



Supercritical CO₂ extraction of PAHs on spiked soil Co-solvent effect and solvent regeneration by ozonization

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ABSTRACT

The supercritical CO₂ extraction of four PAHs (acenaphthene, phenanthrene, anthracene and fluoranthene) from an artificially contaminated soil has been investigated. The effect of temperature (40–60 °C), pressure (300–500 bar) and extraction time (90–150 min) has been assessed by conducting a Box–Behnken experimental design. The results suggest the existence of perturbation variables other than the aforementioned controlled variables leading to a significant dispersion of extraction recoveries. With the exception of anthracene, an optimum in temperature (50 °C) is envisaged when extracting the PAHs. Analogously, with the exception of anthracene (positive effect), pressure does not have a significant influence. The recovery yield increases as extraction time is increased to a value of 120 min. No further improvement is experienced thereafter.

If a co-solvent is used (H₂O₂ aqueous solution) a beneficial effect can be noticed. Hydrogen peroxide concentration did exert no significant influence in the process.

Methanol used to collect the extracted PAHs could be regenerated by gaseous ozone and reused in several consecutive runs.

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1. Introduction

Supercritical fluids (SCFs), in particular supercritical carbon dioxide, are progressively deserving the epithet of “green solvent for the 21st century”. SCFs offer properties that are intermediate between liquids and gases. These properties are obtained through the application of pressures and temperatures above the critical point. They can be summarized in lower viscosity and thermal conductivity than in liquids and better diffusion characteristics. Carbon dioxide shows a relatively mild critical point (72.8 bar and 31.1 °C) not requiring an excessive amount of energy to get supercritical conditions. Other advantages include the low cost of the carbon dioxide, high chemical stability and lack of toxicity [1].

Use of supercritical CO₂ in soil remediation processes is recently being considered. The advantages of using CO₂ include the affinity for non-polar contaminants that are tightly adsorbed into solid particulates [2–4]. The number of factors influencing the efficiency of supercritical carbon dioxide extraction (SCCDE) is considerable [3,5], i.e. soil nature and composition, temperature, pressure, flow-rate, solute sequestration extent, presence of co-contaminants

other than the target compounds, extraction time, etc. For a particular contaminated soil, it seems that the pair temperature/pressure (directly affecting, amongst others, CO₂ density and pollutant solubility) and the operating variables flow-rate and extraction time are the main factors to be taken into account when examining the most influential parameters.

Broadly speaking, temperature improves the kinetics of the extraction process and contaminant desorption, however, it also decreases the extractant density and hence its capability for solute removal. Thus, depending on the soil nature, Elektrowicz et al. [2] report a negative effect of temperature on phenanthrene recovery from clays. Contrarily, other authors [3,6] claim a positive effect of temperature when extracting some polynuclear aromatic hydrocarbons (PAHs) from different soils. Pressure has a lower impact than temperature, although its beneficial effect is assumed. Flow rate is an important parameter when the process is controlled by the solubility of the contaminants, nevertheless, if the process is kinetically controlled no influence is to be expected.

In any case, the errors associated to: (a) soil artificial contamination and/or homogenization, (b) difficulties in controlling the operating parameters in the extraction run, (c) contaminant depositions in lines, (d) Soxhlet extraction and (e) target compounds analysis, indicate that the statement of parameter influence is a rather daunting task. Moreover, most of works focused on the

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elucidation of the temperature effect, pressure influence, etc. on supercritical extraction efficacy have been carried out by investigating “one variable at a time”. In this work, an attempt has been made to analyze the influence of temperature, pressure and extraction time on the recovery of four PAHs from an artificially contaminated soil. For so doing, an experimental design has been proposed and the results statistically analyzed. The complexity of the system just allows for the statement of trends. Accordingly, figures given should be taken as indicative efficiency values.

In the second part of this work, an aqueous solution of hydrogen peroxide has been used as a modifier/oxidising agent. Depending on soil composition (i.e. presence or absence of iron species), H_2O_2 may decompose to generate powerful oxidising agents (free HO° radicals) capable of eliminating either soil-remaining PAHs or PAHs previously desorbed into supercritical CO_2 .

Since CO_2 extraction involves the use of a trapping organic solvent where carbon dioxide is bubbled, finally, some preliminary experiments have been conducted to recycle the fraction of methanol where PAHs were solved after CO_2 bubbling. Due to the high reactivity of ozone with PAHs and relatively high solubility in methanol, ozone can be an appropriate reagent for methanol cleaning and recycling.

2. Experimental

The soil used was taken from an area close to a road in the University of Badajoz (South West of Spain). The soil (mainly clay) was crushed in a mortar and dried for five days at $110^\circ C$. Particle size was below 0.5 mm of diameter. Other properties are: pH 6.8 (water soil ratio 2.5), conductivity $201 \mu S$ (water soil ratio 2.5), weight loss at $500^\circ C$ of 3.23% and oxidability with dichromate of 5.2% (measured as organic carbon).

Artificial contamination of the soil was carried out by mixing an acetone solution of acenaphthene (Ac), phenanthrene (Ph), anthracene (An) and fluoranthene (Fl) (Sigma–Aldrich) with the soil to get a theoretical load of $10 mg kg^{-1}$ in each PAH after acetone natural evaporation. To allow some extent in sequestration, soil was used after no less than three months from artificial contamination.

Extraction experiments were conducted in an ISCO SFX 220 extraction system (Nebraska) basically equipped with a SFX 200 controller, two 100 mL ISCO 100 DX syringe pumps, extraction chamber, restrictor and heater. The extractor is equipped with six motor activated valves controlled by the SFX 200 device. Extracted PAHs were collected into 5 mL of methanol (see Fig. 1).

Ozonation experiments were carried out in semibatch mode. The reactor utilized, basically consisted of a cylindrical glass vessel (0.9 L) equipped with a porous plate to bubble an oxygen–ozone gas mixture, sampling port, thermometer, outlet gas and mechanical agitation (*Heidolph RZR 2020*). Temperature was kept controlled at $20 \pm 0.1^\circ C$ by immersion of the reactor into a thermostatic bath. Ozone was generated in an *Erwin Sander 301.7* laboratory ozone generator capable of producing up to $12 g h^{-1}$ of ozone from pure oxygen. Once the ozonator was stabilised, $30 L h^{-1}$ of the mixture O_2/O_3 was continuously fed to the reactor containing the PAH–methanol solution. Steadily, methanol samples were withdrawn from the reactor and analyzed for the remaining PAH in solution.

Outlet and inlet ozone concentration in the gas phase were monitored by means of an *Anseros Ozomat* ozone analyzer. The analysis based on the absorbance at 254 nm.

Dissolved PAHs were analyzed by injecting $25 \mu L$ of a sample into a HPLC system (Rheodyne injector, 1050 Hewlett Packard

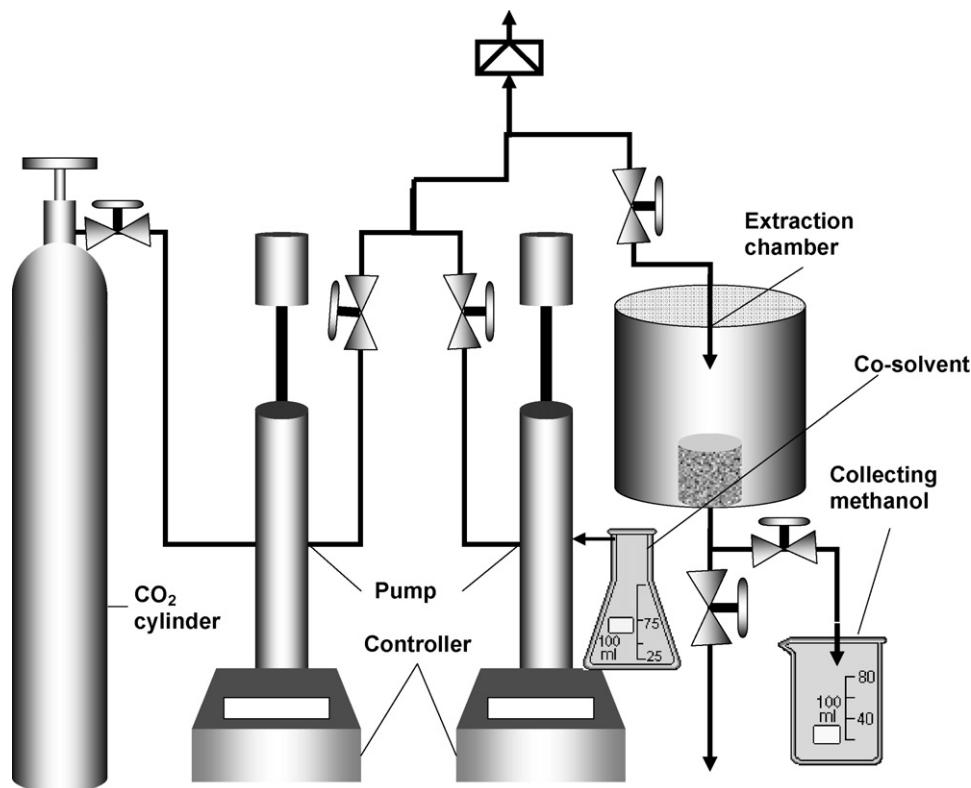


Fig. 1. Experimental setup.

Table 1
Box–Behnken experimental design

Pressure (bar)	Temperature (°C)	Time (min)	Ac	Ph	An	Fl
400	40	90	10.1	2.9	0.9	4.0
400	60	90	17.5	12.8	1.7	11.4
400	40	150	42.9	83.6	27.8	–
300	50	90	41.8	51.5	13.4	56.1
400	50	120	45.9	96.9	35.4	–
400	50	120	47.9	83.5	21.6	117.0
400	50	120	43.2	65.5	16.0	74.7
500	50	90	42.7	73.3	21.9	86.5
300	40	120	33.4	46.2	9.9	51.7
300	60	120	40.9	64.4	14.2	70.3
500	40	120	37.0	71.1	26.1	98.7
400	60	150	38.5	76.5	25.9	110.2
500	60	120	43.0	73.7	20.9	89.9
300	50	150	39.4	68.3	23.3	78.7
500	50	150	41.2	64.7	20.5	83.5

Percentage of PAH recovery.

pump, 1046A, Alltech Prevail C18 column (4.6 mm × 150 mm), Hewlett Packard fluorescence detector, Chromjet Spectra Physics integrator) in isocratic mode using an acetonitrile–water mixture 70:30 (v/v) as mobile phase.

Soxhlet extraction of PAHs (1 g of contaminated soil) was completed with 60 mL of HPLC grade methanol for 6 h. Other solvents like dichloromethane, ethanol, acetone, etc. did not extract PAHs to a higher extent.

3. Results and discussion

3.1. Extraction process

3.1.1. Pure CO₂ extraction

Extraction of PAHs with pure CO₂ was carried out by following the Box–Behnken experimental design with three factors evaluated at three levels. The factors investigated were (in parentheses coded

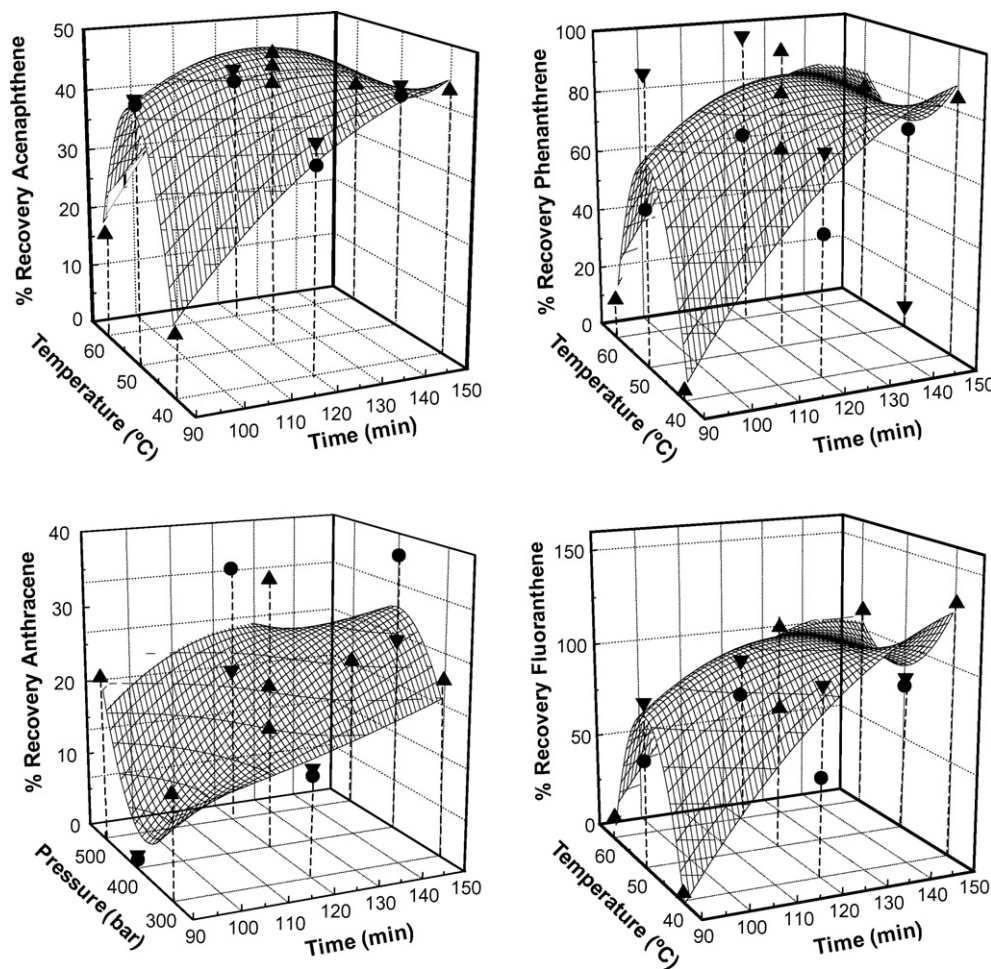


Fig. 2. Supercritical carbon dioxide PAH extraction. Soil mass: 3 g; CO₂ flowrate: $0.4 \pm 0.04 \text{ mL min}^{-1}$; methanol volume: 5 mL. Symbols: (●) 300 bar; (▲) 400 bar; (▼) 500 bar (in anthracene plot, symbols (●), (▲), (▼) represent 40, 50 and 60 °C, respectively).

Table 2Two factors quadratic + interaction model (PAH recovery = $a_0 + a_1 \times T + a_2 \times \text{time} + a_3 \times T \times T + a_4 \times T \times \text{time} + a_5 \times \text{time} \times \text{time} + a_6 \times T \times \text{time} + a_7 \times T \times \text{time} \times \text{time}$)

	Acenaphthene	Phenanthrene	Anthracene ^a	Fluoranthene
R^2	0.96	0.89	0.71	0.76
R^2 adjusted	0.913	0.76	0.42	0.57
F_{signif} (regres)	3.0×10^{-4}	9.2×10^{-3}	0.128	3.4×10^{-2}
F_{signif} (LOF)	1.3×10^{-2}	0.87	0.10	0.70
a_0 (p -value)	-1655.4 (5.63×10^{-4})	-3864.5 (0.011)	803.4 (0.123)	-5767.3 (0.059)
R^2 (parameter a1)	65.8 (2.24×10^{-4})	150.5 (5.96×10^{-3})	-3.95 (0.069)	224.5 (0.037)
a_2 (p -value)	11.1 (0.014)	28.1 (0.085)	-8.5 (0.208)	43.2 (0.215)
a_3 (p -value)	-0.68 (1.12×10^{-4})	-1.56 (3.5×10^{-3})	4.29×10^{-3} (0.077)	-2.3 (0.025)
a_4 (p -value)	-0.42 (2.75×10^{-3})	-1.03 (0.03)	0.039 (0.082)	-1.6 (0.106)
a_5 (p -value)	5.64×10^{-3} (0.658)	4.2×10^{-3} (0.935)	0.015 (0.535)	5.3×10^{-3} (0.964)
a_6 (p -value)	4.8×10^{-3} (2.96×10^{-4})	0.011 (6.4×10^{-3})	-3.6×10^{-5} (0.073)	0.017 (0.036)
a_7 (p -value)	-2.94×10^{-4} (0.262)	-5.0×10^{-4} (0.626)	-4.8×10^{-5} (0.426)	-6.7×10^{-4} (0.773)

^a Factors considered in anthracene recovery were pressure and time.

variable): pressure with values of 300 (-1), 400 (0) and 500 (1) bar, temperature 40 (-1), 50 (0) and 60 (1) °C and extraction time of 90 (-1), 120 (0) and 150 (1) min. The experimental design is displayed in Table 1.

The results are shown in Fig. 2. The percentage of recovery was calculated by considering the maximum amount of PAHs that could be extracted from the raw contaminated soil (i.e. 10 mg kg⁻¹ in each PAHs).

As observed from Fig. 2, no clear trends are easily deduced. In the case of acenaphthene, it is envisaged a positive effect of extraction time from 90 to 120 min, with no further improvement when increasing this parameter to 150 min (with the exception of experiments conducted at 40 °C). Temperature shows an optimum in the vicinity of 50 °C. The existence of an optimum in temperature has also been reported previously. Thus, Hawthorne et al. [6] reported an increased extraction efficiency of benzo[e]pyrene ($P=400$ bar) at 100 °C if compared to results obtained at 150 or 50 °C. This optimum was shifted to 50 °C if working pressure was reduced to 200 bar, indicating the complicated relationships between operating variables in supercritical CO₂ extraction. Phenanthrene recoveries corroborated the results experienced with acenaphthene. It seems that 90 min of extraction is an insufficient time for low (40 °C) or high (60 °C) temperatures, nevertheless, the influence of this parameter decreases when the optimum working temperature is applied. When anthracene extraction yield is analyzed, it is observed a higher effect of the pair pressure–extraction time than the pair pressure–temperature or temperature–extraction time. This is the reason to plot pressure in the anthracene y -axis of Fig. 1. In this case, a slight positive trend is also envisaged by the duration of the extraction process, although the dispersion of the data points does not allow for the statement of consistent conclusions. Similarly the existence of some outliers in fluoranthene recovery precludes the claim of solid inferences. Nevertheless, it seems clear the beneficial effect of extraction time and likely the existence of an optimum in the working temperature. Barnabas et al. [7] in a work similar to this one claimed a negligible role played by temperature and pressure, being the only significant variables the extraction time and modifier (methanol) concentration.

The results obtained confirm the difficulties in experimental replication. Some inherent errors associated to laboratory supercritical CO₂ extraction like short soil beds, CO₂ channeling, etc. should force the investigations to present trends rather than absolute conclusions.

A full quadratic analysis of the results obtained (not shown) for the four PAHs studied demonstrated the deficiencies of this model (see Eq. (1), P = pressure; T = temperature, t = extraction time). Thus, none of the coefficients a_1 to a_9 showed a significance level (p value)

below 0.05 no matter the PAHs extracted.

$$\% \text{PAH recovery} = a_0 + a_1 p + a_2 T + a_3 t + a_4 p^2 + a_5 T^2 + a_6 t^2 + a_7 p t + a_8 T t \quad (1)$$

Moreover, p -values for the regression were always above 0.05, suggesting the inadequacy of the terms in the proposed model.

In order to conduct a rough approach to variables influence, the studied factors were grouped into pairs and the best quadratic plus interaction models plotted. Fig. 2 illustrates the results obtained while Table 2 displays some of the statistical parameters corresponding to the models. Acenaphthene is well described by a simple two factor model including temperature and extraction time, i.e. pressure seems to exert a negligible influence in its extraction within the range of values tested. In contrast, anthracene recovery is best described by a model based on pressure and extraction time. It should be noticed that anthracene is the most insoluble PAH used while acenaphthene is the most soluble hydrocarbon. With the exception of anthracene, F_{signif} (regres) values indicate the suitability of the model to calculate PAHs recovery, although the values of R^2 are in some cases too small. Better R^2 values can be obtained by accounting for the three factors studied and simultaneously rejecting non-influencing terms. Accordingly the following quadratic plus interaction terms were considered (units: °C, min, bar)

Acenaphthene recovery (%):

$$\% \text{PAH} = -1655 + 68.8T + 11.1t - 0.68T^2 - 0.42Tt + 5.6 \times 10^{-3}t^2 + 4.8 \times 10^{-3}T^2t - 2.9 \times 10^{-4}Tt^2 \quad (R^2 = 0.96) \quad (2)$$

Phenanthrene recovery (%):

$$\% \text{PAH} = -3864 + 148T + 27.3t + 2.2 \times 10^{-3}PT - 1.56T^2 - 0.99Tt + 4.2 \times 10^{-3}t^2 + 11.3 \times 10^{-3}T^2t - 5.0 \times 10^{-4}Tt^2 - 8.6 \times 10^{-5}PTt + 6.4 \times 10^{-3}PT \quad (R^2 = 0.94) \quad (3)$$

Anthracene recovery (%):

$$\% \text{PAH} = 587 - 3.76P - 4.91t + 4.2 \times 10^{-3}P^2 + 0.031Pt - 3.6 \times 10^{-5}P^2t - 1.4 \times 10^{-4}PT^2 + 0.014PT - 1.31 \times 10^{-5}Pt^2 \quad (R^2 = 0.79) \quad (4)$$

Fluoranthene recovery (%) [5]:

$$\% \text{PAH} = 1798 - 15.1P + 24.8T - 17.8t + 0.02P^2 + 0.136Pt - 0.25T^2 - 0.03t^2 - 1.7 \times 10^{-4}P^2t \quad (R^2 = 0.83) \quad (5)$$

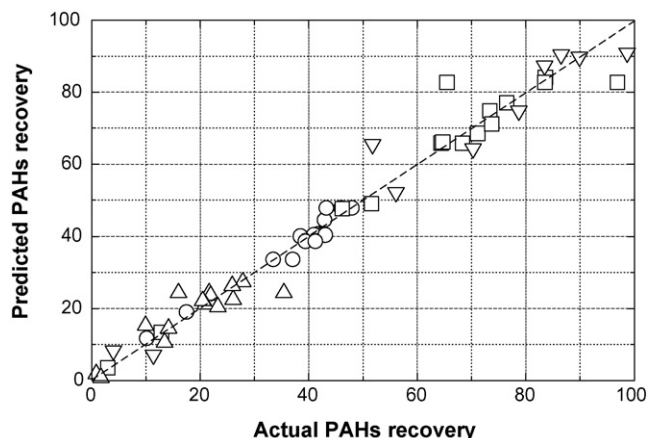


Fig. 3. Supercritical carbon dioxide PAH extraction. Quadratic plus interaction model PAH recovery versus actual PAH recovery. Operating conditions as in Fig. 2.

Fig. 3 illustrates the differences between predicted and actual data for the supercritical extraction of PAHs from soil. Recovery values above 100% (not shown) are difficult to explain. Some hypothesis can be suggested, for instance the lack of homogenization in some of the samples, some errors associated to PAHs analysis, loss of volatile methanol when manipulating some samples, flushing of PAHs adsorbed in pipelines from previous experiments, etc. A priori, although not totally discarded, the first point can be ruled out since control samples analyzed by Soxhlet extraction gave always similar PAH concentrations. PAH deposition in pipes can also be neglected since the system was flushed with methanol between runs. Errors associated to PAHs analysis include methanol volatilization, PAHs sorption onto vial walls (not probable due to high PAHs solubility in methanol), etc. It is considered that errors do exist but do not systematically occur, that is the reason to consider the results from this investigation as “trends” instead of absolute values.

Remaining PAHs in the soil were Soxhlet-extracted for 6 h and the results compared to blank Soxhlet-extractions with soil not previously treated with carbon dioxide. The results indicate that the remaining acenaphthene and fluoranthene were not extracted after the action of CO₂. In the case of anthracene and phenanthrene, the lowest yields (close to 0) were obtained when the extraction time was 150 min. In any case, non CO₂ extracted anthracene and phenanthrene remaining in the soil ranged in the interval 10–15% of the extractable amounts.

3.1.2. CO₂ + co-solvent extraction

Use of co-solvents in supercritical CO₂ extraction is an alternative option capable of enhancing the final extraction yield depending on the co-solvent nature and soil matrix. Thus, this enhancement has been attributed to an increase in the supercritical phase density if compared to pure supercritical carbon dioxide [8]. Additionally, co-solvent nature can affect the diffusivities within the solid by matrix swelling.

In this work a H₂O₂–water solution was used as a co-solvent. Addition of hydrogen peroxide was introduced in an attempt to simultaneously oxidise the target compounds adsorbed into the soil. Thus, at relatively mild conditions of temperature hydrogen peroxide can decompose into free HO° radicals. H₂O₂ decomposition is favoured in soils containing iron oxides in their structures. HO° radicals are powerful oxidising agents capable of reacting with most of organic molecules with rate constants in the order of 10⁸–10¹⁰ M⁻¹ s⁻¹. A double effect can be expected after HO° generation, thus, on one hand, HO° can attack free or sorbed PAHs contributing to the removal of the target compounds from soils. On the other hand, HO° can alternatively attack the organic matter responsible of PAHs adsorption. As a consequence, CO₂ desorption of PAHs can be facilitated.

Table 3 depicts the results obtained by completing the Taguchi experimental design shown. Once again, some recovery values above 100% are found for fluoranthene. The reasons are unclear. In any case, by analyzing the trends, from this table and Fig. 4, a

Table 3
Taguchi experimental design

T (°C)	C _{H₂O₂} (M)	Co-solvent (%)	Acenaphthene	Phenanthrene	Anthracene	Fluoranthene
40	10 ⁻³	1	18.6	24.0	5.4	31.1
70	10 ⁻²	10	21.5	51.4	16.5	75.0
100	0.05	20	9.9	25.6	8.3	41.2
40	0.05	1	12.5	12.8	2.7	15.1
70	0.05	10	50.3	102.7	30.0	147.3
40	10 ⁻²	10	32.7	45.0	12.3	65.4
70	10 ⁻²	1	26.1	62.8	31.4	93.0
100	10 ⁻²	20	31.9	47.4	11.9	64.0
40	10 ⁻³	10	18.8	16.1	3.4	18.2
70	10 ⁻³	20	51.6	103.4	35.1	137.7
100	10 ⁻³	1	17.2	36.0	19.6	53.9
40	5.00E-02	10	15.3	9.2	2.4	8.4
70	5.00E-02	1	17.2	43.5	13.0	63.4
100	5.00E-02	10	15.8	30.6	8.8	43.4
40	10 ⁻³	20	14.6	13.4	2.8	15.9
70	10 ⁻³	1	44.7	95.3	32.3	132.6
70	10 ⁻³	10	12.8	21.2	6.0	28.4
100	10 ⁻³	10	18.5	37.9	12.0	59.5
40	10 ⁻²	1	35.7	61.0	26.2	81.3
100	10 ⁻²	10	37.8	73.2	18.6	107.3
40	10 ⁻²	20	40.2	42.2	13.5	49.8
70	10 ⁻²	20	57.6	117.5	42.7	-
100	10 ⁻²	1	46.2	73.8	22.6	101.3
40	10 ⁻²	20	25.3	16.3	3.2	19.4
70	5.00E-02	20	54.2	127.8	41.2	-
100	5.00E-02	1	36.4	69.4	24.2	92.5
100	10 ⁻³	20	32.0	70.0	52.6	115.0

Percentage of PAH recovery.

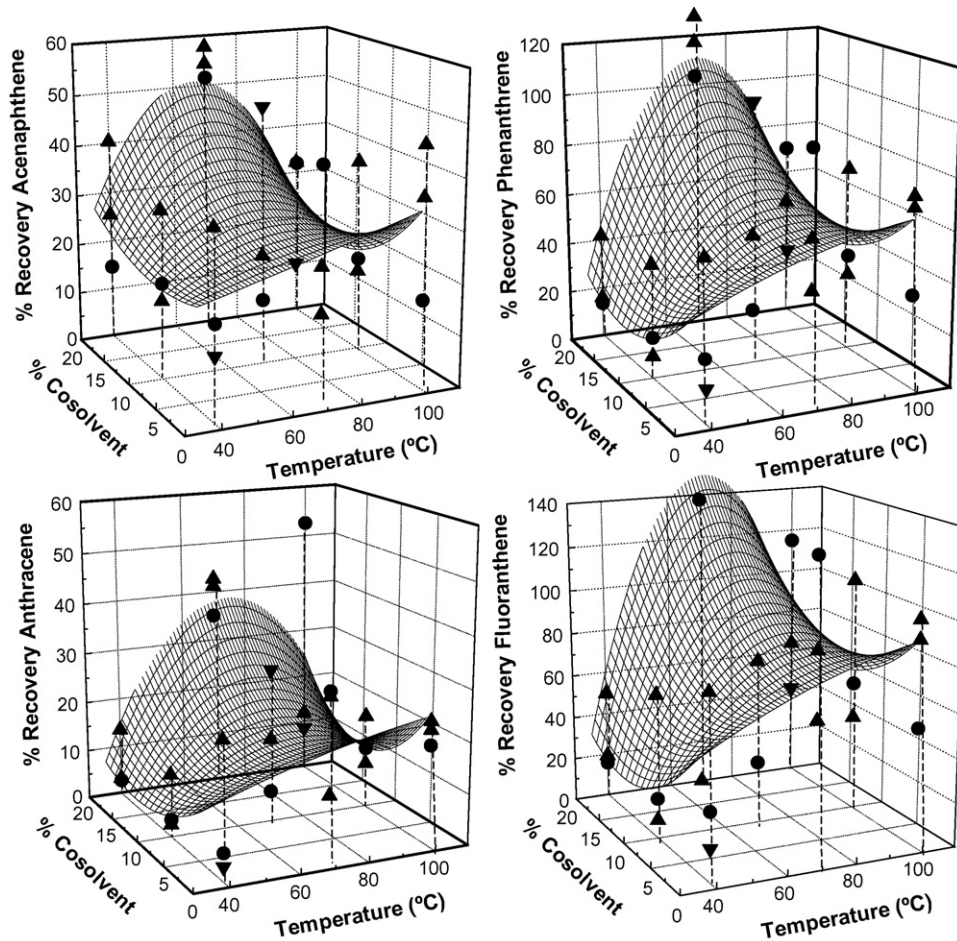


Fig. 4. Supercritical carbon dioxide PAH extraction in the presence of modifiers. Soil mass: 3 g; CO₂ flowrate: 0.3+0.03 mL min⁻¹; P=500 bar; methanol volume: 5 mL. Symbols: (●) 5 × 10⁻³ M of H₂O₂; (▲) 10 × 10⁻³ M of H₂O₂; (▼) 50 × 10⁻³ M of H₂O₂.

positive effect of co-solvent percentage is envisaged. The positive influence can be attributed to a swelling process due to the presence of the co-solvent. Swelling would eventually increase intraparticle diffusivities facilitating, therefore, the extraction of PAHs [8]. Unfortunately, hydrogen peroxide did exert no significant influence in the process. The absence of iron salts in the soil treated seems to be responsible of the slow (if any) decomposition of H₂O₂. Once more, an intermediate temperature appears as the optimum value.

Although surfaces in Fig. 4 have been configured by neglecting the role played by H₂O₂ concentration, higher R² values (not better models) can be obtained by including this variable in a three independent variable expression. Thus, a three-factor model (quadratic+interactions) was applied to the results obtained. Table 4 illustrates the coefficients obtained in each case and the most significant statistic parameters derived from the model.

From Table 4 it is inferred how R² values are not too high, i.e. there is an important data fraction not explained by the model. Nevertheless, F_{sign} for the regression indicates that, with the exception of acenaphthene, the regression is acceptable to model the extraction of PAHs from soil. p-values associated to coefficients are an indicative of terms significance. Thus, p-values below 0.05 involves an important role of the particular term in the regression model, while p-values above 0.05 suggest that terms can be ruled out without experiencing any important deterioration of the model.

Fig. 5 shows the predicted and actual recovery values by using the models displayed in Table 4.

3.2. Solvent regeneration process

Extraction by supercritical CO₂ is normally conducted by collecting the contaminants into an organic solvent. In order to make the whole cleaning process environmentally attractive, regeneration of the solvent is of paramount importance. Ozone is a selective

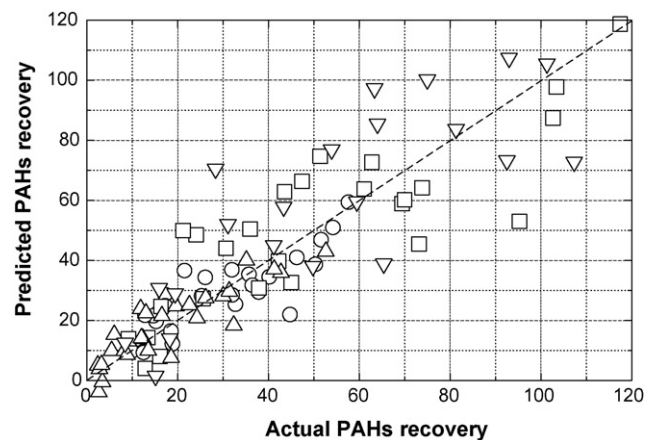


Fig. 5. Supercritical carbon dioxide PAH extraction in the presence of modifiers. Quadratic plus interaction model PAH recovery versus actual PAH recovery. Operating conditions as in Fig. 4.

Table 4

Recovery Ac (%) = $b_0 + b_1 \times T + b_2 \times C_{\text{Cosolv}} + b_3 \times T^2 + b_4 \times T \times C_{\text{H}_2\text{O}_2} + b_5 \times T \times C_{\text{Cosolv}} + b_6 \times C_{\text{H}_2\text{O}_2}^2 + b_7 \times C_{\text{H}_2\text{O}_2} \times C_{\text{Cosolv}} + b_8 \times C_{\text{Cosolv}}^2 + b_9 \times T^2 \times C_{\text{H}_2\text{O}_2} + b_{10} \times T^2 \times C_{\text{Cosolv}} + b_{11} \times T \times C_{\text{H}_2\text{O}_2} \times C_{\text{Cosolv}} + b_{12} \times C_{\text{H}_2\text{O}_2} \times C_{\text{Cosolv}}^2$ ($R^2 = 0.68$)													
ANOVA		SS		SS%		MS		F_{Sign}					
	Regression	3692.8		68		307.73		0.05486					
	Residual	1745.6		32		124.68							
	b_0	b_1	b_2	b_3	b_4	b_5	b_6	b_7	b_8	b_9	b_{10}	b_{11}	b_{12}
Coefficients	60.5	-1.13	-9.83	8.2×10^{-3}	39.8	0.23	-32709	122.8	0.137	-0.229	-0.0016	-0.82	-3.063
p-value	0.145	0.386	0.011	0.380	0.066	0.026	0.012	0.067	0.070	0.166	0.027	0.130	0.217
Recovery Ph (%) = $b_0 + b_1 \times C_{\text{Cosolv}} + b_2 \times T \times C_{\text{H}_2\text{O}_2} + b_3 \times T \times C_{\text{Cosolv}} + b_4 \times C_{\text{H}_2\text{O}_2}^2 + b_5 \times C_{\text{H}_2\text{O}_2} \times C_{\text{Cosolv}} + b_6 \times C_{\text{Cosolv}}^2 + b_7 \times T^2 \times C_{\text{H}_2\text{O}_2} + b_8 \times T^2 \times C_{\text{Cosolv}} + b_9 \times T \times C_{\text{H}_2\text{O}_2} \times C_{\text{Cosolv}} + b_{10} \times C_{\text{H}_2\text{O}_2} \times C_{\text{Cosolv}}^2 + b_{11} \times T \times C_{\text{H}_2\text{O}_2}^2$ ($R^2 = 0.77$)													
ANOVA		SS		SS%		MS		F_{Sign}					
	Regression	22888.9		77		2080.8		0.00418					
	Residual	6946.3		23		463.08							
	b_0	b_1	b_2	b_3	b_4	b_5	b_6	b_7	b_8	b_9	b_{10}	b_{11}	
Coefficients	53.50	-22.55	81.66	0.51	-86206	243.53	0.27	-0.63	-3.3×10^{-3}	-1.72	-5.51	522.62	
p-value	0.001	0.000	0.043	0.001	0.021	0.058	0.060	0.096	0.002	0.073	0.247	0.356	
Recovery An (%) = $b_0 + b_1 \times T + b_2 \times C_{\text{H}_2\text{O}_2} + b_3 \times C_{\text{Cosolv}} + b_4 \times T \times C_{\text{Cosolv}} + b_5 \times C_{\text{H}_2\text{O}_2}^2 + b_6 \times T^2 \times C_{\text{H}_2\text{O}_2} + b_7 \times T^2 \times C_{\text{Cosolv}} + b_8 \times T \times C_{\text{H}_2\text{O}_2}^2 + b_9 \times T \times C_{\text{H}_2\text{O}_2} \times C_{\text{Cosolv}} + b_{10} \times T \times C_{\text{Cosolv}}^2 + b_{11} \times C_{\text{H}_2\text{O}_2}^2 \times C_{\text{Cosolv}} + b_{12} \times C_{\text{H}_2\text{O}_2} \times C_{\text{Cosolv}}^2$ ($R^2 = 0.80$)													
ANOVA		SS		SS%		MS		F_{Sign}					
	Regression	4066.8		80		338.90		0.00367					
	Residual	1003.4		20		71.67							
	b_0	b_1	b_2	b_3	b_4	b_5	b_6	b_7	b_8	b_9	b_{10}	b_{11}	b_{12}
Coefficients	-2.90	0.31	3062.8	-4.76	0.10	-92970	-0.29	9.1×10^{-4}	877.95	-0.79	0.00	2072	-2.90
p-value	0.805	0.078	0.004	0.012	0.057	0.002	0.023	0.015	0.010	0.054	0.005	0.013	0.805
Recovery Fl (%) = $b_0 + b_1 \times C_{\text{Cosolv}} + b_2 \times T^2 + b_3 \times T \times C_{\text{H}_2\text{O}_2} + b_4 \times T \times C_{\text{Cosolv}} + b_5 \times C_{\text{H}_2\text{O}_2}^2 + b_6 \times C_{\text{Cosolv}}^2 + b_7 \times T^2 \times C_{\text{H}_2\text{O}_2} + b_8 \times T^2 \times C_{\text{Cosolv}} + b_9 \times T \times C_{\text{H}_2\text{O}_2} \times C_{\text{Cosolv}} + b_{10} \times C_{\text{H}_2\text{O}_2}^2 \times C_{\text{Cosolv}} + b_{11} \times C_{\text{H}_2\text{O}_2} \times C_{\text{Cosolv}}^2 + b_{12} \times T \times C_{\text{H}_2\text{O}_2}^2$ ($R^2 = 0.76$)													
ANOVA		SS		SS%		MS		F_{Sign}					
	Regression	43900.1		76		3658.3		0.01038					
	Residual	13592.5		24		970.89							
	b_0	b_1	b_2	b_3	b_4	b_5	b_6	b_7	b_8	b_9	b_{10}	b_{11}	b_{12}
Coefficients	50.32	-24.75	2.7×10^{-3}	173.20	0.58	-1.4×10^5	0.32	-1.31	0.00	-1.78	4845	-5.88	537.33
p-value	0.065	0.003	0.509	0.008	0.006	0.013	0.109	0.031	0.009	0.223	0.096	0.334	0.511

oxidant presenting some advantages over other oxidation systems. For instance, ozone is more soluble in methanol than in water, it does not introduce additional contaminants to the reaction matrix and selectively reacts with PAHs at acceptable reaction rates.

The removal of extracted PAHs from methanol was investigated by reusing the organic solvent in four consecutive runs, i.e. the same “cleaned” methanol was used to trap PAHs in four consecu-

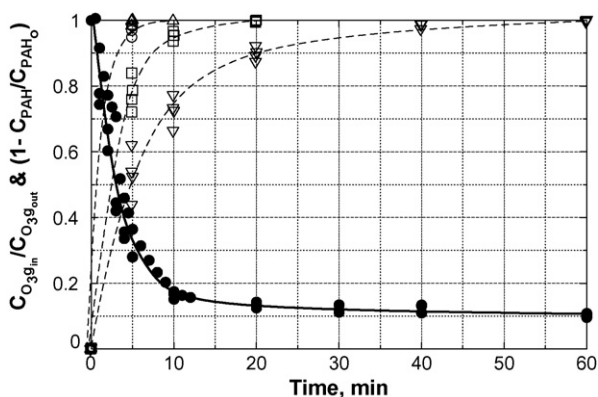


Fig. 6. Ozonation of PAHs containing methanol. Flowrate: 30 L h^{-1} ; $C_{\text{O}_3 \text{ g in}}$: 35 g m^{-3} ; reaction volume: 500 mL. Initial PAH concentration (ppm average values): (○) acenaphthene (6.1); (□) phenanthrene (4.9); (△) anthracene (5.2); (▽) fluoranthene (7.5). Solid symbols: gas outlet ozone.

tive experiments. Fig. 6 suggests that methanol can be reused with no loss of either its capacity of PAH solubilization and the ozone reactivity.

The results revealed that under the experimental conditions used (i.e. 35 ppm of inlet ozone concentration and $Q = 30 \text{ L h}^{-1}$), acenaphthene and anthracene achieve a roughly 100% conversion in just five minutes of ozonation. Phenanthrene disappears in approximately 15–20 min while fluoranthene is the most refractory PAH needing around 1 h to be completely removed. Direct ozonation rate constants in aqueous solutions have been reported to be $2.78 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for anthracene [9], $1.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for acenaphthene and $2.4\text{--}3.1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for phenanthrene [10], agreeing with the reactivity order in methanol (i.e. An > A > Ph > Fl).

The ozone outlet concentration profiles ($C_{\text{O}_3 \text{ g out}}$) obtained decrease as the reaction progresses. This is not the typical behavior observed in aqueous systems. It can be hypothesised that as the reaction proceeds, more ozone consuming intermediates are formed although further investigations should be conducted.

4. Conclusions

From the previous investigation the following conclusions can be derived:

Supercritical CO_2 extraction of contaminants (in this case PAHs), is a complex process dependent on a number of variables. Some of the variables can be acceptably controlled (pressure, temperature, CO_2 flowrate), however, other can be considered as perturbations,

thus, the compacting degree of soil, formation of channels, etc can occur both in the CO₂ extraction cell and in the Soxhlet extraction analytical procedure. Due to perturbation variables the dispersion of results is considerable. As a consequence it is difficult to infer and to articulate accurate effects of controlled variables. From the completion of an appropriate experimental design some effects can be envisaged, for instance:

- Pure CO₂ extraction of PAHs seems to be favoured by extraction time until a maximum efficacy is obtained (around 120 min under the operating conditions used in this work).
- An optimum in the extraction temperature can be guessed around 50 °C for acenaphthene, phenanthrene and fluoranthene. Extraction pressure seems to play a minor role when dealing with these three PAHs.
- Temperature has a low influence in the extraction of anthracene. In the latter case, with caution it can be forecasted a beneficial effect of CO₂ pressure.
- Addition of a co-solvent (H₂O–H₂O₂) gives some indications of positive influence, especially at the optimum working temperature. The presence of H₂O₂ did exert no clear impact in the process, likely the operating conditions used and particularly soil nature were not adequate to promote its decomposition into free radicals. Nevertheless these results do not preclude the possibilities of this oxidant to enhance the efficiency of the cleaning technology. Thus, the combination of supercritical extraction and simultaneous oxidation with oxygen has been previously reported [11].
- Ozone is a suitable option to regenerate the collecting organic solvent in the supercritical CO₂ extraction. A constant reactivity of ozone towards PAHs was experienced in several consecutive reuses of the solvent.

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