



Phenanthrene and pyrene oxidation in contaminated soils using Fenton's reagent

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ARTICLE INFO

Article history:

Received 5 January 2008

Received in revised form 11 April 2008

Accepted 14 April 2008

Available online 20 April 2008

Keywords:

PAH

Soil

AOPs

Process optimization

Factorial design

ABSTRACT

Fenton's reagent has shown its applicability to oxidizing these biorefractory organic contaminants. The purpose of this contribution was to investigate the influence of operating parameters on the process efficiency for soil highly contaminated by PAHs. Five variables were selected: pH, reaction time, UV irradiation, hydrogen peroxide concentration and Fe (II) amendment. Their effects on the oxidation of (i) phenanthrene and on (ii) phenanthrene and pyrene present in freshly contaminated soil samples were studied through batch reactor experiments following factorial designs. For phenanthrene oxidation run with a soil contaminated at 700 mg kg⁻¹, one set of variables enabled us to reach a residual concentration lower than 40 mg kg⁻¹ (Dutch legislation threshold). The most important factor was the reaction time, followed at a certain distance by UV irradiation, Fe (II), H₂O₂ concentration and pH, this last variable being the least significant. The possibility of operating without pH adjustment is of importance in the treatment at the field scale. This shows the feasibility of photo-Fenton-like oxidation for the treatment of soil highly contaminated with PAH and the relative importance of the process variables.

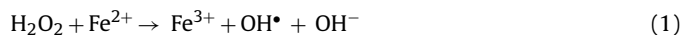
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1. Introduction

Treatment of soils contaminated with Polycyclic Aromatic Hydrocarbons (PAHs) has become a major challenge for stakeholders. PAHs are ubiquitous environmental contaminants that mainly originate from the incomplete combustion of organics. Some of them have carcinogenic and mutagenic potentials [1]. Sixteen PAHs are considered as priority pollutants by the United States Environmental Protection Agency. Contaminated soils may contain up to a few tens of g PAHs per kg soil [2]. These contaminants are persistent in soils because of their hydrophobic nature, their low water solubility and their relative stability. They are strongly sorbed on soils and sediments and their availability decreases with time [3]. Among the 16 PAHs, sorption is known to increase – and availability to decrease – as PAH hydrophobicity (generally measured by the octanol water partitioning constant K_{ow}) increases, that is to say, roughly as molecular weight increases [3]. Thus, the degradation of the low molecular weight PAHs (2–3 aromatic rings) by different remediation techniques has shown to be easier and faster than degradation of high molecular weight PAHs (4–6 rings) [4,5].

For highly contaminated soils, thermal desorption after excavation is the most widely used treatment technology. For lower contamination levels, bioremediation has proved feasible, but its applicability may be limited because of low PAH bioavailability due to sequestration [6]. Chemical techniques are promising alternatives to reach high efficiency in relatively short times. They can also be combined with bioremediation in order to design complete soil treatment processes [7–10]. Among chemical techniques, advanced oxidation processes (AOPs) are widely investigated. Initially widespread for wastewater treatment, they have been increasingly applied to solid matrices such as soils, sediments and sludges [11]. Fenton's reagent is of particular interest because of its high oxidative potential and its simplicity. It has been studied for the treatment of soils contaminated by different types of organics, mainly chlorinated hydrocarbons [12,13], but also petroleum fractions [14–16] and PAHs [7,11,17–25].

Fenton reactions can be catalyzed by different transition metals, iron being the most commonly used for environmental applications. In Fenton's initiation reaction, Fe (II) catalyzes the decomposition of hydrogen peroxide to generate the hydroxyl radical, OH[•], which is a strong and relatively non-specific oxidant [26]:



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Hydroxyl radicals are then involved in complex reaction pathways, leading to the mineralization of organic contaminants. Fenton reaction requires the presence of Fe (II) and is most often run in acid solutions (pH 2–3) to avoid iron salt precipitation. However, naturally occurring iron minerals such as goethite can catalyze hydrogen peroxide decomposition and promote “Fenton-like reactions” [8,14,16,20,27–29]. As well, in some cases, reaction has proved feasible at soil pH, without lowering pH to 2–3 [8,20]. A Fenton reaction can be enhanced by UV radiation, when it is called a “photo-Fenton reaction”.

The reaction pathways are generally not elucidated. Some authors used experimental designs to quantify the effects of the reaction variables on mineralization efficiency [14–16,18]. Using factorial designs allows one to examine simultaneously the effects of multiple independent variables, called factors [30]. Each factor can have a certain number of different values or “levels”. Factorial design is a method to study the effect of each factor on the response variable and the degree of interactions of the factors, by calculating main and interaction effects. A main effect is the average effect of a single factor on the response variable. An interaction effect occurs when the effect of one factor is affected by what happens to the levels of the other factors. The statistical significance of an effect is judged on the basis of a Student's *t*-test [30]. In the present case, the method allows the classification of the experimental variables following their influence on the remediation results and the determination of the optimal set of conditions. This approach must be developed for soil treatment in order to avoid the over dimensioning of the oxidation process and thus to reduce the cost of the treatment.

The present contribution focuses on the study of a model system at the bench scale, with a perspective of scaling up to the field scale. We studied the effects of the experimental variables on the treatment of a soil spiked by one or two PAHs (phenanthrene and pyrene) by the Fenton reaction in (i) Fenton, (ii) Fenton-like, (iii) photo-Fenton and (iv) photo-Fenton-like conditions, *i.e.* with and without Fe²⁺ amendment and without and with exposure to UV. The five variables were pH, reaction time, exposure (or not) to UV radiation, hydrogen peroxide concentration and addition (or not) of Fe (II). Their effects were studied by running batch reactor experiments following factorial designs. The selectivity of the oxidation of both the target PAHs was also considered.

2. Materials and methods

2.1. Chemicals

Phenanthrene (PHE, 98% purity) and pyrene (PYR, 98% purity) were supplied by Aldrich. Hydrogen peroxide (50 vol%) was purchased from VWR and ferrous sulphate (FeSO₄·7H₂O, 99.5% purity) from ACS. Acetonitrile, methylene chloride and *n*-hexane (99.8% purity) were purchased from Fischer Scientific.

2.2. Soil samples

Uncontaminated soil was collected from an agricultural area located in Chenevières, in Northeastern France (Ap horizon, 0–15 cm, sandy loam soil). The soil was composed of 68.9 wt% sand, 22.9 wt% silt, and 8.2 wt% clay. It contained 8.8 g kg⁻¹ organic carbon (C/N: 11.4) and its pH in water was 7.2. Easily exchangeable iron was extracted by citrate-bicarbonate-dithionite extraction [31], and total iron by acid digestion (EPA 3050B) [32]. Iron was analyzed by inductively coupled optical emission spectrometry (ICP-OES): the soil contained 46.1 g kg⁻¹ easily exchangeable iron and 126.5 g kg⁻¹ total iron.

A 4 kg soil sample was air-dried at room temperature for 2 days and sieved to 2 mm, after which it was spiked with PHE and/or PYR. Stock solutions were prepared by dissolving PHE in 40 mL methanol and PYR in 40 mL acetone. Four soil samples were prepared having the same PHE content (C₀ = 700 ± 0.9 mg kg⁻¹), one (S₁) without PYR, the other ones with concentrations of PYR equal to about (i) 2C₀ (S₂: 1406.3 ± 2.7 mg kg⁻¹), C₀/2 (S₃: 271.2 ± 28.2 mg kg⁻¹) and C₀ (S₄: 614.9 ± 18.5 mg kg⁻¹). Appropriate amounts of solutions were added to four dried soil samples, which were immediately vigorously mixed to disperse PAHs. The solvents were then evaporated for 48 h in a hood.

2.3. Statistical design

In the first statistical design, the effects of five variables (or factors, in statistical terms) on PHE degradation were evaluated: pH, reaction time, exposure (or not) to ultraviolet radiation, of H₂O₂ concentration and addition or not of Fe (II) (FeSO₄). Higher and lower levels were chosen for these factors according to the literature [15,16], and a full 2⁵ two-level design was carried out, augmented with a central point in duplicate [30]. The actual levels chosen and their coded values are given in Table 1 (Design 1). In a 2⁵ design, experiments are run at all 32 possible combinations of the higher and lower levels. This allows the calculation, from the experimental results, of the main effects of the five factors and their interactions. The objective of this first design was to find experimental conditions leading to a residual PHE soil concentration lower than 40 mg kg⁻¹, the intervention limit prescribed by Dutch legislation. This limit also applies to residual PYR concentrations. Two other statistical designs were made after the interpretation of the results (see Section 3.2).

2.4. Batch reactor experiments

In all cases, oxidation was conducted as follows: 5 g of spiked soil and 10 mL of ultrapure water were placed into beakers. The reagents were added to the slurry to reach the levels given in Table 1: 4, 6 or 8 mL of H₂O₂ 50% (v/v); 0.9, 1.3, 1.8 mL of FeSO₄, a few drops of 1N H₂SO₄ for pH adjustment. The concentration range of H₂O₂ was chosen assuming that the stoichiometric H₂O₂:PHE ratio was 33:1. Thus, the minimal required volume of H₂O₂ 50% (v/v) was 0.11 mL (density 1.196 kg L⁻¹ at 20 °C). Iron was added at a ratio (H₂O₂):(Fe II) = 10 [8,22,33]. The respective contributions of easily exchangeable iron and total iron were: 4.13 and 11.3 mmol. Both of them were higher than the maximal value of Fe (II) added of 3.4 mmol. In some experimental runs, the samples were irradiated with a 125 W UV high-mercury lamp with major emission output at 365 nm, placed above the beakers to simulate solar irradiation. Blank experiments were also carried out with 5 g soil and 10 mL H₂O without added H₂O₂ and Fe (II). CO₂ bubbling provided sufficient stirring. Temperature was set at 20 °C. At the end of each experiment, PHE and PYR were analyzed in the soil phase.

2.5. PAH extraction from soils and analytical methods

PHE and/or PYR were extracted from the initial and treated soil samples by Soxhlet extraction for 8 h, using hexane/dichloromethane (50:50, v/v) (EPA method 3540) [32]. The solvent was evaporated and the residue was diluted in acetonitrile. HPLC analysis was performed with a Kontron Biosciences system equipped with a photodiode array detector set at 254 nm, using a pre-column (Alltech, 150 mm × 4.6 mm) and a Prosphere column (Alltech, 250 mm × 4.6 mm, particle size 5 μm). The mobile phase was 70% acetonitrile and 30% ultrapure water (flow rate: 1.2 mL min⁻¹). External calibrations were done with standard

Table 1
Real and coded values of the factor levels used in the three sequential factorial designs

Design	Factor	Coding		
		-1	0	+1
1 (Soil sample S ₁)	1. Reaction time (h)	4	6	8
	2. H ₂ O ₂ (mmol)	34	87	140
	3. Fe ²⁺ (mmol)	Endogenous	1.7	3.4
	4. pH	No adjustment	5–6	3–4
	5. Exposure to UV light	Dark	365 nm (3 h)+ Dark (3 h)	365 nm
2 (Soil sample S ₂)	1. Reaction time (h)	4	6	8
	2. H ₂ O ₂ (mmol)	140	210	280
	3. Fe ²⁺ (mmol)	Endogenous	7	14
3 (Soil samples S ₂ , S ₃ , and S ₄)	1. Reaction time (h)	12	18	24
	2. H ₂ O ₂ (mmol)	280	420	560
	3. Fe ²⁺ (mmol)	Endogenous	14	28

Designs 2 and 3 were performed without pH adjustment and under UV irradiation. Details on the contamination of soil samples are given in the text.

solutions of PHE and/or PYR in acetonitrile in the 1–100 mg L⁻¹ range.

3. Results and discussion

3.1. Design 1—degradation in soil sample S₁, contaminated only with PHE

The experimental conditions and results for PHE oxidation in soil sample S₁ are summarized in Table 2. The results showed that PHE

Table 2
Phenanthrene degradation results obtained in the first design (soil sample S₁, spiked with 700 mg kg⁻¹ phenanthrene)

Run	Factor					Residual phenanthrene	
	1	2	3	4	5	(mg kg ⁻¹)	(%)
1	-1	-1	-1	-1	-1	323.9	46.3
2	1	-1	-1	-1	-1	275.3	39.3
3	-1	1	-1	-1	-1	320.0	45.7
4	1	1	-1	-1	-1	257.6	36.8
5	-1	-1	1	-1	-1	325.7	46.5
6	1	-1	1	-1	-1	151.0	21.6
7	-1	1	1	-1	-1	266.0	27.0
8	1	1	1	-1	-1	137.9	19.7
9	-1	-1	-1	1	-1	466.1	66.5
10	1	-1	-1	1	-1	101.5	14.5
11	-1	1	-1	1	-1	275.6	31.1
12	1	1	-1	1	-1	154.4	22.0
13	-1	-1	1	1	-1	264.2	37.4
14	1	-1	1	1	-1	136.0	19.4
15	-1	1	1	1	-1	157.5	22.5
16	1	1	1	1	-1	100.3	14.4
17	-1	-1	-1	-1	1	335.7	48.0
18	1	-1	-1	-1	1	133.0	19.0
19	-1	1	-1	-1	1	214.0	30.6
20	1	1	-1	-1	1	96.1	13.7
21	-1	-1	1	-1	1	200.0	28.6
22	1	-1	1	-1	1	112.2	16.0
23	-1	1	1	-1	1	189.0	27.0
24	1	1	1	-1	1	56.0	8.0
25	-1	-1	-1	1	1	218.1	31.1
26	1	-1	-1	1	1	102.7	14.7
27	-1	1	-1	1	1	231.0	33.0
28	1	1	-1	1	1	91.0	13.0
29	-1	-1	1	1	1	247.2	35.3
30	1	-1	1	1	1	103.7	15.0
31	-1	1	1	1	1	127.5	18.2
32	1	1	1	1	1	18.2	2.6
33, 34	0	0	0	0	0	157.7, 160.1	22.5, 22.9

Coding as in Table 1 (Design 1). The response values are the residual phenanthrene amounts in the soil samples after each treatment. The best and worst results are shown in boldface and italic, respectively.

degradation was always incomplete, with a residual PHE fraction in soil between 2.6% (run #32) and 66.5% (run #9). Only the best run (#32) enabled us to reach a residual PHE level lower than the 40 mg kg⁻¹ limit. Blank experiments showed no PAH desorption.

For a full 2⁵ design it was possible to fit a fifth-order polynomial model to the responses. It was assumed, as usually, that this model could be truncated at the third-order level, which amounted to neglecting higher order interaction effects. These effects were then combined to provide an estimate of the experimental error of a given effect with a larger number of degrees of freedom than if it had been calculated from a few replicates only. With this error estimate, one can evaluate the statistical significance of each effect. The error estimated when a third-order model was fitted to the absolute residual phenanthrene values in Table 2 was 20 mg kg⁻¹, with 8 degrees of freedom. This meant that only the effects with absolute values larger than x (see below) should be considered statistically significant, at the 95% confidence level (Eq. (2)):

$$x = t_8 \times 20 \text{ mg kg}^{-1} = 46.1 \text{ mg kg}^{-1} \quad (2)$$

The value $t_8 = 2.306$ was the two-tailed point from the t -distribution, with eight degrees of freedom [34].

The only effects satisfying this criterion were the main effects of reaction time, UV, Fe²⁺ and H₂O₂, whose values were, respectively, -133.4, -77.4, -62.7 and -50.3 mg kg⁻¹. Neither the interaction effects nor the pH main effect was statistically significant. It should be noted, however, that the pH main effect was also negative (-37.4 mg kg⁻¹), and on the verge of being significant. The relative importance of both main and interaction effects could be visualized in the normal probability plot shown in Fig. 1. In a normal plot, the ordinate scale is chosen in a way that no significant effects fit reasonably well to a straight line passing through the origin. Conversely, the farther a point is from this line, the more significant is the effect to which it corresponds [30]. It was very clear from Fig. 1 that the most important factor was reaction time, followed, at a certain distance, by UV radiation, Fe²⁺, H₂O₂ and pH, respectively (this last one, as we have just seen, a little below the 95% significance threshold).

A main effect describes what happens to the average response when the corresponding factor is raised from its lower to its higher level. Since all five main effects had negative values in this case, raising the levels of all of them should have lead to the lowest response. This was precisely what happened in run #32, where all five factors were at their highest levels. For pH, it should be remembered that this meant more acidic values.

That better oxidation results were obtained at longer reaction times was of course to be expected. As for the other four factors, our findings were in agreement with results reported by other

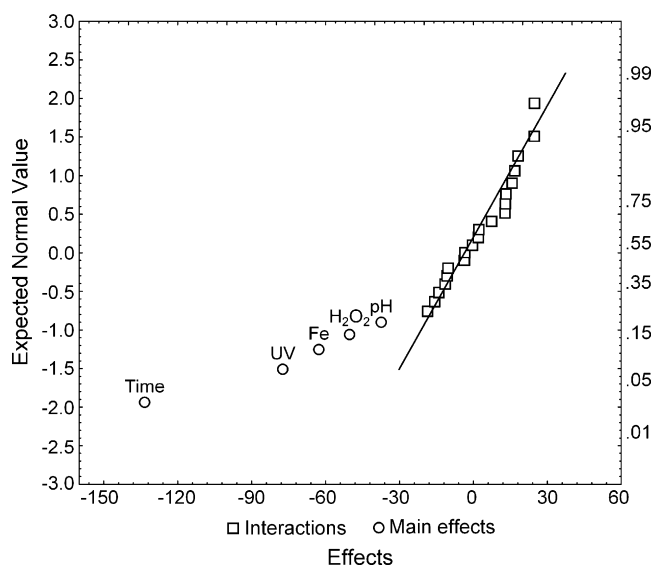


Fig. 1. Normal probability plot of the main and interaction effects of the third-order polynomial model fit to the responses of Table 2 (residual phenanthrene, mg kg^{-1}). The farther a given effect is from the straight line, the more significant it is. Labels as in Table 1.

researchers. The UV irradiation effect could be explained by the photo-reduction of Fe^{3+} to Fe^{2+} , which then acted as an additional source of hydroxyl radicals [35,36].

The addition of Fe^{2+} improved phenanthrene degradation efficiency, although the results obtained with the use of endogenous Fe were also satisfactory. Runs #28 and #32, for example, differed only in the Fe^{2+} source (endogenous vs 3.4 mmol added, respectively), and this single change caused the residual PHE fraction to drop from 13.0 to 2.6%. Several other such paired comparisons (runs #12 and #16 provided another example) confirmed that adding ferrous iron increased the treatment efficiency. The same consequences of ferrous iron addition were observed by Nam et al. [7] with an aged contaminated soil (coal tar): PHE oxidation increased from 11.7 to 100% through the addition of Fe. In the present study, oxidation increased from 87 to 97.4%. In [7], PHE degradation with endogenous Fe was lower than in the present study: endogenous Fe was not available in a sufficient amount to interact with the hydrogen peroxide forming the hydroxyl radical. Moreover, it was a long-standing contamination, and contaminants were less available than in our case, where we used spiked soil samples. Kulik et al. [8] found as well that PAH removal from a creosote spiked soil was enhanced by Fe^{2+} addition.

Similar results have also been reported for other hydrocarbons, e.g. pentachlorophenol and trichloroethylene [37] and toluene [17]. Thus, adding exogenous ferrous ion is generally of great help in

reaching a high oxidation conversion rate. The effect of increasing the amount of H_2O_2 can also be understood as increasing the source of hydroxyl free radicals [38].

Acidifying the reaction medium has often been used to enhance Fenton oxidation results in soil and water [28]. In the present work, however, Fenton oxidation at the natural soil pH also proved to be feasible, as demonstrated by the small pH adjustment main effect. Indeed, the second best result, corresponding to 8% (56 mg kg^{-1}) residual phenanthrene, was obtained in run #24, whose levels were the same as those of run #32, except for the lack of pH adjustment. The efficiency at natural soil pH was also observed by Kanel et al. [20] and Kulik et al. [8]. This is a very important point, because lowering the pH of certain types of soil, especially those with high calcite content, would be impossible.

In summary, this methodology clearly showed the effects of the five variables. In the best experimental run (#32), the removal rate was very high, and compared favorably with other published contributions, particularly taking into account that in the present case the initial PHE concentration was rather high [9,20,39]. These results highlighted the efficiency of Fenton's reagent for PHE removal from contaminated soils.

3.2. Designs 2 and 3—Fenton oxidation efficiency for soils contaminated with PHE and PYR

The first design was followed by two others (Designs 2 and 3 in Table 1) in which pH and UV radiation were kept fixed, and both contaminants were added. pH adjustment was excluded from these subsequent designs because the soil was already approximately neutral, and eliminating this step would reduce costs. On the other hand, UV exposure was maintained, because it proved to have a significant effect in augmenting PHE degradation, and thus the process became a photo-Fenton one. In the two follow-up designs, the goal was to investigate the relative efficiency of the photo-Fenton process with respect to PHE and PYR. Degrading PYR was expected to be more difficult than PHE. For this reason, the levels of the remaining three factors were raised with respect to the first design, as shown in Table 1. In Design 3, three differently contaminated soil samples were used.

Table 3 shows the degradation results of PHE and PYR when the levels specified in Design 2 were used (Table 1). The conclusions were practically the same as those from the first design. All three main effects were negative, and their decreasing order of importance, both for PHE and PYR, was concentration of Fe^{2+} , concentration of H_2O_2 , and reaction time. Once again, the best results were obtained when the three factors were set at their highest levels. However, the 40 mg kg^{-1} limit was satisfied in no experiment. In most experiments, PHE removal was more efficient than that of PYR, but it should be stressed that in this sample, S_2 , the starting PYR concentration was the highest of all, 1406 mg kg^{-1} , which was

Table 3
Phenanthrene and pyrene degradation results obtained in the second design

Run	Factor			Phenanthrene		Pyrene	
	1	2	3	(mg kg^{-1})	(%)	(mg kg^{-1})	(%)
1	-1	-1	-1	205.4	29.4	1207.9	99.0
2	1	-1	-1	180.3	25.8	1032.1	84.7
3	-1	1	-1	135.8	19.4	1071.0	87.9
4	1	1	-1	92.8	13.3	940.3	77.1
5	-1	-1	1	82.5	11.8	875.9	71.9
6	1	-1	1	57.0	8.2	971.9	79.7
7	-1	1	1	42.5	6.1	738.6	52.4
8	1	1	1	43.5	6.2	731.3	43.6
9, 10, 11	0	0	0	82.8, 78.4, 83.2	11.8, 11.2, 11.9	1098.0, 1078.0, 1108.0	90.1, 88.4, 90.9

Coding as in Table 1 (Design 2). The response values are the residual amounts in the soil samples after each treatment.

Table 4
Phenanthrene and pyrene degradation results obtained in the third design

Soil sample	Run	Factor			Phenanthrene		Pyrene	
		1	2	3	(mg kg ⁻¹)	(%)	(mg kg ⁻¹)	(%)
S ₂	a1	-1	-1	-1	89.8	12.9	764.9	54.6
	a2	1	-1	1	45.7	6.5	1010.0	72.2
	a3	-1	1	1	40.6	5.8	709.7	50.7
	a4	1	1	-1	20.9	3.0	336.6	24.1
	a5, a6	0	0	0	33.3, 34.5	4.8, 5.0	460.4, 485.6	33.2, 34.7
S ₃	b1	-1	-1	-1	15.5	2.2	6.1	2.2
	b2	1	-1	1	19.1	2.7	<ql ^a	0
	b3	-1	1	1	10.1	1.4	1.5	0.5
	b4	1	1	-1	3.3	0.5	<ql ^a	0
	b5, b6	0	0	0	6.8, 7.8	1.0, 1.8	<ql ^a , <ql ^a	0, 0
S ₄	c1	-1	-1	-1	10.2	1.5	15.9	2.6
	c2	1	-1	1	12.7	1.8	71.9	11.7
	c3	-1	1	1	10.2	1.5	15.9	2.6
	c4	1	1	-1	8.0	1.2	30.4	3.1
	c5, c6	0	0	0	11.0, 6.34	1.6, 0.9	32.0, 38.7	3.3, 6.7

Coding as in Table 1 (Design 3). The response values are the residual amounts in the soil samples after each treatment.

^a Below the quantification limit. <1 mg kg⁻¹.

twice the PHE concentration, which remained the same in all samples. Since the smallest residual values were 42.5 and 731.3 mg kg⁻¹ for PHE and PYR, respectively, it appeared that approximately the same absolute amount of the two contaminants, 700 mg kg⁻¹, was removed in the best runs.

In Table 3, oxidation of PHE and PYR contaminated soil by H₂O₂ with and without supplementary ferrous ion resulted that PYR was more difficult to remove from soils. This was probably because degradation of PAHs slowed down as molecular weight and the number of benzene rings in PAH structure increased. The present study demonstrated that PYR concentrations (43.6%) remaining in soil were higher than PHE (6.2%) in all treated soils in the best condition (run #8, Table 3). PYR (4 rings) was more recalcitrant than 3-ring PHE. That was expected, and in good coherence with the results of Kulik et al. [8], the degradation of high molecular weight PAHs may be limited mainly by the more complex structure of high molecular weight PAHs from soils.

Taking into account these unsatisfactory results, we decided to carry out a third design, using this time, for economy, half fractions of a full 2³ design, but increasing the levels of reaction time and Fe²⁺ concentration, as specified in Design 3 (Table 1). These oxidizing conditions were applied to soil samples S₂, S₃ and S₄, which had different amounts of PYR, the lowest being that of sample S₃, namely, 271.2 mg kg⁻¹. The results were given in Table 4. This time, the residual amounts of both PYR and PHE fell below the official threshold in several experimental runs. As shown in Table 4, this occurred only three times when soil sample S₂ was employed, and only for PHE. For PYR, the residual values were two orders of magnitude larger. We therefore restricted our analysis to samples S₃ and S₄. The relative efficiency of effects of the three factors on the removal of different target contaminants could best be visualized in Fig. 2, where the PYR initial concentrations were represented with different symbols.

Several conclusions could be drawn from an examination of Fig. 2. In the first place, all but one of the experiments finally complied with the maximum limits for both contaminants. The exception was run #c2, where the level of factor 2 (H₂O₂ concentration) was set at its lower value, and the PYR threshold was overcome. As a whole, the samples labeled with the letter b did quite better than the ones beginning with the letter c, in all likelihood due to the different initial PYR concentrations associated with these labels. It is also worth noticing that varying the factor levels affected much more the residual PYR concentration, as seen by the

larger spread along the abscissa axis. For the residual PHE, represented on the ordinate axis, the spread was much lower, and the limit was satisfied by all experiments.

In Fig. 3, the residual concentrations of PHE and PYR were plotted for each experiment run with soils S₂ to S₄. The PYR initial concentration of soil S₂ was twice the PHE initial concentration. In all cases of soil S₂ the residual PYR concentration was higher than 300 mg kg⁻¹, while the PHE residual concentration was lower than 100 mg kg⁻¹. The results clearly showed that PYR could not be totally mineralized. When the PYR initial concentration was about half the PHE concentration (soil S₃) both PAHs were nearly totally mineralized in all experiments. With similar initial concentrations of PYR and PHE (S₄), the PYR residual concentration was always slightly higher than the PHE residual concentration. These results clearly demonstrated that PHE oxidation was favored compared to PYR. This difference could be assigned to the difference in the number of aromatic rings, as the mineralization and desorption of the chemicals with more aromatic rings were slower. The conse-

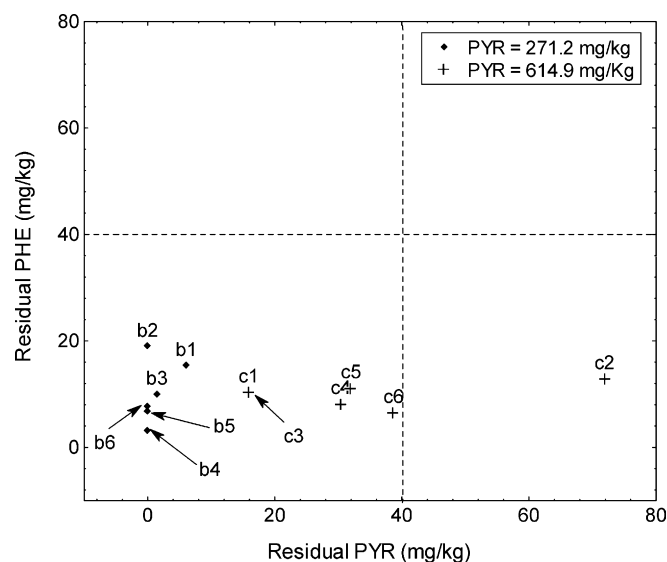


Fig. 2. Residual PHE and PYR amounts for the third design. Values below the quantification limit were assumed, for graphical purposes, to be equal to zero. The dashed lines indicate the maximum allowed limits.

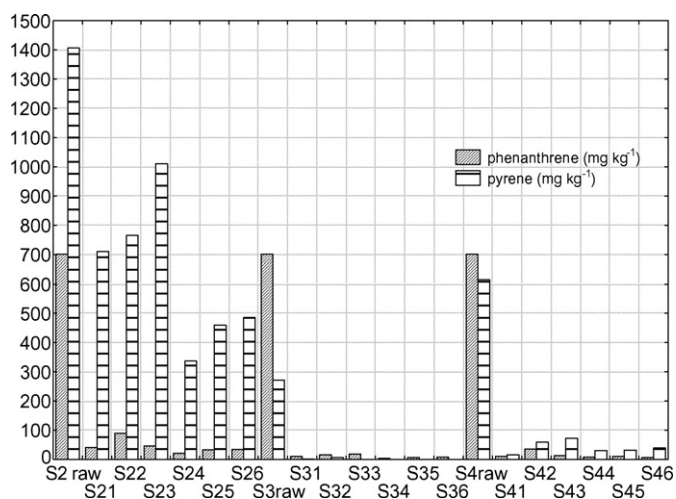


Fig. 3. Comparison of PHE and PYR residual concentrations (soil samples S_2 to S_4).

quence for process applicability is that low molecular weight PAHs are expected to be more easily degraded than higher molecular weight compounds.

4. Conclusions

This work has demonstrated that PAHs such as phenanthrene and pyrene could be eliminated, to a large extent, using oxidation with Fenton's reagent. With a series of factorial designed experiments we have determined conditions that dramatically reduced the concentration of the target pollutants in soil (e.g. from 700 to 18 mg kg⁻¹ PHE). Phenanthrene was more easily degraded than pyrene, reflecting the different molecular weights. To improve the operating conditions of the oxidation process, we have shown the primary importance of factors such as H₂O₂ concentration, Fe (II) concentration, pH, UV radiation, and the reaction time in process performance. Among these parameters, reaction time was the most significant. pH had a rather weak influence on the efficiency of the process, suggesting that the oxidation could be conducted without any pH adjustment, a key-point for field treatment.

However, these conclusions were only valid for freshly contaminated soils. In the case of historically contaminated soils, i.e. former MGP, PAHs are strongly bound to the soil matrix as a result of the pollution "aging" process. Efficiency of the oxidation process run on such soils in the conditions identified in this work should be verified. Also, in our work we have concentrated on Fenton's reaction. Assessment of the performance of this reagent should be compared to other means of oxidation, under lab as well as field conditions. Finally, the ecotoxicological impact of the process should be addressed, as the treated material normally ends up as plant support medium. These questions are currently under study in our groups.

Acknowledgements

The authors gratefully thank the GISFI (<http://www.gisfi.prd.fr>) supported by the French government and the "Région Lorraine". They also thank the "Conselho Nacional de Desenvolvimento Científico e Tecnológico" CNPQ for financial support. They would like to thank two members of the GISFI: Laboratory Soils and Environment (Nancy-Université, INRA) that provided Chenevière soil and LCPME Laboratory (Nancy-Université, INRA) for iron analysis.

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