



ELSEVIER

Journal of Hazardous Materials B67 (1999) 183–196

**Journal of
Hazardous
Materials**

Influence of water on the supercritical fluid extraction of naphthalene from soil

T.J. Smyth, R.G. Zytner, W.H. Stiver *

School of Engineering, University of Guelph, Guelph, Canada, N1G 2W1

Received 1 October 1998; received in revised form 11 March 1999; accepted 11 March 1999

Abstract

Supercritical fluid extraction (SFE) is an innovative soil remediation technology. To aid system evaluation and design, thermodynamic and kinetic parameters have been measured using a naphthalene contaminated, loamy sand at various water contents. The experimental results show that supercritical carbon dioxide can easily extract naphthalene from soil when the water content is below 10%. At low water contents, mass transfer is rapid and the equilibrium partition coefficient is independent of the soil's water content. However, the overall mass transfer coefficient, ($k_{ov} a$), decreases by at least a factor of 200 as the water content increases from 10 to 20%. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Soil remediation; Supercritical carbon dioxide; Organics; Water; Partition coefficient; Mass transfer coefficient

1. Introduction

Supercritical fluid extraction (SFE) is one of a number of innovative soil remediation technologies being developed. SFE is an extraction process which utilizes the solubilizing power and the rapid mass transfer characteristics of supercritical fluids (SCFs) to remove contaminants. McHugh and Krukoniš [1] provide an excellent introduction to the field of supercritical fluids.

The supercritical fluid chosen is almost always carbon dioxide as supercritical carbon dioxide (SCCO₂) requires modest operating conditions ($T_c = 31^\circ\text{C}$; $P_c = 7.4\text{ MPa}$) and it

* Corresponding author. Tel.: +1-519-824-4120, ext. 4862; fax: +1-519-836-0227; e-mail: wstiver@uoguelph.ca

can easily be separated from the solute by depressurization [2]. Additionally, carbon dioxide is cheap, available, and has minimal environmental impact.

On an analytical scale, various contaminants have been removed from soil using SFE, including PCBs, PAHs, DDT, phenolics and metals [3–6]. With respect to soil remediation, Groves et al. [7] indicated that the focus of research has been on factors that control the rate of extraction on a small scale. Laitinen et al. [2] recently reviewed the latest advancements on site remediation. Information is still lacking on thermodynamic and kinetic data.

The distribution coefficient is a fundamental parameter of interest with regard to the development of the SFE process as it indicates the feasibility of the extraction process [8]. It also can be used to estimate the amount of CO₂ required. The literature contains limited information on SCCO₂-soil distribution coefficients [4,9,10].

Mass transfer coefficients between the soil and bulk supercritical fluid depend on both an internal resistance and an external film resistance. The internal resistance is often characterized as an effective diffusion coefficient through a porous structure [11]. The external film resistance is dependent on Reynold's and Schmidt's numbers as in most solvent extraction systems but also depends on the Grashof number owing to a greater importance of natural convection [12]. Measurements of mass transfer coefficients for soil–supercritical fluid systems are limited. Madras et al. [13] and Montero et al. [14] have fitted breakthrough curves for extraction from a dry soil.

Water content of the soil is one factor which has not yet been studied in any detail. Low et al. [15] found little impact as a result of water contents up to 10% by weight on SFE of diesel from loam and silt soils. Champagne and Bienkowski [16] found no statistical differences in the equilibrium distribution with soils up to 10% by weight water content. However, Akgerman and Yeo [17] were only able to recover 11% of the naphthalene from a soil slurry. Water is believed to hinder extraction of non-polar compounds by acting as a barrier to carbon dioxide penetration [18].

Soil at a contaminated site may have a water content that is nearly dry through to 40% by mass. Drying soil in a laboratory setting may be viable but drying tonnes of soil is unlikely to be practical. In addition, a soil washing operation may be one of the first units in an overall treatment process and this will lead to water contents well in excess of 50%. Therefore, the influence of water on the SFC of soil needs to be addressed.

The objectives of this study were to measure the effect of a soil's water content on the equilibrium distribution and the mass transfer rate of contaminants in a SCF–soil system. For these experiments, naphthalene was chosen as the contaminant and the water content of the soil varied from bone dry to 20% by weight.

2. Experimental

Table 1 summarizes the properties of Delhi Loamy Sand (DLS) soil. The soil was sieved through a 2.0-mm sieve and air dried before use. The water content of the air dried soil was approximately 0.5% by mass. The water content was adjusted by adding the desired quantity of water and mixing except in the case of the bone dry (0%) experiment in which oven drying was used (100°C).

Table 1
Delhi loamy sand characteristics

| | |
|-------------------------------|-------|
| Size analysis | |
| % sand | 86.7 |
| % silt | 9.0 |
| % clay | 4.5 |
| Fraction organic matter (g/g) | 0.012 |
| Moisture field capacity (v/v) | 0.22 |
| Porosity (v/v) | 0.42 |
| Density (g cm ⁻³) | 1.49 |
| CEC (mol kg ⁻¹) | 8.27 |

As stated, naphthalene (Fisher, ACS certified) was used as the contaminant and its general properties are provided in Table 2. It has been the subject of numerous solubility studies in SCFs [19] and some distribution studies in SCF–soil systems [9,10].

Table 3 summarizes the experimental conditions tested and reported in this paper. Preliminary experiments indicated that the available stir bar system was unable to mix soils with water contents of 10% or more. Thus, the experiments with 10 and 20% water contents were not mixed and some of the 5% were not mixed to allow comparison.

Fig. 1 illustrates the system that was used to conduct the experiments. A dip tube fitted liquid cylinder supplied CO₂ to the system. A positive displacement HPLC pump (Waters 510A) stepped up the pressure to the desired level. Cooling of the pump heads, by packing them in dry ice, was required to prevent cavitation. A pressure regulator maintained the system pressure at 10.0 MPa (± 0.5) as measured by a downstream pressure transducer. A pressure relief valve provided additional safety and was set at 12.8 MPa.

The extraction vessel (i.d. 4.2 cm; length 3.4 cm) held the contaminated soil, which was contacted with flowing CO₂. The vessel volume is approximately 45 ml (holding 26 g CO₂, when empty, at the operating density). The contents of the vessel were heated to approximately 42°C, which was calculated based on estimated heat transfer properties for the water jacket surrounding the vessel. This was necessary as no direct measure of the temperature inside the vessel was possible for the current configuration of the system. The recirculating water for the water jacket and bath was heated to 48°C.

Two methods were used to measure the chemical concentrations in the SCCO₂. The primary method consisted of an on-line, high pressure UV–Vis (Linear Instruments,

Table 2
Properties of naphthalene [22]

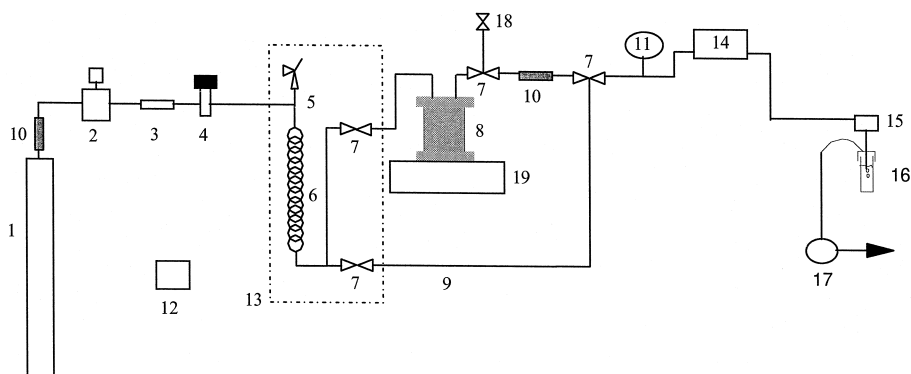
| | |
|--|--------|
| MW (g mol ⁻¹) | 128.2 |
| Melting point (°C) | 80 |
| Log <i>K</i> _{ow} | 3.37 |
| Aqueous solubility (mg l ⁻¹) | 31.0 |
| Vapour pressure (Pa) at 25°C | 10.4 |
| Solubility in SCCO ₂ (mol/mol) at 42°C, 10 MPa [19] | 0.0096 |

Table 3
Summary of experimental conditions

| Water content (%) | Experiment label | Mixing | Static periods initiated at (Duration, min) | | |
|-------------------|------------------|--------|---|----------|-----------|
| 0 | 0/M/C | Yes | None | | |
| 0.5 | 1A/M/C | Yes | None | | |
| | 1B/M/S | Yes | 58 (22) | | |
| 3 | 3/M/C | Yes | None | | |
| 5 | 5A/M/C | Yes | None | | |
| | 5B/M/S | Yes | 34 (21) | 79 (71) | |
| | 5C/NM/S | No | 31 (21) | 66 (88) | |
| | 5D/NM/S | No | 51 (20) | 106 (90) | |
| 10 | 10A/NM/C | No | None | | |
| | 10B/NM/S | No | 58 (20) | 93 (74) | 191 (234) |
| 20 | 20A/NM/C | No | None | | |
| | 20B/NM/S | No | 12 (20) | 46 (69) | 137 (228) |

Model 205), which provided continuous measurements. The wavelengths used were 302 and 305 nm.

The secondary system consisted of a sample collection vial. The SCCO₂ was depressurized by passing it through a heated restrictor (temperature in excess of naphthalene's melting point) to avoid plugging in the restrictor. If plugging appeared to be imminent or had occurred, the power to the heating tape around the restrictor was increased. The flowing CO₂ passed through a sample collection vial and out through a



Legend

- | | | |
|--|---------------------------------|---------------------------|
| 1 CO ₂ cylinder with dip tube and micron filter | 8 Main vessel with water jacket | 13 Water bath |
| 2 HPLC pump | 9 Bypass line | 14 UV-Vis |
| 3 Check Valve | 10 Micron filter | 15 Heated restrictor |
| 4 Pressure regulator | 11 Pressure transducer | 16 Sample collection vial |
| 5 Relief valve | 12 Immersion Circulator | 17 Rotameter |
| 6 Preheating Coil | 13 Water bath | 18 Needle Valve |
| 7 Ball Valves | | 19 Mixer |

Fig. 1. Schematic of SFE system.

rotameter, which measured flow of the gaseous CO₂ (0.4 g min⁻¹). For these experiments the sample collection vials contained no solvent. After the sampling period, methylene chloride was added to the vial to dissolve the precipitated naphthalene and allow measurement using a gas chromatograph (HP5890).

2.1. Experimental procedures

Soil for a specific experiment was prepared by adding the naphthalene dissolved in methylene chloride and evaporating off the solvent over a period of a few hours. The resulting naphthalene concentration on the soil was approximately 10 mg g⁻¹, which was confirmed by taking five random samples for gas chromatograph analysis. The required amount of water was then added to the soil, with three additional samples taken to determine the water content. Following mixing, contaminated soil (15 g) was added to the preheated vessel and the vessel was sealed.

While the vessel was being prepared, carbon dioxide flowed through the bypass line to ensure the downstream lines were clean. Once the vessel was sealed, the carbon dioxide flow was diverted from the bypass line to the vessel to initiate pressurization. Once the vessel reached the desired pressure, the downstream valve was opened and both time and the UV–Vis were zeroed. Pressure and UV–Vis readings were automatically recorded by computer.

Sampling of the carbon dioxide exhaust in the vials were collected over time intervals of 5 to 10 min, with temperature and flow of the exhaust recorded every few minutes. Once the run was complete the vessel was isolated and flow continued through the bypass line to clean out the downstream lines. The vessel was then depressurized through a needle valve and this exhaust was also sampled using the sampling vials. Once depressurized, three soil samples were taken for analysis of the final naphthalene concentration.

For many experiments a static period was included to aid interpretation of the equilibrium status of the system. During the static periods, flow in and out of the vessel was stopped but the bypass flow was continued to clean out downstream lines and reduce the incidence of clogging due to precipitated naphthalene in these lines. Static periods ranged from 20 min to 4 h.

2.2. Gas chromatograph analysis

The soil samples were extracted using methylene chloride using intense shaking over at least a 1-h time period. Methylene chloride samples of the soil and the methylene chloride dissolved carbon dioxide exhaust were analysed by a gas chromatograph equipped with a flame ionization detector. Calibration was by means of external standards.

3. Results and discussion

The overall results and discussion will be presented in three sections. Section 3.1 will focus on the general characteristics of the experimental results. Section 3.2 will consider

the distribution coefficients that prevailed and Section 3.3 will provide the mass transfer results and behaviour.

3.1. General characteristics of experimental results

The experimental procedures and general characteristics are discussed in relation to the general shape of the concentration vs. time, repeatability evidence, agreement between GC and UV–Vis, changes in water content with time and mass closure.

Fig. 2 presents the general behaviour of the three experiments, with static periods, for 5% water content soil. The data presented is the UV signal with the static periods deleted to illustrate a continuous process and ease comparison. In all experiments, the observed concentration, measured by GC or UV–Vis, followed the same trend shown in Fig. 2. The concentration slowly rising to a maximum at around 20 min and then tailing off for the remainder of the run. The time required to reach the maximum concentration was controlled by mass transfer out of the soil and by the time required to reach temperature stability in the vessel.

Runs 5B and 5D are evidently very similar. The lower readings for the run 5C are largely attributable to a lower initial contamination level of 6.4 mg g^{-1} compared with

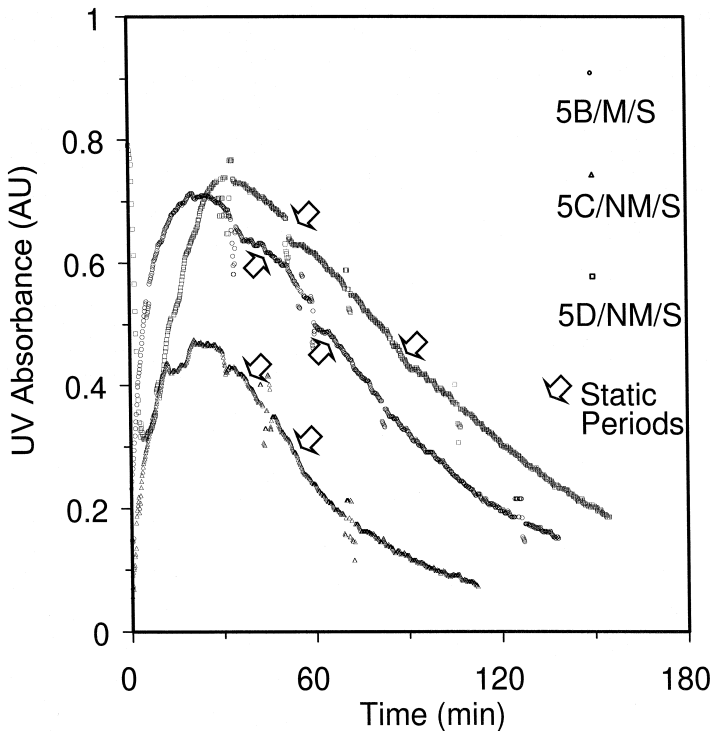


Fig. 2. UV–Vis signal for 5% water content runs with static periods (note: timing of the static periods is identified but the time period has been deleted to facilitate comparison).

8.8 and 8.6 mg g⁻¹ for 5B and 5D, respectively. Further evidence of experimental repeatability is provided in the subsequent sections when the distribution and mass transfer coefficients are calculated.

In all experiments, the GC and UV–Vis data tracked along the same path indicating a consistent measure of the exhaust concentration and that the two measures can be used interchangeably for interpretation purposes. In this work, the UV–Vis signal is used for fine time resolution, whereas, the GC results provide for a mass balance analysis. The fine time resolution of the UV–Vis signal allows for an accurate comparison of the concentration immediately before and after a static period. This comparison forms the basis for interpreting whether the system is operating under equilibrium conditions or not.

A mass balance around the system is necessary in assessing how the system behaved during the extraction experiment. Table 4 lists the percent mass recovered for each experiment, as well as the distribution of this mass between the CO₂ samples, the residual soil and the unknown fraction. The unknown fraction is large and raises a number of challenges in regards to the interpretation of the results.

There are only three possible locations for the unrecovered mass. (1) The mass is still in the soil as a result of inefficient soil analysis. (2) The mass is out of the soil but deposited somewhere downstream of the vessel in the internals of the system. (3) The naphthalene was in the exiting carbon dioxide but that this carbon dioxide was inefficiently sampled or analysed.

Extraction efficiency tests for the soil as a function of water content resulted in greater than 80% recovery in all cases. Two measurements of the naphthalene deposited in the downstream lines resulted in a recovery of only 0.6 and 4%. Related experiments, subsequent to this research [20], added a second stage to the carbon dioxide sampling system and resulted in overall mass closures near 100%. In these related experiments, the amount of naphthalene recovered by this second stage correlated with the mass of carbon dioxide sampled. On this basis, the unrecovered mass of naphthalene has been

Table 4
Mass balance distribution

| Water content (%) | Experiment label | Total recovery (%) | Distribution (%) | | |
|-------------------|------------------|--------------------|--------------------|-----------------|---------|
| | | | in CO ₂ | in soil residue | Unknown |
| 0 | 0/M/C | 68 | 67 | 1.8 | 32 |
| 0.5 | 1A/M/C | 59 | 54 | 4.4 | 41 |
| | 1B/M/S | 47 | 44 | 2.7 | 53 |
| 3 | 3/M/C | 58 | 56 | 1.5 | 42 |
| 5 | 5A/M/C | 51 | 49 | 2.6 | 49 |
| | 5B/M/S | 62 | 59 | 2.4 | 38 |
| | 5C/NM/S | 39 | 37 | 2.8 | 61 |
| 10 | 5D/NM/S | 75 | 69 | 4.8 | 25 |
| | 10A/NM/C | 64 | 53 | 11 | 36 |
| | 10B/NM/S | 61 | 58 | 2.9 | 39 |
| 20 | 20A/NM/C | 59 | 0.1 | 59 | 41 |
| | 20B/NM/S | 72 | 18 | 55 | 27 |

distributed among all of the carbon dioxide samples including the final purge. The distribution has been weighted on the basis of the mass of carbon dioxide associated with each sample.

The water content for each experiment is reported as a single value based on the initial conditions. However, water is partially soluble in SCCO_2 and therefore the water content of the soil did decrease over the duration of the experiment. The 3% water initial condition decreased to about 1.5% and the 20% initial condition dropped to between 17 and 18%.

3.2. Distribution coefficient

The distribution coefficient, K_{cs} ($\text{g}_{\text{soil}}/\text{g}_{\text{CO}_2}$), was calculated for all extraction experiments. The results are summarized in Table 5. All calculations were done on a mass basis to avoid any discrepancies that may arise due to the variability in the volume of CO_2 as a result of changes in temperature and pressure.

The distribution coefficients are reported as an average value over the duration of a run based on the discrete GC samples and as a maximum value for the run. The maximum typically occurred near the peak in the observed outlet concentration. The average value ranges from 60 to 100% of the maximum value. In the case of experiment 20A only a single sample recovered measurable naphthalene.

The four distribution coefficients from the 5% water content experiments (5A–D) all span a narrow range confirming good experimental consistency.

Static periods were included in six of the 12 experiments. For the water contents of 10% and less, the concentration in the exhaust carbon dioxide was the same following the static period as before the static period. This is illustrated in Fig. 3 for the 5% water content experiment (Run 5D). This means that the system was operating at equilibrium

Table 5
Distribution and mass transfer results

| Water content (%) | Experiment label | Distribution coefficient (g/g) | | Mass transfer coefficient ($k_{ov} a$) $\times 10^9 \text{ m}^3 \text{ s}^{-1} \text{ g}_{\text{ds}}^{-1}$ |
|-------------------|------------------|--------------------------------|---------|--|
| | | Maximum | Average | |
| 0 | 0/M/C | 1.5 | 1 | |
| 0.5 | 1A/M/C | 1.7 | 1 | |
| | 1B/M/S | 0.8 | 0.59 | 1.4 |
| 3 | 3/M/C | 1 | 0.81 | |
| 5 | 5A/M/C | 1.5 | 1.1 | |
| | 5B/M/S | 1 | 0.68 | 1.3 |
| | 5C/NM/S | 1.6 | 1.6 | 2.1 |
| | 5D/NM/S | 2.1 | 1.2 | 1.8 |
| 10 | 10A/NM/C | 0.65 | 0.53 | |
| | 10B/NM/S | 1.3 | 0.73 | 1.2 |
| 20 | 20A/NM/C | 0.64 | – | |
| | 20B/NM/S | 0.15 | 0.09 | 0.0073 |

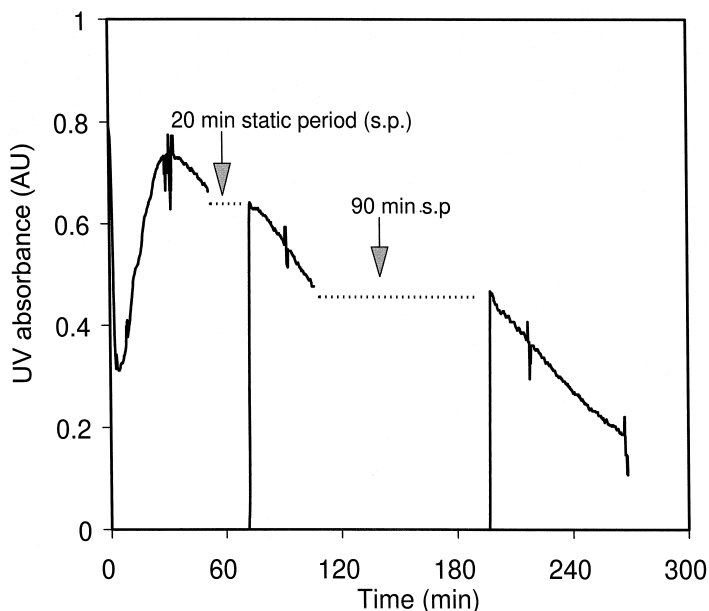


Fig. 3. UV-Vis signal for one 5% water content run (5D) including the static time periods.

between the soil and the carbon dioxide at the point of initiating the static period. Therefore, the distribution coefficients provided, in Table 5, are equilibrium descriptors of the system for water contents of 10% and less.

At low water contents ($\leq 10\%$), high mass transfer rates out of the soil do not control or limit the removal of naphthalene. This situation is true for the specific conditions of these experiments. The quantity of soil relative to the dimensions of the vessel and the flowrate of carbon dioxide are such that equilibrium is achieved. At higher carbon dioxide flowrates, mass transfer may begin to control the extraction process.

The average equilibrium distribution coefficient for water contents between 0 and 10% was $0.92 (\pm 0.31)$ g/g. This compares favourably with the value of $1.7 (\pm 0.7)$ g/g for the same soil, air dry, measured at 35°C and 10.7 MPa by Gray et al. [10]. The difference in the two observed partition coefficients is largely explained by the difference in solubility at the two different supercritical conditions (0.014 mol/mol at $35^\circ\text{C}/10.7$ MPa vs. 0.0096 at $42^\circ\text{C}/10$ MPa [19]).

The equilibrium distribution coefficient for bone dry soil (0/M/C) is the same as the other low water content values. This is unexpected as it is recognized that sorption to bone dry soil increases due to the availability of mineral sites [21]. The oven dried soil likely absorbed some moisture during the necessary handling to contaminate the soil and transfer it to the extraction vessel. In a test, the oven dried soil increased to a water content of 0.11% when exposed to ambient air for 43 min. Since the handling of 0/M/C soil was less than 43 min, the partition coefficient is independent of water content over the water content range of 0.11 to 10%.

Fig. 4 illustrates the system response following static periods for the 20% water content conditions. It is evident that the duration of the static period allows for the concentration in the carbon dioxide to increase and approach equilibrium. Under dynamic operation the system is not able to maintain equilibrium with this water content. Thus, the distribution coefficients for 20% water contents are merely pseudo steady state distribution values dependent on the relative magnitude of carbon dioxide flow and mass transfer coefficient.

The observed distribution coefficients for water contents of 20% are lower than the K_{cs} values for 10% water or less. The reported distribution coefficients have included the unknown naphthalene with the carbon dioxide samples. Although this has been done for consistency, it is likely somewhat less valid for the 20% water content situation. The efficiency of the carbon dioxide sampling was running at around 60% during the lower water content cases. To explain the unknown naphthalene the carbon dioxide sampling efficiency would have to have dropped to about 40% for run 20B and to about 0.2% for run 20A. In addition, with the higher concentrations in the residual soil it is reasonable that modest errors in soil sampling could explain a substantial portion of the unknown naphthalene. Thus, the distribution coefficients reported in Table 5 for the 20% case are likely overestimates.

In run 20B/NM/S, distribution coefficient values are calculated following long static periods. After each static period, the distribution coefficient increased but remained lower than the observations made at the lower water contents. As such, the measured distribution coefficients probably do not represent equilibrium values and a static period longer than 4 h is required to reach equilibrium.

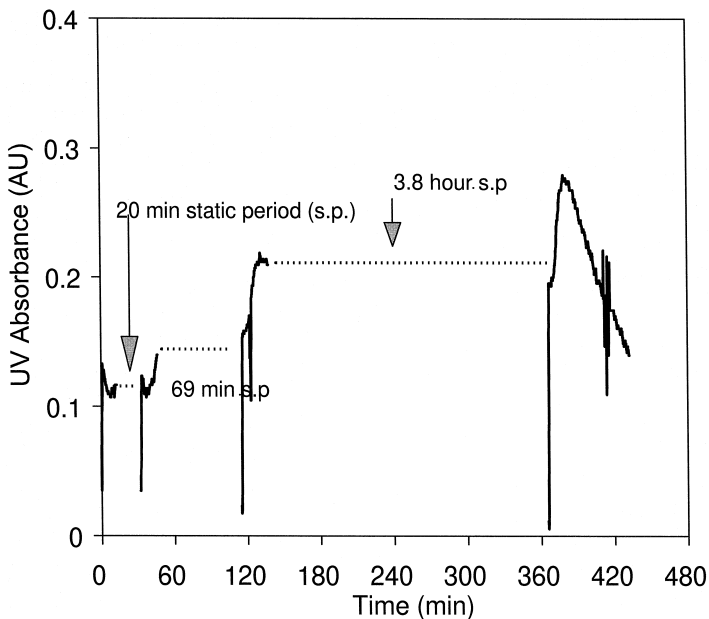


Fig. 4. UV-Vis signal for one 20% water content run (20B) including the static time periods.

3.3. Mass transfer

The mass transfer of the contaminant from the soil to the supercritical fluid is crucial to the development of SFE as a full scale process. The effect of water on mass transfer coefficients has not been quantified. Therefore, an attempt was made to determine values for the mass transfer coefficients for water contents from air dried to 20%.

Overall mass transfer coefficients were calculated for each of the experimental runs involving a static period. Table 5 summarizes the values determined for each experiment with the mass transfer coefficient defined based on Eq. (1).

$$N = (k_{ov} a) M_{ds} \rho_s \left(C_s - \frac{C_{CO_2}}{K_{cs}} \right) \quad (1)$$

where N is the mass transfer rate ($\text{g}_N \text{ s}^{-1}$), M_{ds} is the mass of dry soil (g_{ds}), ρ_s is the soil density ($\text{g}_{ds} \text{ m}^{-3}$), C_s is the naphthalene soil concentration (g_N/g_{ds}), C_{CO_2} is the naphthalene concentration in SCCO_2 ($\text{g}_N/\text{g}_{CO_2}$), and $k_{ov} a$ is the overall mass transfer coefficient ($\text{m}^3 \text{ s}^{-1} \text{ g}_{ds}^{-1}$).

Eq. (1) is consistent with the conventional form of a mass transfer equation but has been written to explicitly identify that all of the parameters are to be used on a mass basis rather than the conventional volume basis. A mass basis is preferred in this application for three reasons: (1) the amount of soil in a system is usually measured by mass rather than by volume; (2) the area for transfer likely scales with the mass of soil in the system rather than the volume of the system particularly when the relevant domain extends all the way to soil slurries; and (3), for supercritical fluids specifying the mass of the fluid is open to less ambiguity than specifying the volume of the fluid.

The use of Eq. (1) requires a measure of the mass transfer rate and a measure of the prevailing driving force. If the system is 'at' equilibrium and if the driving force is considered zero, then the calculated mass transfer coefficient is infinite according to Eq. (1). In reality the system is never 'at' equilibrium, the driving force is only near zero and mass transfer is not infinite. A limiting (minimum) value of the mass transfer coefficient can be quantified when the systems appears to be at equilibrium if a limiting (maximum) value of the driving force can be established. A maximum value of the driving force has been assumed, in this application, to be associated with the system being 10% away from equilibrium. This choice of 10% was based on the judgement that it is the maximum driving force that could have prevailed and might not have been observed following a static period.

For the low water content cases ($\leq 10\%$), reliable measures of the mass transfer rate were available during the dynamic period and thus the dynamic period was used to determine the mass transfer coefficient. For the 20% water content case, the effluent concentrations during the dynamic period were at or near detection limits and as such reliable mass transfer rates were not available during this period. However, during a static period the concentrations changed measurably in the vessel and therefore reliable mass transfer rates were available. Thus, the dynamic periods were used to determine mass transfer coefficients for the low water content cases ($\leq 10\%$) and the static periods for the 20% case. The mass transfer coefficients have only been calculated for the runs with static periods.

The resulting overall mass transfer coefficients for the low water content cases averaged $1.6 \times 10^{-9} \text{ m}^3 \text{ s}^{-1} \text{ g}_{\text{ds}}^{-1}$. For the 20% water content case the value is $7.3 \times 10^{-12} \text{ m}^3 \text{ s}^{-1} \text{ g}_{\text{ds}}^{-1}$. Two aspects warrant discussion: (1) the consistency of the values for water contents of 10% or less, and (2) the significantly lower value for the 20% water content case.

The consistency of the mass transfer coefficients for the low water contents is an artefact of the calculation procedures and the limitations of the resolution of these experiments. For all of the low water content cases, the system was operating 'at' equilibrium and this required the 10% deviation from equilibrium assumption to define the limiting driving force and calculate a limiting mass transfer coefficient. The same deviation was chosen for all of these runs leading to essentially the same mass transfer coefficient. All of these mass transfer coefficients represent minimum values due to the choice of a maximum value for the driving force. The calculated minimum value (10^{-9}) is a measure of the mass transfer coefficient resolution capability of this equipment as it was operated. A substantial increase in the flowrate of carbon dioxide is required to provide resolution capability at higher mass transfer coefficients.

The substantial difference between the mass transfer coefficients for water contents of 10% or less and for the 20% water content case has important implications to extraction efficiencies in both remediation and analytical contexts. In considering the magnitude of the difference in the mass transfer coefficient it is important to remember that the value for 10% water content is a minimum and to recognize that the value for 20% water content is likely a maximum. In determining the 20% value, the system was assumed to reach to within 10% of equilibrium at the end of the third static period. At the end of the third static period, the distribution coefficient was only 0.15 g/g whereas the actual partition coefficients may be as high as 0.92 g/g. Using a low value for the partition coefficient leads to a maximum estimate of the mass transfer coefficient.

Understanding the manner in which water has such a large impact on the mass transfer coefficients may be useful in terms of improving mass transfer and in terms of extraction vessel design. Consider a soil aggregate suspended in SCCO_2 . The aggregate consists of individual soil mineral grains and natural organic matter and has a finite internal porosity [11]. The removal of contaminants from the soil requires the desorption of the contaminant from the soil surface into the fluid within the internal pores. The contaminant must then diffuse through the tortuous internal pores to the perimeter of the aggregate and eventually transfer to the bulk external fluid. Consider the effective internal diffusion to control the overall mass transfer process. If the soil aggregate is dry, then for a 200 μm diameter, an internal porosity of 13 vol.% [11], and a partition coefficient of 0.92 g/g, the resulting overall mass transfer coefficient is $1.9 \times 10^{-7} \text{ m}^3 \text{ s}^{-1} \text{ g}_{\text{ds}}^{-1}$. At a water content of 5 wt.%, sufficient to fill the internal pores, the overall mass transfer coefficient becomes $1.7 \times 10^{-8} \text{ m}^3 \text{ s}^{-1} \text{ g}_{\text{ds}}^{-1}$. Both of these values are faster than $10^{-9} \text{ m}^3 \text{ s}^{-1} \text{ g}_{\text{ds}}^{-1}$ which would be consistent with equilibrium observations in these experiments for the low water content conditions. As the water content increases beyond 5% an external water film will develop and the contaminant must diffuse through this additional layer or resistance. For 10% water content, the resulting overall mass transfer coefficient decreases to $1.6 \times 10^{-8} \text{ m}^3 \text{ s}^{-1} \text{ g}_{\text{ds}}^{-1}$ and at a 20% water content the coefficient drops to $1.4 \times 10^{-8} \text{ m}^3 \text{ s}^{-1} \text{ g}_{\text{ds}}^{-1}$. Using different particle

diameters and different internal porosities does not significantly change a weak dependence on water content. Clearly, this picture of an isolated soil aggregate with the water within the internal pores and as a film on the outside cannot explain the several order of magnitude drop in the observed mass transfer coefficient as the water content increases from 10 to 20%.

The soil in the vessel under no mix conditions will not exist as isolated aggregates but as a packed bed of soil aggregates. Thus, as the water content of the soil exceeds the quantity necessary to fill the internal pore volume the excess water will no longer just create a thin uniform film around each particle. The water film around each particle will begin to bridge between particles and in so doing significantly increase the water path length for transfer of some of the contaminant and decrease the area of contact between the carbon dioxide and water film. Estimating the extent of path length increase and the degree to which the area diminishes as a function of water content would be difficult. However, one extreme can be estimated. Once the water content fills all of the internal and external pores, that is, the soil is water saturated, the path length becomes of the order of the depth of soil and the area becomes the cross-sectional area of the vessel. The overall mass transfer coefficient in this situation is estimated at $1.3 \times 10^{-12} \text{ m}^3 \text{ s}^{-1} \text{ g}_{\text{ds}}^{-1}$ and applies to a water content of 29 wt.%. It would seem that this picture of the controlling aspects of mass transfer has general agreement with the observed mass transfer coefficient.

If water bridging, leading to longer path lengths and lower interfacial areas, is the dominant factor in causing the strong dependence of the mass transfer coefficient on a soil's water content, then dramatic improvements in mass transfer rates should be possible. Mixing energy sufficient to suspend the soil particles in a SCCO_2 solution will break the water bridges and lead to high mass transfer coefficients.

4. Summary

The results obtained from this series of SFE experiments with soil of varying water contents has shown that contaminants from soil with water contents below 10% are easily extracted with SCCO_2 . Equilibrium distribution coefficients were independent of water content in these relatively dry soils. Mass transfer was rapid with an overall mass transfer coefficient greater than $1.7 \times 10^{-9} \text{ m}^3 \text{ s}^{-1} \text{ g}_{\text{ds}}^{-1}$.

The mass transfer coefficient was only $7.3 \times 10^{-12} \text{ m}^3 \text{ s}^{-1} \text{ g}_{\text{ds}}^{-1}$ at a soil water content of 20%. It is believed that this lower value is largely due to water bridging between particles of a packed bed of soil.

Acknowledgements

Funding for this research has been provided by the Natural Sciences and Engineering Research Council of Canada. Mr. Paul Found's assistance in modifying the vessel to minimize leaks is gratefully acknowledged.

References

- [1] M.A. McHugh, V.J. Krukoni, *Supercritical Fluid Extraction, Principles and Practice*, 2nd edn., Butterworth-Heinemann, Boston, MA, 1994.
- [2] A. Laitinen, A. Michaux, O. Aaltonen, Soil cleaning by carbon dioxide extraction: a review, *Environ. Technol.* 15 (1994) 715–727.
- [3] B.O. Brady, C.P.C. Kao, K.M. Dooley, F.C. Knopf, R.P. Gambrell, Supercritical extraction of toxic organics from soils, *Ind. Eng. Chem. Res.* 26 (1987) 261–268.
- [4] A.T. Andrews, R.C. Ahlert, D.S. Kosson, Supercritical fluid extraction of aromatic contaminants from a sandy soil, *Environ. Prog.* 9 (1990) 204–210.
- [5] A. Akgerman, C. Erkey, S.M. Ghoreishi, Supercritical extraction of hexachlorobenzene from soil, *Ind. Eng. Chem. Res.* 31 (1992) 333–339.
- [6] N. Saito, Y. Ilkushima, T. Goto, Liquid/solid extraction of acetylacetone chelates with supercritical carbon dioxide, *Bull. Chem. Soc. Jpn.* 63 (1990) 1532–1534.
- [7] F.R. Groves, B. Brady, F.C. Knopf, State-of-the-art on the supercritical extraction of organics from hazardous waste, *CRC Crit. Rev. Environ. Rev.* 15 (1985) 237–274.
- [8] R.K. Roop, R.K. Hess, A. Akgerman, Supercritical extraction of pollutants from water and soil, in: K.P. Johnston, J.M.L. Penninger (Eds.), *Supercritical Fluid Science and Technology*, Chap. 29, ACS Symposium Series #406, 1989, pp. 468–476.
- [9] C. Erkey, G. Madras, M. Orejeula, A. Akgerman, Supercritical fluid extraction of organics from soil, *Environ. Sci. Technol.* 27 (1993) 1225–1231.
- [10] D.J. Gray, R.G. Zytner, W.H. Stiver, Supercritical carbon dioxide—soil partition coefficients, *J. Supercrit. Fluids* 8 (1995) 149–155.
- [11] S.-C. Wu, P.M. Gschwend, Sorption kinetics of hydrophobic organic compounds to natural sediments and soils, *Environ. Sci. Technol.* 20 (1986) 717–725.
- [12] P. Debenedetti, R.C. Reid, Diffusion and mass transfer in supercritical fluids, *AIChE J.* 32 (1986) 2034–2046.
- [13] G. Madras, C. Thibaud, C. Erkey, A. Akgerman, Modelling of supercritical extraction of organics from solid matrices, *AIChE J.* 40 (1994) 777–785.
- [14] G.A. Montero, T.D. Giorgio, K.B. Schnelle, Jr., Removal of hazardous contaminants from soils by supercritical fluid extraction, in: K.W. Hutchenson, N.R. Foster (Eds.), *Innovations in Supercritical Fluids: Science and Technology*, Chap. 19, ACS Symposium Series #608, 1995, pp. 281–297.
- [15] G.K.C. Low, G.J. Duffy, S.D. Sharma, M.D. Chenesse, S.W. Weir, A.R. Tibbett, Transportable supercritical fluid extractor unit for treating of contaminated soils, in: G. Brunner, M. Perrut (Eds.), *Proceedings of the 3rd International Symposium on Supercritical Fluids*, Vol. 2, October 17–19, 1994, pp. 275–280.
- [16] A.T. Champagne, P.R. Bienkowski, The supercritical fluid extraction of anthracene and pyrene from a model soil: an equilibrium study, *Sep. Sci. Technol.* 30 (1995) 1289–1307.
- [17] A. Akgerman, S.-D. Yeo, Supercritical Extraction of Organic Components from Aqueous Slurries, ACS Symposium Series #514, 1993, pp. 294–304.
- [18] V. Camel, A. Tambuté, M. Caude, Analytical-scale supercritical fluid extraction: a promising technique for the determination of pollutants in environmental matrices, *J. Chromatogr.* 642 (1993) 263–281.
- [19] S.E. Guigard, W.H. Stiver, A density-dependent solute solubility parameter for correlating solubilities in supercritical fluids, *Ind. Eng. Chem. Res.* 37 (1998) 3786–3792.
- [20] T. Laplante, *Supercritical Fluid Extraction of Naphthalene from Soil Slurries*, MSc Thesis, University of Guelph, 1998.
- [21] C.T. Chiou, T.D. Shoup, Soil sorption of organic vapors and effects of humidity on sorptive mechanism and capacity, *Environ. Sci. Technol.* 19 (1985) 1196–1200.
- [22] D. Mackay, W.Y. Shiu, K.C. Ma, *Illustrated Handbook of Physical–Chemical Properties and Environmental Fate for Organic Chemicals: Vol. II. Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins, and Dibenzofurans*, Lewis Publishers, Boca Raton, FL, 1992.