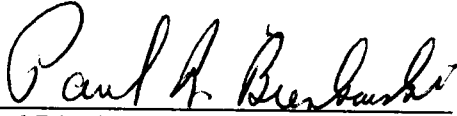
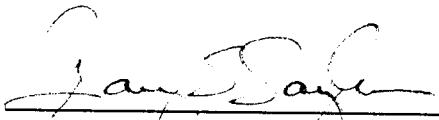
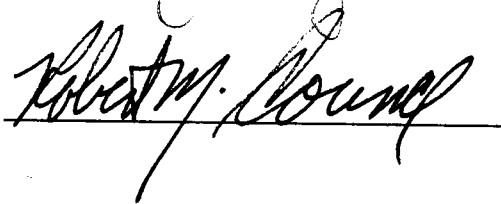


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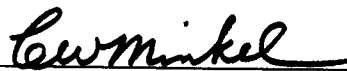
I am submitting herewith a thesis written by Justin Thomas Shingleton entitled "Thermodynamic Analysis of Supercritical CO₂ as a Fluid Phase for Naphthalene Adsorption onto Soil in a Packed Bed Column." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.


Paul Bienkowski, Major Professor

We have read this thesis
and recommend its acceptance:

Accepted for the Council:


Associate Vice Chancellor and
Dean of the Graduate School

THERMODYNAMIC ANALYSIS OF SUPERCRITICAL CO₂ AS A FLUID PHASE
FOR NAPHTHALENE ADSORPTION ONTO SOIL IN A PACKED COLUMN

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Justin Thomas Shingleton

August 1996

DEDICATION

This thesis is dedicated to my parents,

Dr. Royce Shingleton

and

Mrs. Ruth Shingleton.

ACKNOWLEDGMENTS

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ABSTRACT

A comparison of supercritical CO₂ and dichloromethane as fluid phases for the adsorption of naphthalene onto a sandy loam soil is presented. In order to compare the solvents a thermodynamic study on the naphthalene-soil-supercritical CO₂ system is necessary. The isotherms for naphthalene adsorption onto soil from the supercritical CO₂ phase are modeled using the classical Freundlich isotherm model. The equilibrium partition coefficients are also determined from experimental data and they are found to increase with temperature. The heat of adsorption of naphthalene at 308K is determined by a thermodynamic analysis in terms of standard chromatographic terminology and is in the range of weak physical adsorption for the soil used in this study.

Dichloromethane is a popular solvent for producing control contaminated soils. It readily dissolves PAHs and has a low viscosity and surface tension. However, the extent of interaction with the soil matrix is unknown. Supercritical CO₂ may be a superior solvent to create a simulated *in situ* contaminated soil based on its enhanced solvent and mass transfer properties relative to liquid solvents. An exploration of the differences in qualitative and quantitative adsorption between these two solvents is conducted. Experimental batch desorption curves are found to be similar for both control soils when dichloromethane is used as the extraction solvent. Neither supercritical CO₂ nor dichloromethane has any apparent deleterious effect on the indigenous microbial population.

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LIST OF SYMBOLS

C	fluid phase concentration	g/cm^3
C_s	saturated fluid phase concentration	g/cm^3
D_L	axial dispersion coefficient	cm^2/s
D_{AB}	molecular diffusion coefficient	cm^2/s
D_e	effective diffusion coefficient	cm^2/s
f_c	fractional organic content	g/g
G_r	ratio of bouancy to viscous forces	dimensionless
h_2^{IG}	ideal gas enthalpy of the solute in the mobile phase	cal/mol
$\bar{h}_2^{\text{m}}$	partial molar enthalpy of the solute in the mobile phase	cal/mol
ΔH_2^{ads}	change in enthalpy of the solute upon adsorption	cal/mol
$\Delta \bar{H}^{\text{trans}}$	change in enthalpy as it moves from the stationary to the mobile phase	cal/mol
k_2	capacity factor	dimensionless
K_2	partition coefficient of the solute	cm^3/g
k_c	mass transfer coefficient	cm/s
K_b	BET adsorption model constant	dimensionless
K_f	Freundlich model constant	dimensionless
K_p	partition coefficient	dimensionless
K_{oc}	organic carbon based partition coefficient	dimensionless
K_{ow}	octanol-water partition coefficient	dimensionless
m	mass of naphthalene collected in the impingers	g

m_q	mass of naphthalene adsorbed onto the soil matrix	g
n	Freundlich constant	dimensionless
L	characteristic bed length	cm
P	total system pressure	atm
P_c	critical pressure	atm
P_2^s	saturation pressure of the solute	atm
q	adsorbed phase concentration	g/g
$\bar{q}$	average adsorbed phase concentration	g/g
q_m	monolayer adsorbed phase concentration	g/g
Re	Reynolds number	dimensionless
Sh	Sherwood number	dimensionless
Sc	Schmidt number	dimensionless
T	temperature	K
T_b	boiling point temperature at 1 atm	K
T_c	critical temperature	K
T_m	melting point temperature	K
v_1	volume of CO ₂ passed through the system at ambient conditions	ml
v_2	volume of CO ₂ passed through the system at system T, P	ml
V	volume	cm ³
y_2	mole fraction solute in the supercritical phase	mol/mol
y_{exp}	experimental mole fraction of the solute in the supercritical CO ₂ phase	mol/mol
y_{lit}	literature mole fraction of the solute in the supercritical phase	mol/mol
z	length of an elemental section of packed bed	cm
Z	compressibility factor	dimensionless
ϵ	packed bed void fraction	cm ³ /cm ³

ϕ_2^f	solute fluid phase fugacity	atm
ϕ_2^s	solute saturation fugacity	atm
μ	viscosity	cP
ρ	density	g/cm^3
ρ_b	packed bed density	g/cm^3
ρ_f	fluid phase density	g/cm^3
$\Delta\rho_A$	density gradient	g/cm^3
v_2	molar volume	cm^3/mol
ω	acentric factor	dimensionless

CHAPTER 1

INTRODUCTION

1.1 PROBLEM STATEMENT

Research on the remediation of polynuclear aromatic hydrocarbons(PAHs) requires a control, or model, contaminated soil that simulates *in situ* contaminated soil.

Contaminant distribution in environmental soil is complex, and current methods for developing control soils do not accurately simulate the contaminant distribution. Control soils are necessary to conduct quantitative studies of the physical and chemical processes governing contaminant separation from a soil matrix. Knowledge of these processes is fundamental for successful remediation of PAH contaminated soil. The goal of this investigation is to explore the use of supercritical fluids as a medium to distribute PAHs uniformly over the entire soil matrix.

1.2 PAH CONTAMINATION

There are different sources of PAH contamination in the environment. Fossil fuels are a primary source of energy and are also a main source for industrial PAH production. Combustion, coal coking, and petroleum catalytic cracking are major sources of airborne PAHs contamination in the environment. The resulting airborne PAHs can cause

respiratory problems and some are known carcinogens. Transportation and processing of petroleum can result in contamination of the water environment(Pucknat, 1981). Another potential source of PAH contamination in the water environment are the former manufactured gas plant(MGPs) facilities. PAHs are found in the soil at these facilities, and contamination of a water supply is possible if the PAHs leach from the contaminated soil(Remediation Technologies, 1990).

From the 1850's to the 1950's, the manufactured gas industry produced approximately 15×10^{12} ft³ of gas for lighting and heating(Eng, R., 1985). Gas production processes varied among plant location and time. MGPs first used coal carbonization to produce synthetic gas. Most facilities phased in carburetted water gas with coke or soft coal as feedstocks. Some facilities converted to oil gas operations to produce manufactured gas. Oil feedstocks changed from light naphthas to the heavier gas oils and finally to heavy residuum. Based on 87 typical gas plants, 30% used coal carbonization, 36% used carburetted water gas, 7% used oil gas, and 15% used a combination of coal carbonization and carburetted water gas(Remediation Technologies, 1990). By the 1950's, interstate natural gas pipelines provided a cheaper and higher quality product than MGPs; therefore, during the 1950's MGPs were decommissioned in the United States of America(Mattson, 1995).

The processes, such as coal carbonization, produced 11×10^9 gal of coal tar by-product. Coal tar was mainly sold as fuel or used in other chemical processes. The by-product was either stored in underground tanks, consumed, sold, or discarded. Soil contamination at approximately 1,500 manufactured gas plant sites occurred primarily through leaking pits or tanks used for by-product storage. A generic site contains 15,000ft³ of contaminated soil.

Coal tar by-product was not considered hazardous when the plants were operating or when the plants were decommissioned. The MGP by-product and its residuals are now

considered hazardous. Table 1 lists the commonly detected PAHs according to whether they are potential carcinogens or toxins.

1.3 DESIGN OF SOIL REMEDIATION PROCESSES

Numerous remediation technologies exist. They can be classified into four main processes: thermal, desorption, biological, and chemical oxidation. According to Brown, existing technologies can achieve three levels of treatment. First, the gross reduction of high concentration contaminants alleviates immediate health threats. The second is to reduce concentrations below leachable levels and to prevent migration of contaminants. The last level of treatment involves meeting a specific standard for soil and/or groundwater contamination(Brown, 1995).

The effective use of any remediation technique is dependent upon the degree of contamination and the desired reduction in contaminant concentration. The following is a description of five remediation technologies in use or in the developmental stage(Brown, 1995):

1. Thermal desorption - Heat is used to strip coal tars from soil. Seaview has developed an innovative process to produce a low grade fuel.
2. Co-Burning - Soils with high PAH concentrations are mixed with crushed coal or wood chips. The mixture is a fuel for industrial boilers.
3. Surfactant flushing - Surfactant blends are used to desorb PAHs from soils. Initial concentrations of 3-5% can be reduced to less than .05%.
4. Surfactant assisted bioremediation - Surfactants increase the aqueous phase solubility of PAHs. The increase in substrate concentration will increase the rate of biodegradation.
5. Chemical/biological treatment - Strong oxidants, like hydrogen peroxide, are added to soils and groundwater contaminated with PAHs. The PAHs are partially oxidized and are degraded.

TABLE 1. Common PAHs at MGP sites

Potential Carcinogens	Toxins
Benzo(a)anthracene	Acenaphthene
Benzo(a)pyrene	Anthracene
Benzo(b)fluoranthene	Dibenzofurans
Benzo(g,h,i)perylene	Fluoranthrene
Benzo(k)fluoranthene	Fluorene
Chrysene	2-Methylnaphthalene
Dibenzo(a,h)anthracene	Naphthalene
Indeno(1,2,3-cd)pyrene	Phenanthrene
	Pyrene

Source: Srivastava, V.J. "Field Demonstration of MGP-REM Process: A low Cost Reliable Approach to Successful Remediation of MGP Sites," IGT Conference, Colorado Springs, CO, 1995.

PAHs present inherent difficulties in remediation design. Soil in MGP sites is often weathered, and the PAHs are strongly adsorbed deep within the soil matrix. Adsorption deep within the soil matrix can present mass transfer limitations. Microbial degradation of PAHs in an aqueous phase is limited by the solubility of the large hydrophobic molecules. PAHs are relatively non-volatile, and liquid coal tars have a low viscosity. MGP soil obtained by Remediation Technologies, Inc. from six different sites are reported to contain total PAH concentrations from 200-31,000 mg/kg. Mean naphthalene concentrations range from 11-11,000 mg/kg and represent between 5-37% of total PAHs in the samples. With the wide range in deposition amounts and composition coal tar liquids can be present as both LNAPLs(light non aqueous phase liquids) and DNAPLs(dense non aqueous phase liquids). Given the level of complexity associated with PAH contamination, the requisite goal is often not achieved with a single type of remediation technology. Some technologies will only cost effectively achieve a gross reduction in contamination. Some processes achieve low levels of contamination, but work efficiently when initial concentrations of PAHs are low(Brown, 1995).

Understanding convective mass transfer processes is essential for engineering design of remediation processes. Remediation processes inherently involve interfacial transfer with at least one fluid phase in bulk motion relative to another phase(e.g. solid-liquid and gas-liquid interfaces). For instance, the three mechanisms of mass transfer that determine solute desorption from soil into a fluid phase are: pore and/or surface diffusion from the particle's interior to the external surface, transfer across the fluid/solid interface, and diffusion due to the bulk flow of a fluid.

Adsorption/desorption equilibria and thermodynamic modeling are necessary for engineering design. Knowledge of the adsorption equilibria for the contaminant-soil system is necessary for developing a desorption model. An equilibrium adsorption isotherm model is used to determine the amount of solute on an adsorbent as a function of

the bulk fluid concentration. Once this relationship is determined it can be used in conjunction with an elemental mass balance to develop a desorption model.

According to Nakles, one area of research that needs to be pursued is the nature of the physical and chemical interactions that bind contaminants to the soil matrix (Remediation Technologies, 1995). Thermodynamic models also allow a better understanding of the physical and chemical interactions that bind PAHs to the soil matrix. Equilibrium partition coefficients can be used to determine the nature of the soil-PAH bond. The interaction between the PAH and the soil will govern the method of remediation. Soil-PAH bonds and equilibrium partition coefficients are discussed more in Chapter 2.

Adsorbed contaminant concentrations in the soil matrix are crucial variables in modeling mass transfer and thermodynamics. For example, in the case of bioremediation, microbial activity is affected by the presence of multiple substrates (Webb, 1992). Soil with known contaminant concentrations must be used to evaluate the characteristic kinetic and mass transfer properties of a system. Therefore, in order to develop a fundamental understanding of the biodegradation process the number of contaminants and the contaminant concentration must be controlled variables.

In addition to the quantitative contamination of soil, the qualitative association between a contaminant and the soil matrix is important. Desorption time is dependent upon the strength of adsorption bonds within the soil matrix and the extent of adsorption in the soil matrix. A study on the effect of aging chemicals in soils questions the effectiveness of bioremediation of sites contaminated with aged chemicals (Hatzinger, 1995). Aged chemicals are chemicals that have been adsorbed to the soil for an extended period such that strong interactions with the soil organic matter have formed. Hatzinger concludes more research is necessary to determine the effects of aging on desorption rates and the mechanisms involved. The adsorptive properties and mass transfer characteristics of a PAH-soil system must be known to successfully develop a remediation technology that

involves transport of a contaminant from the soil surface to a fluid in bulk motion.

Control, or model, soil can be prepared in the lab with known contaminant concentrations. It is often prepared by dissolving a known mass of contaminant in a liquid solvent and adding the solution to the soil. The solvent evaporates, and the contaminant remains on the soil. The method is frequently referred to as "spiking" (Reimer, 1995; Camel, 1995). Dichloromethane is a popular solvent based on its relatively low viscosity and high vapor pressure. The extent of adsorption within the soil particle is unknown for spiking methods. In addition, the residual solvent from spiking the soil may affect adsorption or desorption of the contaminant. In the case of bioremediation spiking the soil with a solvent may affect the indigenous microbial population. Degradation rates are affected by differences in soil type, moisture content, temperature, and nutrients. Discrepancies in reported rate data are also explained by uncertainties in sorption/desorption processes between the soil and the contaminant. This echoes the need for a control soil with defined contaminant distribution.

Supercritical fluids have certain properties that make them attractive extraction solvents. They have the ability to dissolve organic molecules from soil. Figure 1 shows that small changes in pressure and temperature near the critical point can control the density, or solvent power of a pure component. The density has the primary effect on the solvent power of supercritical CO₂. Figure 2 shows the solubility of naphthalene in supercritical CO₂ as a function of density. The solvent power increases with density at constant temperature and increases with temperature at constant density. In addition, solute separation is accomplished simply by flashing the CO₂. This eliminates costly solvent recovery systems. In addition, supercritical CO₂ is also cheap, non-toxic, non-reactive, and non-flammable.

Supercritical fluids also have certain properties that enhance mass transfer. They have lower viscosities (Figure 3) and higher diffusivities (Figure 4) relative to liquid

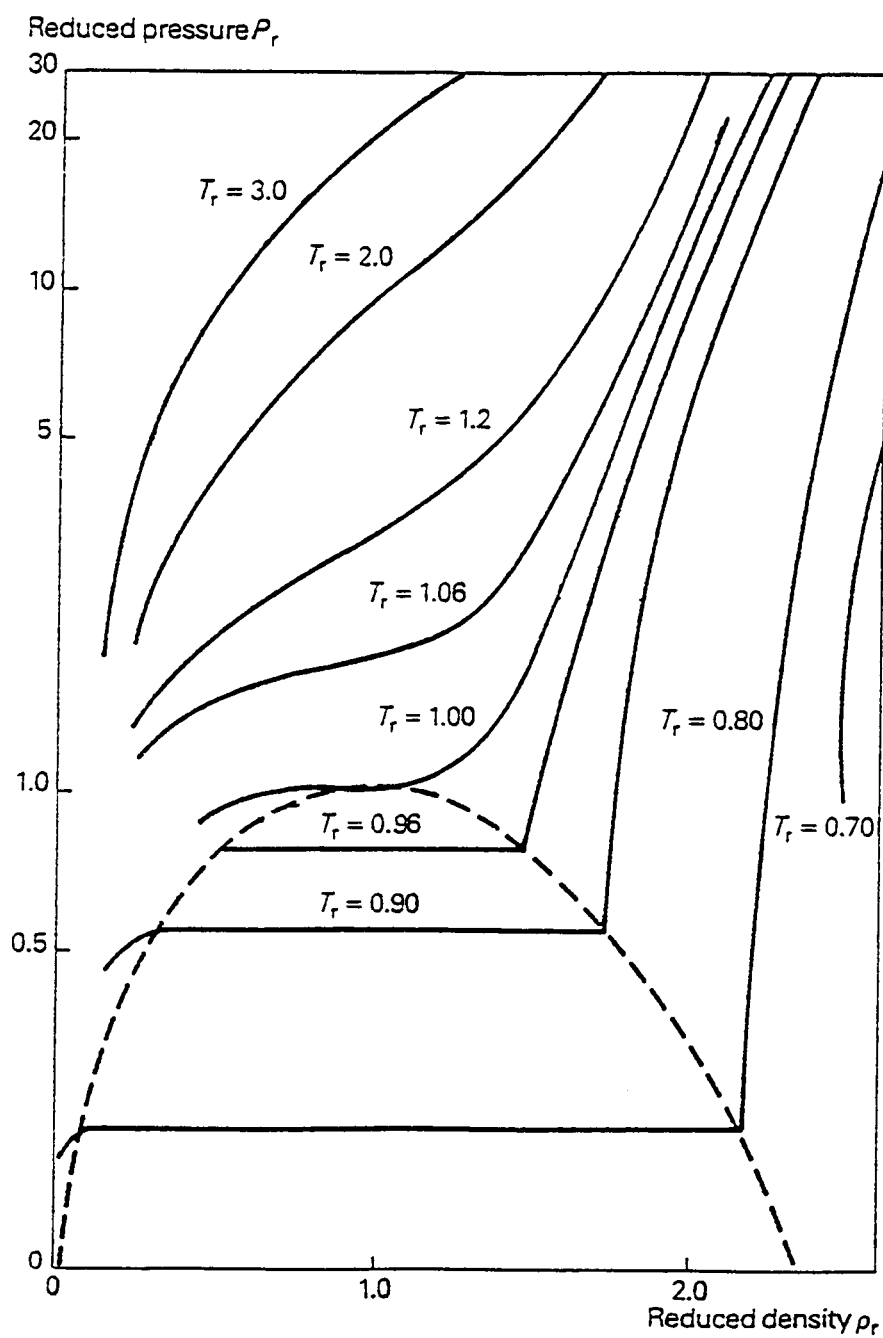


FIGURE 1. Phase Diagram of CO₂

Source: Bott, T. Reg, "Fundamentals of CO₂ in Solvent Extraction," *Chemistry and Industry*, June, 1982.

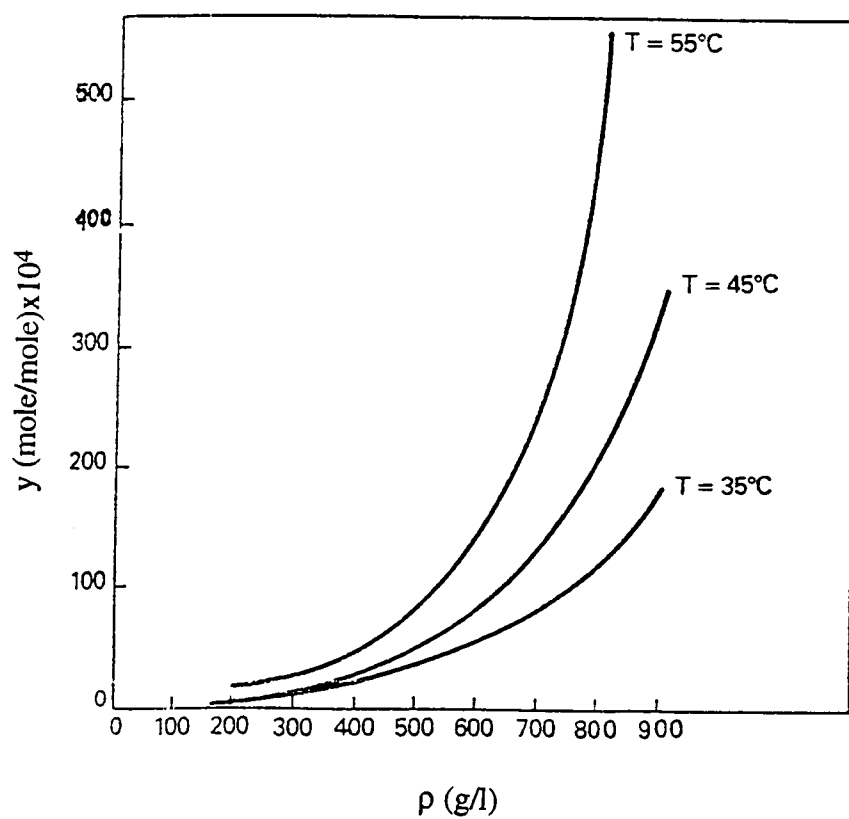


FIGURE 2. Solubility of naphthalene in CO₂ as a function of density

Source: Brogle, Heidi, "CO₂ as a solvent: its properties an applications," *Chemistry and Industry*, June, 1982.

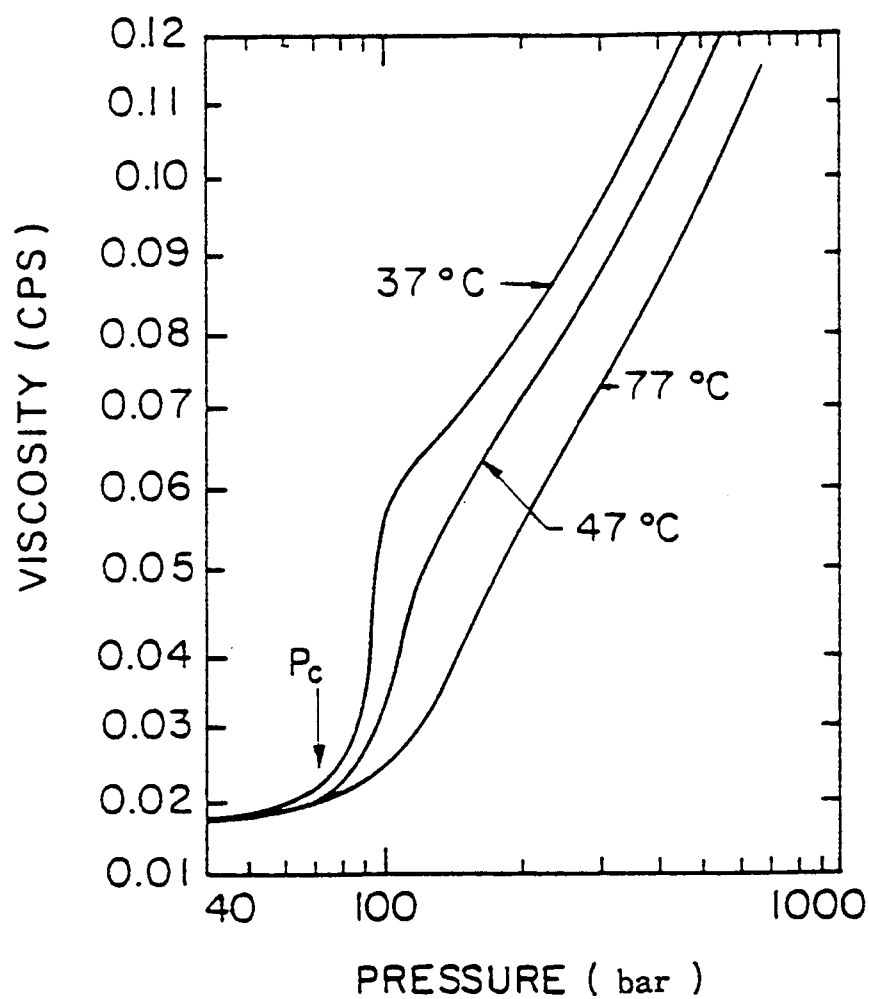


FIGURE 3. Viscosity Behavior of CO₂

Source: McHugh, Mark; Krukonis, Val, *Supercritical Fluid Extraction*, Butterworth-Heinemann, 2nd ed., 1994.

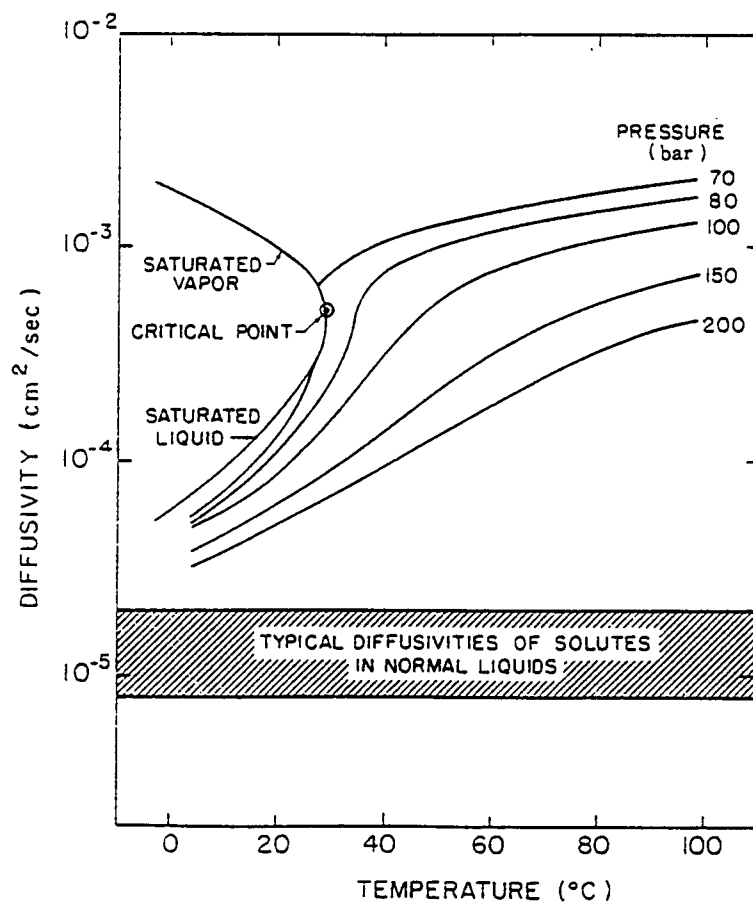


FIGURE 4. Diffusivity Behavior of CO_2

Source: McHugh, Mark; Krukonis, Val, *Supercritical Fluid Extraction*, Butterworth-Heinemann, 2nd ed., 1994.

solvents. Interfacial density gradients are significant and result in high buoyant forces that increase mass transfer rates. Low surface tension allows penetration into particle pores. Such properties can result in faster and more efficient extraction of PAHs from soil than conventional extraction methods(Reimer, 1995; Hawthorne, 1994). Table 2 compares the properties of supercritical CO₂ and liquid dichloromethane. The mass transfer properties, μ and D_{AB} , are both an order of magnitude more favorable for supercritical CO₂ than dichloromethane. The solvent property, ρ , is more favorable for dichloromethane.

TABLE 2. Properties of supercritical CO₂ and liquid dichloromethane

Solvent	$\rho(\text{g/cm}^3)$	$\mu(\text{cP})$	$D_{AB}(\text{cm}^2/\text{s})$
carbon dioxide	0.2-0.7	0.025-0.065 ^(a)	$1.0\text{-}1.4 \times 10^{-4}(\text{b})$
dichloromethane	1.3 ^(c)	0.41 ^(d)	$\sim 10^{-5}$

Sources: ^aStephan, K.;Lucas, K., *Viscosity of Dense Fluids*, Plenum Press, New York, 1979. ^bImotev, M.B.; Tsekhanskaya, Y.V., "Diffusion of Naphthalene in Compressed Ethylene and Carbon Dioxide," *Russian Journal of Physical Chemistry*, **38**(4), 1964. ^cWeast, Robert C.Ed., *CRC Handbook*, 68th ed., CRC Press, Boca Raton, 1987. ^dYaws, C.L., *Chem.Eng.*, **83**(25), p.153, 1976.

The objective of this study is to compare supercritical CO₂ and dichloromethane as solvents for naphthalene adsorption onto soil. Naphthalene is the chosen solute for these two control contaminated soils based on its abundance in MGP sites and its popularity among researchers involved in remediation technology. Naphthalene is readily soluble in supercritical CO₂, and thermodynamic models are established to predict the solubility. Three experimental studies are conducted to obtain the objective. First, modeling the soil-naphthalene-supercritical CO₂ thermodynamics in a packed bed adsorber will determine the equilibrium relationship of naphthalene between the two phases. Second, the rates of

naphthalene desorption from both types of control soils are compared. The third study involves comparing the rate of naphthalene biodegradation from the soil contaminated in supercritical CO₂ to the biodegradation rate from the soil contaminated in liquid dichloromethane. The effects of each soil preparation method on the indigenous microbial population is also investigated in the third study.

The enhanced solvent and mass transfer properties of supercritical CO₂ serve as a basis for supercritical CO₂ to be a superb solvent for model soil preparation. Theoretically, the supercritical CO₂ phase should penetrate further into the soil matrix than dichloromethane and will subsequently create a more uniform distribution of naphthalene on the soil. Therefore, naphthalene adsorption onto soil from a CO₂ supercritical phase will produce a simulated weathered soil superior to that produced by dichloromethane.

CHAPTER 2

LITERATURE REVIEW

2.1 ADSORPTION

The term "adsorption" was introduced by Kayser in 1881 to denote the condensation of gaseous molecules on a surface. Adsorption is defined as the enrichment of one or more components on an interfacial layer (Gregg, 1982). Adsorption is caused by the forces acting between a solid surface, the adsorbent, and molecules in a fluid phase, the adsorbate. The forces are either physical or chemical. Physical adsorption involves weak intermolecular forces. Chemical adsorption, or chemisorption, involves the formation of a covalent bond between the adsorbate and the adsorbent surface. Table 3 lists the general features of each type of adsorption.

Adsorption onto a solid surface is governed by intermolecular forces. The forces and energies of physical adsorption include a van der Waals force, a dispersion-repulsion interaction which is always present. Electrostatic interactions are also present and include polarization, dipole interactions, and quadrupole interactions (Ruthven, 1984). The type of forces present depend upon the solvent and solute polarity. Table 4 summarizes the intermolecular forces associated with adsorption.

Ionic forces and dipole interactions are significant in polar solvents. Aqueous solvents can deactivate polar adsorption sites if the solute is non-ionic or nonpolar. Hydrophobic and van der Waals interactions are the only mechanisms for physical PAH

TABLE 3. Distinguishing features of physical and chemical adsorption

Physical	Chemical
• Low heat of adsorption (<2 or 3 times the latent heat of evaporation) • Non specific • Monolayer or multilayer • No dissociation of adsorbed species • Significant at relatively low temperatures • Rapid, non-activated, reversible • No electron transfer although polarization of adsorbate may occur	• High heat of adsorption (>2 or 3 times the latent heat of evaporation) • Highly specific • Monolayer only • May involve dissociation • Possible over a wide range of temperature • Activated, may be slow and irreversible • Electron transfer leading to bond formation between sorbate and surface

Source: Ruthven, Douglas M., *Principles of Adsorption and Adsorption Processes*, Wiley, 1984.

TABLE 4. Intermolecular forces involved in adsorption

System	Forces	Energy (kcal/mole)
Aqueous Systems	ionic	≈20
	dipole interactions	<10
	hydrogen bonding	5-10
	hydrophobic interaction	entropic mechanism
	covalent bonds	50-100
Non-aqueous Systems	hydrogen bonding	5-10
	charge/dipole interactions	<10
	non-specific van der Waals	<5
	covalent bonds	50-100

Source: Andrews, A.T.; Ahlert, Robert C.; Kosson, David S., "Supercritical Fluid Extraction of Aromatic Contaminants from a Sandy Loam Soil," *Environmental Progress*, 9:4, 204, 1990.

adsorption in aqueous systems(Dzombak, 1984). However, ionic forces are relatively non-existent in solvents like supercritical CO₂. The interaction of PAHs with polar sites occurs through the delocalization of the π electrons on the conjugated rings(Schnitzer, 1978). This leads to hydrogen bonding interactions between the solute and the adsorption site. Silica, humic acid, and edge defects contain hydroxyl groups for hydrogen bonding. Hydroxyl groups on hydrated alumina are other possible hydrogen bonding sites.

Karikoff *et al.* studied the effect of soil organic carbon on PAH adsorption. They showed PAH adsorption increases proportionally with organic carbon content. The equilibrium correlation they proposed is:

$$K_p = f_c \cdot K_{oc} \quad (1)$$

where f_c is the weight fraction of organic content in the sediment and K_{oc} is the organic carbon-based partition coefficient. K_{oc} expresses the tendency of a chemical to be adsorbed, and is almost independent of the properties of the soil or sediment. By normalizing for soil organic content the variation in sorption coefficients among various soils and sediments is almost eliminated. The remaining variation may be due to differences in clay content, surface area, cation exchange capacity, pH, or the nature of the organic matter on the soil. Variations in laboratory procedures may also account for differences in sorption coefficients(Lyman, 1982). Published K_{oc} values for naphthalene on a variety of soils and sediments range from 455-1476(Kan, 1994). Karikoff developed a linear relationship between K_{oc} and the octanol-water partition coefficient, K_{ow} (Karikoff, 1979):

$$K_{oc} = 0.63 \cdot K_{ow} \quad (2)$$

These equations provided a means of calculating the partition coefficient based only on the solute and sorbent characteristics.

For uncharged organic compounds hydrophobic interactions dominate the partitioning between an aqueous phase and the organic content of the sorbent. The key thermodynamic property is the aqueous phase activity coefficient, a measure of the chemicals affinity for aqueous phase. Hydrophobic compounds tend to have similar affinities for a organic sorbent surfaces, so the affinity for the aqueous phase accounts for the differences in adsorptive behavior among hydrophobic compounds(Karikoff, 1984).

PAHs can also interact with soil organic matter in the presence of CO₂. Although the weight fraction of organic substances in soil is small, the surface area covered by the organic substances can be large(Robinson, 1994). Polarization of π electrons through London dispersion results in aromatic-aromatic binding. Carbon dioxide is a nonpolar solvent, so it does not compete with the interactions(Pratt, 1977). If covalent bonding to the soil organic matter occurs very high adsorption energies between 50-100 kcal/mole are possible.

Addition of polar co-solvents has significant effects on adsorption of PAHs to soil. When methanol is added to a supercritical CO₂-PAH-soil system, the amount of PAH adsorbed is less than if no co-solvent is added. Adsorption is hindered by competition for polar adsorption sites on the soil. This phenomenon highlights the importance of polar adsorption sites in PAH adsorption onto soil(Andrews, 1990).

2.2 ADSORPTION IN PACKED BEDS

The dynamic behavior of an adsorption column can be described by a differential mass balance on an element of the column and on an adsorbent particle within the element. An element of the bed is defined as the differential column section, dz , in Figure 5 (Ruthven, 1984). Assuming the axial diffusion coefficient is constant, the differential fluid phase mass balance is

$$-D_L \frac{\partial^2 C}{\partial z^2} + \frac{\partial}{\partial z}(v \cdot C) + \frac{\partial C}{\partial t} + \left(\frac{1-\epsilon}{\epsilon} \right) \frac{\partial \bar{q}}{\partial t} = 0 \quad (3)$$

Information regarding the transfer of the solute to the adsorbent is necessary for a solution of equation 3. In general the information is provided by an adsorption rate expression of the form

$$\frac{\partial \bar{q}}{\partial t} = f(q, C) \quad (4)$$

The dynamic response is determined by the solution of equations 3 and 4 with the appropriate initial and boundary conditions for the column.

Certain non-dimensional groups are associated with convective mass transfer. The equation that describes convective mass transfer can be written as

$$f(\text{Sh}, \text{Re}, \text{Sc}, \text{Gr}) = 0 \quad 5$$

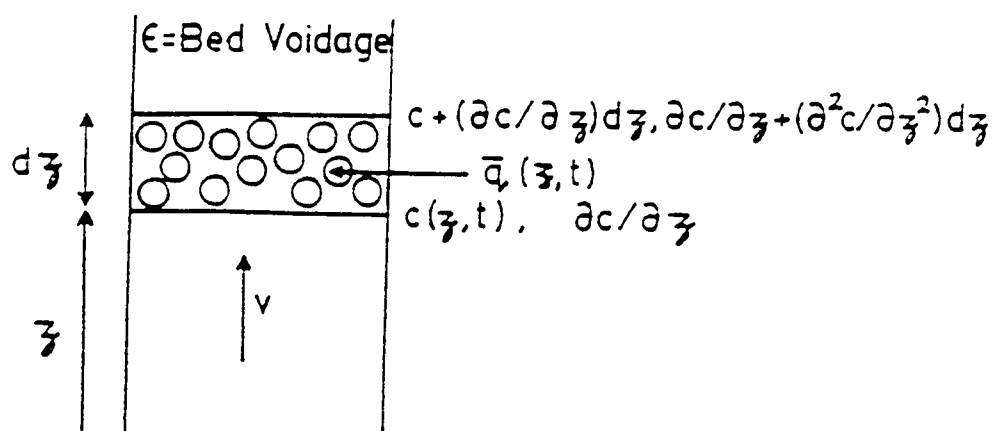


FIGURE 5. An element of a packed bed defined as the differential column section dz

Source: Ruthven, Douglas M., *Principles of Adsorption and Adsorption Processes*, Wiley, 1984.

where Sh is the Sherwood number, Re is the Reynolds number, Sc is the Schmidt number, and Gr is the Grashof number. Mass transfer rates can be estimated by developing mass transfer coefficient correlations based upon the non dimensional groups. The non-dimensional groups are listed in Table 5.

TABLE 5. Dimensionless groups for mass transfer

Group	Definition	Interpretation
Sherwood number (Sh)	$\frac{k_c \cdot L}{D_{AB}}$	Dimensionless concentration gradient
Reynolds number (Re)	$\frac{\rho \cdot v \cdot L}{\mu}$	Ratio of the inertia and viscous forces
Schmidt number (Sc)	$\frac{\mu}{\rho \cdot D_{AB}}$	Ratio of the momentum and mass diffusivities
Grashof number (Gr_{AB})	$\frac{L^3 \cdot g \cdot \Delta \rho_A}{\mu \cdot v}$	Ratio of bouancy to viscous forces

In 1945, Brunauer classified equilibrium isotherms for the adsorption of vapors into five forms as shown in Figure 6. The type I isotherm is know as the Langmuir isotherm. It is characterized by monolayer adsorption on a fixed number of adsorption sites. The heat of adsorption is the same for all sites and does not depend on the fraction of occupied sites. The type II isotherm is characteristic of multiple layer adsorption for nonporous solids. In this case the first layer of molecules adsorbed on localized sites serves as a set of sites for the second layer of adsorbent molecules, etc. The heats of adsorption for the second and subsequent layers are equal to each other and also equal to the heat of liquefaction.

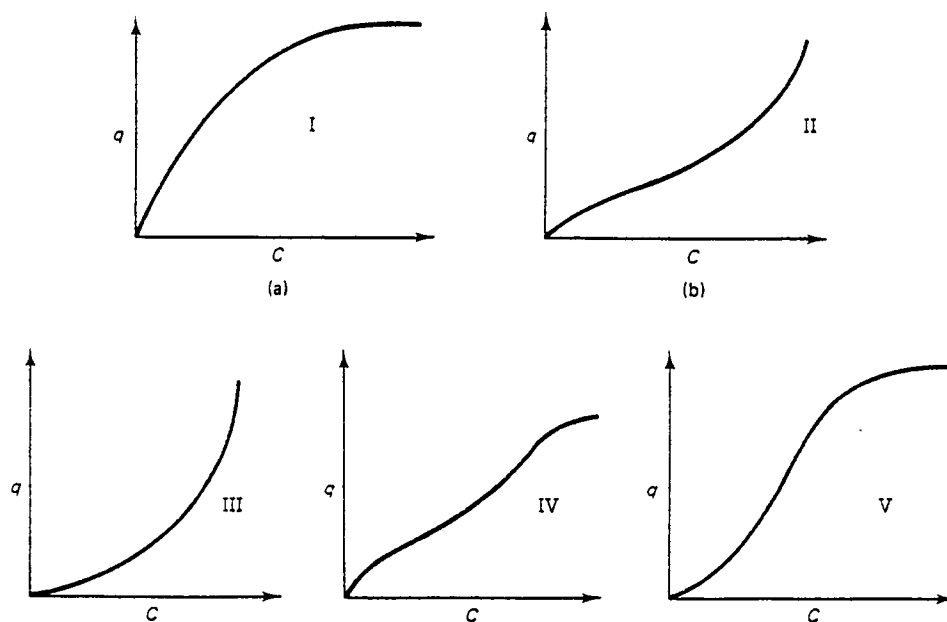


FIGURE 6. Brunauer's classification showing amount adsorbed as a function of fluid concentration

Source: Hines, Anthony L.; Maddox, Robert N., *Mass Transfer Fundamentals and Applications*, PTR Prentice Hall, New Jersey, 1985.

Type III isotherms are relatively rare, but are indicative of multiple layer adsorption. Types IV and V reflect capillary condensation since the amount adsorbed becomes constant as the saturation pressure of the adsorbant is reached. These are characteristic of porous adsorbents.

Common equilibrium isotherm models for the soil-supercritical CO₂-PAH system are the Freundlich and the Brunauer-Emmett-Teller(BET) models. The Freundlich isotherm model is a semiempirical equation used in the low to intermediate concentration range. It is expressed as

$$q = K_f \cdot C^{1/n} \quad (6)$$

where q is the mass of adsorbate per mass of adsorbent, K_f and n are constants for the adsorbent-adsorbate system, C is the equilibrium adsorbate concentration in the mobile phase. For values of $n > 1$ the Freundlich equation exhibits type I behavior and type III behavior for values of $n < 1$. For $n=1$ Henry's law behavior is obtained. Equation 6 can be written in logarithmic form

$$\log q = \log K_f + 1/n \log C \quad (7)$$

Equation 6 can be used to model equilibrium adsorption data, but no relationship to the adsorption mechanism can be made directly(Hines, 1985).

The BET isotherm is used for multilayer adsorption which is characteristic of type II isotherms. The BET equation assumes:

- adsorbed molecules are attached at definite sites
- each site can accommodate only one adsorbed molecule

- the energy of the adsorbed molecule is the same for all sites and is independent of the presence of adsorbed molecules at neighboring sites
- the first layer of adsorbed molecules serves as a set of sites for the second layer, etc.
- the heats of adsorption of the second and subsequent layers are equal and are equal to the heat of liquefaction of the gas
- the heat of adsorption of the first layer is not equal to the heat of liquefaction

The BET equation can be expressed as

$$\frac{q}{q_m} = \frac{K_b \cdot \left(\frac{C}{C_s}\right)}{\left(1 - \frac{C}{C_s}\right) \cdot \left[1 + K_b \cdot \frac{C}{C_s} - \frac{C}{C_s}\right]} \quad (8)$$

where q is the adsorbed phase concentration, q_m is the monolayer concentration, K_b is the BET adsorption model constant, C is the fluid phase concentration, and C_s is the saturation concentration in the fluid phase. Equation 8 can be written as

$$\frac{C}{C_s} = \frac{C}{q \cdot (C_s - C)} \cdot \frac{q_m \cdot K_b}{K_b - 1} - \frac{1}{K_b - 1} \quad (9)$$

From equation 9 a plot of C/C_s vs. $C/[q(C_s - C)]$ yields

$$\text{slope} = \frac{q_m \cdot K_b}{K_b - 1} \quad (10)$$

$$\text{intercept} = \frac{1}{K_b - 1} \quad (11)$$

2.3 SUPERCRITICAL FLUIDS

In 1822 Baron Cagniard de la Tour discovered the vapor-liquid transition to the supercritical state. Dr. Thomas Andrews investigated the phase behavior of carbon dioxide in the mid-1800s. At a meeting of the Royal Society of London in 1879 Hannay and Hogarth described the solubility of inorganic salts in supercritical ethanol and were the first researchers to describe the potential of a supercritical fluid to dissolve non-volatile solids(Booth, 1949). Villard studied the solubility of liquid and solid hydrocarbons in supercritical carbon dioxide, ethylene, methane, and nitrous oxide in 1896. In 1906 E.H. Buchner investigated the solubility of several organic molecules in supercritical fluids. He was the first known researcher to investigate the solubility of naphthalene in supercritical CO₂(Booth, 1949).

In 1948 Diepen and Sheffer published a study of ethylene-naphthalene phase behavior and solubility. Their paper was the first of a dozen by them and their colleagues. These publications spawned numerous other investigations into the solubility of naphthalene in supercritical fluids. From the 1960s through the 1980s at least a dozen researchers measured the solubility and phase behavior of naphthalene in supercritical fluids(Mchugh and Krukonis, 1994).

Supercritical fluid separations are potential alternatives to many conventional processes. McHugh and Krukonis summarize 107 patents issued on supercritical fluids. They discuss patents on petroleum and fossil fuel separations, coffee decaffeination, vegetable and animal material extraction, polymer processing, organic-water separation, and materials processing. Many supercritical large-scale processes, such as hop extraction, coffee decaffeination, wastewater treatment, and chemical analysis, are successful. Research into separations of polymers, pharmaceuticals, and hazardous wastes is progressing.

The properties of supercritical fluids(SCFs) are advantageous for manipulating and enhancing chemical reactions. Small changes in pressure and/or temperature can produce a large change in the density, or SCF solvent strength, as seen in Figure 1 in section 1.3. The solvent strength can be used to control rate and equilibrium constants or reactant and product concentrations(Johnston, 1989). Pressure and/or temperature can also control product selectivities. SCF reactions can be coupled with SCF separation processes for easy and highly selective separation of product. SCF provides a homogenous environment for chemical reactions. This improves transport properties and saves energy. SCFs can reduce capillary condensation and pore plugging associated with heterogeneous catalysis(Johnston, 1989).

The use of supercritical CO₂ in the analytical industry is increasing. The environmentally benign properties of CO₂ make it unique. Supercritical fluid chromatography(SFC) is being used to separate low-volatility organic compounds. In 1995 instrument manufacturers sold about \$35 million in SCF analytical devices, and sales in 1996 are expected to grow to \$40 million(Black, 1996). Supercritical CO₂ extraction is faster and more selective than conventional methods like Soxhlet extraction(Black, 1996; Reimer, 1995; Hawthorne, 1994). It can reduce extraction and recovery times by 2 orders of magnitude(Hawthorne, 1990). The EPA has approved supercritical CO₂ for the extraction of petroleum hydrocarbons(Method 3560) and PAHs(Method 3561), and the protocols are to be published in 1996(Black, 1996).

SFC is effective for determining mass transfer coefficients in fluid-solid systems at supercritical conditions. Lee and Holder have determined mass transfer coefficients using the moment analysis. They developed a generalized mass transfer correlation based on optimized fluid-solid mass transfer coefficients. According to their results mass transfer under supercritical conditions is not limiting during adsorption. Thus, assuming mass

transfer resistances are negligible is a valid assumption in predicting breakthrough curves at supercritical pressures(Lee and Holder, 1995).

Supercritical fluid extraction(SCFE) with CO₂ is an alternative to organic solvents in soil remediation. Erkey *et al.* measure the desorption profiles of naphthalene, phenanthrene, hexachlorobenzene, and pentachlorophenol from soil. Assuming a linear adsorption isotherm, negligible mass transfer resistances, and negligible axial dispersion, they present a simple model for the desorption profile. Champagne measures the desorption profile for anthracene and pyrene and develops an intraparticle diffusion model that neglects axial dispersion. Both of these models neglect axial dispersion, but Tan and Liou have found that dispersion increases with density and viscosity of the SCF, and the particle diameter of the adsorbent(Tan, 1989). In a 1989 publication Tan and Liou present a single-parameter model to describe desorption of ethyl acetate or toluene from activated carbon(Tan; Liou, 1989). Kothandaraman *et al.* use the same single parameter model to fit anthracene and pyrene desorption profiles for a sandy loam soil(Kothandaraman, 1992).

2.4 SOLUBILITY OF PAHs IN SUPERCRITICAL CO₂

Phase equilibria models for nonideal systems generally use cubic or virial equations of state, activity coefficients, or statistical mechanics to establish phase behavior. The virial equation of state does not model the dense fluid region near the critical point even when third order virial coefficients are included. The activity coefficient model requires two parameters, k_{ij} and γ_i^∞ . The partial molar volume at infinite dilution is required to estimate γ_i^∞ , the infinite dilution activity coefficient, and is difficult to obtain. The cubic equations of state model phase behavior well and require fitting parameters, k_{ij} . Examples are the

Peng-Robinson, Redlich-Kwong, or Soave models, and these models are accurate over a broad range of temperatures and pressures.

Assuming an incompressible solid phase and a saturation fugacity coefficient equal to unity, the solubility of a solute in the supercritical fluid phase is expressed as

$$y_2 = \frac{P_2^s}{P} \cdot \left\{ \frac{\phi_2^s \cdot \exp\left[\frac{v_2(P - P_2^s)}{R \cdot T}\right]}{\phi_2^f} \right\} \quad (12)$$

where y_2 is the solute mole fraction in the fluid phase, P_2^s is the saturation vapor pressure, P is the total system pressure, ϕ_2^s is the saturation fugacity of the solute, ϕ_2^f is the fugacity coefficient of the fluid phase, v_2 is the molar volume of the solute, T is the system temperature, and R is the gas constant. The exponential term is the Poynting correction factor and corrects for compressibility due to high pressures.

The fugacity coefficient, ϕ_2^f , accounts for the non-ideality of the solute in the fluid phase and is developed from an equation of state. The fugacity coefficient in terms of independent variables, V and T

$$\ln \phi_2^f = \frac{1}{R \cdot T} \int_V^\infty \left[\left(\frac{\partial P}{\partial n_2} \right)_{T, V, n_1} - \frac{R \cdot T}{V} \right] dV - R \cdot T \cdot \ln Z \quad (13)$$

where Z is the compressibility factor. The calculation of ϕ_2^f requires the evaluation of the partial derivative in equation 13 and the compressibility factor, Z . The Peng-Robinson equation of state can be used to calculate the fugacity coefficient. It is expressed as

$$P = \frac{R \cdot T}{V - b} - \frac{a}{V \cdot (V + b) + b \cdot (V - b)} \quad (14)$$

At low pressures solubility is dominated by naphthalene vapor pressure, and the solubility of naphthalene increases with temperature. Between 60 and 120atm naphthalene solubility decreases with temperature. This is known as retrograde vaporization. As the temperature increases there are two competing effects on solubility, vapor pressure and CO₂ density. Between 60 and 120atm the vapor pressure of naphthalene increases with temperature, and the density of CO₂ decreases with temperature. In this region the density effect dominates and solubility decreases with temperature. Below 60atm and above 120atm CO₂ density is relatively insensitive to temperature. In these regions the solubility increases with temperature because the vapor pressure effect dominates naphthalene solubility.

2.5 ADSORPTION IN SOIL-PAH-SUPERCRITICAL CO₂ SYSTEMS

Andrews *et al.* give BET adsorption isotherms for anthracene, perylene, triphenylene, and phenanthrene (Andrews, 1990). Erkey *et al.* model naphthalene and phenanthrene isotherms using the Freundlich isotherm model. Champagne uses the Freundlich model to fit anthracene and pyrene adsorption isotherms. Table 6 presents K and n for four PAH-soil-supercritical CO₂ systems. The properties of the soil vary between the two sources referenced.

The temperature dependence of K, the equilibrium partition coefficient, for adsorption in supercritical chromatography systems is given by the temperature derivative of the capacity factor (Kelly, 1990). Kelly proposed an approximation by assuming:

TABLE 6. Freundlich constants for selected PAHs

Solute	T (K)	K _f (cm ³ /g)	1 / n
Anthracene ^a	308	1.44	1
	318	1.49	1
	328	1.54	1
Naphthalene ^b	308	0.172	1
	318	0.458	1
	328	2.28	1
Phenanthrene ^b	308	1.24	1
	318	3.06	1
	328	16.4	1
Pyrene ^a	308	1.39	1
	318	1.43	1
	328	1.52	1

Sources: ^aChampagne, Andrew T., "The Supercritical Extraction of Anthracene and Pyrene from a Model Soil: An Equilibrium and Mass Transfer Study," Ph.D. Dissertation, University of Tennessee Knoxville, 1994. ^bErkey, Can; Madras, Giridhar; Orejuela, Mauricio; Akgerman, Aydin, "Supercritical Carbon Dioxide Extraction of Organics from Soil," *Environmental Science and Technology*, **27**, 6, 1993.

- dilute mobile phase
- constant pressure
- solute residual enthalpy is dominant in determining variations in capacity factors with temperature
- small fractional coverage on the adsorbent

The expression is approximated by

$$\left(\frac{\partial \ln k_2}{\partial T} \right)_{P, y_2} = \frac{\Delta \bar{H}^{\text{trans}}}{RT^2} + \alpha^m \quad (14)$$

where k_2 is the capacity factor for species 2, naphthalene, $\Delta \bar{H}^{\text{trans}}$ is defined as the enthalpy change per molecule of solute as it moves from the fluid phase to the stationary phase, and α^m is the volume expansivity. The relationship for α^m is

$$\alpha^m = \frac{1}{v^m} \cdot \left(\frac{\partial v^m}{\partial T} \right)_P \quad (15)$$

The capacity factor is defined as

$$k_2 = \frac{\rho_b \cdot q_2}{\varepsilon \cdot y_2 \cdot \rho_f} \quad (16)$$

Capacity factors are similar to equilibrium partition coefficients which are defined as

$$K_2 = \frac{q_2}{y_2 \cdot \rho_f} = \frac{q_2}{C_2} \quad (17)$$

The factor ρ_b/ϵ is dependent on the physical structure of the bed. Equation 14 can be written (Kelley, 1990)

$$\left(\frac{\partial \ln k_2}{\partial T}\right)_{P,y_2} = \frac{\left[h_2^{\text{IG}} - \bar{h}_2^{\text{m}}\right] + \Delta H_2^{\text{ads}}}{RT^2} + \alpha^{\text{m}} \quad (18)$$

where k_2 is the capacity factor, h_2^{IG} is the ideal gas enthalpy of the solute, $\bar{h}_2^{\text{m}}$ is the partial molar enthalpy of the solute in the fluid phase, and ΔH_2^{ads} is the heat of adsorption of the solute on the stationary phase. The $\Delta \bar{H}^{\text{trans}}$ can be determined for a particular system from the slope of a plot of $\ln K$ vs. $1/T$. Literature values for $h_2^{\text{IG}} - \bar{h}_2^{\infty}$ are given by Shim *et al.* for naphthalene and phenanthrene for a range of temperatures and pressures, or the Peng-Robinson equation of state can be used to determine $\bar{h}_2^{\infty}$. Assuming a dilute supercritical phase $\bar{h}_2^{\infty}$ may substitute for $\bar{h}_2^{\text{m}}$ when calculating ΔH_2^{ads} . Therefore, an equation to calculate ΔH_2^{ads} is

$$\Delta H_2^{\text{ads}} = \bar{h}_2^{\infty} - h_2^{\text{IG}} + \Delta \bar{H}^{\text{trans}} \quad (19)$$

CHAPTER 3

EXPERIMENTAL METHODS

3.1 EXPERIMENTAL DESIGN

Three different experiments were conducted to accomplish the objective of this study. The purpose of the first experiment is to model the thermodynamics of naphthalene adsorption onto soil from a supercritical CO_2 fluid phase. In the experiment a packed bed column is used to adsorb the naphthalene onto the soil. The isotherms for a naphthalene-saturated CO_2 feed are developed at 308K, 318K, and 328K. The pressure range is between 800 and 2000 psia. Partition coefficients are determined and used to determine the heat of adsorption of naphthalene onto soil. The heat of adsorption serves as evidence of adsorption in the packed bed. Preliminary experiments were conducted to develop a breakthrough curve for the packed bed. The breakthrough curve serves as additional evidence for adsorption.

In the second set of experiments desorption rates of naphthalene are measured. Naphthalene desorption from soil contaminated in dichloromethane is compared to naphthalene desorption from soil contaminated in supercritical CO_2 . The purpose of these experiments is to explore differences between the adsorption solvents.

Biotic experiments were conducted to determine the residual effects on the indigenous microbial population of the model soil. The growth curves for microorganisms in soil contaminated by each method were measured. Sterile soil samples from each

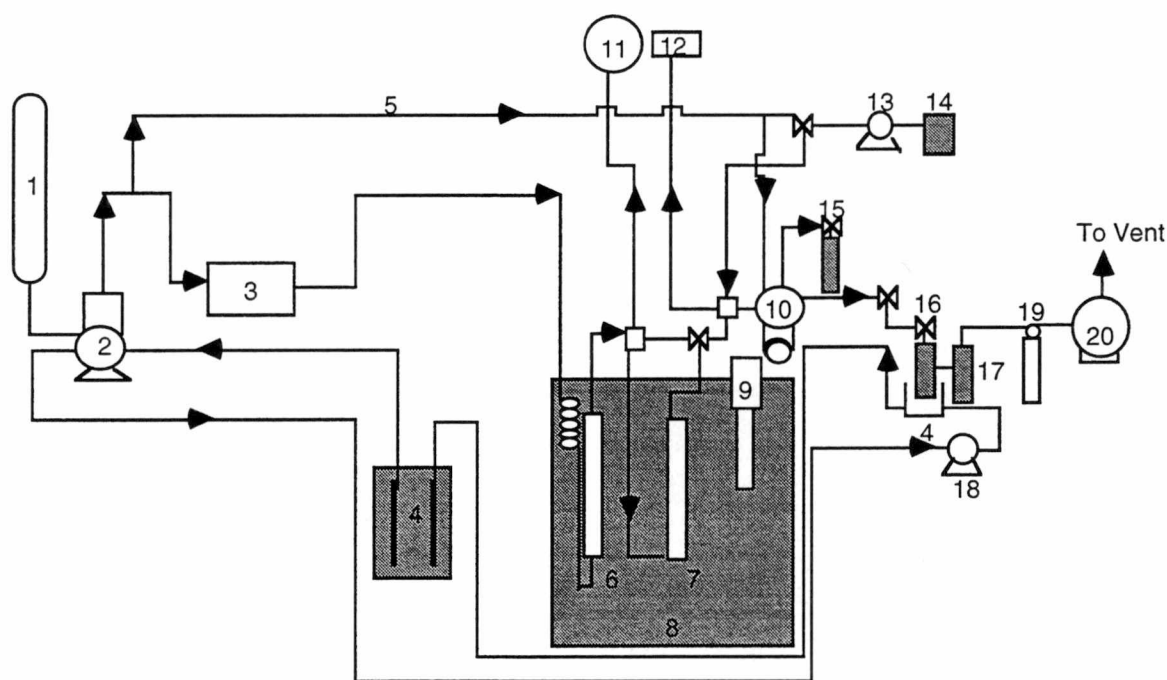
contamination method served as controls for naphthalene volatilization. Soil samples with no naphthalene contamination served as controls for naphthalene degradation.

3.2 ADSORPTION WITH SUPERCRITICAL CO₂

System Specifications and Control

The original SCF system for liquid-SCF equilibrium experiments was constructed by Kaiser(Kaiser,1988). The system was modified for solid-SCF equilibrium experiments by Ko. Further modifications were made for SCF extraction of PAHs from soil(Champagne, 1994). The current system is a rebuilt design of Champagne's system to simplify operation and control.

A schematic of the SCF system is shown in Figure 7. Liquid CO₂ flowed into a -20°C ethylene glycol bath to prevent vaporization . The LCD Analytical positive displacement pump was equipped with brass head heat exchangers to prevent vaporization and maintain pump efficiency. CO₂ was then fed through a 500cm³ surge tank to dampen pulses which may disrupt plug flow through the system. CO₂ entered a thermal equilibrium coil in the constant temperature bath. A Haake E3 Immersion Circulator provided heat for the bath with a temperature control accuracy of $\pm 0.02^{\circ}\text{C}$. The bath temperature was measured with Platinum Resistant Thermometers connected to a Keithley 135A Digital Multimeter. Next, CO₂ entered an 18 cm³ saturator packed with solute and glass wool. The glass wool prevented entrainment of solid solute and channeling of the CO₂ stream. Pressure after the saturator was measured by a Heise Bourdon Tube Gauge model CMM. A 3-way valve diverted flow of the saturated CO₂ stream into the adsorption



- | | |
|-----------------------------------|---------------------------------|
| 1. CO ₂ tank | 11. Bourdon tube pressure gauge |
| 2. Piston pump | 12. Digital pressure gauge |
| 3. Surge tank | 13. Solvent pump |
| 4. Cooling bath | 14. Solvent reservoir |
| 5. Purge line | 15. Impinger A |
| 6. Saturator | 16. Impinger B |
| 7. Packed bed adsorber | 17. Impinger C |
| 8. Water bath | 18. Pump |
| 9. Bath heater | 19. Water saturator |
| 10. Switching valve & sample loop | 20. Wet test meter |

FIGURE 7. Supercritical CO₂ system

bed. The 18cm³ adsorption bed was packed with adsorbent and enclosed by two metal frits. It was packed uniformly to maintain plug flow and reduce pressure drop effects. A Heise Digital Indicator measured the system pressure after the bed.

A cumulative sample was collected in impinger B and C by flashing the stream across a heated micrometering valve. The purpose of impinger C was to collect entrained naphthalene exiting impinger B. The continuous stream exited through a calibrated wet-test meter with an accuracy of $\pm 0.5\%$ of volume through the meter. It was used to measure the total volume of CO₂ passed through the system. Stream samples were collected in impinger A using a six port Rheodyne Model 7010 sampling valve. The sample lines were flushed with toluene using a Waters Associates Liquid Chromatography Pump to collect any residual naphthalene. Samples are analyzed by a Varian Vista Series 6000 gas chromatograph with a 3% OV-101 CWHP 80/100 packed column. The chromatographic peaks were integrated by a Hewlett Packard 3390A Reporting Integrator.

The sampling valve was located outside the constant temperature bath, so a heating tape was used to warm the lines to the proper temperature. The proper temperature range of the sampling valve was determined by the constant system temperature and the system pressure. If the system was in the region of retrograde vaporization the sampling valve temperature was maintained lower than the system temperature. Otherwise, the temperature of the sampling valve was maintained higher than the system temperature.

Adsorption Procedure

First, naphthalene and glass wool were packed in the saturator, and the mass was recorded. Then, soil was packed uniformly into the adsorption vessel, and the mass was

recorded. The average mass packed into the saturator and the adsorber was 13.0g and 25.0g, respectively. The vessels were put online and the water bath was heated to the desired operating temperature. Then, the heating tapes were allowed to reach their desired temperatures.

Once the temperatures were stable the system was pressurized by the CO₂ tank. High CO₂ velocities through the saturator and solute entrainment were prevented by pressurizing the system slowly. When the system reached 800psia the high pressure pump was activated at full displacement of the piston. When the system reached the desired operating pressure the piston displacement was decreased to about 20% of the maximum. The heated micrometering valve was adjusted and the system was allowed to reach a steady state.

Initially, the supercritical stream flowed through the saturator, but the adsorption bed was bypassed. Samples of the saturator outlet were taken until the saturator effluent was saturated. At steady state the CO₂ flow rate was in the range of 100 - 500cm³/min at ambient conditions. According to Champagne, different volumetric flow rates had no effect on the equilibrium mole fraction(Champagne, 1994).

Using a 3-way valve the flow was diverted through the adsorption bed. The effluent concentration was measured until it reached the saturation concentration. At that time the adsorption bed was saturated with naphthalene. The volume of CO₂ that passed through adsorber was recorded. The system was slowly depressurized. After the system was depressurized the soil was removed from the bed. A 2.00g sample was Soxhlet extracted to determine the concentration of naphthalene on the soil.

A mass balance on naphthalene was initially used to calculate the mass of adsorbed naphthalene. However, the mass of naphthalene adsorbed is approximately 10⁻³ less than the initial naphthalene mass in the system. Therefore, small experimental error can cause significant errors. In addition, the error associated with the gas chromatograph alone was

10%. A mass balance on naphthalene was used to show the system operated as described and the average relative error was shown in Table 10.

3.3 ADSORPTION WITH DICHLOROMETHANE

In this method, naphthalene was adsorbed onto the soil using dichloromethane as the solvent. The procedure was often referred to as "spiking"(Brady, 1987; Camel, 1995; Champagne, 1994, Hatzinger, 1995; Reimer, 1995). A known amount of naphthalene was dissolved into 25 ml of solvent. The solution was added to 25g of soil and stirred. The slurry was placed in a fume hood to allow the solvent to evaporate. The solvent evaporated in 4-6 hours. The soil was transferred to a sample vial to prevent naphthalene vaporization.

3.4 BATCH DESORPTION EXPERIMENTS

Desorption rates from contaminated soil from the supercritical and spiking methods are compared. Dichloromethane served as the extraction solvent for these experiments. Two g of contaminated soil were placed in five 20ml sample vial. Ten ml of dichloromethane were added to each vial. The vials were placed on an a shaker at 220cycles/min. One vial was removed for each time point between 1 and 30 minutes for a total of five time points.

The concentration of naphthalene in the vial was determined using a 9AM Shimadzu Gas Chromatograph with a flame ionization detector. A 30m x 0.25 μ m capillary column with a (5% phenyl)-methylpolysiloxane bonded phase was used for separation. One μ L samples were injected into the column by an AOC-17 Shimadzu Auto-Injector. The peaks

were integrated by a Shimadzu C-R3A Chromatopac Integrator.

3.5 BIOTIC COMPARISON

For the first biotic experiment, an 18cm³ vessel was used to contaminate the soil with supercritical CO₂. The temperature was 308K, and the pressure was 1250psia for the supercritical case. The concentration of naphthalene on the soil after adsorption was approximately 5,000ppm. Since the 18cm³ adsorption cell can hold approximately 25g of soil, two batches of soil were contaminated and mixed. For the second and third experiments a 300cm³ vessel was used to contaminate the 36g of soil in one batch.

For all the dichloromethane samples, naphthalene was added to 25ml of dichloromethane. The solution was then added to the soil in a 500ml beaker and allowed to evaporate. The beaker was in a fume hood at ambient conditions with air flow of approximately 100fpm. Once the dichloromethane evaporated, the soil was placed in a sealed container to prevent vaporization of the naphthalene.

Control samples were also prepared for the second and third experiments. Sterile soil served as a control for naphthalene volatilization by eliminating any degradation by indigenous bacteria. The saturator, adsorption cell, and beakers were sterilized to prevent contamination. For each solvent type, 12g of sterile soil was contaminated. A second control, using original soil, was not contaminated. This control was used to determine the effects of naphthalene on the indigenous microbial population.

For each contamination method, triplicate 2g samples were placed in 20ml amber sample vials. For the control samples, a 2g sample was placed in a 20ml amber vial. This procedure was done for 6 time points. The 54 vials were placed in a box in a 298K incubator.

At each time point, the vials were taken from the incubator. One ml samples of each vial were added to 9ml of .01% sodium pyrophosphate buffer solution. Subsequent 1:10 dilutions were made to create a dilution series. Then, 100 μ l of the solution was pipetted onto a plate containing YEPG media with 50mg cycloheximide/l. The plates were placed in the 298K incubator. After three days the total colony forming units were counted(Sayler, 1979).

After the 1ml samples were taken from the vials, the vials were placed in a freezer. The samples were frozen to cease any biotic activity. The samples were then Soxhlet extracted with dichloromethane for 18 hours to remove the remaining naphthalene. The dichloromethane solution was analyzed using a 9AM Shimadzu Gas Chromatograph with a flame ionization detector. A 30m x 0.25 μ m capillary column with a (5% phenyl)-methylpolysiloxane bonded phase was used for separation. One μ L samples were injected into the column by an AOC-17 SHimadzu Auto-Injector. The peaks were integrated by a Shimadzu C-R3A Chromatopac Integrator.

3.6 PARAMETERS AND PROPERTIES

The density of the supercritical CO₂ phase was determined using a FORTRAN program written by Champagne. He used the Peng-Robinson equation of state to calculate the compressibility factor(Champagne, 1994). The solubility of naphthalene in supercritical CO₂ was calculated using the Peng-Robinson equation of state. The binary interaction parameter, k_{ij} , is used as fitting parameter to fit the equation of state to the literature data. The parameter is obtained by minimizing the average absolute deviation(AAD) between the calculated mole fractions and the literature data. The equation for AAD is

$$AAD = \frac{1}{N} \cdot \sum_{i=1}^N \frac{|y_{lit} - y_{exp}|}{y_{lit}} \quad (1)$$

where y_{lit} is the literature mole fraction, y_{calc} is the mole fraction calculated using the Peng-Robinson equation, and N is the number of mole fractions used to fit the data. The program is given in Appendix B.

The Peng-Robinson equation of state requires certain physical properties of the solvent and any dissolved molecules. The parameters for the present system are in Table 7. The solubility calculations require a value for P_2^s . A vapor pressure correlation for naphthalene was used

$$\log P_2^s(\text{Pa}) = A - B / (T - C) \quad (2)$$

where $A = 13.575$, $B = 3729.3$, $C = 0.0$, and T in K^{-1} (Ambrose, 1975).

Soil for all experiments is a loamy agricultural soil. The properties of the soil were determined by Dr. Mike Essington at the University of Tennessee, Knoxville. The soil is course sieved through 1/4 inch mesh, and air dried. Sayler *et al.* show low background levels of a Nah A containing microorganism (Sayler, 1996). Table 8 summarizes the characteristics of the packed bed and soil.

TABLE 7. Physical properties for carbon dioxide and naphthalene

Compound	MW	T _c ^a	P _c ^a	T _b ^b	T _m ^b	ω ^a	v ^a
	(g/mole)	(K)	(bar)	(K)	(K)		(cm ³ /mole)
carbon dioxide	44.01	304.2	73.8	-78.6	-56.6	0.239	----
naphthalene	128.2	748.4	40.5	217.8	80.0	0.302	111.9

Sources: ^aWhite, Gary L.; Lira, Carl T. "Multiphase Behavior of Carbon-Dioxide with Solid Aromatics," *Fluid Phase Equilibria*, **78**, p.269-284, 1992. ^bFelder, Richard M.; Rousseau, Ronald M. *Elementary Principles of Chemical Processes*, 2nd ed., John Wiley and Sons, New York, 1986.

TABLE 8. Properties of the packed bed and soil

bed length, cm	15.0
bed diameter, cm	1.25
bed void fraction, ε	0.5
average particle diameter, cm	0.03
water capacity, g/g	0.3
total organic carbon, g/g	0.0129
total sand	41.74%
total clay	18.15%
total silts	40.10%
cation exchange coefficient, cmol/kg	9.96

CHAPTER 4

RESULTS AND DISCUSSION

4.1 ADSORPTION ISOTHERMS

Equilibria data is given to show the supercritical CO₂ apparatus is capable of obtaining reliable data. Experimental solubility isotherms at 308, 318, and 328K are shown in Figures 8-10. The experimental values are compared to literature values from Tsekhanskaya(Tsekhanskaya, 1964). The Peng-Robinson equation of state is also used as a comparison by predicting the solubility of naphthalene in CO₂. The thermodynamics of calculating solid solubilities in supercritical fluids are discussed in section 2.4. The computer code is written in Matlab® and is given in Appendix B. The experimental data shown agrees with both the literature data and the equation of state model.

The solubility of naphthalene in supercritical CO₂ as a function of density at constant temperature is shown in Figure 11. This graph shows an increase in solubility with an increase in temperature at constant density. Also, the solubility increases as the density increases at constant density. The general trends are similar to Figure 2 in section 1.3. Champagne shows the equilibrium mole fraction is independent of the superficial velocity through the packed soil bed(Champagne, 1994). Given the agreement between the literature data, thermodynamic model, and the experimental data, the equilibrium adsorption isotherms can be determined with the experimental apparatus and sampling procedure.

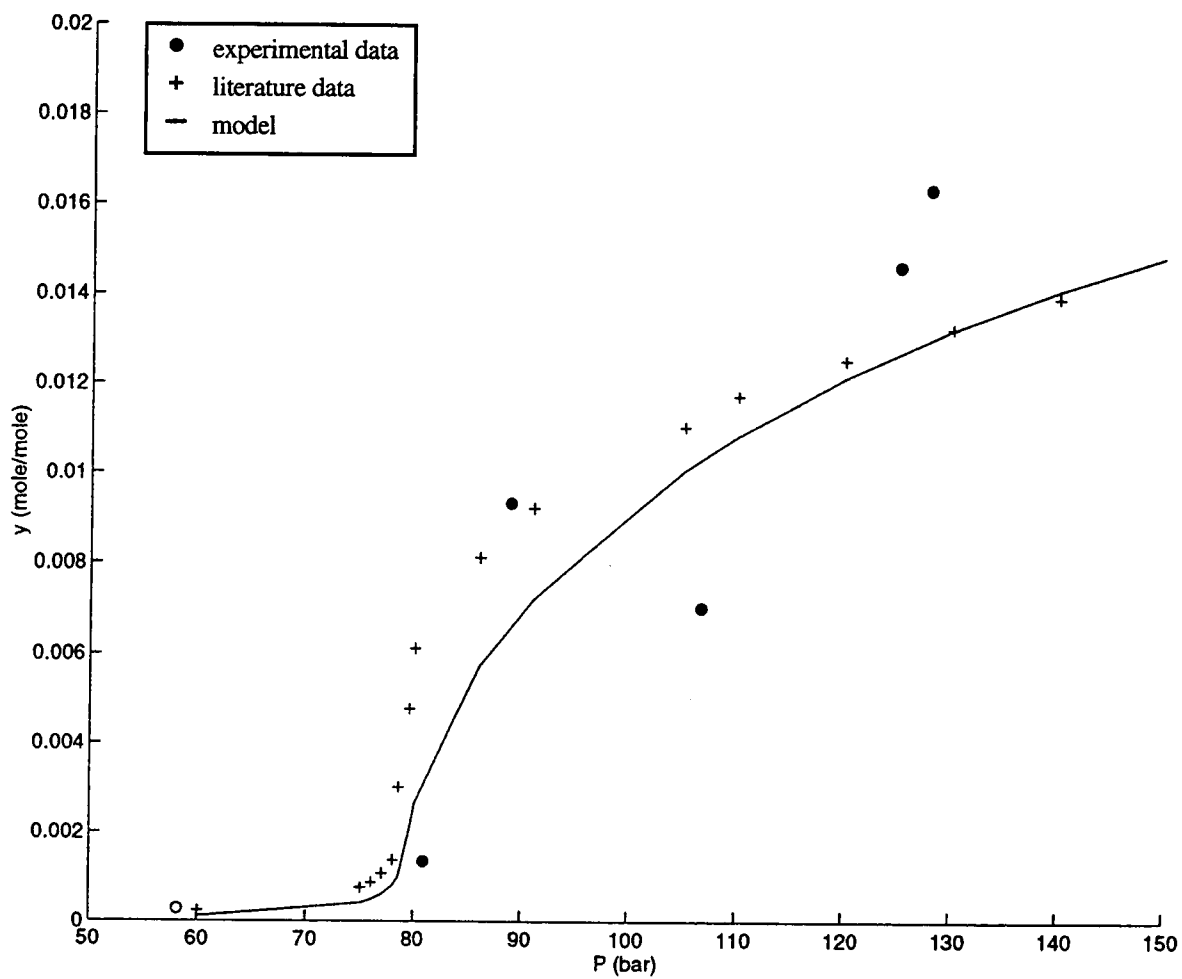


FIGURE 8. Solubility of naphthalene in supercritical CO₂ at 308K

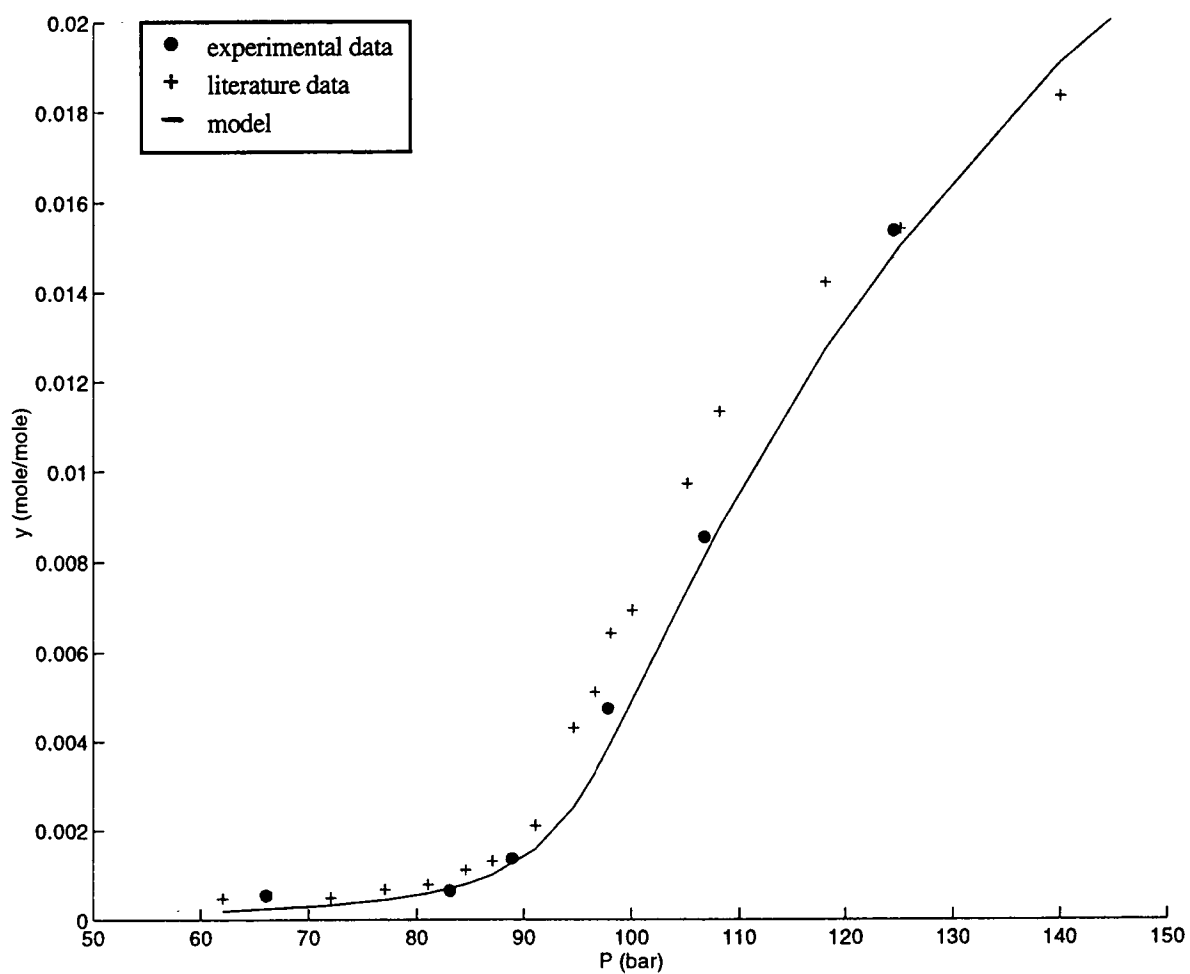


FIGURE 9. Solubility of naphthalene in supercritical CO₂ at 318K

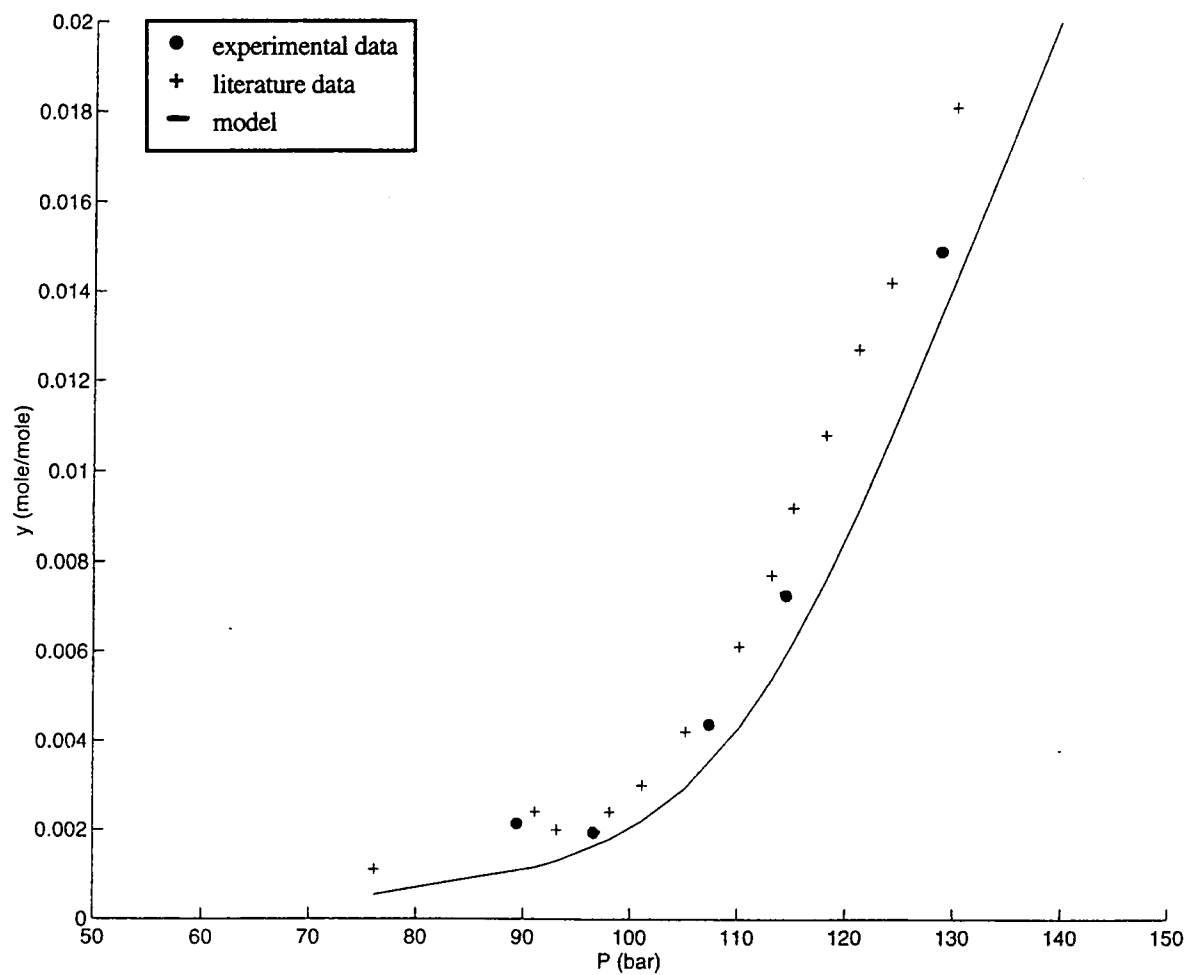


FIGURE 10. Solubility of naphthalene in supercritical CO₂ at 328K

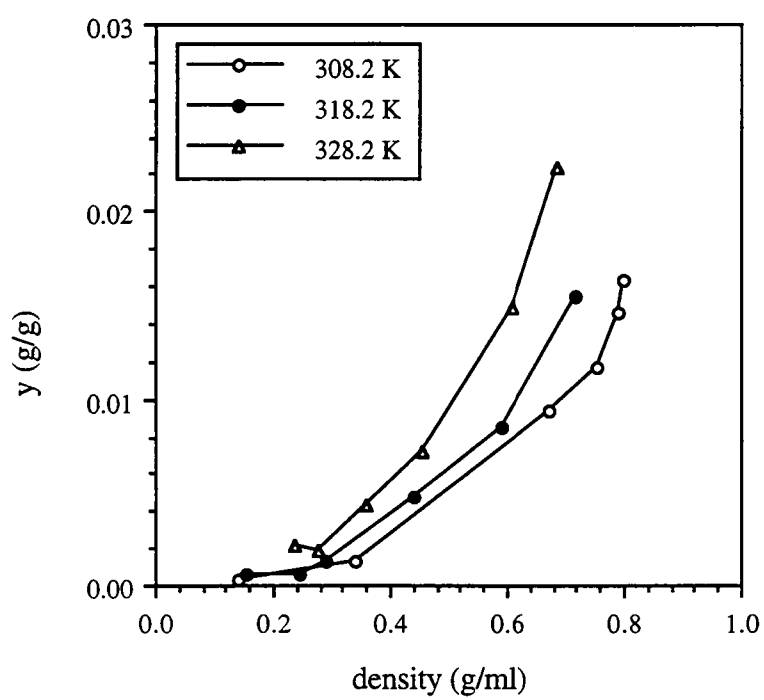


FIGURE 11. Solubility isotherms for naphthalene in supercritical CO₂ as a function of density

A knowledge of equilibrium between the two phases must be known in order to model mass transfer processes. The rate of naphthalene extraction from soil is dependent upon the mass transfer resistance across the phase boundary, and the resistance is associated with the local concentration difference between the soil particle surface and the bulk supercritical CO₂ phase. An equilibrium isotherm describes the local equilibrium at an interface. The local equilibrium between the surface of the soil particle and the bulk supercritical CO₂ phase is described by an equilibrium isotherm.

Figure 12 shows the equilibrium isotherms for naphthalene in the soil-supercritical CO₂ system. The Freundlich isotherm is used to describe equilibrium for the system, and the constants are given in Table 9. The constants were determined by plotting the data to the following equation

$$\log q = \log K_f + 1/n \log C \quad (1)$$

The data is non-linear, and the exponential constant ranges from 0.31 for 308.2K to 0.59 for 328.2K. K_f increases with temperature indicating that the fraction of the adsorbed phase increases with temperature at constant supercritical CO₂ concentration. That is, uptake by the soil increases with temperature. Table 10 gives the average error in naphthalene mass balances for each temperature. The error ranges from 3-14%.

Experimental isotherms obtained by Erkey *et al.* for a naphthalene-soil-supercritical CO₂ system are linear in nature. The data given in Table 9 are for a supercritical CO₂ saturated with naphthalene. Erkey's data is for unsaturated conditions and is the type of information needed for supercritical desorption experiments at constant temperature and pressure. Assuming the unsaturated isotherms are linear over a range of pressures, temperatures, and soil types the data used in Table 9 can be used to determine the unsaturated isotherms at a given temperature and pressure by the slope of the saturated

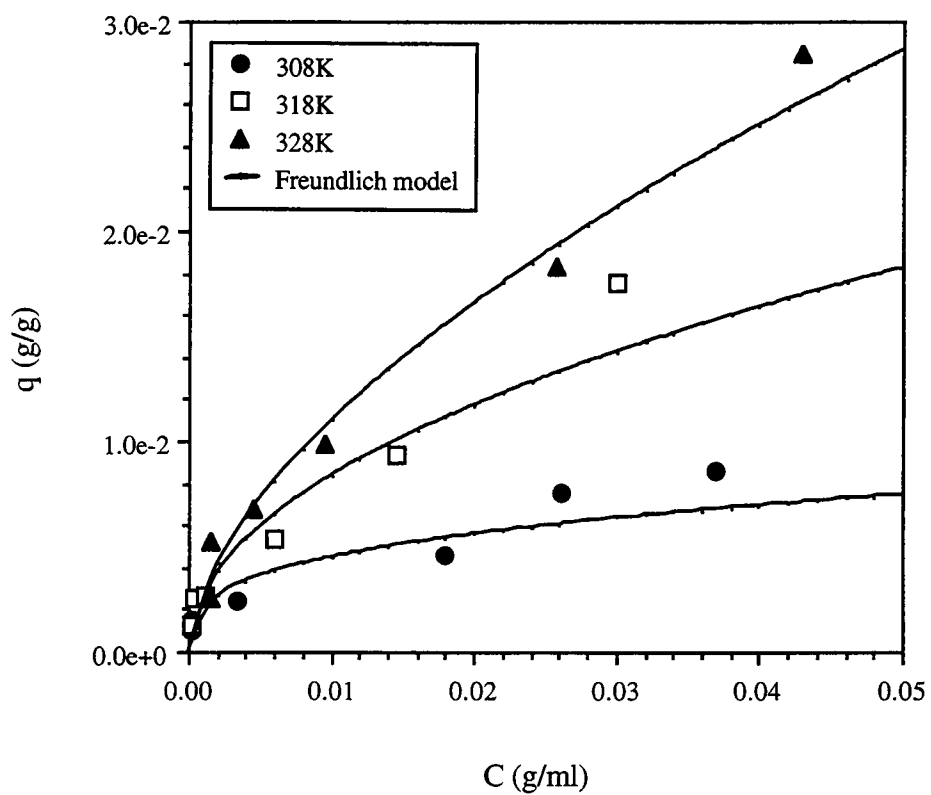


FIGURE 12. Adsorption isotherms for the naphthalene-soil-supercritical CO₂ system

TABLE 9. Freundlich isotherm constants

T(K)	K_f	1/n
308.2	0.019	0.31
318.2	0.078	0.48
328.2	0.17	0.59

TABLE 10. Average relative error in naphthalene mass balances

T(K)	% error
308.2	14.4
318.2	11.5
328.2	3.0

isotherm at a given temperature and pressure. That is, the slope of the saturated isotherm for a given T and C_s can be taken as the slope of a linear unsaturated isotherm for the same operating conditions.

The experimental partition coefficients as a function of pressure are shown in Figure 13. The general trend of the graph is for the partition coefficient, K_2 , to increase with temperature at constant pressure. This is anomalous to the expected behavior of decreasing partition coefficient with increasing temperature. Figure 14 is a plot of $\ln K_2$ vs. $1/T$. According to equation 14 in section 2.5 the slope of the line is equal to $-\Delta H^{\text{trans}} / R$. The ΔH^{ads} can be determined by equation 19. For this system the $\Delta H^{\text{ad}} = -2.6$ kcal/mole. Erkey et al give $\Delta H^{\text{ad}} = -1.42$ kcal / mole for their particular naphthalene-soil-supercritical CO_2 system(Erkey, 1993). Table 11 lists the values for four PAHs. These values for the heat of adsorption at constant pressure are indicative of weak physical adsorption.

The increasing uptake by the soil with temperature as shown in Figure 13 is explained by a supercritical fluid chromatography(SFC) analysis by Kelly *et al.* He presents this relationship as the condition for retrograde solubility behavior

$$h_2^{\text{IG}} - \bar{h}_2^{\text{m}} > \Delta H_2^{\text{ads}} \quad (2)$$

The sign of equation 2 determines how equilibrium partition coefficients change with temperature. When the equation is satisfied, K, or the uptake by the soil, will increase with temperature. In the compressible retrograde region equation 2 is always satisfied(Kelly, 1990).

Evidence of adsorption is shown in Figures 15-17. The equilibrium mole fraction of naphthalene in supercritical CO_2 phase at constant temperature is shown as a function of pressure. If adsorption did not occur the naphthalene-soil-supercritical CO_2 isotherm would emulate the pure naphthalene-supercritical CO_2 isotherm also shown. The

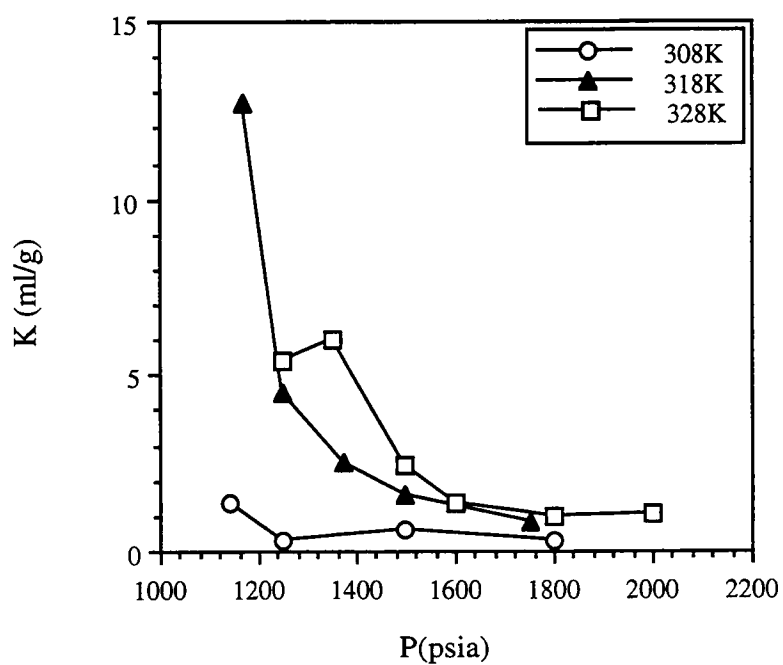


FIGURE 13. Experimental partition coefficients as a function of system pressure at constant temperature

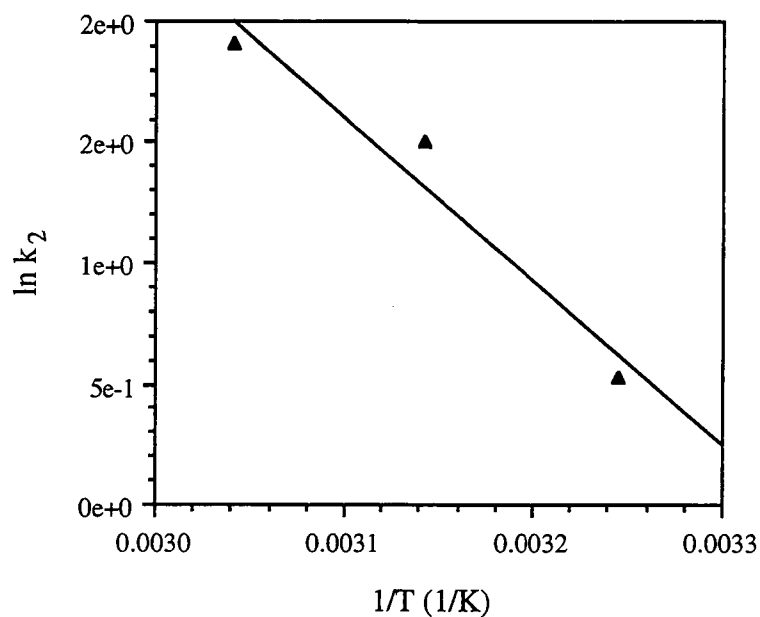


FIGURE 14. The $\ln(k_2)$ as a function of T^{-1} to determine ΔH_2^{ads}

TABLE 11. Heats of adsorption at 308K

Solute	$\bar{h}_2^\infty - h_2^{\text{IG}}$ (kcal/mol)	$\Delta \bar{H}^{\text{trans}}$ (kcal/mol)	ΔH_2^{ads} (kcal/mol)
naphthalene ^a	-16.12	13.5	-2.6
naphthalene ^b	-16.12	14.8	-1.42
phenanthrene ^b	-19.74	14.8	-4.94
hexachlorobenzene ^b	-13.12	8.96	-4.16
pentachlorophenol ^b	-13.12	10.38	-3.74

Sources: ^aThis work. ^bErkey, Can; Madras, Giridhar; Orejuela, Mauricio; Akgerman, Aydin, "Supercritical Carbon Dioxide Extraction of Organics from Soil," *Environmental Science and Technology*, **27**, 6, 1993

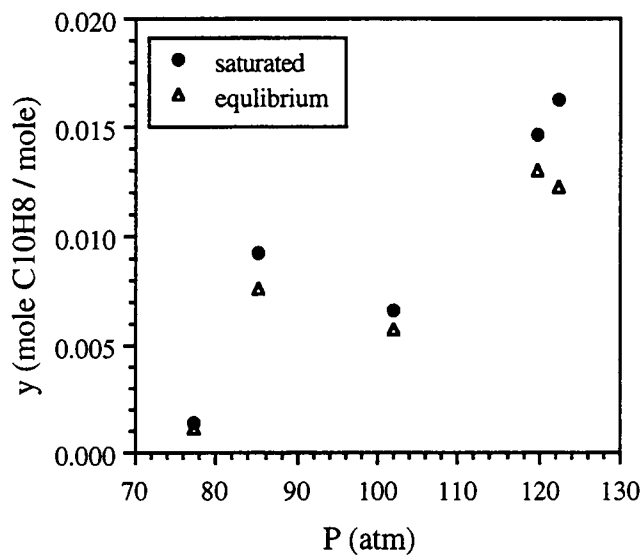


FIGURE 15. Equilibrium mole fraction of naphthalene in the supercritical CO₂ phase compared to the saturated mole fraction of naphthalene in supercritical CO₂ at 308K

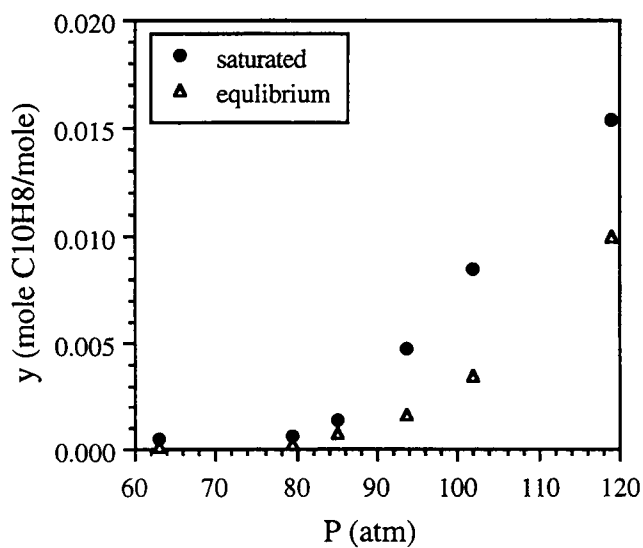


FIGURE 16. Equilibrium mole fraction of naphthalene in the supercritical CO₂ phase compared to the saturated mole fraction of naphthalene in supercritical CO₂ at 318K

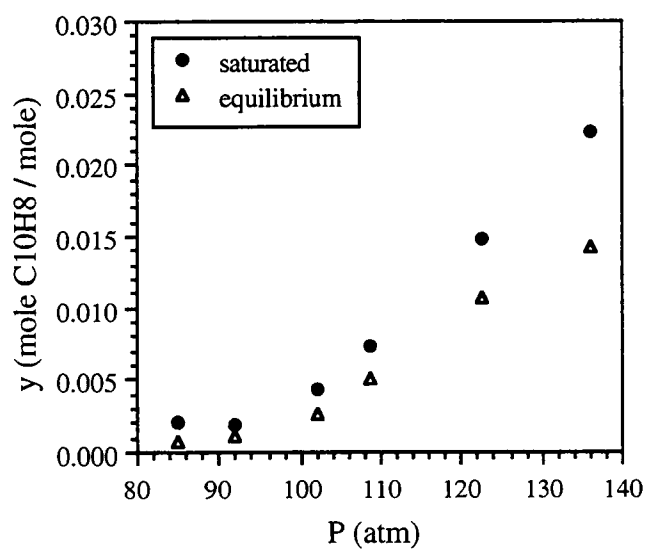


FIGURE 17. Equilibrium mole fraction of naphthalene in the supercritical CO₂ phase compared to the saturated mole fraction of naphthalene in supercritical CO₂ at 328K

difference between the two isotherms on a given plot increases as the pressure increases at constant temperature. The increased difference is explained by an increase in the fraction of total naphthalene that is adsorbed to the soil and is reflected by the positive slope of the adsorption isotherms.

Figure 18 is an experimental breakthrough curve for the supercritical system at 1250psia, and 308K. The breakthrough curve shows the effluent concentration, C , of the packed bed approaches the feed concentration, C_0 , in 30-40min. The experimental data points reflect a typical breakthrough profile for a packed bed adsorber. Figure 18 serves as evidence that adsorption is occurring in the packed bed.

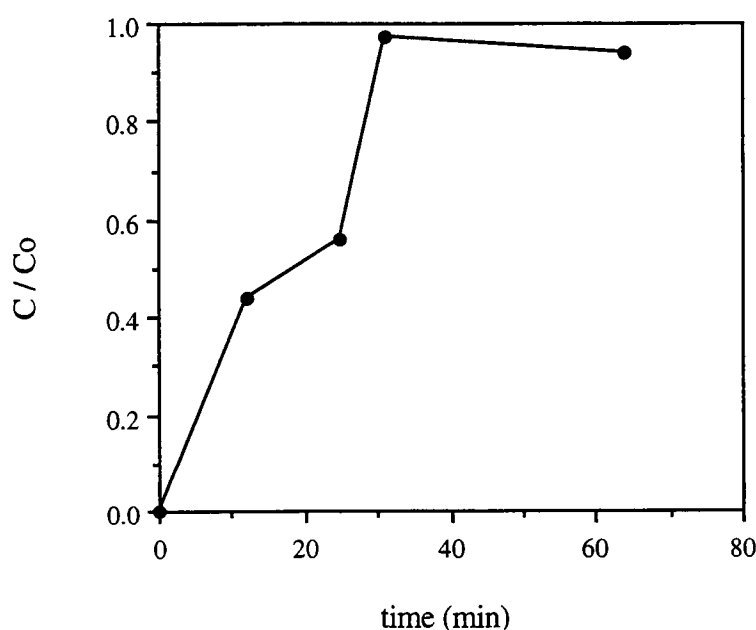


FIGURE 18. Experimental breakthrough for naphthalene at 1250psia and 308K

4.2 DESORPTION RESULTS

The results of batch desorption experiments are shown in Figures 19-20. Figure 19 shows the desorption curves for naphthalene from a soil contaminated using supercritical CO₂ as the solvent. Figure 20 shows the desorption curves for naphthalene from a soil using dichloromethane as the solvent. The initial desorption rates given by the slope of the curves is approximately equal for both solvents used in the contamination method. Equilibrium is approached in approximately 30 minutes for both cases. Both figures show a fast desorption rate for the first minute. After the first minute the rate decreases for both cases and seems to be independent of soil concentration.

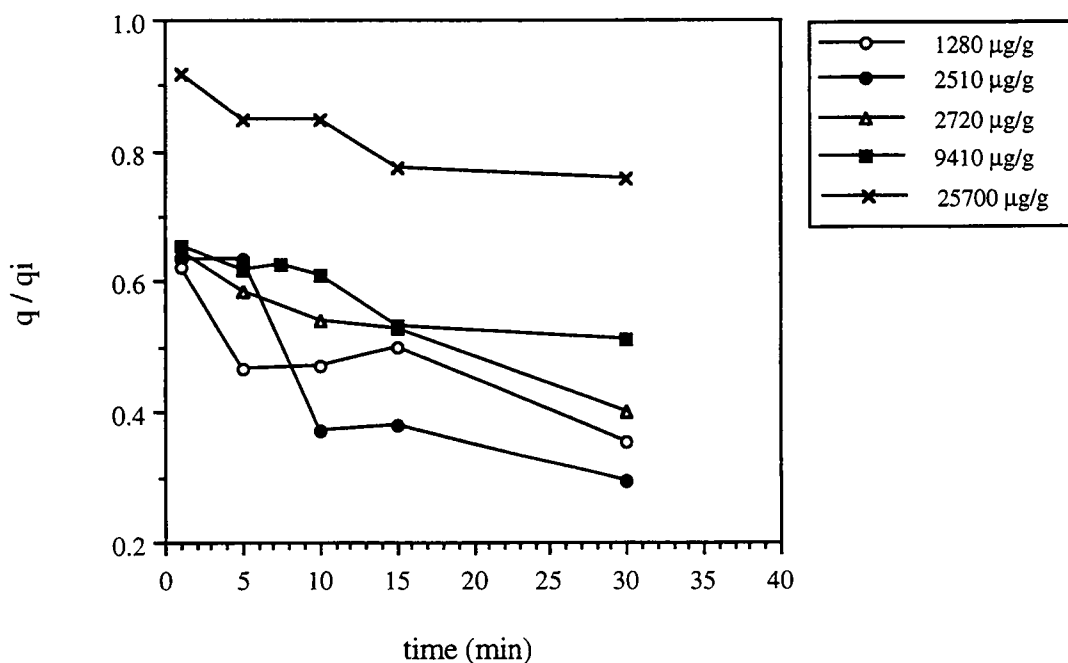


FIGURE 19. Desorption of naphthalene from soil contaminated in supercritical CO₂

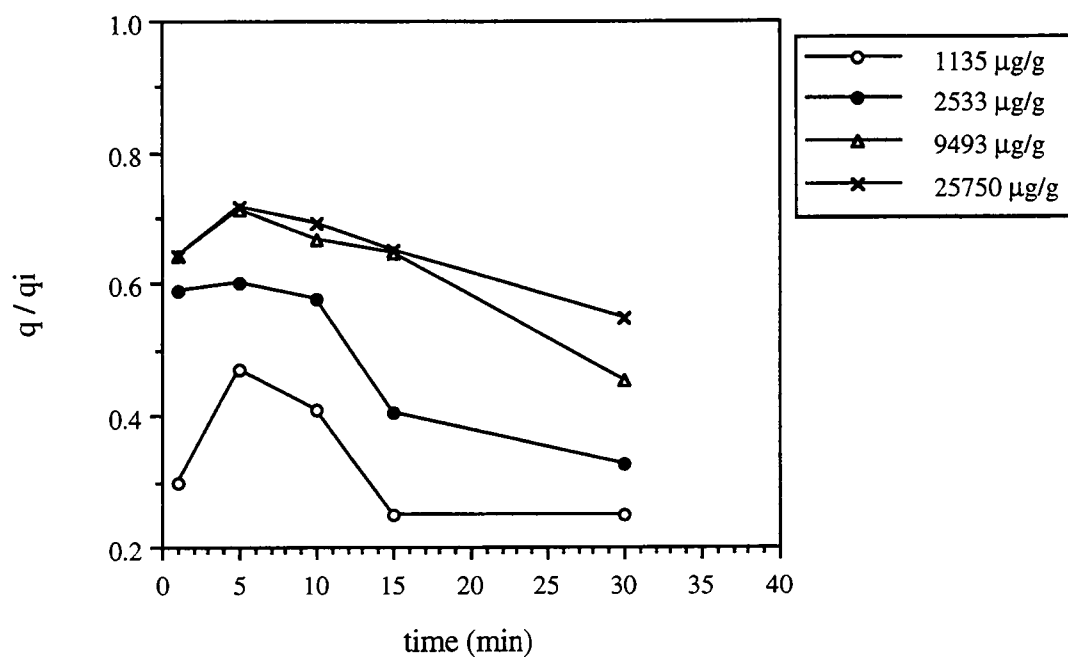


FIGURE 20. Desorption of naphthalene from soil contaminated in dichloromethane

4.3 BIOTIC RESULTS

Three biotic experiments were conducted to determine the effects of each solvent on the indigenous microbial population. The experimental procedures were the same as given in section 3.5, but the initial concentrations on each type of soil differed. Table 12 gives the initial naphthalene concentrations for each experiment.

TABLE 12. Initial naphthalene concentration in the batch solution

Experiment	Solvent	$C_o \times 10^3$ (g/ml)
1	CH ₂ Cl ₂	0.70
	CO ₂	1.7
2	CH ₂ Cl ₂	2.0
	CO ₂	4.6
3	CH ₂ Cl ₂	2.1
	CO ₂	4.3

Figures 21-23 show the growth curves for the three biotic experiments. Trends are evident in the growth curves shown in Figures 21-23. First, neither solvent destroys the indigenous microbial population on the soil. The high pressure CO₂ does not lyse the cells, and the dichloromethane does not dissolve cell membranes. Second, exponential growth is observed in the first 5-10 days. The growth curves in Figure 24 for the control soil with no naphthalene are the same order of magnitude as the contaminated soils. Therefore, naphthalene can not be considered to be the principle substrate for indigenous cell growth.

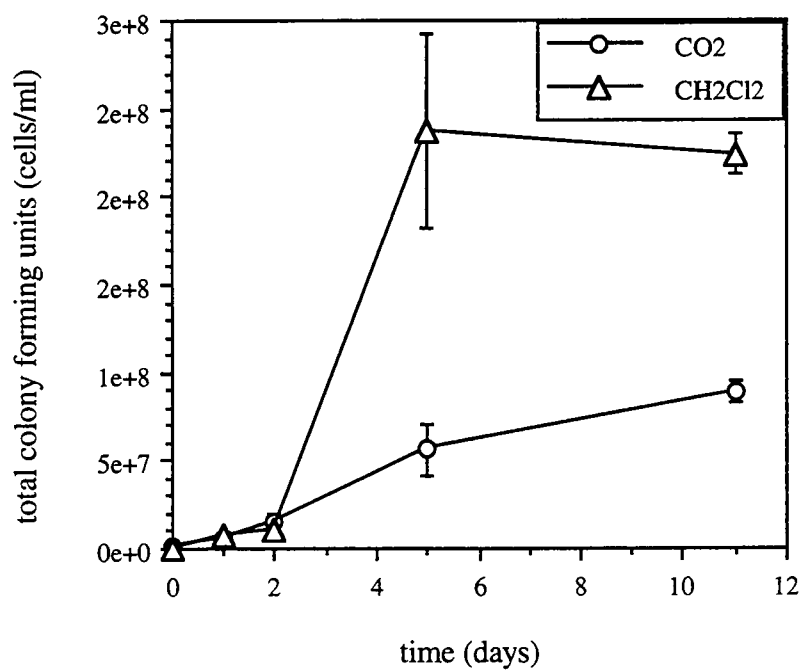


FIGURE 21. Persistence of the indigenous microbial population in a sandy loam soil contaminated with naphthalene in either supercritical CO₂ or dichloromethane for experiment #1

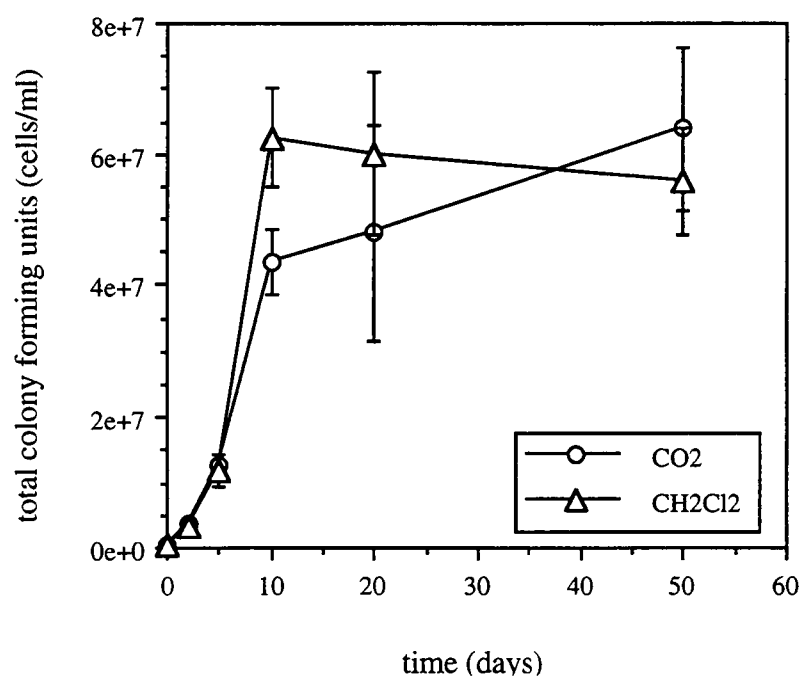


FIGURE 22. Persistence of the indigenous microbial population in a sandy loam soil contaminated with naphthalene in either supercritical CO₂ or dichloromethane for experiment #2

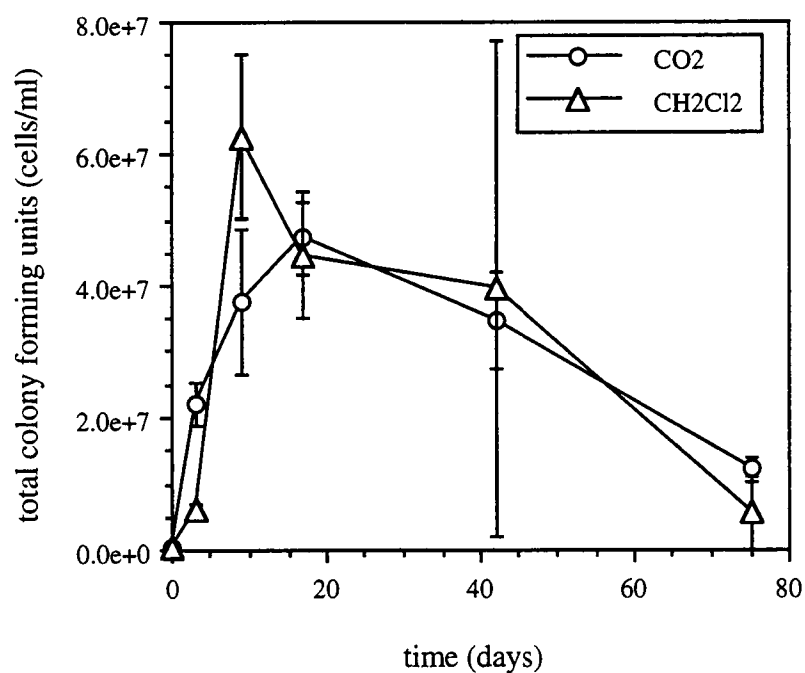


FIGURE 23. Persistence of the indigenous microbial population in a sandy loam soil contaminated with naphthalene in either supercritical CO₂ or dichloromethane for experiment #3

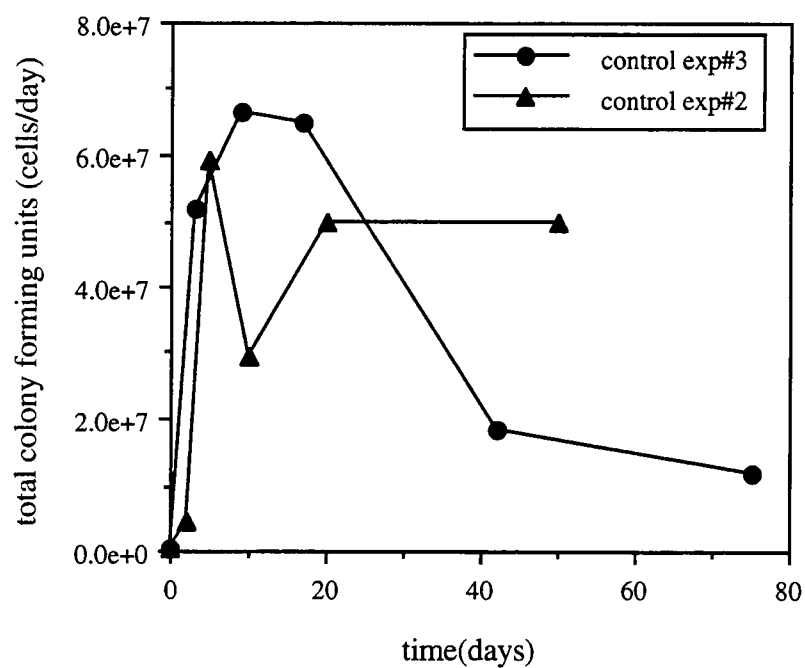


FIGURE 24. Persistence of the indigenous microbial population in a sandy loam soil with no adsorbed naphthalene($q=0$) for experiments #2 and #3

Rate constants can be measured using a variety of techniques and operating systems. The operating modes are either batch or continuous systems. The types of assays are typically biotransformations or mineralizations. Biotransformations studies measure naphthalene disappearance in the system. Mineralizations involve measuring the production of $^{14}\text{CO}_2$. The samples are usually slurries, groundwater, or sludges. Digrazia highlights the large variances in reported degradative activity(Digrazia, 1991). For biotransformation batch systems the rate constant varies from $0.05\text{-}8.4\text{day}^{-1}$, and for mineralization studies the reported rate constants range from $0.0024\text{-}3.8\text{day}^{-1}$. Digrazia notes the experimental conditions between the studies varied significantly.

Naphthalene disappearance is used to develop a first order rate constant for naphthalene degradation. In the present study the operating mode is a batch system, and the biotransformation is measured from a slurry sample. A plot of $\ln C_0/C$ vs. time(days), where C_0 is the initial naphthalene concentration in the slurry, C is the naphthalene concentration in the slurry for each time, gives the first order rate constant as the slope of a linearly regressed line. Figures 25 and 26 show the plots for each type of soil. The points correspond to the exponential growth phase of the batch culture. After the exponential growth phase naphthalene degradation rate appears to be different than first order in naphthalene concentration. Therefore, the degradation rates represent initial degradation rates for the batch system. The first order rate constants and the 95% confidence intervals are listed in Table 13.

TABLE 13. Kinetic parameters for naphthalene degradation

Contamination method	$k(\text{day}^{-1})$
supercritical CO_2	$.033 \pm .01$
dichloromethane	$.051 \pm .12$

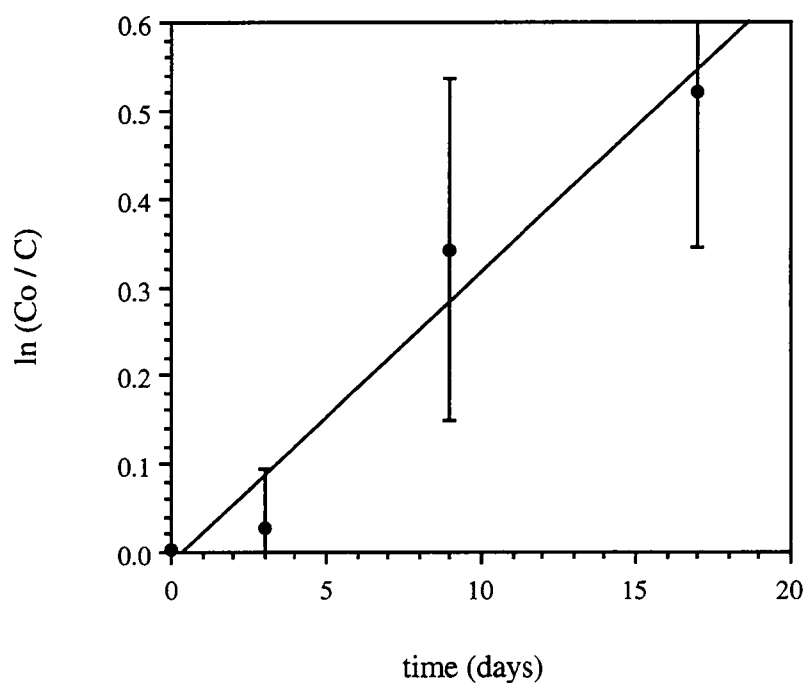


FIGURE 25. The $\ln(C_0/C)$ as a function of time to determine the first order rate constant for naphthalene degradation in soil slurry contaminated using supercritical CO_2 as the fluid phase

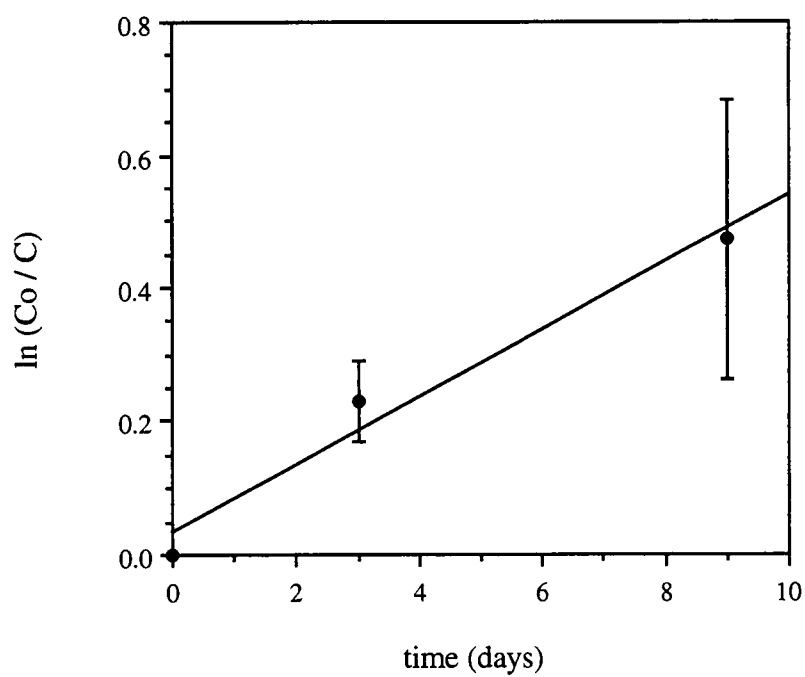


FIGURE 26. The $\ln(C_0/C)$ as a function of time to determine the first order rate constant for naphthalene degradation in soil slurry contaminated using dichloromethane as the fluid phase

The rate constants are similar to those reported in the literature. Variation within controlled experimental conditions can range from one to three orders of magnitude. This supports the conclusion that *a priori* determination of degradation is difficult to predict (Digrazia, 1991). The experimental degradation of naphthalene from soil contaminated by supercritical adsorption is less than the degradation rate from soil contaminated by dichloromethane.

A control sample with gamma irradiated sterile soil was prepared for each time point to account for any losses in naphthalene to vaporization. The sterile soil was obtained from Dr. Charles Steward (University of Tennessee, Knoxville). However, contamination of the sterile soil occurred during the incubation period. Therefore, the vapor pressure of naphthalene above the slurry in the sealed sample vial was utilized to determine if naphthalene losses were only a result of degradation. Using equation 2 in section 3.6 the vapor pressure of naphthalene at 300K is 0.00014 atm. Using Raoult's law the maximum mass of naphthalene in the 15ml head space was 0.000012g. An average value of Henry's constant for naphthalene is .00865 (Digrazia, 1991). Using Henry's law the mass of naphthalene vapor in equilibrium with the mass of naphthalene in the a saturated liquid phase is approximately 4×10^{-6} g. Using Raoult's law and Henry's law 4×10^{-6} g in the 15ml head space is negligible compared to a change in naphthalene mass of 0.005g in the soil slurry. Therefore, a decrease in naphthalene concentration in the experimental system is attributed to degradation.

CHAPTER 5

CONCLUSIONS

The following conclusions are made regarding naphthalene adsorption onto soil from the supercritical CO₂ phase:

1. The experimental apparatus is modified from the previous design to facilitate operation and control.
2. Equilibrium partition coefficients are determined using the supercritical apparatus. The coefficients increase with temperature at constant pressure. Results of a thermodynamic analysis are consistent with the literature.
3. The isotherms for naphthalene adsorption onto soil are determined and modeled based on the Freundlich isotherm. Uptake by the soil increases with temperature.

The following conclusions are made regarding the comparison of supercritical CO₂ and dichloromethane as solvents for naphthalene adsorption onto soil:

1. The initial desorption rates for each soil are similar.
2. Neither supercritical CO₂ nor dichloromethane has apparent deleterious effects on the indigenous microbial population of the soil.
3. Initial naphthalene degradation rates are similar to literature values for both

types of model soil.

4. Supercritical CO₂ is a suitable solvent for adsorbing naphthalene onto soils. As shown by the adsorption isotherms the amount of naphthalene on the soil can be controlled when using supercritical CO₂.
5. Vaporization of naphthalene occurs when the soil is contaminated in dichloromethane. Naphthalene concentration is difficult to control with this solvent.

CHAPTER 6

RECOMMENDATIONS

The quality of the experimental equilibrium data obtained with the supercritical apparatus can be improved by developing an online method of analysis. One notable problem with measuring breakthrough curves is the relatively large pressure drops (20-50psi) created by sampling. The large pressure drops may disrupt equilibrium in the packed bed. Small sample volumes relative to the system volume alleviate this problem. A large packed bed volume to sample volume ratio may require impracticable quantities of material. Many analytical techniques are possible, and different schemes depend on whether the stream is sampled at supercritical conditions (Randall, 1983).

Experimental comparisons of dichloromethane and supercritical CO₂ as adsorption solvents can be expanded. Supercritical CO₂ desorption of naphthalene from soil is an alternative route to using a liquid extraction solvent. Analysis of different soil types other than sandy loam is necessary to determine if the solvents are indeed similar. The soil porosity and fractional organic content may influence the adsorption phenomena. Experiments should be conducted to determine whether the solvents change the structure or properties of the soil matrix. For example, the solvent effects on the soil organic matter can be explored.

If online sampling capability is added chromatography experiments can be conducted to determine the mass transfer properties of the naphthalene-soil-supercritical

fluid system. A moment analysis on the breakthrough curve from a pulse input can be used to determine optimized mass transfer coefficients. The coefficients can be used to model desorption of naphthalene and other PAHs from soil.

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APPENDICES

APPENDIX A

APPENDIX B

```
%This program plots the three isothermal solubility curves. The cubic form of the
%Peng-Robinson EOS is used. The fitting parameter, kij, is obtained by minimizing the
%average absolute deviation(AAD) between the calculated mole fraction and the literature
%values given by Tsevhessankaya(1964).
```

```
%
```

```
%      1 = supercritical CO2
```

```
%      2 = naphthalene
```

```
clear all
format short E
clg
```

```
R = 83.14; % gas constant [cm3*bar/mol/K]
T = [308.2 318.2 328.2]; % system temperature [K]
```

```
for t = 1:1 % outside loop for temperatures
```

```
ynew = 0; % reset new mole fraction for loop
```

```
if t == 1 % 308.2 K data
```

```
T = T(1);
```

```
kij = .0703;
```

```
P2sat = .0002984;
```

```
Pexp = [817 1138 1250 1500 1760 1800];
```

```
Pexp = Pexp.* .071154;
```

```
yexp = [.00028254 .00134 .009311 .007 .01459 .01629];
```

```
Pset = [60 75 76 77 78 78.5 79.5 80 86 91 105 110 120 ...
        130 140 150 160 190 220 240 290 330];
```

```
ylit = [2.4 7.5 8.7 10.7 13.7 30.1 47.6 61.1 81 92 110 ...
        117 125 132 139 146 151 163 174 177 184 187];
```

```
points = 22;
end
```

```
if t == 2 % 318.2 K data
```

```
T = T(2);
```

```
kij = .066;
```

```
P2sat = .0007162;
```

```
Pexp = [1500 1750 1375 1168 928 1250];
```

```
Pexp = Pexp.* .071154;
```

```
yexp = [.008514 .01536 .004727 .0006424 .000540809 .001360];
```

```
Pset = [62.0 72.0 77.0 81.0 84.5 87.0 91.0 94.5 ...
        96.5 98.0 100 105 108 118 125 140 153 200 275 310 ];
```

```
ylit = [4.7 4.8 6.7 7.8 11.0 13.0 21.0 43.0 51.0 64.0 69.0 ...
        97.0 113 142 154 183 197 245 285 294];
```

```
points = 20;
end
```

```
if t == 3 % 328.2 K data
```

```
T = T(3);
```

```

kij = .066;
P2sat = .00163;
Pexp = [1250 1350 1500 1600 1800 2000];
Pexp = Pexp .* .07154;
yexp = [.002131 .001931 .004360 .007244 .01490 .02232];
Pset = [76.0 91.0 93.0 98.0 101 105 110 113 115 118 121 124 ...
        130 141 150 160 170 180 195 230 250 320];
ylit = [11.0 24.0 20.0 24.0 30.0 42.0 61.0 77.0 92.0 108 127 ...
        142 181 234 264 300 324 356 399 459 485 550];
points = 22;
end

Pset = Pset .* 14.07 .* .071154;           % Pressure [bar]
ylit = ylit./10^4;

V2sat = 111.5;                             % molar volume of pure naphthalene
                                           % ref. White, Gary L. [cm3/mole]
for n = 1:points                            % loop for n data points in each isotherm

    y2 = ylit(n);
    y1 = 1-y2;

    P = Pset(n);

    false = 1>2;                            % Begin convergence loop for EOS
    true = ~false;
    converged = false;
    thta = 0;
    while ~converged

        Tr1 = T / 304.2;                    % reduced temperatures
        Tr2 = T / 748.4;

        a1c = (.45724*83.14^2*304.2^2)/73.8; % critical point parameters
        a2c = (.45724*83.14^2*748.4^2)/40.5;

        w1 = .239;                          % acentric factors
        w2 = .302;

        K1 = .37464+1.54226*w1-.26992*w1^2;
        K2 = .37464+1.54226*w2-.26992*w2^2;

        alph1 = (1+K1*(1-(Tr1)^.5))^2;
        alph2 = (1+K1*(1-(Tr2)^.5))^2;

        a1 = a1c * alph1;                  % pure component parameters
        a2 = a2c * alph2;
        b1 = .0778*83.14*304.2/73.8;
        b2 = .0778*83.14*748.4/40.5;

        a12 = (1-kij)*(a1*a2)^.5;

```

```
am = y1^2*a1+2*y1*y2*a12+y2^2*a2;
bm = y1*b1+y2*b2;
```

```
A = am*P/R^2/T^2;
B = bm*P/R/T; % P-R EOS parameters
```

```
c1 = 1;
c2 = (B-1);
c3 = (A-3*B^2-2*B);
c4 = (B^3+B^2-A*B);
c = [c1 c2 c3 c4];
Z = roots(c); % Solves for compressibility factor
% if statements choose largest real root
```

```
if abs(imag(Z(1))) > 0
    if abs(imag(Z(2))) > 0
        Znew = Z(3);
    end
end
if abs(imag(Z(2))) > 0
    if abs(imag(Z(3))) > 0
        Znew = Z(1);
    end
end
if abs(imag(Z(3))) > 0
    if abs(imag(Z(1))) > 0
        Znew = Z(2);
    end
end
```

```
Z = Znew;
```

```
f1 = b2/b1*(Z-1); % calculate the fugacity coefficient
f2 = log(Z-B);
f3 = A/2.828/B;
f4 = 2*y1*(a1*a2)^.5*(1-kij)/a1 - b2/b1;
f5 = log((Z+(1-1.4142)*B)/(Z+(1+1.4142)*B));
```

```
phi = exp(f1-f2+f3*f4*f5); % fugacity coefficient
```

```
y2new = P2sat/(P*phi)*exp(V2sat*(P-P2sat)/(R*T)); % solve for solubility
```

```
err = abs((y2new - y2)/y2new); % set convergence tolerance
tol = .0001;
if err <= tol
    converged = true;
end
```

```
y2 = y2new;
```

```

y1 = 1- y2new;

end
ynew(n) = y2new;
end

% calculate the AAD
AAD(t) = sum (abs(ynew-ylit)./ ylit) * 100 / points

hold on % plot the results
plot(Pset,ynew, 'y-')
plot(Pset,ylit, 'c+')
plot(Pexp, yexp, 'go')
axis([50.0 150 0 .020])

end

```

VITA

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