Products Co., Dayton, OH). A calibration curve is given in Appendix A. During mixing, the beads were not completely dispersed in the liquid phase. Furthermore, part of the oil was dispersed into the water whereas part of it remained either at the surface of water or stuck to the blades of the propeller.

Because of the non-uniformity of the dispersion/suspensions, monitoring of pyrene concentration during experiments could not be based on sampling the liquid phase of the beaker. In addition, the oil amount was always small and its separation from a small water/oil sample was practically impossible. For this reason, the whole contents of a beaker were used in obtaining measurements at each particular instant of time. This means that six beakers loaded with the same amounts of beads, oil and water were used for one experiment which yielded six points in the time profile of pyrene transfer from the surface of the beads to the water/oil suspension.

At the end of a particular time interval, mixing was stopped and the following procedure was used.

The blades of the propeller were washed with 15 mL of hexane. The washings were collected in a clean beaker and then diluted to 25 mL with hexane in a volumetric flask. Samples were taken and analyzed in the HPLC unit.

The liquid contents of the beaker used in the experiment were placed in a separatory funnel whereas the beads were left in the beaker itself. The beads and beaker were washed four times with 10 mL of hexane. The washings were combined and diluted with more hexane to 50 mL before they were analyzed by HPLC.

After separation of the liquid phases, the oil was diluted with 20 mL of hexane, placed in a volumetric flask, and diluted to 50 mL with hexane before HPLC analysis.

The water phase (ca. 450 mL) was collected from the separatory funnel into a 1L Erlenmeyer flask and placed in a clean separatory funnel where it was shaken with 20 mL hexane. After separation, the hexane phase was combined with an another amount of hexane (ca. 20 mL) which was used for washing the flask employed in the original transfer. The combined solution was placed in a volumetric flask and diluted to a final 50 mL volume with more hexane. Samples from the final solution were analyzed in the HPLC unit.

The amount of pyrene recovered in each of four steps above were used in closing the mass balance relative to the amount of pyrene originally present on the surface of the beads used in the experiment.

Initial experiments in which the water phase was not analyzed for pyrene led to results which did not make sense since the mass balance could not be closed. In these experiments, it was assumed that negligible amounts of pyrene go into the water phase. This proved incorrect as discussed in the results section.

4.5 Coating of Sand with Pyrene

In these experiments, 00-grade sand of 30-50 mesh size, i.e., 300-600 μm diameter (Morris Industries, Pomptons Plains, NJ) was used. A measured amount (50 g) of sand was added to a solution of pyrene in methylene chloride present in a 250 mL flask. Part of the methylene chloride was evaporated in a stream of nitrogen under intermittent shaking of the flask for uniform coating of the sand with pyrene. The flask was subsequently transferred to an incubator shaker operating at 150 rpm and 50°C.

The flask was left in the shaker for 1.5 h for the sand to completely dry. The sand was transferred to another flask and the original flask was washed with hexane to determine the amount of pyrene lost during coating.

To check the uniformity of the coating procedure some control experiments were performed as follows. The sand was divided into five equal parts and each part was washed twice with hexane in a 250 mL flask as follows. First, 25 mL hexane were used and the flask was placed for 30 min in an incubator shaker (150 rpm). The liquid (hexane) was then removed and placed in a 50 mL volumetric flask. An amount of 15 mL pure hexane was added to the sand-containing flask which was placed in the incubator shaker (150 rpm) for another 15 min. The second washing (hexane) was combined with the first and the combination was brought to 50 mL with an additional amount of pure hexane. Samples of the final solution were subjected to HPLC analysis. Results are shown in Table B-2 of Appendix B and indicate that coating was relatively uniform.

4.6 Mass Transfer of Pyrene Between Sand and Oil/Water Suspensions

The experiments with sand were similar to those with glass beads and were performed with 1 and 10 mL oil (speed of agitation = 389 rpm). The effect of speed of agitation (450 and 520 rpm) was also studied for the case where 1 mL mineral oil was used.

It should be mentioned that while in the case of glass beads complete separation of the solid and liquid phases occurs, this is not the case with sand. In fact, some sand is present in the water phase (step 4 in the procedure of section 4.4) as discussed in the results section. In one case, the 450 mL water was divided into two equal parts. One was extracted with 20 mL hexane as discussed in section 4.4 whereas the second part was first filtered under vacuum and then extracted with 20 mL hexane. Some sand was seen on the filter paper. The results, shown in Table F-1 of Appendix F, showed that the outcome of the two approaches is completely different. Filtering led to a tremendous decrease in pyrene detected in the water phase. This decrease could not be attributed to pyrene being on the sand. It was most likely due to pyrene crystals detached from the sand particles but retained by the filter paper. Because of this uncertainty, it was decided not to use the filtering procedure since this extra step could not lead to an unequivocal explanation of the data.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 Mass Transfer and Partitioning of Pyrene Between Oil and Water

Results from two experiments performed in order to determine the rate of mass transfer of pyrene from the oil to the water phase are shown in Tables 5.1 and C-1 of Appendix C. These experiments required determining the amount of pyrene in the water and oil phases as a function of time. Since, as described in section 4.1.1, the experimental protocol required sacrificing a flask every time analysis was performed, each entry of Tables 5.1 and C-1 represents essentially a different experiment.

Table 5.1 Results from Experiments Regarding the Rate of Mass Transfer of Pyrene into Water from the Mineral Oil. Effect of Time.

Time h	A[1] μg	B[2] μg	C[3] μg	D[4] μg /mL
6.70	24,738.5	24,142.1	1.4	0.056
20.32	24,358.0	22,461.0	0.6	0.026
54.80	24,916.1	26,819.6	0.8	0.033
77.53	23,749.0	24,758.9	0.6	0.025
196.13	22,480.4	25,923.4	2.0	0.082

[1] Amount of pyrene in the mineral oil added to the flask in the beginning of the experiment.
[2] Amount of pyrene in the oil phase at the corresponding time.
[3] Amount of pyrene in the water phase at the corresponding time.
[4] Concentration of pyrene in the water phase at the corresponding time.

Although an effort was made so that all experiments in Table 5.1 and all experiments in Table C-1 started with the same amount of pyrene, there were variations as seen from the second columns of the tables. These variations stem from the way the mineral oil was added to the flasks (section 4.1.1).

The third column of Table 5.1 shows the amount of pyrene present in the oil phase at the corresponding time. These amounts were calculated based on the concentration determined by HPLC and the volume of the oil phase. Clearly, the last three entries of the table do not make sense as the amount of pyrene found in the oil phase is higher than that originally added to the flask. This may be explained by the fact that samples from the oil phase needed a 4:1 dilution with hexane before the HPLC analysis. Hence, the smallest analytical error and errors in reading of volumes can result into very large errors when the total amount of pyrene in the flask is calculated based on a HPLC reading.

Comparisons should really be made between the second and the fourth column of Tables 5.1 and C-1. The fourth column is indicating the amount of pyrene found in the water phase which translates into the concentration shown in the fifth column. Although the results may again be affected by the lengthy procedure of extracting pyrene as discussed in Section 4.1.2, it is clear that the mass transfer rate is extremely slow. It is worth noticing that even after 200 h the concentration is no way near (especially in Table C-1) the value of the solubility of pyrene in water reported as 0.14 mg/L (Cerniglia 1993).

The experiments reported in Table 5.2 were performed in order to see what is the effect of the initial pyrene concentration in the mineral oil on the mass transfer of the compound into the water phase. All flasks were analyzed 72 h after the initial contact between the two phases. The expected trend is that the concentration of pyrene in water (at t = 72 h) increases with the initial pyrene concentration in mineral oil since this implies a higher driving force for mass transfer. Once again the complexity of the procedure does not allow to see this trend with confidence (especially with the last entry of Table 5.2).

Table 5.2 Results from Experiments Regarding the Rate of Mass Transfer of Pyrene into Water from the Mineral Oil. Effect of Initial Concentration.

Concentration of pyrene in mineral oil (mg/L)		Concentration of pyrene in water (mg/L)
t = 0	t = 72 h	t = 72 h
5.2	5.4	0.0035
117.1	115.0	0.0075
595.8	574.5	0.0060
1,169.6	1,172.4	0.0045

Although the data shown in Tables 5.1, 5.2, and C-1 are problematic, they certainly show that the rates of mass transfer of pyrene from the oil to the water phase are extremely low. In fact, these rates are way below the rates of pyrene mineralization reported by Jimenez (1995). If nothing else, the data obtained here suggest that the conclusion of Jimenez that mineral oil enhances pyrene mineralization rates due to direct contact of cells with oil droplets is correct.

5.2 Mass Transfer of Pyrene Between Oil and Glass Beads

The coefficient of mass transfer of pyrene from the glass beads to the oil was found by monitoring the change in concentration of pyrene in the oil as a function of time. The data were modeled with a first order expression.

5.2.1 Mathematical Model

Because of the extremely high solubility of pyrene into mineral oil, it can be assumed that the contact of beads coated with pyrene and mineral oil will eventually lead to a complete transfer of pyrene from the surface of the beads to the mineral oil phase. Hence, the transfer of pyrene from the surface of the beads to the oil phase can be described by the following mass-balance equation,

$$\frac{dC}{dt} = k_L \left(C^* - C\right) \qquad (5.1)$$

where, C is the pyrene concentration in the mineral oil, C^* is the value of C when all pyrene originally on the surface of the beads has been transferred into the mineral oil phase, and k_L is an overall mass transfer coefficient.

Equation (5.1) when solved subject to the initial condition: $C = 0$ at $t = 0$ yields,

$$\ln\left[\frac{C^*}{C^* - C}\right] = k_L t \tag{5.2}$$

or,

$$C = C^*\left(1 - e^{-k_L t}\right) \tag{5.3}$$

According to equation (5.2) a plot of data leads to a line the slope of which, is the value of k_L . Data were regressed to equation (5.2) using the least square regression method.

5.2.2 Effect of Speed of Flask Shaking on k_L

In order to determine the effect of the speed of flask-shaking on k_L , experiments were performed at 50, 75, 100, and 200 rpm following the methodology described in section 4.3.1. The data are shown (as measured concentrations) in Tables 5.3 and D-1 of Appendix D. The data from each experiment were regressed to equation (5.2) as shown in Figure D-1 of Appendix D. Since each experiment employed 200 beads coated with 2,314.4 μg pyrene placed in 20 mL oil the value of C^* (see section 5.2.1) for the regressions was 115 mg/L.

The slopes of the lines shown in Figure D-1 gave values for k_L of 0.0587, 0.1047, 0.1307, and 0.2447 min^{-1} at 50, 75, 100, and 200 rpm respectively. Using the values of k_L and C^* , concentrations were calculated according to equation (5.3) and are shown for comparison in Tables 5.3 and D-1. As can be seen, the agreement between measured and calculated values is not good especially at 100 and 200 rpm. This could be anticipated from the R^2 -values for the regressions shown in Figure D-1.

As expected, the value of k_L increases with the speed of shaking the flask. The values of k_L were regressed to the following equation:

$$k_L = k_{Lo} + \alpha f \tag{5.4}$$

where k_{Lo} is the value of k_L when the flask is not shaken, f is the speed of flask shaking, and α is a proportionality constant.

Table 5.3 Change of concentration of Pyrene in Mineral Oil. Effect of Speed.

CONDITIONS

Original solution : 28,851 μg pyrene in 30 mL methylene chloride

Number of beads used : 1,400

Number of beads per experiment : 200

Amount of pyrene lost to surface of original flask : 12,650 μg

Amount of pyrene on surface of 1,400 beads : 16,201 μg

Amount of pyrene on surface of 200 beads : 2,314.4 μg

Volume of mineral oil used : 20 mL

Speed of shaking of flasks carrying coated beads and mineral oil : 50 rpm

Expected pyrene concentration in mineral oil, if all pyrene is transferred from the surface of the beads to the mineral oil : 115.72 mg/L

Table 5.3 *cont.*

DATA

Time min.	Concentration of pyrene in mineral oil (mg/L)	
	Measured	Calculated
4	36.9	24.2
11	55.6	55.0
16	76.5	70.5
24	85.7	87.4
34	91.7	100.0
58	112.6	111.9

The results of the regression are shown graphically in Figure 5.1 and imply values for α and k_{Lo} of 1.25 x 10^{-3} min^{-1} rpm^{-1} and 0.0 min^{-1}. Although the value of k_{Lo} is expected to be small, it should be positive. The zero-value obtained for k_{Lo} , suggests that k_L is, most probably, not directly proportional to f as equation (5.4) suggests.

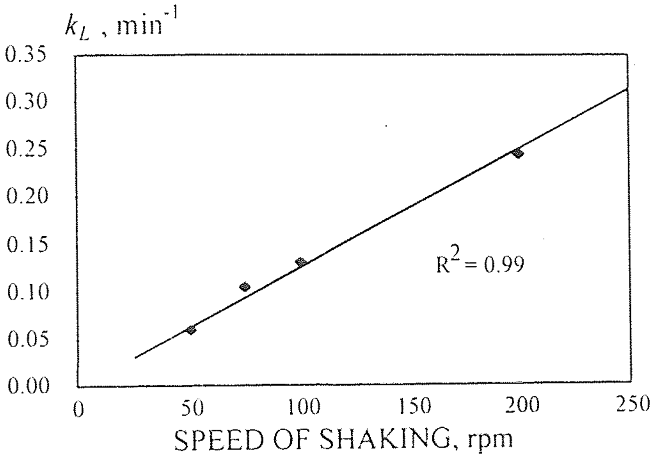


Figure 5.1 Variation of mass transfer coefficient, k_L with speed of shaking, rpm.

5.2.3 Effect of Initial Pyrene Amount on Beads

Two experiments were performed with identical conditions (see section 4.3.2) except for the amount of pyrene coated on the beads. Experimental results (measured concentrations) and calculated values [based on equation (5.3)] are shown in Tables 5.4 and 5.5. Regression of the data to equation (5.2) is shown graphically in Figure D-2 of Appendix D. The values of k_L were 0.0864 and 0.1354 min^{-1} for experiment 1 (Table 5.4) and experiment 2 (Table 5.5), respectively.

Table 5.4 Experiment 1 with Glass Beads and Mineral Oil.

CONDITIONS

Original solution : 2,761.8 μg pyrene in 25 mL methylene chloride

Amount of pyrene lost to surface of original flask : 572 μg

Amount of pyrene on surface of beads : 2,189.8 μg

Volume of mineral oil used : 40 mL

Speed of shaking of flasks carrying coated beads and mineral oil : 90 rpm

Expected pyrene concentration in mineral oil, if all pyrene is transferred from the surface of the beads to the mineral oil : 54.8 mg/L

Table 5.4 *cont.*

DATA

Time (min)	Pyrene concentration in mineral oil (mg/L)	
min	Measured	Calculated
6	32.9	22.1
11	42.5	33.6
16	46.8	41.0
26	48.9	49.0
36	52.3	52.3
50	55.1	54.0
66	55.1	54.6

Table 5.5 Experiment 2 with Glass Beads and Mineral Oil.

CONDITIONS

Original solution : 792.5 μg pyrene in 25 mL methylene chloride

Amount of pyrene lost to surface of original flask : 206.3 μg

Amount of pyrene on surface of beads : 586.2 μg

Volume of mineral oil used : 40 mL

Speed of shaking of flasks carrying coated beads and mineral oil : 90 rpm

Expected pyrene concentration in mineral oil, if all pyrene is transferred from the surface of the beads to the mineral oil : 14.7 μg

Table 5.5 *cont.*

DATA

Time min.	Pyrene concentration in mineral oil (mg/L)	
	Measured	Calculated
4	11.0	6.1
9	11.0	10.3
15	11.8	12.7
22	14.0	13.9
27	14.2	14.3
37	14.7	14.6
47	14.8	14.6

The data (measured values in Tables 5.4 and 5.5) do in fact suggest that the rate of pyrene transfer increases with C^* as dictated by equation (5.1). However, the difference in k_L values, which should be the same, suggests that equation (5.1) does not really describe the process. It may also be possible that equation (5.1) is correct and the discrepancies are due to experimental errors.

5.3 Mass Transfer of Pyrene Between Beads and Oil/Water Suspensions

Before experiments were performed according to the methodology described in section 4.4, experiments during which the water phase was not analyzed for its pyrene content were performed. This was done because the solubility of pyrene in water is negligible. However, this methodology led to puzzling results as the mass balance on pyrene could not be closed, especially at low amounts of mineral oil and during the initial phase of the experiments (e.g., Table E-2 of Appendix E). Data shown in Table E-3 of Appendix E seem to be better but they are in fact inconclusive as measurements started 10 min after initiation of the experiments. In fact, after 10 min the mass balance on pyrene closes equally well for the experiments reported in Tables E-2 and E-3. Because of these problems, the methodology was modified as described in section 4.4 and results from two experiments are shown in Tables 5.6 and E-1 of Appendix E.

Table 5.6 Results from Experiment to Measure the Amount of Pyrene Transferred from the Glass Beads to the Oil/Water Suspension.

CONDITIONS

Original solution : 21,115 μg pyrene in 40 mL methylene chloride

Amount of pyrene lost to surface of original flask : 2,997.2 μg

Amount of pyrene on surface of 3,000 beads : 18,117.8 μg

Diameter of glass beads : 3 mm

Number of glass beads : 500/beaker

Volume of mineral oil used : 1 mL

Volume of water : 450 mL

Speed of agitation of beakers carrying coated beads and oil/water suspension :389 rpm

Expected amount of pyrene in mineral oil, if all pyrene is transferred from the surface of the beads to the mineral oil : 3,019.6 μg

Table 5.6 *cont.*

DATA

Time	Measured weight of pyrene (µg)				Total weight of pyrene	Total weight of pyrene	% recovery
min	Blades	Oil	Water	Beads	pyrene in the oil (µg)	pyrene recovered (µg)	of pyrene
1	283.1	624.0	668.7	1,078.1	907.1	2,653.9	87.9
3	443.7	848.1	813.5	1,041.4	1,291.8	3,146.8	104.2
5	528.7	803.5	831.5	429.0	1,332.2	2,592.7	85.9
8	1,035.6	1,225.0	538.6	211.9	2,260.6	3,011.1	99.7
12	1,122.3	1,475.0	424.7	303.4	2,597.3	3,325.4	110.1
20	1,082.0	1,654.4	430.0	125.1	2,736.4	3,291.5	109.0

These two experiments differ in the number of beads used and the amount of pyrene originally coated on the beads.

From the detailed experiments two things became clear, as can be seen from Tables 5.3 and E-1. First, there is a very substantial amount of pyrene found in the water phase. Second, an amount of pyrene was found on the blades of the mixer.

Regarding the pyrene found on the blades, it was determined that it is contained in mineral oil attached to the blades. What is interesting is that experiments showed that the volume of mineral oil attached to the blades is varying with time. This variation is kind of random and does not help the analysis. The amount of pyrene actually found in the mineral oil phase of the suspension plus the amount found on the blades is reported as "total amount of pyrene in the oil" in Tables 5.6 and E-1.

Regarding the amount of pyrene found in the water phase, it cannot be explained based on solubility. The only explanation is that crystals (fragments) of pyrene get detached from the surface of beads and are suspended in the dominant water phase. Such pyrene fragments were actually observed during some of the experiments. As can be seen from Tables 5.6 and E-1, the amount of pyrene detected in the water phase initially increases with time and it subsequently decreases. This can be explained as follows. Mixing causes pyrene detachment which increases with time. However, as time increases there is more time for the detached pyrene to be transferred from the water to the mineral oil phase. It was also observed that dispersion of oil in water is incomplete during the initial stages of an experiment. Hence, as time increases there is a better contact between oil and pyrene fragments suspended in water and thus, more pyrene is found in the oil phase.

As can be seen from Tables 5.6 and E-1 the pyrene mass balance is much better satisfied at all instants of time when compared to the experiments in which the water phase was not analyzed (Tables E-2 and E-3). However, the observations discussed in the preceding paragraph led to the conclusion that the transfer of pyrene from the solids to the mineral oil is complex and cannot really simulate the transfer of pyrene from sludges to mineral oil. Hence, experiments with glass beads were abandoned and sand was used instead as discussed is the following section.

5.4 Mass Transfer of Pyrene Between Sand and Oil/Water Suspensions

The experiments performed with sand were similar to those with beads. The key difference between the two classes of experiments was that the transfer of the amount of pyrene adsorbed on sand to the mineral oil takes more time when compared to the case of glass beads.

The data for the experiment with 1 mL of mineral oil and an agitation speed of 389 rpm are presented in Table 5.7. As seen from the sixth column of the table, the rate of transfer of pyrene to the mineral oil is very slow. In fact, even after 80 min only 19% of pyrene was transferred to the oil whereas in the experiments with beads there was complete transfer in about 20 min. However, an average 17% of pyrene is also observed in water as seen from the fourth column of the table. The presence of pyrene

Table 5.7 Results from Experiment 1 to Measure the Amount of Pyrene Transferred from Sand to the Oil/Water Suspension.

CONDITIONS

Original solution : 10,293 μg pyrene in 16 mL methylene chloride

Amount of pyrene lost to surface of original flask : 828.6 μg

Amount of pyrene coated on 50 g of sand : 9,464.4 μg

Weight of sand per beaker : 10 g

Volume of mineral oil used : 1 mL

Volume of water : 450 mL

Speed of agitation of beakers carrying sand and oil/water suspension : 389 rpm

Expected amount of pyrene in mineral oil, if all pyrene is transferred from the surface of sand to the mineral oil : 1,892.9 μg

DATA

Time	Measured weight of pyrene (μg)				A[1]	B[2]	C[3]
min.	Blades	Oil	Water	Sand	μg	μg	
5	20.8	25.4	362.0	1,359.4	46.2	1,767.6	93.4
10	23.1	42.5	329.0	1,182.3	65.6	1,576.9	83.3
15	45.2	77.4	271.4	1,304.8	122.6	1,698.8	89.7
30	55.6	71.8	340.4	1,343.5	127.4	1,811.3	95.7
80	164.8	203.8	346.6	1,292.8	368.6	2,008.0	106.1

[1] Total weight of pyrene transferred to mineral oil (blades + oil).
[2] Total weight of pyrene recovered from the experiment.
[3] Percentage recovery of pyrene from the experiment.

in water may be because of its weak adsorption on sand and due to the sand being unable to settle down completely when mixing is stopped for measurement of pyrene in the various phases.

In the subsequent experiments (reported in Appendix F), the weight of sand was measured at the end of each analysis. The measurements showed that the weight of sand lost to the water phase was (in most cases) less than 0.3 g (Note: weight of sand per beaker = 10 g). Based on the amount of pyrene used in the experiments, the amount present in 0.3 g sand is in the order of 60 μg which is way below the amounts detected in the water phase (Tables 5.7 and F-1 through F-4). Hence, detachment of pyrene from sand occurred as in the case of glass beads.

Comparing the data (blades plus oil) shown in Tables 5.6, F-1, and F-2 one can see that the mass transfer of pyrene to the oil phase increases (as expected) when the amount of mineral oil is increased. Transfer is also faster when the speed of mixing increases as can be seen from Tables 5.6, F-3, and F-4.

The results discussed in sections 5.3 and 5.4 show that sand is much better than glass beads in the sense that pyrene detachment is less in the case of sand. Hence, sand should be used in experiments which try to simulate industrial sludges.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

Because of the complexity of the processes involved, most of the results obtained during the course of this thesis are qualitative rather than quantitative in nature.

It has been established that pyrene dissolved in mineral oil does not really get transferred to water even after very long periods of contact. In reality, some type of equilibrium is established but the amount of pyrene in water (given also its low solubility limit) can be safely neglected.

However, in cases where pyrene is to be transferred from a solid phase (either glass beads or sand) to water/oil suspensions, there is a substantial presence of pyrene in the water phase. This amount of pyrene is not dissolved in water but rather, it is in the form of pyrene fragments (crystals) suspended in the water phase. Pyrene gets detached from the solid surface because of mixing. Whether this phenomenon actually occurs when pyrene-contaminated soil or sludges are used, is not clear and should be investigated in the future.

When pyrene-coated beads were in contact with mineral oil only and the environment (flask) was shaked rather than mixed, data were analyzed and led to determination of mass transfer coefficients which were found to be proportional to the speed of environment (flask) shaking.

Data on the transfer of pyrene from solids to water/oil suspensions were not quantified. Qualitative results show that the rate of transfer depends on the type of solid surface (beads, fast transfer vs. sand, slow transfer), the amount of mineral oil, the speed of agitation, and the extent of dispersion of oil into the water phase.

Since sand is much closer to soil and sludges, the results suggest that pyrene is transferred from the soil very slowly. Given the fact that mineralization rates based on experiments with dissolved pyrene (Jimenez 1995) are high, the results of the present thesis suggest that soil and sludge decontamination in slurry reactors is, most probably, mass-transfer limited.

Further experiments are needed for determining the mass transfer coefficients in a quantitative way. If detachment of pyrene (or PAHs in general) from real solid surfaces (soil, sludges) proves to be actually occurring, it would need to be also described and quantified.

APPENDIX A

CALIBRATION CURVES

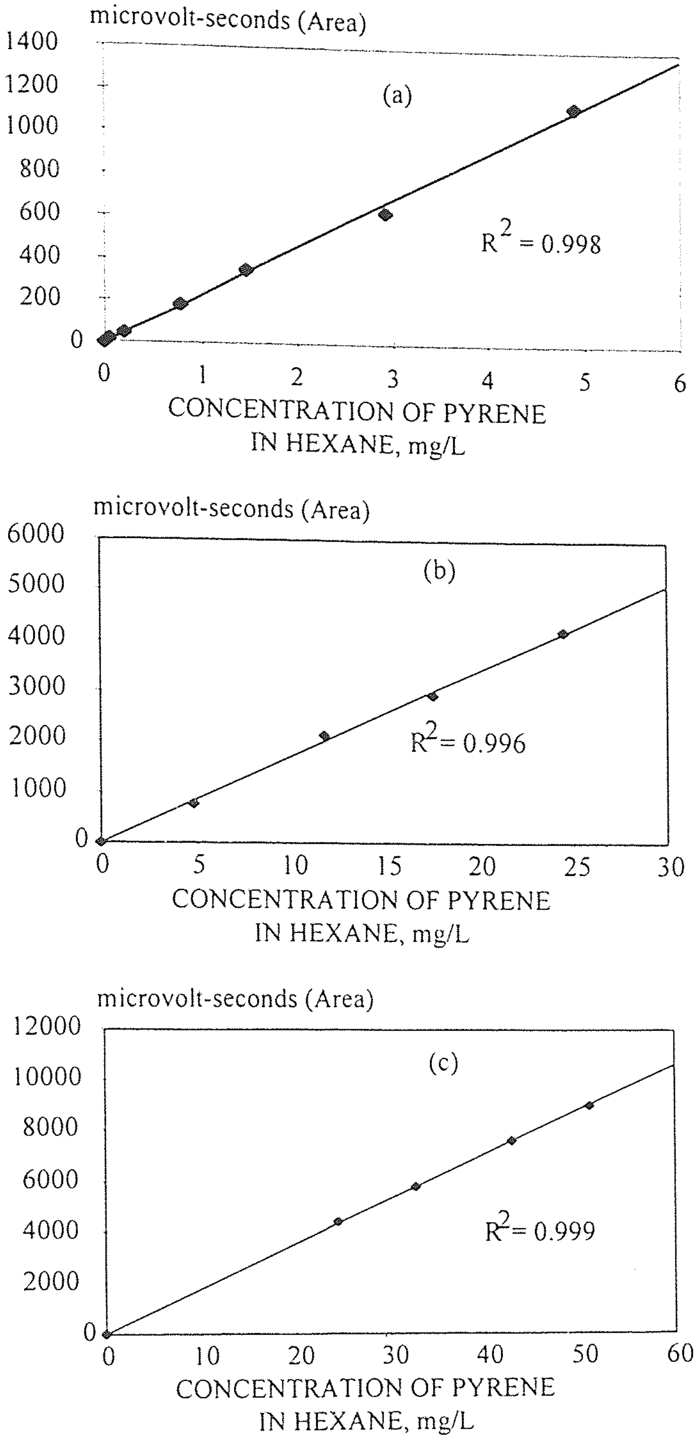


Figure A-1 Calibration curves for three different ranges of pyrene concentration in hexane: (a) 0.049 to 4.9 mg/L, (b) 4.9 to 24.508 mg/L, and (c) 24.508 to 51.06 mg/L.

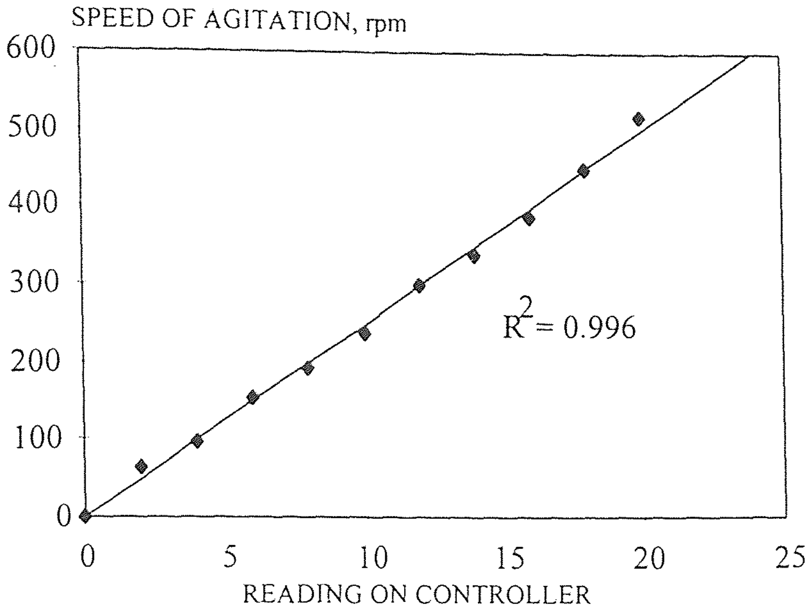


Figure A-2 Calibration curve of controller for speed of agitation.

APPENDIX B

UNIFORMITY OF GLASS BEADS AND SAND COATING WITH PYRENE

Table B-1 Results from Experiments to Check Uniformity of Coating on Glass Beads.

CONDITIONS

Original solution : 20,021 μg pyrene in 40 mL methylene chloride

Number of beads used : 3,000

Diameter of beads : 3 mm

Number of beads per flask : 500

Amount of pyrene lost to surface of original flask : 3,662.5 μg

Amount of pyrene on surface of 3000 beads : 16,358.5 μg

Amount of pyrene on surface of 500 beads : 2,726.4 μg (assuming uniform coating)

DATA

Flask #	Weight of pyrene recovered (μg)	% recovery of pyrene
1	2,755.0	101.0
2	2,592.5	95.1
3	2,695.0	98.8
4	2,858.8	104.9
5	2,698.8	99.0
6	2,586.3	94.9

Table B-2 Results from Experiment to Check Uniformity of Coating on Sand.

CONDITIONS

Original solution : 10,874 µg pyrene in 16 mL methylene chloride

Weight of sand : 50 g

Weight of sand per flask : 10 g

Amount of pyrene lost to surface of original flask : 152.8 µg

Amount of pyrene coated on 50 g of sand : 10,721.2 µg

Amount of pyrene coated on 10 g of sand: 2,144.2 µg (assuming uniform coating)

DATA

Flask #	Weight of pyrene recovered (µg)	% recovery of pyrene
1	2,137.0	99.7
2	2,069.2	96.5
3	2,098.0	97.8
4	2,068.9	96.5
5	2,093.5	97.6

APPENDIX C

MASS TRANSFER AND PARTITIONING OF PYRENE BETWEEN OIL AND WATER

Table C-1 Results from Experiments Regarding the Rate of Mass Transfer of Pyrene into Water from the Mineral Oil. Effect of Time.

Time h	A[1] µg	B[2] µg	C[3] µg	D[4] µg /mL
1.0	4,588.8	3,958.4	0.188	0.0074
23.0	5,094.3	5,353.3	0.351	0.0145
47.0	5,308.7	4,771.9	0.259	0.0103
114.5	4,901.5	4,339.5	0.663	0.0353
145.0	5,088.6	4,824.7	0.166	0.0066
263.0	5,026.3	4,158.5	0.303	0.0121

[1] Amount of pyrene in the mineral oil added to the flask in the beginning of the experiment.

[2] Amount of pyrene in the oil phase at the corresponding time.

[3] Amount of pyrene in the water phase at the corresponding time.

[4] Concentration of pyrene in the water phase at the corresponding time.

APPENDIX D

MASS TRANSFER OF PYRENE BETWEEN OIL AND GLASS BEADS

Table D-1 Change of concentration of Pyrene in Mineral Oil. Effect of Speed.
(Note : Conditions as mentioned in Table 5.3)

(a) Speed of shaking of flasks carrying coated beads and mineral oil : 75 rpm

Time	Concentration of pyrene in mineral oil (mg/L)	
min.	Measured	Calculated
3	8.4	31.2
6	51.1	54.0
12	81.8	82.8
24	106.9	106.3
40	130.3	114.0

(b) Speed of shaking of flasks carrying coated beads and mineral oil : 100 rpm

Time	Concentration of pyrene in mineral oil (mg/L)	
min.	Measured	Calculated
4	53.1	47.1
10	81.7	84.4
15	107.7	99.4
25	109.1	111.3
55	120.0	115.6

Table D-1 *cont.*

(c) Speed of shaking of flasks carrying coated beads and mineral oil : 200 rpm

Time	Concentration of pyrene in mineral oil (mg/L)	
min.	Measured	Calculated
3	90.1	60.2
7	107.2	94.9
12	108.6	109.6
21	114.8	115.0

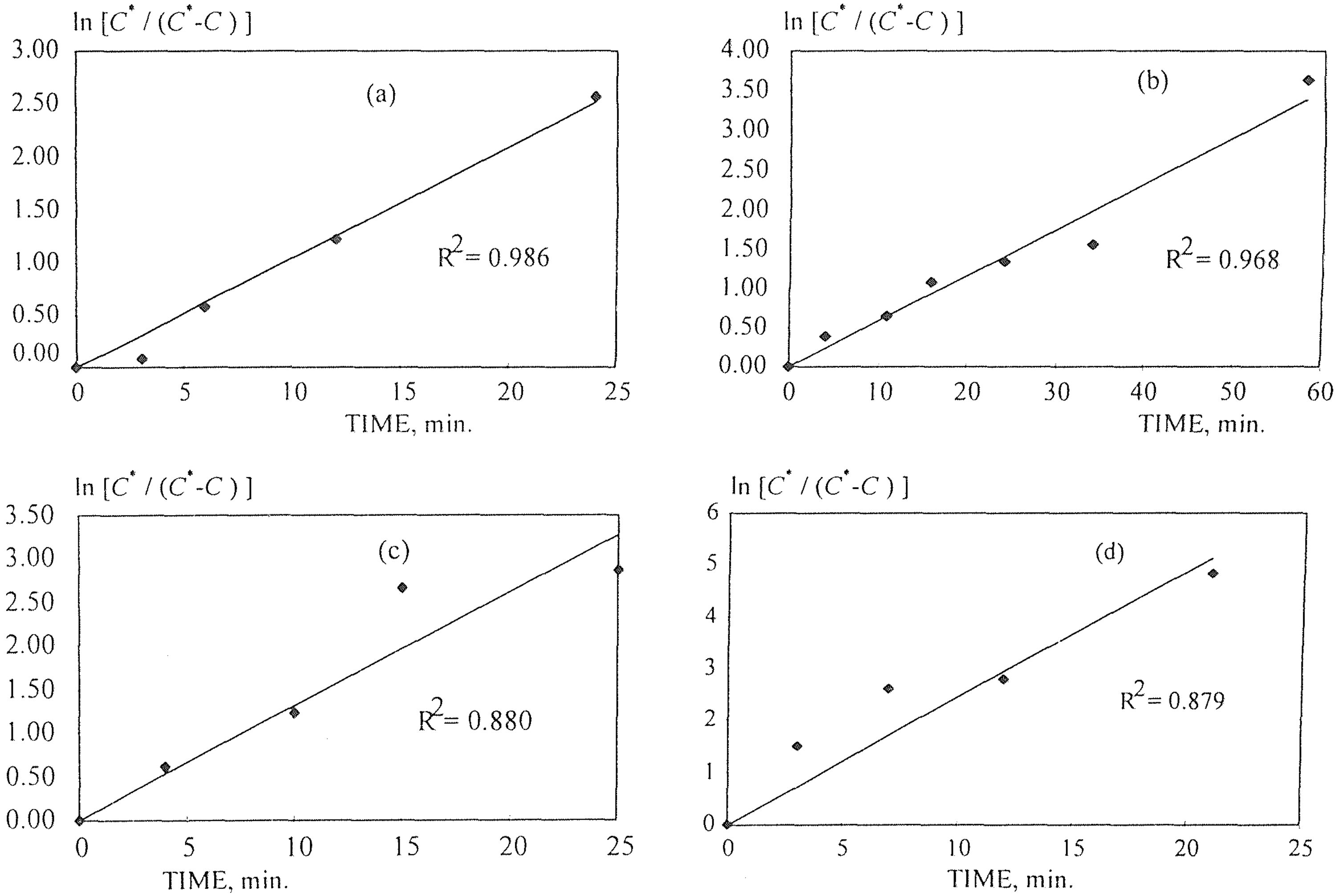
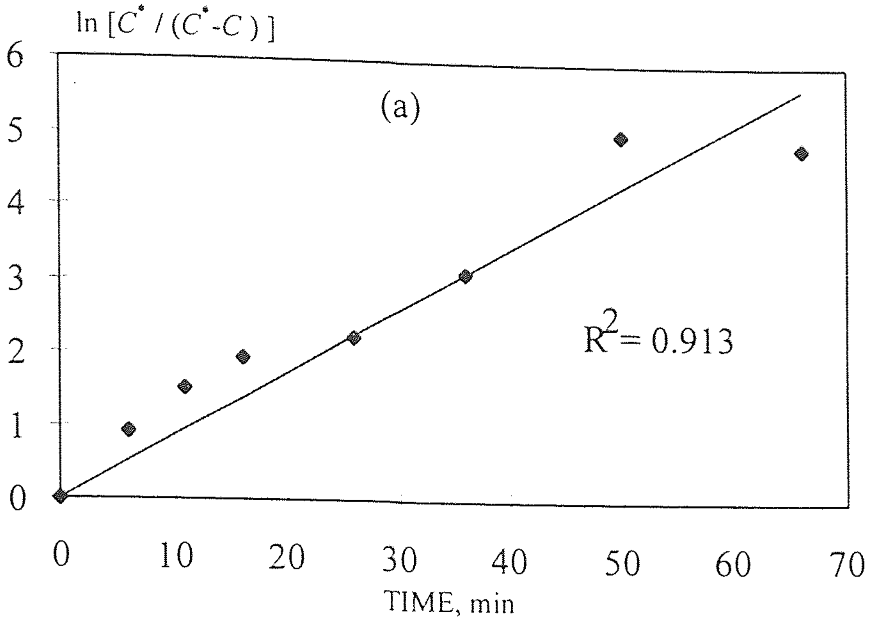


Figure D-1 Plots of $\ln[C^* / (C^*-C)]$ vs. time, t for determination of overall mass transfer coefficient. (a) 50 rpm, (b) 75 rpm, (c) 100 rpm, and (d) 200 rpm, corresponding to Tables 5.3 and D-1.



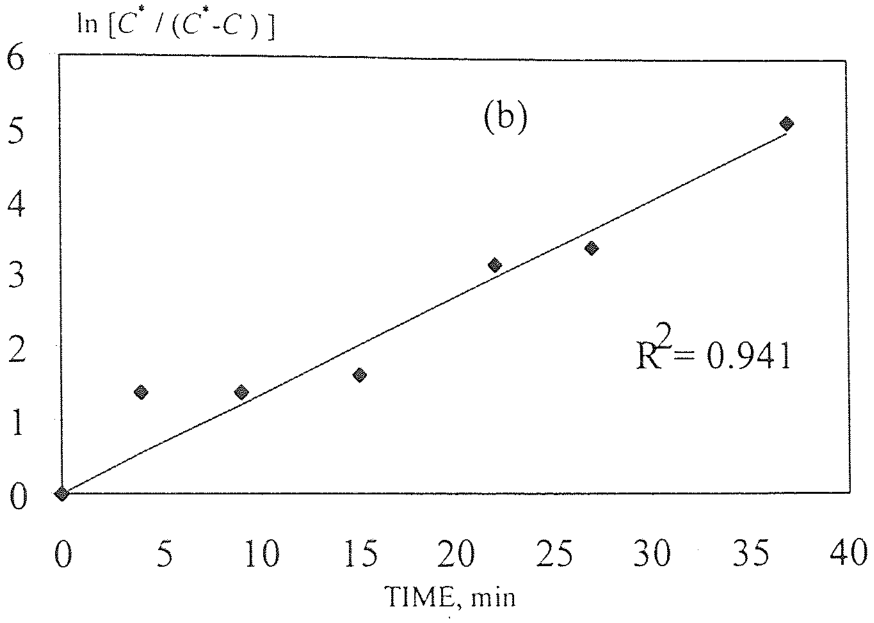


Figure D-1 Plots of ln[C^* / (C^*-C)] vs. time, t for determination of overall mass transfer coefficient. (a) C^* = 54.8 mg/L, and (b) C^* = 14.7 mg/L., corresponding to Tables 5.4 and 5.5 respectively.

APPENDIX E

MASS TRANSFER OF PYRENE BETWEEN GLASS BEADS AND OIL/WATER SUSPENSIONS

Table E-1 Results from Experiment to Measure the Amount of Pyrene Transferred from the Glass Beads to the Oil/Water Suspension.

CONDITIONS

Original solution : 38,737 μg pyrene in 60 mL methylene chloride

Amount of pyrene lost to surface of original flask : 4,547.8 μg

Amount of pyrene on surface of 6,000 beads : 34,189.2 μg

Diameter of glass beads : 3 mm

Number of glass beads : 1,000/beaker

Volume of mineral oil used : 1 mL

Volume of water : 450 mL

Speed of agitation of beakers carrying coated beads and oil/water suspension :389 rpm

Expected amount of pyrene in mineral oil, if all pyrene is transferred from the surface of the beads to the mineral oil : 5,698.2 μg

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Table E-1 *cont.*

DATA

Time	Measured weight of pyrene (µg)				Total weight of pyrene	Total weight of pyrene	% recovery
min	Blades	Oil	Water	Beads	pyrene in the oil (µg)	pyrene recovered (µg)	of pyrene
1	330.9	1,011.4	1,395.7	2,641.8	1,342.3	5,379.8	94.4
3	727.6	1,672.2	2,107.9	1,121.6	2,399.8	5,629.3	98.8
5	886.3	2,212.0	1,916.6	610.1	3,098.3	5,625.0	98.7
12	1,548.2	2,725.5	698.1	491.9	4,273.7	5,463.7	95.9

Table E-2 Results from Experiment to Measure the Amount of Pyrene Transferred from the Glass Beads to the Oil/Water Suspension. No Analysis of Water Phase.

CONDITIONS

Original solution : 41,597 μg pyrene in 40 mL methylene chloride

Amount of pyrene lost to surface of original flask : 1,263 μg

Amount of pyrene on surface of 6,000 beads : 40,334 μg

Diameter of glass beads : 3 mm

Number of glass beads : 500/beaker

Volume of mineral oil used : 1 mL

Volume of water : 450 mL

Speed of agitation of beakers carrying coated beads and oil/water suspension :389 rpm

Expected amount of pyrene in mineral oil, if all pyrene is transferred from the surface of the beads to the mineral oil : 6,722.3 μg

DATA

Time	Measured weight of pyrene (μg)		Total weight of	% recovery
min	mineral oil	beads and beaker	pyrene recovered (μg)	of pyrene
1	2,786.3	2,409.0	5,195.3	77.3
3	4,629.0	672.0	5,301.0	78.9
5	4,616.5	701.1	5,317.6	79.1
10	5,947.5	233.2	6,180.7	91.9
30	6,643.8	82.3	6,726.1	100.1
250	6,823.8	54.3	6,878.1	102.3

Table E-3 Results from Experiment to Measure the Amount of Pyrene Transferred from the Glass Beads to the Oil/Water Suspension. No Analysis of Water Phase.

CONDITIONS

Original solution : 3404.3 μg pyrene in 25 mL methylene chloride

Amount of pyrene lost to surface of original flask : 672.8 μg

Amount of pyrene on surface of 1000 beads ; 2731.5 μg

Diameter of glass beads : 3 mm

Number of glass beads : 200/beaker

Volume of mineral oil used : 10 mL

Speed of agitation of beakers carrying coated beads and oil/water suspension :389 rpm

Expected amount of pyrene in mineral oil, if all pyrene is transferred from the surface of the beads to the mineral oil : 546.3 μg

DATA

Time	Measured weight of pyrene (μg)		Total weight of	% recovery
min	mineral oil	beads and beaker	pyrene recovered (μg)	of pyrene
10	435.9	78.7	514.6	94.2
34	450.3	68.0	518.3	94.9
69	501.1	31.7	532.8	97.5
118	515.8	28.3	544.1	99.6
217	527.2	17.6	544.8	99.7

APPENDIX F

MASS TRANSFER OF PYRENE BETWEEN SAND AND OIL/WATER SUSPENSIONS

Table F-1 Results from Experiment 2 to Measure the Amount of Pyrene Transferred from Sand to the Oil/Water Suspension.

CONDITIONS

Original solution : 10,346 μg pyrene in 16 mL methylene chloride

Amount of pyrene lost to surface of original flask : 626.6 μg

Amount of pyrene coated on 50 g of sand : 9,719.4 μg - (A)

Weight of sand per beaker : 10 g

Volume of mineral oil used : 5 mL

Speed of agitation of beakers carrying sand and oil/water suspension : 389 rpm

Expected amount of pyrene in mineral oil, if all pyrene is transferred from the surface of sand to the mineral oil : 1,943.9 μg

DATA

(a) Rate of Transfer of Pyrene to Oil as function of time.

Time	Measured weight of pyrene (μg)			B[1]	C[2]	D[3]
min.	Blades	Oil	Sand	μg	μg	
33	49.7	430.8	1,128.3	480.5	1,608.8	116.7
95	77.4	787.7	885.4	865.1	1,750.5	96.3
152	82.6	788.0	831.0	870.6	1,701.6	92.7
218	38.7	846.8	846.7	885.5	1,732.2	91.2
360	66.1	969.9	622.4	1,036.0	1,658.4	86.1

[1] Total weight of pyrene transferred to mineral oil, i.e., sum of the amounts of pyrene measured on blades and directly in oil.

[2] Total weight of pyrene recovered from sand and oil.

[3] Percentage recovery of pyrene from the experiment [based also on data from (b) below, values without filtration times two]

(b) Experiment for Analysis of Pyrene in Water*.

Time	Measured weight of pyrene (μg)		
min	Without filtration	With filtration	Total
33	329.8	3.1	332.9
95	60.5	1.5	62.0
152	50.5	1.4	51.9
218	20.4	0.4	20.8
360	7.7	0.1	7.8

* Amounts found in 225 mL of water as water phase was divided into two parts.

(c) Analysis of Sand.

Time	Weight of sand (g)			Weight of pyrene
min.	Initial	Final	Difference	lost (μg) *
33	10.00	9.91	0.09	17.5
95	10.00	9.75	0.25	48.6
152	10.00	9.83	0.17	33.0
218	10.00	9.86	0.14	27.2
360	10.00	9.30	0.70	136.1

* Assuming no transfer from this part of the sand to the other phases.

Table F-2 Results from Experiment 3 to Measure the Amount of Pyrene Transferred from Sand to the Oil/Water Suspension.

CONDITIONS

Original solution : 10,783 μg pyrene in 16 mL methylene chloride

Amount of pyrene lost to surface of original flask : 325.8 μg

Amount of pyrene coated on 50 g of sand : 10,457.2 μg

Weight of sand per beaker : 10 g

Volume of mineral oil used : 10 mL

Volume of water : 450 mL

Speed of agitation of beakers carrying sand and oil/water suspension : 389 rpm

Expected amount of pyrene in mineral oil, if all pyrene is transferred from the surface of sand to the mineral oil : 2,091.4 μg

DATA

Time	Measured weight of pyrene (μg)				A[1]	B[2]	C[3]
min.	Blades	Oil	Water	Sand	μg	μg	
33	25.4	614.7	313.9	1,096.9	640.1	2,050.9	98.1
98	36.6	880.4	195.4	1,025.6	917.0	2,138.0	102.2
175	44.4	1,121.8	50.9	813.0	1,166.2	2,030.1	97.1
228	42.0	1,211.8	30.8	924.8	1,253.9	2,209.5	105.6
318	48.2	1,340.6	16.4	638.4	1,388.8	2,043.6	97.7

[1] Total weight of pyrene transferred to mineral oil (blades + oil).
[2] Total weight of pyrene recovered from the experiment.
[3] Percentage recovery of pyrene from the experiment.

Table F-3 Results from Experiment 4 to Measure the Amount of Pyrene Transferred from Sand to the Oil/Water Suspension.

CONDITIONS

Original solution : 10,850 μg pyrene in 16 mL methylene chloride

Amount of pyrene lost to surface of original flask : 67.4 μg

Amount of pyrene coated on 50 g of sand : 10,782.6 μg

Weight of sand per beaker : 10 g

Volume of mineral oil used : 1 mL

Volume of water : 450 mL

Speed of agitation of beakers carrying sand and oil/water suspension : 450 rpm

Expected amount of pyrene in mineral oil, if all pyrene is transferred from the surface of sand to the mineral oil : 2,156.5 μg

DATA

Time	Measured weight of pyrene (μg)				A[1]	B[2]	C[3]
min.	Blades	Oil	Water	Sand	μg	μg	
32	58.9	257.4	467.2	1,296.3	316.3	2,079.8	96.4
100	55.6	470.2	365.7	1,284.4	525.8	2,175.9	100.9
156	40.9	611.0	354.1	1,176.5	651.9	2,182.5	101.2
240	60.3	686.9	255.6	1,153.6	747.2	2,156.4	100.0
361	81.4	809.7	303.4	954.0	891.1	2,148.5	99.6

[1] Total weight of pyrene transferred to mineral oil (blades + oil).
[2] Total weight of pyrene recovered from the experiment.
[3] Percentage recovery of pyrene from the experiment.

Table F-4 Results from Experiment 5 to Measure the Amount of Pyrene Transferred from Sand to the Oil/Water Suspension.

CONDITIONS

Original solution : 10,739 μg pyrene in 16 mL methylene chloride

Amount of pyrene lost to surface of original flask : 376.5 μg

Amount of pyrene coated on 50 g of sand : 10,362.5 μg

Weight of sand per beaker : 10 g

Volume of mineral oil used : 1 mL

Volume of water : 450 mL

Speed of agitation of beakers carrying sand and oil/water suspension : 520 rpm

Expected amount of pyrene in mineral oil, if all pyrene is transferred from the surface of sand to the mineral oil : 2,072.5 μg

DATA

Time	Measured weight of pyrene (μg)				A[1]	B[2]	C[3]
min.	Blades	Oil	Water	Sand	μg	μg	
30	33.2	525.6	378.9	1,232.4	558.8	2,170.1	104.7
90	61.6	709.8	241.5	1,109.9	771.4	2,122.8	102.4
163	48.0	832.6	221.5	1,029.9	880.6	2,132.0	102.9
240	88.3	963.2	90.7	993.9	1,051.6	2,136.2	103.1
372	64.4	1,007.2	81.5	970.2	1,071.6	2,123.3	102.5

[1] Total weight of pyrene transferred to mineral oil (blades + oil).
[2] Total weight of pyrene recovered from the experiment.
[3] Percentage recovery of pyrene from the experiment.

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