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A. Firus[a]; W. Weber[a]; G. Brunner[a]
[a] TU HAMBURG-HARBURG, THERMISCHE VERFAHRENSTECHNIK, HAMBURG, GERMANY

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Supercritical Carbon Dioxide for the Removal of Hydrocarbons from Contaminated Soil

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A. FIRUS,* W. WEBER, and G. BRUNNER
TU HAMBURG-HARBURG
THERMISCHE VERFAHRENSTECHNIK
EISSENDORFER STR. 38, 21073 HAMBURG, GERMANY

ABSTRACT

Soil material contaminated with hydrocarbons can be cleaned by supercritical water extraction. Due to the high critical data of supercritical water (T_c = 647 K, P_c = 22.1 MPa), supercritical carbon dioxide (T_c = 304 K, P_c = 7.3 MPa) was investigated as an alternative solvent. The amount of hydrocarbons removed from weathered contaminated soil material with supercritical carbon dioxide was less than 21%.

INTRODUCTION

Cleaning of contaminated soil is of great importance for agricultural recultivation and to avoid groundwater pollution, to mention only two examples. Conventional thermal decontamination techniques like incineration and pyrolysis involve toxic flue gases. Therefore, alternative solutions should be found for the handling of contaminated soil areas.

A new method for cleaning contaminated soil is extraction using supercritical solvents. Supercritical fluids are unique solvents owing to their low viscosity and high density. There is no phase transition between the liquid and vapor phases above the critical point of a substance. This point is reached for carbon dioxide at 304 K, 7.3 MPa. Solvent power can change significantly under supercritical conditions. Supercritical carbon dioxide and polycylic aromatic hydrocarbons still show limited solubility, whereas

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* To whom correspondence should be addressed.

supercritical water ($T_c = 647$ K, $P_c = 22.1$ MPa) and organic compounds are completely miscible (1, 4).

Former investigations proved that weathered, contaminated soil material can be cleaned by supercritical water extraction and supercritical water oxidation (1). Although the operating temperature of supercritical water extraction (653 K) is lower than of other thermal treatment methods (e.g., incineration > 1300 K), it is much higher than the critical temperature of carbon dioxide. Due to its moderate critical data, carbon dioxide was examined as an alternative solvent. Furthermore, it is nontoxic, nonflammable, nonreactive, and easy to regenerate by pressure release.

During the last decade several soil materials have been treated on an analytical scale by supercritical fluid extraction using carbon dioxide, and the dependence of temperature, pressure, addition of modifier, and soil pretreatment was thereby investigated (2, 3). In this study the applicability of carbon dioxide to the industrial-scale extraction of contaminated soil was investigated.

EXPERIMENTAL

Figure 1 shows a flow scheme of the laboratory plant. The main part of the apparatus is the extraction autoclave (d) containing a fixed bed of soil material (c, $V_{fb} = 0.46$ l). First, the soil material is compressed and fixed in the autoclave. Then the apparatus is filled with solvent and pressurized. After the extractor is heated to operating temperature, solvent is pumped continuously through the fixed bed. A compressor (a) is used to reach the supercritical pressure conditions of carbon dioxide (purity: 99.95%). The preheated (c) solvent enters the extraction autoclave at the top. In the tubular gap between the inner wall of the autoclave and the outer wall of the fixed bed the fluid is heated to operating temperature and enters the fixed bed at the bottom. After having passed a heat exchanger (e) and a backpressure regulator (f), the loaded solvent leaves the apparatus at ambient conditions. Gaseous compounds are separated in a volumetric flask (g) from the liquids. The gas flow rate is measured by a gas meter (h), and the extracted amount of oil is determined gravimetrically.

The oil content of the soil material was measured before and after the extraction by supersonic extraction with cyclohexane/acetone (vol: 1:1) as solvent. Three grams of dry soil was mixed with 10 mL of solvent and placed in a supersonic bath for 30 minutes. Then the loaded solvent was replaced by fresh cyclohexane/acetone and the supersonic extraction was repeated two times. Subsequently the soil material was dried 1 day at a temperature of 313 K. The amount of hydrocarbons was determined gravimetrically by weighing the dry soil material. Due to heterogenity of

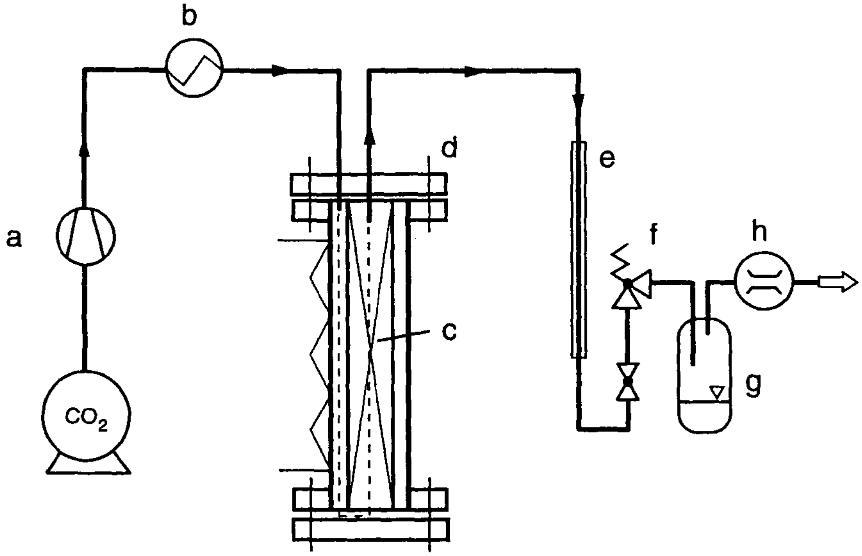

FIG. 1 Flow scheme of the extraction apparatus: (a) compressor, (b) preheater, (c) fixed bed, (d) extraction autoclave, (e) cooler, (f) backpressure regulator, (g) separator, (h) gas meter.

the hydrocarbon load, analysis was carried out three times. The soil material was mixed before and after the extraction process, and finally random samples were drawn from each batch.

For qualitative determination of oil compounds, the loaded solvent was collected after each extraction, concentrated under nitrogen flow, and dried for 1 day at a temperature of 313 K. Then the hydrocarbons were dissolved in hexane for GC analysis.

Two types of soil material were used for the experiments. The first was a contaminated soil material weathered for 20 years, a clayey loam with an equivalent particle diameter of $d_{p,v} = 18$ μm. It contained 13 wt% hydrocarbons (37% long alkanes, 34% monoaromatic hydrocarbons, 16% diaromatic hydrocarbons, 12% polyaromatic hydrocarbons). The second soil material was a loamy sand ($d_{p,v} = 182$ μm) which was contaminated artificially with 5 and 10 wt% diesel fuel. Soil material and diesel fuel were mixed mechanically without any solvent. It was aged for 1 month in dark glass bottles under exclusion of air. The diesel fuel contained 71.7% aliphatic hydrocarbons, 16.4% monoaromatic hydrocarbons, 8.0% diaromatic hydrocarbons, and 3.9% polyaromatic hydrocarbons.

RESULTS AND DISCUSSION

Experimental extraction data with carbon dioxide as the solvent show that the extraction result of weathered and artificially contaminated soil material is quite different. This is shown in Fig. 2. The fresh contamination can be extracted to 95% from the soil material using only a small amount of solvent (<1 g CO_2/g dry soil material), whereas weathered soil material can be cleaned only up to 21%, even if the solvent-to-soil ratio is greater than 10 g CO_2/g dsm. Experimental results cited in the literature show that the stationary point of extraction is reached at 4–6 g CO_2/g dsm (5, 6). Therefore it is not expected that the degree of extraction can be improved by increasing the solvent-to-soil ratio further. In contrast to artificially contaminated soil material, the contamination has diffused into the micropores over a long period of time and has become strongly adsorbed.

Reiss et al. (5) found that an increase in temperature of 20 K at 30 MPa results in an increase of the extraction result of approximately 2.5%. By increasing the temperature from 353 to 473 K at 35.5 MPa, Yang et al. (7) could raise the extraction result of phenanthrene from a marine sediment by 40%. Furthermore, Michel (6) improved the removal of perylen

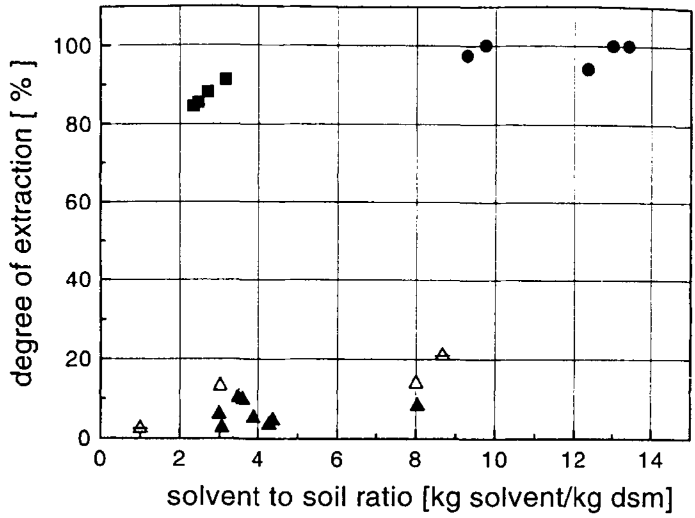

FIG. 2 Extraction results of contaminated soil material with supercritical carbon dioxide and water versus solvent-to-soil ratio: (≜) carbon dioxide, weathered, 323 K, 20 MPa; (▲) carbon dioxide, weathered, 353 K, 20 MPa; (△) carbon dioxide, weathered, 373 K, 20 MPa; (■) carbon dioxide, artificial, 353 K, 20 MPa; (●) water, weathered, 653 K, 25 MPa.

from an artificially contaminated soil material between 313 and 353 K at 34 MPa about 42%. In our case the temperature was varied between 323 and 373 K. No clear influence on the degree of extraction of weathered soil material could be observed, as can be seen in Fig. 2. One reason is the inhomogenous distribution of contamination in the soil material. The conditions of the fixed bed are not exactly reproducible because the density as well as the humidity of the soil package varies slightly, and therefore the residence time.

The nonpolar solvent carbon dioxide is not capable of disrupting dipole interactions of hydrocarbons and soil material. Several polar entrainers have been investigated on an analytical scale (7–9). Most often methanol, but also toluene, hexane, and acetonitrile were employed. Owing to its polarity and nontoxicity, water was used as a modifier for our experiments. Figure 3 shows that a higher soil humidity leads to a higher degree of extraction, but even then, acceptable clean-up results cannot be achieved. Water does not improve the solubility of hydrocarbons in carbon dioxide; nevertheless, the extraction result could be raised. The water covers free space on the particle surface and therefore avoids readsorption of hydrocarbons. The degree of extraction is strongly affected by the choice of entrainer in connection with the soil matrix (8), so that other entrainers may lead to better extraction results.

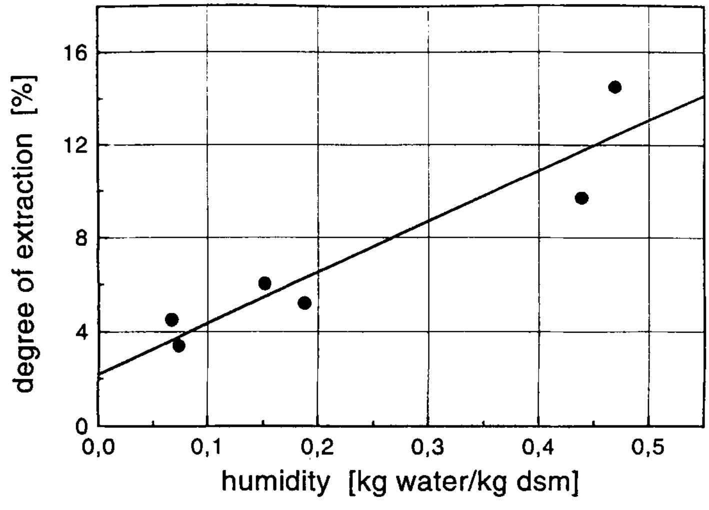

FIG. 3 Degree of extraction with supercritical carbon dioxide versus humidity of weathered soil material at 353 K, 20 MPa.

In comparison to the extraction of weathered soil material with supercritical water, carbon dioxide is an inefficient solvent for the extraction of field-weathered hydrocarbon residues (see Fig. 2).

MODELING

The model as applied to supercritical carbon dioxide extraction is described in detail elsewhere (1). The fixed bed is divided into a fluid phase and agglomerates, which consist of a solid phase and a pore phase. The different volumes are expressed as follows. Fixed bed:

$$V_{\mathrm{fb}} = L_{\mathrm{fb}} \frac{d_{\mathrm{fb}}^2 \pi}{4}$$

Fluid:

$$V_{\mathrm{f}} = \Phi(V_{\mathrm{fb}} - V_{\mathrm{s}})$$

Pore:

$$V_{\mathrm{p}} = (1 - \Phi)(V_{\mathrm{fb}} - V_{\mathrm{s}})$$

Solid:

$$V_{\mathrm{s}} = \frac{m_{\mathrm{s}}(1 + c_{\mathrm{s}})}{\rho_{\mathrm{s}}}$$

where:

$$\Phi = \frac{\text{actually trickled fixed bed volume}}{1 - V_{\mathrm{fb}}/V_{\mathrm{s}}}$$

Different mass transport effects were taken into consideration. The mass transfer from the solid phase into the pore phase is described as a reversible first-order reaction (Eq. 1). Furthermore, the mass transport in the pore phase is assumed as unstationary diffusion in a sphere (Eq. 2). The extent of axial dispersion is taken into consideration in an ideal stirred tank model. The fixed bed is divided into *n* equivolume sections with a constant fluid concentration within each section (Eq. 3). These sections are connected in series. The greater the number of units, the more the flow can be regarded as plug flow. These assumptions can be described mathematically by a system of dimensionless linked partial differential equations with the corresponding boundary and initial conditions (Eqs. 1–3).

Solid phase:

$$\frac{\partial X_s}{\partial F_0} = -\mathrm{Da}\cdot X_s\left(1 - \frac{X_p}{X_p^{\max}}\right); \qquad X_s(\xi, F_0 = 0) = 1 \tag{1}$$

Pore phase:

$$\frac{\partial X_p}{\partial F_0} = \mathrm{Da}\cdot X_s\left(1 - \frac{X_p}{X_p^{\max}}\right) \tag{2}$$

$$+ \frac{1}{\epsilon_p}\left[\frac{\partial^2 X_p}{\partial \xi^2} + \frac{2}{\xi}\frac{\partial X_p}{\partial \xi} + \mathrm{Da}\cdot X_s\left(1 - \frac{X_p}{X_p^{\max}}\right)\right];$$

$$X_p(\xi, F_0 = 0) = 0; \qquad \xi = 0: \frac{\partial X_p}{\partial \xi} = 0;$$

$$\xi = 1: \frac{\partial X_p}{\partial \xi} = \mathrm{Bi}(X_{F,n} - X_p|_{\xi=1})$$

Fluid phase (section n):

$$\frac{\partial X_{F,n}}{\partial F_0} = \frac{\psi}{4}\mathrm{Pe}_p(X_{F,n}^{\mathrm{in}} - X_{F,n}) + 3\,\frac{(1 - \epsilon_{fb})}{\epsilon_{fb}}\,\mathrm{Bi}(X|_{\xi=1} - X_{F,n});$$

$$X_F(\xi, \mathrm{F}_0 = 0) = 0; \qquad n = 1: X_{F,1}^{\mathrm{in}} = 0; \qquad n > 1: X_{F,n}^{\mathrm{in}} = X_{F,n-1} \tag{3}$$

Two parameters, the porosity of the fixed bed (ϵ_{fb}) and the agglomerate diameter (d_p), have to be estimated. The rate constant of solubilization or desorption (k_1) and the extent of axial dispersion (n) are adjustable to experimental data. The density of carbon dioxide was determined by the Bender equation of state (10) with coefficients from Sievers (11). The molecular diffusion coefficient ($D_{1,2}$) was estimated from experimental data for the binary system carbon dioxide–naphthalene (12). Finally, the mass transfer coefficient β was calculated by a correlation of Dwivedi and Upadhyay (13). Diesel fuel and weathered lubricating oil are a mixture of a variety of hydrocarbons. Due to the lack of phase equilibrium data concerning multicomponent mixtures of hydrocarbons and supercritical carbon dioxide, hexadecane was determined as a key component for the diesel fuel and pyrene for the weathered lubricating oil. For the correlation, solubility data of Kordikowski and Schneider (14) and Miller et al. (4) were used.

Former investigations showed that the model could be successfully used for correlation of the extraction of weathered soil material with supercritical water (see Fig. 4, Table 1). It is also suitable for modeling the extraction of artificially contaminated soil material with supercritical carbon dioxide as shown in Fig. 4. The correlation parameters are listed in Table 1. The limited solubility of hydrocarbons in supercritical carbon dioxide has no significant influence on the extraction results. The dimensionless rate-constant Damköhler number (see Table 1), which represents the relation of desorption and diffusion, shows that desorption is the rate-limiting mass transfer step for artificially and weathered contaminated soil material.

The model could not be used for correlating the extraction of weathered contaminated soil material with supercritical carbon dioxide. This process is modeled as a linear function of solvent-to-soil ratio (correlation parameters are in Table 1). Because of the minor influence of phase equilibrium, the bad extraction results of weathered contaminated soil material cannot be explained by the limited solubility of hydrocarbons in supercritical carbon dioxide. The reason is the nonpolar structure of carbon dioxide, which is not suitable for removing the strong interaction of soil material and hydrocarbons.

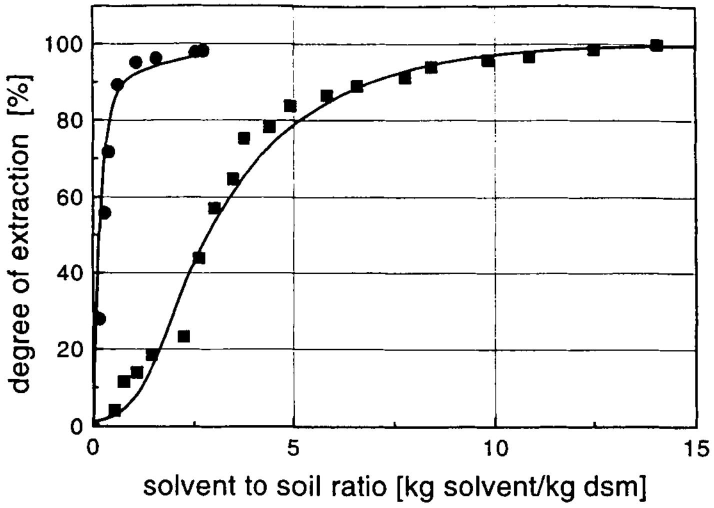

FIG. 4 Modeling of the extraction of weathered contaminated soil material with supercritical carbon dioxide at 673 K, 20 MPa and water at 653 K, 25 MPa (1) (for correlation data, see Table 1). Experimental data: (●) carbon dioxide, artificial, 353 K, 20 MPa; (■) water, weathered, 653 K, 25 MPa (1); (——) correlated data.

TABLE 1
Correlation Data for Supercritical Carbon Dioxide and Water Extraction of Contaminated Soil Material (see Fig. 4)

	Solvent/contamination		
	Water/weathered	Carbon dioxide/ artificial	Carbon dioxide/ weathered
T	653 K	353 K	353 K
P	25 MPa	20 MPa	20 MPa
d_{fb}	39 mm	39 mm	39 mm
L_{fb}	390 mm	390 mm	390 mm
$\dot{m}$	2 kg/h	0.77 kg/h	0.77 kg/h
m_s	356 g	696 g	334 g
ρ_s	1930 kg/m^3	2529 kg/m^3	1930 kg/m^3
c_s^0	140 g/kg	50 g/kg	114 g/kg
Humidity	100 g/kg	10 g/kg	470 g/kg
Solubility data	(1)	(14)	(4)
d_p	100 μm	200 μm	100 μm
ϵ_{fb}	0.4	0.2	0.13
k_{De}	1.5×10^5 l/m^2	0.5×10^5 l/m^2	6×10^3 l/m^2
n	1	1	1
Da	0.001	0.01	8.7×10^{-5}

In conclusion, results of a semibatch fixed-bed extraction can be predicted for both solvents, carbon dioxide and water. Former investigations showed that the model can be applied to supercritical water extraction of three different field-weathered and an artificially contaminated soil materials (1), whereas with carbon dioxide as solvent only the extraction of artificially contaminated soil material can be predicted.

CONCLUSION

Supercritical carbon dioxide has been investigated for the decontamination of weathered and artificially contaminated soil material. The extraction results for long weathered contaminated soil material were not better than 21%. In contrast to this, up to 95% of an artificial diesel contamination could be removed from sandy soil material.

The present model can be used to predict extraction results for different soil materials and different supercritical solvents at given operating conditions and physical properties. If desorption is strongly limited, the model is not suitable.

So far, supercritical carbon dioxide cannot be regarded as an alternative to supercritical water for the decontamination of long weathered soil material on an industrial scale, even if water is added. Other extrainers will be investigated in the future. Finally, a supersonic pretreatment of soil material may be helpful for disrupting the strong interaction bonding between soil material and contamination.

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DEFINITIONS

Independent variables:

Time: $F_0 = \dfrac{D_{\mathrm{eff}} t}{(d_p/2)^2}$

Coordinate on the radius: $\xi = r/R$

Concentrations:

$$X_s = \frac{c_s}{c_s^0};\quad X_p = \frac{c_p}{\rho_s c_s^0};\quad X_{f,n} = \frac{c_{f,n}}{\rho_s c_s^0};\quad X_p^{\max} = \frac{c_p^{\max}}{\rho_s c_s^0};\quad X_{f,n}^{\mathrm{in}} = \frac{c_{f,n}^{\mathrm{in}}}{\rho_s c_s^0}$$

Rate coefficients:

Dissolution: $\mathrm{Da} = \dfrac{k_1 D_{1,2}(d_p/2)^2}{D_{\mathrm{eff}}}$, whereas $D_{\mathrm{eff}} = D_{1,2}\epsilon_p/(2 - \epsilon_p)$

Mass transfer: $\mathrm{Bi} = \dfrac{\beta(d_p/2)}{D_{\mathrm{eff}}}$

Superficial velocity: $\mathrm{Pe} = \dfrac{u d_p}{D_{\mathrm{eff}}\epsilon_{fb}}$

Other:

Geometrical ratio: $\psi = \dfrac{d_p}{\Delta L_{fb}}$

NOMENCLATURE

Bi	Biot number
c_s^0	initial concentration of hydrocarbons in the solid material (mg/kg)
c_s, c_p, c_f	current concentrations of hydrocarbons in the solid, pore, and fluid phase, respectively (mg/kg)
$c_{f,n}^{\mathrm{in}}$	concentration of hydrocarbons in the fluid phase at the entrance of a section n (mg/kg)

c_p^{max}	maximum solubility in the pore phase determined by phase equilibrium (mg/kg)
d_{fb}	diameter of the fixed bed (m)
d_p	agglomerate diameter (m)
dsm	dry solid material
$D_{1,2}$	molecular diffusion coefficient (m^2/s)
Da	Damköhler number
D_{eff}	effective diffusion coefficient (m^2/s)
k_1	velocity of dissolution ($1/m^2$)
ΔL_{fb}	height of one section in the fixed bed (m)
L_{fb}	length of fixed bed (m)
m_s	mass of dry solid material (kg)
n	number of sections in the fixed bed
P_c	critical pressure
Pe	Peclet number
r	radius within agglomerate (m)
R	outer radius of agglomerate (m)
t	time (s)
T_c	critical temperature
T_{red}	reduced temperature
u	velocity of solvent flow in the empty tube (m/s)
$V_{fb,s,p,f}$	volume of fixed bed, solid, pore, and fluid phase, respectively (m^3)

Greek Symbols

β	mass transfer coefficient (m/s)
ϵ_{fb}	porosity of fixed bed (—)
ϵ_p	porosity of agglomerate (—)
ρ_s	density of solid material and hydrocarbons (kg/m^3)

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