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Remediation of Soils Contaminated with Total Petroleum Hydrocarbons and Polycyclic Aromatic Hydrocarbons: Extraction with Supercritical Ethane

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In this work two natural certified soils were extracted with supercritical ethane. One sample was polluted with total petroleum hydrocarbons (THP−soil) and the second one with polycyclic aromatic hydrocarbons (PAH−soil). The extraction studies were carried out using a high-pressure experimental device constructed in our laboratory. The extraction conditions for the TPH−soil were 27.1 MPa and 308.15 K, whereas those for the PAH−soil were 23.7 MPa and 308.15 K. Four independent extractions were performed on each test soil varying the volume of solvent: 10, 20, 30, and 40 L. Infrared spectroscopy was used to quantify the hydrocarbons in the residues after supercritical extraction of the TPH−soil, whereas high-performance liquid chromatography was employed, with a photodiode array detector and a fluorescence detector, to analyze seven polycyclic aromatic hydrocarbons (PAHs) in the residues after supercritical extraction of the PAH−soil. The extraction results show that there is a reduction of hydrocarbons of 76% using 10 L of ethane while the reduction is 90% using 40 L of ethane for the TPH−soil sample. For the sample of PAH−soil there is a reduction greater than 80% for the concentration of six of the seven PAHs studied. Naphthalene behaves as a refractory compound; hence, it presents the lowest reduction in concentration.

1. Introduction

Supercritical solvents have been used in a very wide range of scientific and technological fields because of several advantages, such as high efficiency, ease of separation of solutes from solvent, fast mass transfer rate, low energy consumption for solvent recovery, and elimination of conventional toxic solvents.[1−3] It has been claimed that supercritical extraction of pollutants from soils can be carried out at relatively low temperature, requiring less energy than thermal treatment, and that the soil structure and nutrients remain relatively intact. Therefore, in recent years the use of supercritical fluids (SCFs) has been proposed as an efficient alternative for the remediation of contaminated soils as well as in the recovery of hydrocarbons from different types of matrices.[4,5] There are reported several studies related to the extraction of complex mixtures of hydrocarbons from different matrices. Emery et al.[6] carried out extraction studies for the recovery of diesel from spiked clays using supercritical CO_2. Eckert-Tilotta et al.[7] extracted total petroleum hydrocarbons (TPH) from spiked and polluted natural soils using supercritical CO_2. A sample of soil contaminated with gasoil was studied for decontamination with supercritical CO_2 by Alonso et al.[8] Al-Marzouqi et al.[9] focused on the extraction of hydrocarbons from a spiked oil-saturated soil using supercritical CO_2. The supercritical fluid extraction (SFE) of four different bitumens was studied by Subramanian and Hanson[10] employing propane as solvent, and the recovery of complex mixtures of hydrocarbons from crude oil tank bottom sludges with supercritical ethane was reported by Ávila-Chávez et al.[11] Other works have reported the extraction of polycyclic aromatic hydrocarbons (PAHs) from different types of solid matrices with supercritical CO_2.[12−15] Laitinen et al.[16] included organic compounds of different nature and their removal from soils using supercritical CO_2. Becnel and Dooley[17] reported a review on the supercritical fluid extraction of PAHs from a wide variety of matrices such as soil, river sediment, urban dust, clay, loam, and petroleum sludge.

The solubility of individual paraffins of high molecular mass in SCFs has been widely studied due mainly to the fact that these compounds may be used as a model to represent different petroleum fractions. Although several supercritical solvents such as carbon dioxide, argon, ethane, ethylene, and propane have been used in different investigations, in general carbon dioxide is the most common solvent used both in solubility and in SFE studies.[18−23] However, based on a comparison of experimental results from solubility studies reported in the literature of high molar mass hydrocarbons in supercritical ethane and supercritical carbon dioxide, at the same intervals of pressure and temperature it was evident that hydrocarbons are much more soluble in ethane than in CO_2.[24−28] Nonetheless, there are reported in the literature few works in which a supercritical hydrocarbon is used as a solvent to extract hydrocarbons from different types of matrices. In particular Rose et al.[29] using ethane as supercritical solvent extracted a Peace River bitumen (Alberta, Canada) blended with sand. Therefore, the decision to use ethane in this work to extract different hydrocarbons from contaminated soils was a natural selection in view of previous experimental evidence. Furthermore, there exists other undeniable advantages since ethane possesses a gas−liquid critical temperature (T_c = 305.4 K),[30] which is similar to that of CO_2 (T_c = 304.2 K)[30] whereas its critical pressure (p_c = 4.88 MPa)[30] is much lower than that of CO_2 (p_c = 7.39 MPa).[30]

In this work two certified natural soil samples (certified reference materials, CRMs) polluted with known concentrations of TPH and PAHs were extracted with supercritical ethane. The objective was to quantitatively demonstrate that polluted soils, after a relatively short extraction time with a supercritical solvent, hence low solvent consumption, can reduce their hydrocarbon concentration to levels below environmental regulations, thus yielding soils that can be reused for different human activities.

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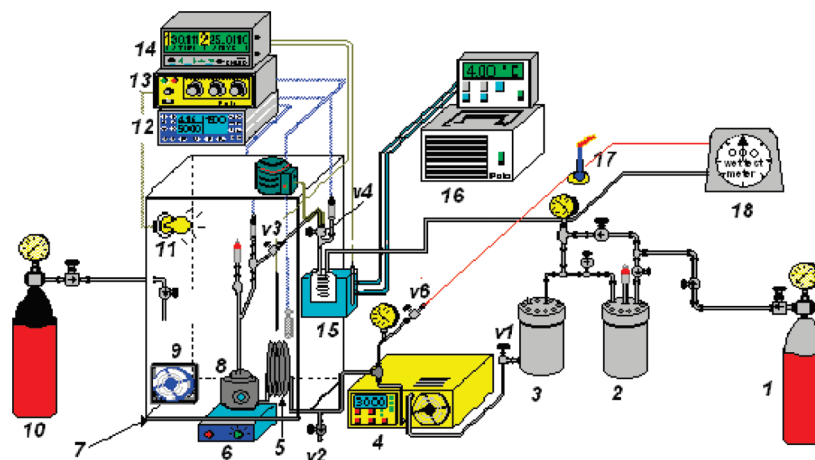
Figure 1. Experimental system for the extraction of hydrocarbons from solid matrices using supercritical solvents: (1) ethane commercial cylinder, (2 and 3) stainless steel storage cells, (4) high-pressure positive displacement pump, (5) 2 m stainless steel coil, (6) stirring plate, (7) constant temperature air bath, (8) extraction cell, (9) electric fan, (11) heat source, (12) digital pressure indicator, (13) proportional temperature controller, (14) digital thermometer, (15) recovery cell, (16) circulating bath, (17) burner, and (18) wet test meter.

2. Experimental Section

2.1. Reagents. A standard mixture, about 1 cm^3, of 16 different PAHs dissolved in acetonitrile (CSM-8310 rpm) was purchased from Chem Service (West Chester, PA). This standard was used to obtain the chromatographic calibration curves for each of the seven PAHs studied. The standard calibration sample for TPHs was a mixture of hydrocarbons, in accordance with U.S. EPA method 418.1, purchased from Buck Scientific (East Norwalk, CT). The ethane was supplied by Praxair, Mexico (>99 mol % purity). Solvents dichloromethane (HPLC grade, 99.9 mol % purity) and acetone (HPLC grade, 99.9 mol % purity) were from J.T. Baker, Mexico. Acetonitrile (HPLC grade, ≥99.9 mol % purity) was obtained from EM Science (EMD Chemicals, Gibbstown, NJ). 1,1,2-Trichlorotrifluoroethane, 99.9 mol % purity, was purchased from Dupont de Nemours (Wilmington, DE). Silica gel, 60−200 mesh, for chromatography was from J.T. Baker (Xalostoc, Mexico) as well as the anhydrous sodium sulfate (Na$_2$SO$_4$). Water was type 1 reagent from an UltraPure water system, model Easypure RF (Barnstead Thermoline; Dubuque, IA).

2.2. Soil Samples. Two certified natural soil samples were purchased as Environmental Reference Materials (TRCorp, WY). The TPH-sandy clay loam (CRM350-100, lot J435) is a typical soil sampled from around a leaking storage tank of diesel. The PAH-loamy sand (CRM115-100, lot JC115) was obtained from the western region of the United States. The CRMs are natural matrix material whose certified concentration or reference value is established through interlaboratory analysis. The samples were used as received and kept refrigerated at 4 °C in the dark until experiments were performed.

2.3. Extraction Device. The apparatus used in this work to carry out the extractions of the certified samples of TPH−soil and PAH−soil was constructed in our laboratory. The equipment is an updated version of a device previously used to study the solubility of saturated linear hydrocarbons in supercritical carbon dioxide[22,31] and to regenerate used lubricant oils with supercritical ethane.[32] The device has been used in a previous work to recover complex mixtures of hydrocarbons from crude oil tank bottom sludges.[11] The assembly of the whole experimental apparatus is shown in Figure 1.

The apparatus consists of three main subsystems: the solvent feeding system, the extraction system, and the separation of solutes from the solvent system. The feeding system is composed of an ethane commercial cylinder (1) which feeds

solvent into two 220 cm^3 stainless steel storage cells (2 and 3). Ethane from the storage cells is sent to a high-pressure positive displacement pump (4), LabAlliance, model SFC-24 (State College, PA), which pressurizes ethane up to the desired working pressure into the extraction cell. The positive displacement pump provides a reliable, accurate, and reproducible flow of ethane during the extraction process. The pump feeds ethane into the extraction system, which is placed into an insulated constant temperature air bath (7). The extraction system is formed by a 2 m stainless steel coil (5) to ensure thermal equilibrium of the solvent and the extraction cell (8), which contains the soil sample to be studied at the selected equilibrium temperature and pressure. The extraction cell, constructed in 316 stainless, with an internal volume of 14 cm^3, was adapted with two optical-quality sapphire windows (25 mm o.d. × 5 mm thick) provided by Thoughtventions Unlimited LLC (Glastonbury, CT). Also, a magnetic stirring bar was placed inside the extraction cell to improve mass transfer from the solid matrices into the solvent phase with the help of a stirring plate (6). The temperature in the extraction section was kept at the desired value by means of a heat source (11) regulated through a YSI proportional temperature controller (13), model 72 (Yellow Springs, OH). Homogeneity of the temperature in the extraction system was reached by means of an electric fan (9). The thermometer (14) used to register the temperature in the extraction system was a Systemteknik AB digital thermometer, model S1220 (Lindigo, Sweden), with a precision of ±0.001 K, adapted with a platinum resistance sensor for surfaces, which was compared with the readings from an F-250 Automatic Systems Laboratory digital thermometer (MA) with a Pt-100 probe calibrated at the factory and traceable to the US NIST with an accuracy of ±0.005 K. The average uncertainty of the temperature measurements obtained in the extraction system was ±0.15 K. The equilibrium pressure during the extraction process was registered through a digital Druck multifunction pressure indicator (12), model DPI 145 (Leicester, U.K.). The pressure indicator was calibrated against a dead weight pressure tester from Pressurements Ltd., model T2200/3LP (Dunstable, Bedfordshire, U.K.) with an accuracy of ±0.03% in the full range. Considering all possible sources of uncertainty the average uncertainty for the equilibrium pressure measurements was estimated to be ± 0.21 MPa.

The extractions were performed through a dynamic process, i.e., the solvent is continuously fed into the extraction or

equilibrium cell, always attaining thermodynamic equilibrium. Subsequently, the solvent together with the extract proceed to the separation system which is composed of separation or recovery cell (15), which is under conditions of low pressure, with the help of a micrometering valve, and constant temperature of 277 K, with the aid of a Julabo F70 circulating bath (Vista, CA) using water as thermal fluid (16). These conditions ensure total separation of the extracted hydrocarbons from ethane. With the aim of avoiding the dragging of solid particles from the extraction cell a Hoke micrometer filter, model 6313G4B, was adapted in the stainless steel line after the recovery cell. Finally, ethane is sent to the wet test meter (18) to measure the total volume used in each experimental run.

Soil samples from 7.2 to 8.2 g were used in the different supercritical extraction experiments.

2.4. Methods. In order to test the analytical infrastructure of our laboratory we decided to verify in-house the pollution levels reported in the certificate of each purchased soil. It is of interest to mention that this work is part of a long-term research program to analyze and remediate contaminated soils from Mexico as well as recovering hydrocarbons from different matrices.[11,33] Both certified soils were extracted using Soxhlet devices according to EPA method 3540C.[34] Approximately 7.5 g of each soil was placed in extraction thimbles with 1 g of Na_2SO_4 (dried at 150 °C overnight). The thimbles containing the soil samples were extracted with 200 cm^3 of a mixture of acetone−dichloromethane (50:50 v/v) during 16 h. After the extraction the liquid samples were concentrated in a Kuderna-Danish apparatus. The TPHs were analyzed according to EPA method 418.1,[35] while the PAHs were analyzed following EPA method 3600C.[36]

2.4.1. Analysis of TPHs and PAHs. As mentioned above, the determination of TPHs in the corresponding certified soil sample was based on EPA method 418.1. Infrared spectroscopy was performed with equipment from Buck Scientific (East Norwalk, CT), model HC-404, at a wavelength of 2930 cm^{-1}. The calibration curve of absorbance−concentration was obtained using the standard calibration sample for TPHs dissolved in 1,1,2-trichlorotrifluoroethane. Therefore, the value of TPHs for the certified soil sample was estimated after extraction by interpolations from the equation of a straight line fitted to seven pairs of experimental points of absorbance−concentration.[37] Each calibration point is the average of at least five readings of absorbance.

Identification and quantification of PAHs in the certified soil sample were carried out with dual detection using a Waters HPLC system consisting of a solvent delivery system, model 626, with a controller, model 600S, a fluorescence detector, model 474, a photodiode array detector, model 996, and a solvent degasser unit, model 6324 Degassit (MetaChem Technologies, Torrance, CA). For the separation of the PAHs a stainless steel analytical column of 125 mm length × 4.6 mm internal diameter, with polymeric bonded phase, Phenomenex Envirosep PP (Torrance, CA), was used. The analysis was based on EPA method 8100.[38]

The best chromatographic conditions to separate and quantify the studied PAHs were established to be the following: isocratic elution with acetonitrile−water 40:60 (v/v) for 5 min was performed, changing to a gradient for 25 min to reach acetonitrile−water 100:0 (v/v). The flow was kept constant throughout at 1.2 cm^3/min. These conditions yielded the best separation and resolution of the different PAHs. Identification of each PAH was performed with the UV detector (photodiode array detector), whereas quantification was carried out with a

Table 1. Reference Value, Confidence Interval, and Prediction Interval for the Concentration of Several Analytes of Two Samples of Certified Soils (Certified Reference Materials)^a

compound	reference value (mg/kg)	confidence interval (mg/kg)	prediction interval (mg/kg)	this work (mg/kg)	recovery (%)
TPH	8296	7387–9203	4262–12 329	5083 ± 277	61.3
acenaphthene	4.60	4.06–5.15	6.31–17.8	14.40 ± 1.51	313.0
naphthalene	1.34	1.21–1.47	0.72–1.96	1.42 ± 0.11	106.0
fluorene	13.0	11.4–14.6	5.19–20.8	6.32 ± 2.61	48.6
fluoranthene	22.1	19.8–24.5	11.9–32.3	20.32 ± 1.16	91.9
pyrene	7.66	6.78–8.54	3.44–11.9	7.69 ± 1.36	100.4
benzo(a)anthracene	12.1	10.8–13.3	6.31–17.8	11.72 ± 0.75	96.9
chrysene	16.8	14.5–19.0	6.15–27.4	18.60 ± 1.10	110.7

^{a} The last two columns give the experimental values of concentration obtained in this work for the same two samples of soils and the recovery in percent with respect to the reference values, respectively. All values from the certificates are expressed on a dry weight basis.

fluorescence detector (scanning fluorescent detector). The wavelengths of excitation and emission (λ_{ex} and λ_{em}, respectively) of the fluorescence detector were changed throughout the elution process to obtain the highest resolution: 0−17 min, 280 λ_{ex} and 340 λ_{em}; 17−21 min, 240 λ_{ex} and 425 λ_{em}; 21−25 min, 265 λ_{ex} and 385λ_{em}. The concentration of each of seven PAHs in the certified natural soil sample was obtained by interpolation from an external five-point calibration curve which was prepared from the purchased standard mixture of different PAHs dissolved in acetonitrile.[33,39] Each calibration point is the average of at least five injections.

The final or combined uncertainty of the values of concentration was evaluated through a complete statistical analysis on the propagation of uncertainties for all the known variables involved in the experimental work which considered the use of the so-called Student's t distribution.[39,40] Therefore, the uncertainty was always determined with 95% confidence.

In all the calibration experiments only fresh solutions of known concentration were used in order to avoid errors caused by possible adsorption of the hydrocarbons on the walls of the glassware.

2.4.2. Volume of Ethane. After supercritical extraction the extract of each soil studied in this work is sent to a separation cell whose temperature and pressure are those to ensure complete separation of the solutes from the solvent ethane. Once this separation is carried out ethane is fed to a calibrated wet test meter (Precision Scientific Co., Chicago, IL) in order to obtain the volume of ethane used in each extraction. The volume was measured at ambient conditions of temperature and pressure and corrected to standard conditions of temperature and pressure (STP), i.e., 293.15 K and 101.325 kPa.

3. Results and Discussion

3.1. Comparison of Analyte Concentration Against Certificates. Table 1 reproduces the analyte concentration or reference value reported by the certificate of each of the two CRMs, i.e., TPH−soil and PAH−soil. The table also includes the confidence interval (95%) for the reference value and the prediction interval around the reference value (95%), which indicates that measurements should fall within the prediction interval range 19 of 20 times. The different values obtained in this work are given in the Table 1, together with their experimental uncertainty. The experimental values of the concentrations for the TPH−soil and PAH−soil of this work are the mean of two independent samples from each soil. The last column in Table 1 contains the recovery percentage obtained in this work with respect to the reference concentrations reported in the certificates.

Table 2. Values of Pressure, Temperature, Volume of Ethane, Mass of Solvent to Mass of Sample (Phase Ratio), and Extraction Time Used in the Supercritical Extraction of Natural Soil Samples with TPHs and PAHs

| sample	P^a (MPa)	T^b (K)	V^c (L)	V^d (L)	g of C_2H_6/g of soil^e	t^f (min)
TPH-10	27.10 ± 0.18	308.18 ± 0.02	10.00	6.86	1.18	21.88
TPH-20	27.04 ± 0.17	308.15 ± 0.03	20.00	14.40	2.44	38.98
TPH-30	27.11 ± 0.19	308.13 ± 0.01	29.99	20.71	3.58	67.50
TPH-40	27.09 ± 0.16	308.15 ± 0.03	40.00	29.41	4.92	73.87
PAH-10	23.72 ± 0.16	308.15 ± 0.01	10.00	6.23	0.94	30.68
PAH-20	23.71 ± 0.15	308.15 ± 0.01	20.00	12.10	1.96	37.78
PAH-30	23.70 ± 0.15	308.14 ± 0.01	30.15	19.29	3.26	51.23
PAH-40	23.62 ± 0.21	308.15 ± 0.03	40.00	27.55	4.54	89.53

^{a} Extraction pressure. ^{b} Extraction temperature. ^{c} Volume of ethane used in the extraction at ambient conditions. ^{d} Volume of ethane at standard conditions of pressure and temperature (i.e., 101.325 kPa and 293.15 K). ^{e} Mass of ethane to mass of soil ratio. ^{f} Total time of extraction.

It is observed that the concentration value obtained in this work for the TPH−soil is in agreement with the prediction interval given by the certificate. Regarding the PAH−soil, the concentration for five of the seven PAHs is in agreement with both the confidence and the prediction intervals; furthermore, for naphthalene, pyrene, and benzo(*a*)anthracene the concentration agrees, within experimental uncertainty, with the corresponding reference value. The concentration of acenaphthene and fluorene is in agreement with the prediction interval.

It can be noted that the set of seven PAHs studied here contains compounds of low molar mass (naphthalene), medium molar mass (acenaphthene and fluorene), and high-molar mass (fluoranthene, pyrene, benzo(*a*)anthracene, and chrysene).

3.2. Extractions. Table 2 shows the thermodynamic parameters that were controlled in each of the eight extractions carried out. The nomenclature used in the first column indicates TPH for certified soil samples with total petroleum hydrocarbons and PAH for certified soil samples with polycyclic aromatic hydrocarbons. The number after each acronym identifies the volume of solvent used in each extraction. Two sets of values are given for the volume of ethane used in each extraction: the actual readings from the wet test meter and the corrected values at standard conditions. From the latter we derived the mass of solvent to obtain the mass ratio of solvent to soil sample for each extraction. Table 2 also includes the time of each extraction. Also, it is of interest to mention that under the average extraction conditions of pressure and temperature for the TPH−soil the density of pure ethane was obtained to be 14.250 mol/L and for the PAH−soil it is 13.968 mol/L.[41]

Previous work from the literature and from our laboratory agree on the best conditions of temperature and pressure to reach
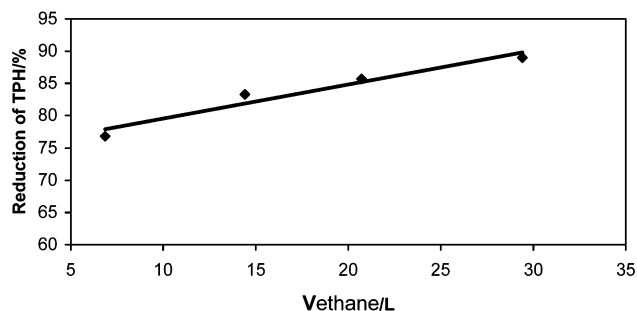
Figure 2. Reduction of the concentration of total petroleum hydrocarbons in the residual soil samples after supercritical extraction as a function of solvent volume at 27.1 MPa and 308.15 K. Line is drawn to show tendency of the results.

high extraction yields and low extraction time. At relatively low temperature and high pressure the solvent density reaches values similar to those in its liquid state, hence obtaining high solubility or extraction yield. We chose a low temperature of 308.15 K and pressure close to the working limit of our experimental device, 30 MPa, since at high density of the solvent pressure has little effect on extraction recoveries.[17]

3.3. Total Petroleum Hydrocarbons. Table 3 shows the experimental results for the concentration of hydrocarbons that remained in the soil residues after the different supercritical extractions were accomplished. The first column contains the analyte of interest and the second column the initial concentration determined in this work for TPHs and seven different PAHs. The concentration of hydrocarbons in the residues is given as a function of the corrected ethane volume used in each extraction. We also included in parentheses the concentration reduction in percent with respect to the concentration determined here. The concentration reduction in percent is equivalent to the extraction yield. It is important to place emphasis on the fact that the different results for the concentration of TPHs were obtained from independent extractions, that is, they do not correspond to cumulative extractions. Also, a replicate extraction was performed for the 10 L run, and the concentration of each sample was within the determined experimental uncertainty; hence, the TPH concentration included in Table 3 for the corrected ethane volume of 6.86 L is the average of two values.

Figure 2 shows the reduction in concentration of the TPHs in percent as a function of the corrected volume of ethane. It is clearly observed that a large reduction of TPHs occurs for the extraction with only 6.86 L of ethane or 1.18 g of ethane/g of soil, i.e., 76.8%. For the extraction with 14.40 L (2.44 g of ethane/g of soil) the reduction of TPHs is 83.3%, which is higher, only 6.5%, with respect to the extraction with 6.86 L; however, the volume or mass of ethane used is now more than

Table 3. Experimental Results for the Concentration of Hydrocarbons in the Residua after Supercritical Extraction as a Function of the Corrected Ethane Volume Used in Each Independent Extraction

compound	initial concentration (mg/kg)	concentration in the residual soil (mg/kg) (**concentration reduction or extraction yield (%)**)			
		6.86 L	14.40 L	20.71 L	29.41 L
TPHs	5083 ± 277	1178 ± 66 (**76.8%**)	850 ± 45 (**83.3%**)	726 ± 63 (**85.7%**)	557 ± 98 (**89.0%**)

compound	initial concentration (mg/kg)	concentration in the residual soil (mg/kg) (**concentration reduction or extraction yield (%)**)			
		6.23 L	12.10 L	19.29 L	27.55 L
acenaphthene	14.40 ± 1.51	1.74 ± 0.10 (**87.6%**)	2.34 ± 0.19 (**83.4%**)	2.36 ± 0.20 (**83.2%**)	2.47 ± 0.43 (**82.4%**)
naphthalene	1.42 ± 0.11	0.58 ± 0.09 (**59.0%**)	0.49 ± 0.09 (**65.2%**)	0.40 ± 0.10 (**71.8%**)	0.59 ± 0.09 (**58.2%**)
fluorene	6.32 ± 2.61	0.89 ± 0.11 (**85.8%**)	1.24 ± 0.12 (**80.4%**)	1.04 ± 0.11 (**83.5%**)	1.10 ± 0.12 (**82.6%**)
fluoranthene	20.32 ± 1.16	2.37 ± 0.18 (**88.3%**)	3.06 ± 0.21 (**85.0%**)	3.07 ± 0.22 (**84.9%**)	2.36 ± 0.39 (**88.4%**)
pyrene	7.69 ± 1.36	1.29 ± 0.08 (**83.2%**)	1.46 ± 0.09 (**81.1%**)	1.45 ± 0.10 (**81.1%**)	0.78 ± 0.07 (**89.8%**)
benzo(*a*)anthracene	11.72 ± 0.75	2.02 ± 0.12 (**82.8%**)	1.53 ± 0.09 (**86.9%**)	2.18 ± 0.12 (**81.4%**)	0.96 ± 0.15 (**91.8%**)
chrysene	18.60 ± 1.10	6.61 ± 0.55 (**64.5%**)	2.69 ± 0.23 (**85.5%**)	4.73 ± 0.39 (**74.6%**)	2.20 ± 0.19 (**88.2%**)

double. It is also observed that by increasing the volume of ethane from 14.40 to 20.71 L and from 20.71 to 29.41 L the reduction percentage of TPHs is small. It is adequate to note that a maximum value of 89.0% for the reduction of TPHs was obtained with 29.41 L (4.92 g of ethane/g of soil). All observations remain valid if instead of analyzing the results for reduction in concentration of the TPHs in percent as a function of the corrected volume of ethane we use as an independent variable either the ratio of the mass of ethane to mass of soil sample, so called phase ratio, or the extraction time, both given in Table 2.

These results are of great importance considering that the pollution of soils is unfortunately a common subject in different parts of the planet as a result of human activities. The results show that solid matrices contaminated with a complex mixture of hydrocarbons can efficiently be remediated by the use of adequate solvents, mainly hydrocarbons, under optimal super-critical conditions. Specifically, the results fulfill Mexican regulations published by the Ministry for the Environment[42] regarding the use of soils contaminated with hydrocarbons. There exist three types of soils according to their use, i.e., agricultural, residential, and industrial soils. Pollution limits for agricultural soils are stricter than in soils for industrial activities; furthermore, pollution limits depend on the type of hydrocarbons, e.g., light hydrocarbons have a lower concentration limit. For example, a soil polluted with a light hydrocarbon fraction (e.g., gasoline) has a limit of 200 mg/kg (parts per million), while soils with heavy hydrocarbon fraction can have up to 6000 mg/kg. Hence, in this context the certified TPH–soil studied in this work can be considered as an example of a polluted industrial soil, which after extraction with 6.86 L of ethane (or 1.18 g of ethane/g of soil) can be considered to be clean for reuse in industrial areas. The same polluted soil after extraction with 29.41 L of ethane (or 4.92 g of ethane/g of soil) reached a very low concentration of hydrocarbons, i.e., 557 mg/kg, which is only the 11.0% of the original concentration of hydrocarbons. This value now meets the environmental legislation for low concentration of contaminants, and the soil could be used for agricultural activities.

Emery et al.[6] extracted hydrocarbons typical of a diesel from a spiked soil and obtained extractions over 75%; however, they obtained low recovery of high molar mass hydrocarbons as a consequence of the low solubility of large molecules in supercritical CO_2. The thermodynamic extraction conditions reported by these authors to give the highest extraction yield were 37 MPa and 80 °C. It is clear that these values are much higher than those used in this work. Brooks and Uden[43] studying a spiked soil reported extraction yields greater than 90%, although the extractions were performed at subcritical conditions of temperature (296–298 K) for CO_2. Liang and Tilotta[44] extracted gasoline and fuel oils independently from spiked sand, loam, and clay samples using supercritical argon. The extraction conditions were 50 MPa and 150 °C. The reduction in the concentration of hydrocarbons was about 80% with respect to the original concentration. This result is similar to the values reported in Table 3, although it is important to note that the values of the thermodynamic parameters used for the extraction by those authors are much higher than the ones used in this work, and after 100 min it was not possible to extract quantitatively a fuel oil from loam and clay matrices.

The ratios (mass of ethane/mass of soil), also called phase ratio, used in the four extractions of TPHs are indeed substantially lower than those reported in other works, even for solid
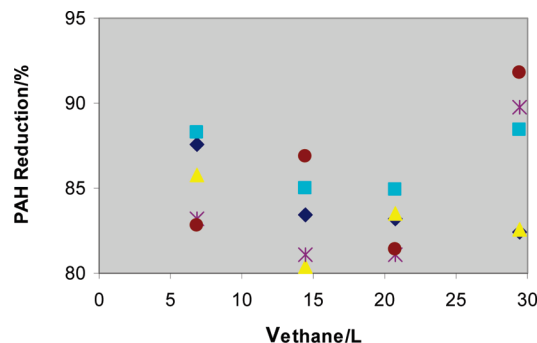
Figure 3. Reduction of the concentration of polyaromatic hydrocarbons in the residual soil samples after supercritical extraction as a function of solvent volume at 23.7 MPa and 308.15 K: (◆) acenaphthene, (▲) fluorene, (*) pyrene, (•) benzo(*a*)anthracene, (■) fluoranthene.

matrices spiked with contaminants, which are considered to be easier for desorption.[7,17,45]

3.4. Polycyclic Aromatic Hydrocarbons. The experimental concentration results for seven different PAHs determined in the residual soil samples, i.e., after the certified PAH–soil was subjected to extraction with supercritical ethane, are given in Table 3. The latter also includes, for comparison purposes, the initial concentration of each PAH experimentally determined in this work. The concentration results, together with the percentage of reduction or extraction yields, are given for each ethane volume used in the extractions. Here again it is adequate to emphasize that the results for the concentration of the PAHs and consequently the reduction percentages were obtained from independent extraction experiments; hence, they are not cumulative results.

The results show that the reduction of concentration for acenaphthene, fluorene, fluoranthene, pyrene, and benzo(*a*)an-thracene is higher than 80% with the lowest corrected ethane volume used, i.e., 6.23 L (or 0.94 g of ethane/g of soil). It is also observed that an increase of ethane volume in the studied range, i.e., 6.23–27.55 L, does not produce an important increase in the extraction capacity for four of these five PAHs, whereas the concentration reduction for benzo(*a*)anthracene changes from 82.8% to 91.8%. The concentration reduction for chrysene reaches a high value of 85.5%, which is similar to the corresponding value for the five mentioned PAHs, with an ethane volume of 12.10 L, and its concentration reduction percentage with 19.29 and 27.55 L of ethane is also similar to that achieved for the five PAHs mentioned, with the same ethane volume. As a whole it can then be stated that six PAHs present similar results for the extraction yield with supercritical ethane. It is clear that naphthalene behaves in a different way since its concentration reduction is lower than that for the other six PAHs with 6.23 L of ethane, and its maximum concentration reduction, 71.8%, is achieved with 19.29 L (or 3.26 g of ethane/g of soil). Figure 3 shows the change of the concentration reduction for some of the PAH's as a function of the volume of ethane used in each individual extraction experiment.

The experimental results indicate that naphthalene, a low molar mass contaminant, shows a refractory behavior to extraction, whereas the medium molar mass contaminants, acenaphthene, phenanthrene, and anthracene, and the high molar mass contaminants, pyrene and chrysene, present high affinity toward supercritical ethane. Therefore, the results in Table 3 lead us to infer that the relative molar mass, i.e., a coarse measure of the molecular size, and the volatility of the different PAHs studied are not the only factors that influence the extraction from a solid matrix, but their molecular structure

should also play an important role in the overall interactions with the solid matrix, with the solvent, and surely among themselves. Several different factors that affect the efficiency of the supercritical extraction should be considered simultaneously if rationalizing of the experimental results is attempted. For example, naphthalene is formed by two aromatic rings and is the PAH with the lowest relative molar mass; nonetheless, its concentration reduction after extraction is relative small with respect to the other PAHs compounds which are larger in size and less volatile, i.e., the relatively high volatility of naphthalene does not help to increase the extracted amount, for a given ethane volume. Chrysene is on the other extreme; it is a four aromatic ring compound and consequently less volatile than naphthalene; however, its concentration reduction with 6.86 L of ethane is higher than that for naphthalene. Benzo(a)anthracene, being an structural isomer of chrysene, presents concentration reduction values which are slightly higher than those for chrysene for any value of the ethane volume. Pyrene also has four aromatic rings, although arranged in a different way that gives a slightly lower molar mass than that for chrysene and benzo(a)anthracene, and presents concentration reduction values which are very close to those for benzo(a)anthracene. Fluoranthene has a molar mass equal to that for pyrene, although only three aromatic rings bonded together through a cyclopentane; however, it presents concentration reduction percentages very close to those for pyrene and benzo(a)anthracene. Acenaphthene and fluorene are formed by essentially the same structural units, two aromatic rings and a cyclopentane, although their arrangement is different; hence, the relative molar mass for the former is 154.21 g/mol and 166.22 g/mol for the latter. It is observed from Table 3 that the extraction yield is essentially the same for both compounds in the range of studied ethane volumes.

The extraction behavior observed in this work for naphthalene is consistent with that obtained in native samples of railroad bed soil, petroleum waste sludge, and urban air particulate matter extracted with supercritical CO_2 at 40 MPa and 60 °C.[14] Also, a similar behavior was observed for pyrene and chrysene. The results obtained here for fluorene, fluoranthene, and benzo(a)anthracene are similar to those reported by Hawthorne et al.[15] These authors carried out extractions of PAHs from soil samples from a wood treatment facility and from a railroad bed at 40 MPa and 60 °C using CO_2 as a solvent. It should be noted that the extraction parameters of both literature works cited above are higher than the values applied here for both equilibrium temperature and pressure.

As in the results discussed above for the extraction of TPHs, the ratios (mass of ethane/mass of soil) used in the extractions of PAHs are indeed lower than those used in other works reported in the literature, including the study of solid matrices spiked with contaminants, which are generally considered easier to extract.[12−14,17,46]

The extraction yields obtained in this work are very high considering that native solid heterogeneous matrices were studied as compared with spiked matrices, since it is well known that contaminants on spiked matrices may be bound primarily by interactions with the matrix surface while those on weathered soils are more strongly bound.

4. Conclusions

We studied the extraction of contaminants from natural heterogeneous soils instead of spiked native soils or model solid matrices since the latter do not have the same difficulties, e.g., strong interactions between contaminants and matrix, to remove toxic components. Furthermore, extractions from spiked matrices tend to overestimate the efficiency of the extraction methods used.

The experimental results obtained in this work make it clear that supercritical fluid extraction, with ethane as a solvent without a modifier, is highly feasible to quantitatively remediate natural soils contaminated with TPHs and PAHs. Furthermore, the temperature and pressure conditions are easy to handle and the amount of solvent is small as well as the extraction time. All these factors lead to a less energy-intensive process than, for example, incineration of the soil.

The experimental methods and results obtained in this work will be the basis for studying the extraction of contaminants from natural soil samples taken from sites around industrial facilities of the oil industry in Mexico. These results will be the subject of a future report.

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