

## Use of solvent extraction to remediate soils contaminated with hydrocarbons

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### Abstract

The main objective of this research is to exploit the possibility of using an *ex situ* solvent extraction technique for the remediation of soils contaminated with semi-volatile petroleum hydrocarbons. The composition of the organic phase was chosen in order to form a single phase mixture with an aqueous phase and simultaneously not being disturbed (forming stable emulsions) by the soil particles hauling the contaminants. It should also permit a regeneration of the organic solvent phase.

As first, we studied the miscibility domain of the chosen ternary systems constituted by ethyl acetate–acetone–water. This system proved to satisfy the previous requirements allowing for the formation of a single liquid phase mixture within a large spectrum of compositions, and also allowing for an intimate contact with the soil.

Contaminants in the diesel range within different functional groups were selected: xylene, naphthalene and hexadecane. The analytical control was done by gas chromatography with FID detector.

The kinetics of the extractions proved to be fast, leading to equilibrium after 10 min. The effect of the solid–liquid ratio on the extraction efficiency was studied. Lower S/L ratios (1:8, w/v) proved to be more efficient, reaching recoveries in the order of 95%. The option of extraction in multiple contacts did not improve the recovery in relation to a single contact. The solvent can be regenerated by distillation with a loss around 10%. The contaminants are not evaporated and they remain in the non-volatile phase.

The global results show that the *ex situ* solvent extraction is technically a feasible option for the remediation of semi-volatile aromatic, polyaromatic and linear hydrocarbons.

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### 1. Introduction

Solvent extraction is a promising technology for soil remediation. It is an *ex situ* separation and concentration process in which a non-aqueous liquid is used to remove organic contaminants. The effectiveness of the extraction of pollutants from the soil depends on the realization of an intimate contact between the soil and the mixture of solvents. Consequently, some solvent extraction processes use water miscible

solvents or else the soils must be dried before applying the solvent extraction technique [1].

Although variants to this technology have been thoroughly described [2–5] some authors refer to complex mixtures of solvents, not always easy to find at lower costs, and some of them with a potential negative environmental impact.

The solvent extraction method have been accepted as an alternative for the remediation of soils contaminated with polychlorinated biphenyls (PCBs), when integrated with a complementary dechlorination technology [6]. Recently, the results of a study to assess the suitability of the solvent extraction soil remediation process have been tested for Aro-

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clor 1016, as an example of PCB in which solvent extraction is combined with solids agglomeration. A two-stage extraction process, with a series of three wash steps incorporated into the solid–liquid separation operation produced a treated soil with recovery rates of Aroclor 1016 above 94% [7].

The remediation of soils contaminated with polycyclic aromatic hydrocarbons (PAHs) has also been researched and several solvents are reported: ethanol, 2-propanol, acetone, 1-pentanol and water. The extraction data for several PAHs compounds indicate that while 1-pentanol was more effective in removing naphthalene and less effective with four-ring PAHs, removals were generally comparable for ethanol, 2-propanol, acetone and 1-pentanol. Since water was present in the soil moisture, it was considered as a component of the extracting solvent. From the various mixtures of solvents, the ternary one composed by 5% 1-pentanol, 10% water and 85% ethanol was selected for further optimization of the extraction process, using 1 h of contact time between soil and solvent mixture. A three-stage crosscurrent solvent washing train was capable of removing more than 95% of the PAH contamination from highly contaminated field soils [8].

The use of hot water in a subcritical state, at approximated 250 °C, was described reporting removals of PAH's between 79 and 99% depending on the molecular weight of the contaminant, for an optimized extraction time of 2 h [9].

Solvent washing was evaluated as a method to remove pentachlorophenol (PCP) from aged field soils contaminated with wood treating wastes. The 50% ethanol solution proved to be as effective as more concentrated solutions of ethanol in removing PCP from field soils in batch extraction tests. Maximum observed PCP removal from field soils occurred within an hour of contact time between soil and solvent [10]. A cross-current soil washing procedure was developed and at least two wash stages with 50% ethanol were needed to remove more than 77% of the PCP. Ethanol recoveries were greater than 92% when the crosscurrent washing processes were followed by water rinse stages. In three-stage solvent washing process counter current washing removed nearly three times more PCP per volume of solvent than a similar crosscurrent solvent washing process. This study was also conducted to determine whether soil solvent washing would also be considered as a cleanup alternative for petroleum hydrocarbons [11].

The mixture acetone–ethyl acetate–water became interesting because it consists of environmental friendly solvents, and specially because for certain compositions, they form a single phase mixture [1], which allows a more efficient contact with the soil, allowing the application in wet soils and sediments without a previous drying operation. To study the capacity of this mixture to remove petroleum compounds from the soil, we selected three compounds belonging to the diesel range [12]: xylene, naphthalene and hexadecane. The selection criterion was based on the choice of hydrocarbons with different structures, namely one aromatic

(xylene), one polyaromatic (naphthalene) and one linear (hexadecane).

## 2. Materials and methods

### 2.1. Reagents

The reagents *n*-pentane, xylene, naphthalene, potassium dichromate, ammonium iron sulphate were all p.a. grade and supplied by Merck. The hexadecane was supplied by Sigma–Aldrich and also at p.a. grade. Acetone and ethyl acetate were supplied by Merck at pure grade. The water used was deionised and had a conductivity less than 0.1 µS/cm.

### 2.2. Analytical conditions

The analytical method used in the quantification of the contaminants was based on the Texas Natural Resource Conservation Commission (TNRCC) Method 1005, which is a generic procedure for the determination of hydrocarbons in soil samples using a chromatographic procedure [13].

The gas chromatograph used was a Chrompack CP-9000, equipped with a FID detector and a split injector. The separations were performed using a CP-SIL 8 CB Chrompack fused silica capillary column (25 m × 0.25 mm i.d. × 0.12 µm of film thickness). The chromatographic conditions were the following: an initial oven temperature of 50 °C for 3 min, followed by an increase in the temperature of 25 °C/min until 310 °C. The injector and the detector temperatures were kept at 285 and 325 °C, respectively. The gases used in chromatographic analysis were hydrogen (34 mL/min), air (300 mL/min) and nitrogen (20 mL/min), the last one used as carrier. Quantification was based one the area count obtained for the peaks of the extracts and they were compared to standards used in the calibration curve. The solvent used in the analysis was the *n*-pentane chosen because it does not interfere in the analytical process. The injection volume used was 1 µL.

### 2.3. Ternary diagram

For the experimental determination of the ternary diagram acetone–ethyl acetate–water, different volumes of acetone–water and acetone–ethyl acetate were taken, after which an accurate volume of the third compound was added until the occurrence of immiscibility was observed. The experiment was done at room temperature.

### 2.4. Soil preparation

The soil used was collected at an agricultural area in north of Portugal, without previous history of industrial activities, or suspicion of previous hydrocarbons contamination. It was put in an oven, at 50 °C for 24 h, to equalize the moisture

content and after screening (10 mesh) to exclude the fractions larger than 2 mm.

### 2.5. Soil characterization methods

The main properties assessed in the soil were the pH, the bulk density, the moisture content, the organic carbon content and the size distribution.

The pH was measured directly in the supernatant with a combined glass electrode [14]. The bulk density was evaluated by using the relation mass and volume [14,15], and the moisture content was measured by mass difference after 24 h drying at 105 °C [14]. The organic carbon content was determined by wet oxidation at 200 °C in the presence of potassium dichromate [16]; the excess of dichromate was evaluated by titration with ammonium iron sulphate [14,15].

### 2.6. Soil contamination

Approximately 2.5 kg of soil was contaminated with 7.04200 g of xylene, 6.11336 g of naphthalene and 7.34473 g of hexadecane. Because naphthalene is solid at room temperature, this contaminant was previously dissolved in trimethylpentane before it was spiked in the soil. After the contamination, the soil remained in a closed box for 2 weeks to allow the dispersion and sorption of the contaminant in the soil matrix.

### 2.7. Solid–liquid extraction

To evaluate the capacity of the acetone–ethyl acetate–water mixture to remove the contaminants from the soil, the following procedure was adopted: to a rigorous mass of contaminated soil, around 25 g, a know volume of solvent mixture was added. The contact between the phases was promoted by magnetic agitation and the separation was done by vacuum filtration. Samples of soil and samples of the extract mixture were collected for later gas chromatographic analysis.

### 2.8. Distillation

The solvent regeneration experiments were performed in a vigreux column with 30 cm of length and 10 cm of diameter; 100 mL of mixture was used in each experiment.

## 3. Results and discussion

### 3.1. Soil characterization

Detailed physical and chemical characteristics of the soil sample used for this study were determined and the results are summarised in Table 1.

Table 1  
Soil characteristics

Parameter	Value
pH	5.84
Moisture (%)	7.79
Bulk density (g/L)	950.2
Organic carbon (%)	1.314
Clays (%)	6.89
Silts (%)	63.41
Sand (%)	29.70

### 3.2. Analytical

For each one of the studied pollutants, a calibration curve was obtained using a large frame of standards solutions to include all the possible working areas. All the determinations were made in triplicate. A chromatogram of a standard in the optimized conditions is presented, as example, in Fig. 1.

A standard calibration method was used to quantify the pollutant in soil, using nine standard solutions, with concentrations in the 5–800 mg/L range; a linear response was obtained. The linear correlation parameters [17] slope, intercept, detection limit and the correlation coefficient ( $R^2$ ) are presented in Table 2.

### 3.3. Ternary diagram

The experimental data conducive to the isothermal ternary phase diagram of ethyl acetate, acetone and water are shown in Table 3, where all values are expressed as mass fractions. A non-miscibility region is present, owing to the partial mutual miscibility of ethyl acetate and water [1]. These results agree well with the diagram described by Nardella et al. The miscibility gap is above the points represented in Fig. 2.

From the ternary phase diagram several mixtures were selected from A to H to evaluate the influence of composition of the extract mixture in the removal of pollutants from contaminated soil.

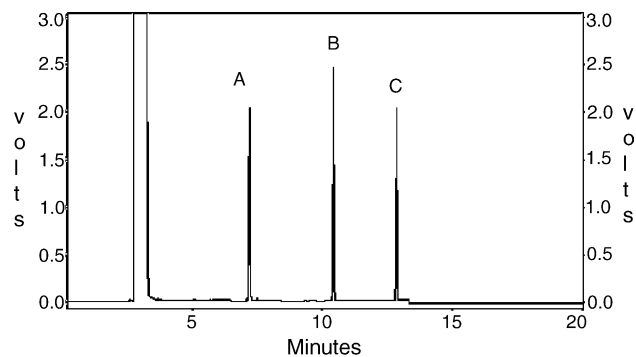


Fig. 1. Chromatogram of standard approximately 200 mg/L in each pollutant: (A) xylene, (B) naphthalene and (C) hexadecane.

Table 2  
Calibration parameters

Pollutant	Slope	Intercept	Detection limit (mg/L)	R <sup>2</sup>
Xylene	16546 ± 128.56	84369 ± 42025.21	1.31	0.9993
Naphthalene	18331 ± 95.20	29867 ± 31211.28	4.39	0.9998
Hexadecane	17849 ± 125.88	20401 ± 37304.84	1.31	0.9997

Table 3  
Data obtained for the ternary phase diagram (%)

Ethyl acetate	Acetone	Water
0.394	0.356	0.250
0.416	0.358	0.226
0.439	0.356	0.205
0.508	0.339	0.153
0.130	0.120	0.750
0.150	0.270	0.570
0.210	0.310	0.480
0.250	0.330	0.410
0.710	0.190	0.100
0.620	0.270	0.100
0.238	0.336	0.426
0.322	0.356	0.322
0.384	0.361	0.254
0.409	0.362	0.229
0.431	0.361	0.208
0.123	0.120	0.758
0.155	0.272	0.573
0.209	0.306	0.484
0.252	0.330	0.418
0.544	0.335	0.121
0.602	0.302	0.096
0.555	0.332	0.112

### 3.4. Solvent extraction

Batch extraction experiences were conducted with various ethyl acetate–acetone–water mixtures using a volume of 50 mL for each mixture and a contact time of 15 min. The results obtained are shown in Table 4.

Table 4  
Removal values obtained for the studied mixtures

	Composition (%)			Removal (%)		
	Water	Acetone	Ethyl acetate	Xylene	Naphthalene	Hexadecane
A	0	0	100	86.66	86.65	87.36
B	10	40	50	83.37	84.24	83.78
C	100	0	0	26.84	15.87	–
D	30	40	30	64.11	65.81	64.52
E	40	40	20	79.17	71.11	57.73
F	10	50	40	75.21	73.97	77.06
G	20	60	20	74.45	70.53	74.30
H	0	100	0	78.21	77.62	79.04

By observing these results it can be concluded that ethyl acetate is the compound that has a higher contribution to the removal efficiency, in contrast to the water. Multivariable linear regressions confirmed this conclusion. The choice of a mixture of 50% ethyl acetate, 40% of acetone and 10% of water was made because it was necessary to assure the existence of a single liquid phase, in order to promote an efficient contact between solid and liquid.

### 3.5. Kinetics of the hydrocarbons removal

The removal of the contaminants from the soil was studied as a function of time using a mixture composition of 50% ethyl acetate, 40% acetone and 10% water. The kinetics data are presented in Fig. 3a–c.

The results show that the extraction process rapidly reaches equilibrium, at a time of approximately 10 min, for

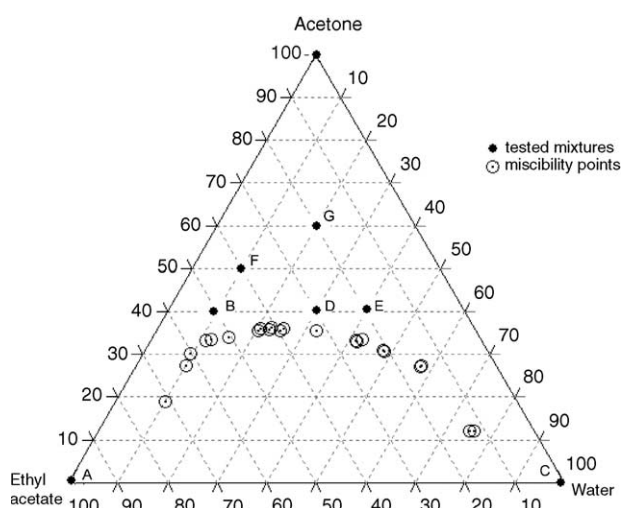


Fig. 2. Experimental ternary phase diagram ethyl acetate–acetone–water and selected mixtures.

Table 5  
Variation of the removal rate, with the increase of the extraction mixture volume

Solid–liquid ratio	Removal rate (%)		
	Xylene	Naphthalene	Hexadecane
1:1	66.83	67.94	68.78
1:2	86.24	86.33	87.33
1:3	90.63	90.29	89.40
1:4	94.04	93.60	93.10
1:8	94.81	94.96	95.16

Table 6  
Removal rates obtained in soil and sand

	Removal (%)	
	Sand	Soil
Naphthalene	95.96	84.49
Hexadecane	96.26	84.98

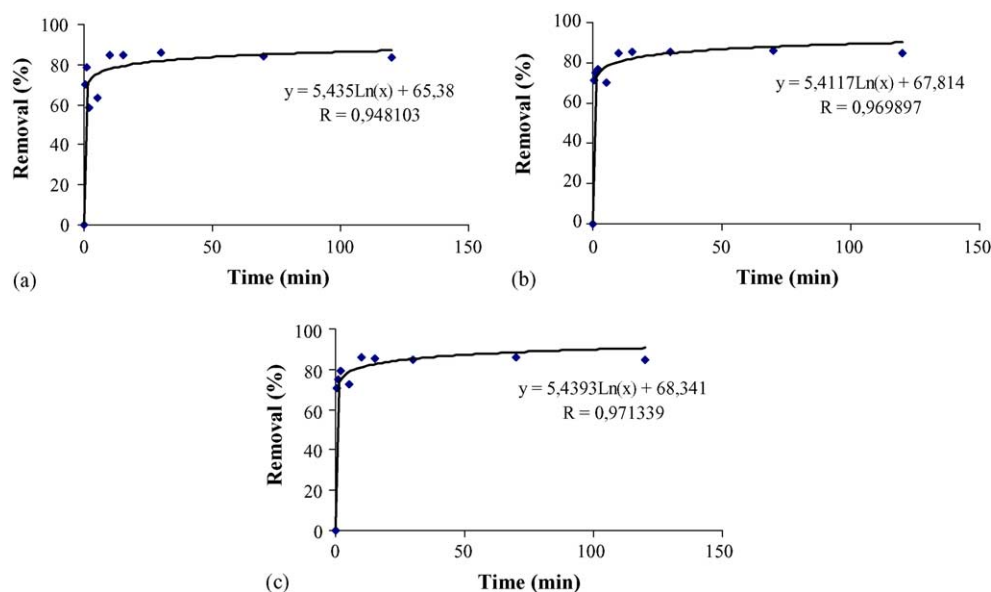


Fig. 3. Extraction kinetics for (a) xylene, (b) naphthalene and (c) hexadecane.

Table 7  
Distillation mass balance

	Initial mass (mg)	Mass in the organic phase (mg)		Mass in the aqueous phase (mg)	
		First experience	Replicate	First experience	Replicate
Xylene	2.84	0.17	0.52	2.27	1.88
Naphthalene	22.98	0.31	0.18	20.21	20.64
Hexadecane	28.84	0.54	0.33	24.44	24.17

each hydrocarbon; after this period no considerable changes in the removal rates were observed.

### 3.6. Soil/solvent ratio

Following the kinetics studies, and using the optimized contact time of 15 min, the solid–liquid ratio was considered. For a constant mass of soil (25 g), different volumes of the extracting mixture were used: 25, 50, 75, 100 and 200 mL corresponding to solid–liquid ratios of 1:1, 1:2, 1:3, 1:4 and 1:8 (w/v). The results are shown in Table 5.

These results indicate that the three pollutants have a similar behaviour. The recovery efficiency increases when the liquid/soil ratio increases. For all contaminants, the removal rate improved in average 40% when the liquid phase was eight times higher than the solid one, conducting to removal level near 95%. Increase in the liquid phase provides a higher mass transfer from the soil under study. This is a result of two main factors: improve of the contact between phases and the increases on concentrations gradient. From the results indicated in Table 5, it seems that the three contaminants present similar physico-chemical behaviour at the experimental condition under study.

The option of operating with successive contact stages of the solvent mixture was also considered, but the levels of

remediation obtained were not significantly different from the results achieved when the same volume of the extracting mixture was used in a single contact stage.

To evaluate the influence of organic carbon content, an experience was performed with soil and sand in similar conditions. The results obtained (Table 6) show that the removal rates in sand, a matrix with low organic carbon content (0.017%), are 13% higher than the removal rates in soil. Xylene does not sorbs enough in the sand to be measured so was not considered in this experience.

### 3.7. Solvent regeneration

After solid–liquid separation the single phase spent liquid mixture used in each extraction was used to perform the regeneration experiments. Distillation was selected as the regeneration technique, in the experimental conditions described in 2.8. Acetone and ethyl acetate distil together at 65 °C of vapour temperature. The results obtained in the regeneration experiments are summarised in Table 7.

The mass balance indicates losses of approximately 10% in the distillation process. These results indicate that the distillation is an effective technique to regenerate the spent solvent mixture. The aqueous phase after distillation can be remitted to a water treatment station.

#### 4. Conclusions

These studies show that the environmentally friendly mixture of ethyl acetate, acetone and water is effective in removing hydrocarbon compounds from the soils. In this mixture, the compound that contributes more to the remediation efficiency is the ethyl acetate.

The extraction kinetics is fast reaching equilibrium after 10 min, corresponding to a hydrocarbon removal of 85%.

A solid–liquid ratio of 1:2 is sufficient to achieve an acceptable remediation level, but when that ratio is increased to 1:8 the removal further increases 8% in average. The multiple contact options were considered but no significant difference in the results was observed. In future applications, it will be necessary to adjust these two parameters to optimize the extraction efficiency and the target concentration.

As it is expected, carbon content is an important parameter in the extraction efficiency.

Distillation proves to be an applicable method to perform the solvent regeneration.

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