

# Influence of pyrene combination state in soils on its treatment efficiency by Fenton oxidation

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Received 18 March 2006; received in revised form 1 March 2007; accepted 16 March 2007

Available online 22 May 2007

## Abstract

Interactions of hydrophobic organic compounds (HOCs) with soil organic matter (SOM) determine their combination state in soils, and therefore strongly influence their mobility, bioavailability, and chemical reactivity. Contact time (aging) of an HOC in soil also strongly influences its combination state and environmental fate. We studied Fenton oxidation of pyrene in three different soils to reveal the influences of SOM, contact time, and combination state on the efficiency of vigorous chemical reactions. Pyrene degradation efficiency depended strongly on the dose of oxidant ( $\text{H}_2\text{O}_2$ ) and catalyst ( $\text{Fe}^{2+}$ ); the greatest degradation was achieved at an oxidant to catalyst molar ratio of 10:1. Pyrene degradation differed among the three soils, ranging from 65.4% to 88.9%. Pyrene degradation efficiency decreased with increasing SOM content, and the aromatic carbon content in SOM was the key parameter. We hypothesize that pyrene molecules that combine with the compact net structure of aromatic SOM are less accessible to Fenton oxidation. Furthermore, pyrene degradation efficiency decreased considerably after aged for 30 days, but further aging to 60 and 180 days did not significantly change degradation efficiency. The Fenton oxidation efficiency of pyrene in both unaged and aged soils was greater than the corresponding desorption rate during the same period, perhaps because Fenton reaction can make pyrene more accessible to the oxidant through the enhancement of HOCs' desorption by generating reductant species or by destroying SOM through oxidation.

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*Keywords:* Fenton oxidation; Aging; Combination state; Pyrene; Desorption; SOM

## 1. Introduction

The combination state of hydrophobic organic compounds (HOCs) in soils is an important factor controlling their fate, reactivity, and bioavailability in the environment. When an HOC enters soil, its combination state can vary greatly as a result of the high heterogeneity of the soil. Soil organic matter (SOM) is believed to be the key structure that binds HOCs (Chiou et al., 2000). Based on its solubility in acids and bases, SOM is divided into three fractions: fulvic acid (FA) is the fraction soluble in both acids and bases, humic acid (HA) is the fraction soluble in bases but not acids, and humin is the residue soluble in neither bases nor acids. HOCs combined with these different fractions of the SOM behave differently because the fine structures of the three fractions differ (Huang et al.,

2003). FA and HA have relatively flexible and amorphous structures; in contrast, humin has a relatively condensed, rigid, three-dimensional structures. Therefore, it has been proposed that HOC molecules exist in SOM as different combination states: some are combined with those "easily desorbing and available sites", some combined with "difficultly desorbing and less available sites", and the others with "irreversible and non-available sites" (Sun and Li, 2005).

Moreover, it has been reported that HOCs become increasingly unavailable with increasing contact time (aging) in soils (Alexander, 2000), which suggests that the combination state of the HOC changes further during aging, with some molecules moving from the "easily desorbing and available sites" to the "difficultly desorbing and less available points", and even to the "irreversible and non-bioavailable sites". It has been well documented (Walker et al., 2005; Conrad et al., 2002; Macleod and Semple, 2000; Kan et al., 1994) that desorption of HOCs in

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soils, their availability to bio-uptake and biodegradation, and their extraction by mild solvents all decrease considerably during aging. However, whether or not the combination state of an HOC, which is controlled by soil properties and contact time, influences its reactivity in chemical reactions such as Fenton oxidation, has seldom been studied (Bogan and Trbovic, 2003).

Polycyclic aromatic hydrocarbons (PAHs) have attracted much attention for a long time due to their potential carcinogenic or mutagenic effects on human beings. Therefore, it is important to find an effective technique for purifying PAH-contaminated soils. However, biodegradation of PAHs is slow and incomplete, especially at high concentrations (Mueller et al., 1991). Recently, in-situ chemical oxidation (ISCO) has been shown to be an efficient and economical remediation technique for PAH-contaminated soils (Goi and Trapido, 2004; Watts et al., 2002; Kang and Hua, 2005). Fenton reaction, which uses  $\text{H}_2\text{O}_2$  as oxidant and  $\text{Fe}^{2+}$  as catalyst to generate hydroxyl radicals ( $\bullet\text{OH}$ ), is a promising ISCO technique due to its high efficiency, low cost, and environmental benignancy. It has been successfully applied in the remediation engineering of PAH-contaminated sites (Quan et al., 2003; Martinez et al., 2003). Moreover, several studies have reported that Fenton oxidation can enhance the biodegradability of PAHs (Nam et al., 2001; Lee and Hosomi, 2001; Kulik et al., 2005; Palmroth et al., 2006). Several studies have reported that the treatment efficiency of HOCs by ISCO is affected by soil type (Gates-Anderson et al., 2001; Goi and Trapido, 2004). Bogan and Trbovic (2003) have found that total organic carbon, humin content, and soil porosity all influenced the degradability of sorbed PAH by Fenton oxidation. The susceptibility of PAH to chemical oxidation was a function of SOM in four of the soils (those with SOM greater than approximately 10%), but was strongly dependent on soil porosity for low-SOM soils. There have also been many studies of aging effects on the bioavailability of HOCs in soils (Laor et al., 1996; Harkey et al., 1995; Conrad et al., 2002). However, the effect of aging on Fenton oxidation efficiency has seldom been discussed in literature (Bogan and Trbovic, 2003). Hence, the objectives of the present study were: (1) to determine the influence of soil type and aging on the treatment efficiency of a representative PAH (pyrene) in soil slurries using Fenton reaction; (2) to examine the effect of pyrene combination state on Fenton oxidation efficiency by comparison with its desorption. To determine the optimum conditions for Fenton reaction, the influences of the doses of the oxidant and the catalyst on reaction efficiency were observed first, then the optimal combination of the two reactants was used in subsequent experiments.

## 2. Materials and methods

### 2.1. Soil samples

Uncontaminated Chinese soils were sampled as the surface (0–20 cm) horizontal soils in Henan Province, and

in Tianjin. These soils were named Soil 1, 2, and 3, respectively, and their characteristics are shown in Table 1. The soil samples were air-dried, passed through a 2-mm sieve, and stored in closed containers in a dry place, in the dark at room temperature, prior to use. The content of SOM was determined using the potassium dichromate outside-heating method (Liu et al., 1996) after removing visible plant residues. HA is soluble in bases, but not acids; FA is soluble in both acids and bases; and humin is the insoluble residue that remains after HA and FA extractions. The content of each of the three fractions can thus be measured using a series of extractions: 0.1 mol/L diphosphoric acid and 0.1 mol/L sodium hydroxide to remove HA and FA, followed by 0.5 mol/L sulfuric acid (pH = 2–3) to remove FA. pH was measured in a 1:1 (w/w) soil– $\text{CaCl}_2$  water suspension. The grain-size distribution was determined using a densimeter. Iron content was determined using the *o*-phenanthroline photometric method.

### 2.2. Chemicals

Pyrene (98% purity) was purchased from the Aldrich Chemical Company, US. Pyrene stock solution (1 g/L) was prepared in HPLC-grade methanol. Aqueous solution containing 0.01 mol/L  $\text{CaCl}_2$  and 200 mg/L  $\text{NaN}_3$  was adopted as the test solution in the desorption experiments in order to create a specific ionic strength and to prevent microbial activity, respectively. Ethyl acetate used as organic solvent to extract pyrene from soils, and  $\text{H}_2\text{O}_2$  and  $\text{FeSO}_4$  were of analytical grade. Acetonitrile used for the mobile phase in the high-performance liquid chromatography (HPLC) analysis was of HPLC grade.

### 2.3. Preparation of unaged and aged soil samples

To obtain pyrene-contaminated soil samples, specific volume of pyrene–methanol stock solution (1 g/L) was added to a given mass of soil in tubes to make up a final pyrene concentration of 40 mg/kg (dry soil). The tubes were then shaken using a Vortex Mixer for 1 min at 15-min intervals for 1 h in a hood to evaporate the methanol and disperse pyrene molecules in the soils. Specific amount of 200 mg/L  $\text{NaN}_3$  aqueous solution was added to inhibit

Table 1  
Selected properties of the tested soils

	Soil 1	Soil 2	Soil 3
pH	7.46	7.72	7.66
SOM (%)	1.55	1.86	5.20
Fulvic acid (%)	0.24	0.22	1.22
Humic acid (%)	0.75	0.80	1.24
Humin (%)	0.56	0.84	2.74
Sand (%)	70.10	49.95	67.79
Silt (%)	23.25	34.55	25.27
Clay (%)	6.62	15.50	6.90
Iron (%)	2.79	2.98	2.60
Texture type	Loamy sand	Sandy loam	Loamy sand

biological activity and keep soil moisture at 30% (wet weight basis). The tubes were then tightly capped with Teflon septum and kept in the dark at  $25 \pm 1$  °C overnight or for 30, 60, and 180 days to obtain unaged and 30-, 60-, and 180-day-aged soils, respectively.

#### 2.4. Characterization of HA and humin

Solid-state cross-polarization magic-angle-spinning and total-side band-suppression (CPMAS-TOSS)  $^{13}\text{C}$  NMR spectra of the extracted HA and humin were obtained using a Varian Infinity Plus 400 spectrometer operated at the  $^{13}\text{C}$  frequency of 100.5 MHz. The instrument was run under the following conditions: contact time, 1 ms; spinning speed, 5 kHz;  $90^\circ$   $^1\text{H}$  pulse, 2.2  $\mu\text{s}$ ; acquisition delay, 4 s; and from 5000 to 10,000 scans (Kang and Xing, 2005).

#### 2.5. Treatment of the soil samples by Fenton oxidation

In the Fenton oxidation, 2 g of pyrene-contaminated soil samples were slurried in 10 mL of de-ionized water containing certain concentration (0–80 mM) of  $\text{FeSO}_4$ . Henceforth, we will refer to this mixture as the 1:5 slurry. pH of the tested solution was adjusted to 3.0 ( $\pm 0.2$ ) with appropriate amounts of 1 M HCl and 1 M NaOH. Specific concentrations (0–500 mM) of  $\text{H}_2\text{O}_2$  were then added according to the design of the experiments. The slurry was stirred using a magnetic bar to ensure complete mixing of the reactants for a certain period (15–180 min). The soil samples were then recovered and analyzed to determine their pyrene content. All Fenton oxidation experiments were conducted in duplicate.

#### 2.6. Tenax beads—assisting desorption

To compare pyrene desorption and oxidation, desorption of pyrene from unaged and 30-day-aged soils was measured using Tenax beads (35–60 mesh, Chromatographic Specialties, Canada) to assist desorption. The procedure is similar to that previously described in the literature (Sun and Li, 2005). In this approach, 1 g of the contaminated soils was suspended in round-bottom glass tubes containing 10 mL of the test solution and 0.5 g of Tenax beads. The tubes were capped with Teflon septum and shaken at 150 rpm for a designated period of time (0–10 days). At the end of each desorption period, the tubes were centrifuged for 20 min at 3500 rpm. The Tenax beads were then carefully removed using a clean stainless-steel spatula and transferred into a clear 25-mL glass flask. An additional 0.5 g of clean Tenax beads was added into the tube to continue the desorption. The contaminated Tenax was then extracted with a 1:1 (v/v) mixture of acetone and *n*-hexane in three successive extractions, with each extraction carried out in a horizontal shaker overnight. The combined acetone and *n*-hexane was evaporated to near-dryness under a gentle stream of nitrogen in a water bath held at 40 °C, and the residue was re-dissolved

to certain volume using acetonitrile. The contaminant concentration in the acetonitrile was analyzed by means of HPLC. Pyrene recovery from the Tenax beads using this method was more than 98%, which was determined by adding a known quantity of pyrene onto Tenax beads. The percentage of pyrene desorbed from the soils was then calculated. Desorption experiments were conducted in duplicate.

#### 2.7. Soxhlet extraction

Soil samples were obtained after centrifugation of the slurry. The separated solid phase was mixed with anhydrous  $\text{Na}_2\text{SO}_4$  (1:1 w/w), allowed to stand overnight, and ground into a fine powder prior to Soxhlet extraction. For the Soxhlet extraction, the soil sample was transferred into a cellulose extraction thimble, which was then placed in a Soxhlet extraction apparatus. A 200-mL round-bottom flask containing 85 mL of ethyl acetate was connected to the apparatus, and the extraction was performed for 6 h with a reflux cycle of 5 cycles per hour (Ravelet et al., 2001). After extraction, the solvent was evaporated to near-dryness under a gentle stream of nitrogen in a water bath held at 40 °C. The residue was dissolved in 10 mL of acetonitrile for HPLC analysis. Recovery of pyrene in the Soxhlet extraction of the contaminated soil samples ranged from 85% to 90%, and the oxidation percentage was calculated using the sample concentration after an average extraction recovery of 88% was accounted for.

#### 2.8. Analytical procedure

The pyrene concentration in the solvent was quantified by means of HPLC. The HPLC system was a model SCL-10AVP HPLC (Shimadzu, Japan) equipped with a programmable fluorescence detector. A reverse-phase column (VP-ODS Kromasil  $\text{C}_{18}$ , 150 mm  $\times$  4.6 mm  $\times$  5  $\mu\text{m}$ , Shimadzu, Japan) was employed at ambient temperatures. The mobile phase, containing 85% acetonitrile and 15% water (MilliQ quality), flowed at 1.0 mL/min, and the injection volume was 20  $\mu\text{L}$ . Fluorescence detection was performed at an excitation wavelength of 260 nm and an emission wavelength of 373 nm. The amount of pyrene was determined using an external standard for calibration.

### 3. Results and discussion

#### 3.1. Effect of $\text{H}_2\text{O}_2$ and $\text{FeSO}_4$ dosage on pyrene degradation

Fenton oxidation efficiency for HOCs varies greatly as a function of the reaction conditions, and this variation has been well-documented in aqueous phase (Martinez et al., 2003). The optimum conditions for Fenton oxidation in soil slurries appear to be similar to those in aqueous solutions (Watts et al., 2002). In the present study, the optimum dosages of the oxidant ( $\text{H}_2\text{O}_2$ ) and the catalyst

( $\text{Fe}^{2+}$ ) for pyrene oxidation in soil slurries were determined at a fixed pH of 3. This pH was chosen because Fenton reaction efficiencies are the highest at a pH around 3 in both aqueous and soil systems (Quan et al., 2003). To investigate the effect of  $\text{H}_2\text{O}_2$  dosage, batch experiments were carried out on 40 mg/kg (dry soil) pyrene in a soil slurry at different  $\text{H}_2\text{O}_2$  concentrations (0–500 mM) with 20 mM  $\text{Fe}^{2+}$  as the catalyst and the solution temperature held at  $25 \pm 1$  °C. The resulting levels of pyrene degradation are shown in Fig. 1. Not surprisingly, the degradation percentage increased with increasing  $\text{H}_2\text{O}_2$ . For example, the percentages were  $40.3 \pm 2.4\%$ ,  $31.3 \pm 1.2\%$ , and  $15.5 \pm 1.3\%$  at 25 mM  $\text{H}_2\text{O}_2$  in Soils 1, 2, and 3, respectively. When the  $\text{H}_2\text{O}_2$  concentration increased to 200 mM, the degradation percentage increased to  $88.9 \pm 2.7\%$ ,  $79.4 \pm 2.1\%$ , and  $65.4 \pm 2.0\%$ , respectively. However, when the  $\text{H}_2\text{O}_2$  concentration continued increasing beyond this level (to 400 and 500 mM), the oxidation efficiency did not increase significantly.

To observe the effect of the  $\text{Fe}^{2+}$  concentration, pyrene degradation was analyzed at  $\text{FeSO}_4$  concentrations ranging from 5 to 80 mM at a fixed  $\text{H}_2\text{O}_2$  concentration of 200 mM (Fig. 2). Fig. 2 shows that pyrene degradation increased with increasing  $\text{Fe}^{2+}$  concentration for  $\text{Fe}^{2+}$  concentrations less than 20 mM, then stabilized or decreased slightly; the greatest degradation was achieved at 20 mM  $\text{FeSO}_4$ . Hence, the optimum condition for pyrene oxidation in soil slurry appears to be 200 mM  $\text{H}_2\text{O}_2$  plus 20 mM  $\text{FeSO}_4$ , with a resulting oxidant to catalyst molar ratio of 10:1.

The greatest oxidation efficiency was achieved at the above-mentioned optimum oxidant to catalyst ratio, which agrees with previous results (Lunar et al., 2000). This is because Fenton oxidation is a complicated reaction system. The Fenton initiation reactions are (Walling and Goosen, 1973):

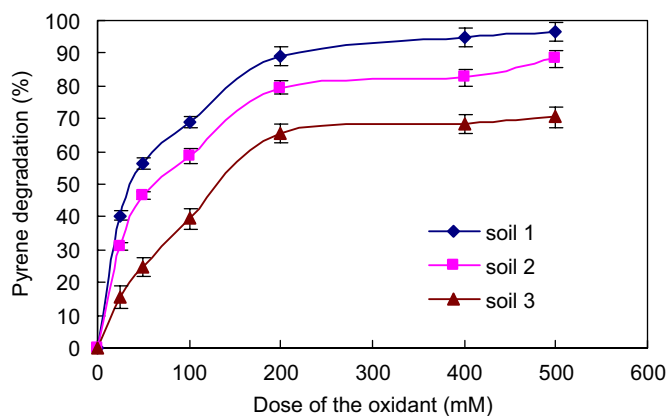
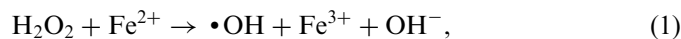


Fig. 1. Effects of  $\text{H}_2\text{O}_2$  dose on pyrene degradation in three different soils using the Fenton reaction (30-min reaction time in a 1:5 slurry with 20 mM  $\text{Fe}^{2+}$  at pH 3).

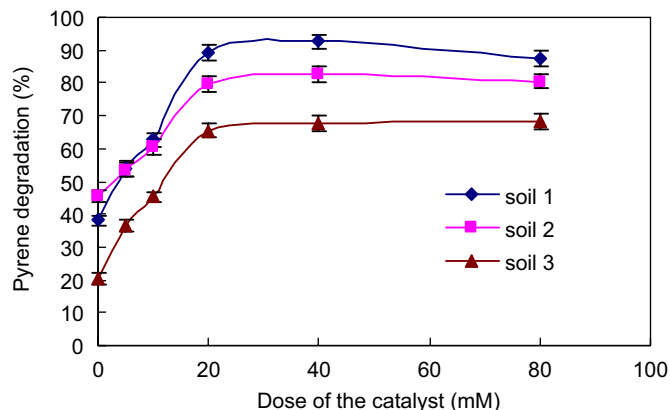


Fig. 2. Effects of  $\text{Fe}^{2+}$  dose on pyrene degradation in three different soils using Fenton reaction (30-min reaction time in a 1:5 slurry with 200 mM  $\text{H}_2\text{O}_2$  at pH 3).

As demonstrated in Eq. (1),  $\text{H}_2\text{O}_2$  acts as the oxidant, and soluble  $\text{Fe}^{2+}$  serves as the catalyst in Fenton oxidation. Attack on HOCs by the  $\cdot\text{OH}$  radicals generated through the reaction in Eq. (1) is believed to be responsible for destruction of the HOCs (Watts et al., 2002). In order to continually generate  $\cdot\text{OH}$ , the  $\text{Fe}^{3+}$  produced in Eq. (1) must be reduced to  $\text{Fe}^{2+}$  via additional steps (Eq. (2)). Additionally, it has been pointed out that the generation of  $\cdot\text{OH}$  and the subsequent free-radical attack on the target HOCs will proceed when soluble  $\text{Fe}^{2+}$  species are present. Hence, if the total soluble  $\text{Fe}^{2+}$  concentration decreases, the catalytic cycles of soluble  $\text{Fe}^{2+}$  cease and the rate of Fenton oxidation decreases (Bogan and Trbovic, 2003). This is why, at certain concentrations, pyrene degradation increased with increasing dosages of both  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$ . The removal rate of pyrene was limited by the availability of soluble  $\text{Fe}^{2+}$  when  $\text{H}_2\text{O}_2$  was present in excess (Fig. 1), thereby consuming too much  $\text{Fe}^{2+}$  and consequently creating a low level of  $\text{Fe}^{2+}$  in the reaction system. On the other hand, when  $\text{Fe}^{2+}$  concentration was too high (>20 mM in this study; Fig. 2), a considerable quantity of  $\text{H}_2\text{O}_2$  may have been consumed in vain (i.e., not used to generate  $\cdot\text{OH}$  but instead used to generate water via other reactions). Hence, an optimum oxidant to catalyst ratio exists for Fenton oxidation of HOCs in soil systems, and the mechanisms are the same as in aqueous systems.

### 3.2. Effect of SOM on pyrene oxidation efficiency

The time-dependent oxidation efficiencies of pyrene in the three soils with different SOM content are shown in Fig. 3. Oxidation took place quickly, and the majority of the reaction finished within 30 min. The percentage of pyrene degradation differed noticeably among the three soils, with values of  $88.9 \pm 2.7\%$ ,  $79.4 \pm 2.1\%$ , and  $65.4 \pm 2.0\%$  for unaged Soils 1, 2, and 3, respectively. Lower degradation efficiency was found for soils with a higher SOM content. It has been well-documented that SOM plays an important role in determining the mobility and

bioavailability of HOCs in soils (Sun and Li, 2005; Walker et al., 2005) because the combination state of HOCs bound in soils varied greatly with respect to SOM content and structure. Usually, soils with higher SOM content possess more “difficultly desorbing and less available sites”, and hence HOCs in these soils are less available for desorption and biological uptake. In the present study, we found that even in the face of a vigorous Fenton reaction, SOM still played an important role through its impact on the combination state of the HOC. In addition, the fact that Fenton oxidation efficiency decreased with increasing SOM content might also result from greater consumption of hydroxyl radicals at high SOM content, which would lead to a lower rate of pyrene degradation.

SOM is a highly heterogeneous system of macromolecules. From the view of solubility in acids and bases, SOM can be divided into three fractions: FA (soluble in acids), HA (soluble in bases), and humin (insoluble in either acids or bases). The three SOM fractions have different effects on the mobility and bioavailability of the HOC that combines with them due to differences in their fine structure. In order to identify the key factor that affects the efficiency of Fenton oxidation, the percentages of the three SOM fractions were measured (Table 1), and the fine structures of HA and humin in the three soils were observed by CPMAS-TOSS  $^{13}\text{C}$  NMR (Table 2). The resulting NMR spectrum revealed that humin contains more aromatic carbons (108–160 ppm) than HA does, and that their aliphaticity is lower than that of HA; in contrast, HA contains a higher content of amide or carboxylic acid groups (160–190 ppm) than humin does. These groups are polar, thus sorption of HOCs on these groups is reported to be weak (Kang and Xing, 2005). We analyzed the correlation between pyrene degradation in the three soils and their SOM fractions (Table 3). The pyrene degradation percentage was negatively correlated with all the parameters analyzed, but the strongest correlation ( $R^2 = -0.955$ ) was for the percentage of aromatic carbon in both HA and humin, which equals the sum of the

percentage of aromatic carbon in each fraction (Table 2) multiplied by the corresponding HA and humin percentages (Table 1). From these results, the aromatic carbon component of SOM appears to be the key factor affecting pyrene degradation, and HOCs that combine with aromatic carbons become less available to Fenton oxidation. This conclusion should be verified using additional soil samples. Bogan and Trbovic (2003) also reported that humin in SOM could reduce the susceptibility of PAHs to Fenton oxidation.

### 3.3. Effect of contact time on pyrene oxidation efficiency

The effect of contact time (aging) on Fenton oxidation is shown in Fig. 4. The results reveal that the rate of pyrene degradation had decreased considerably after 30 days of aging, with the pyrene degradation percentage decreasing to  $74.7 \pm 3.1\%$ ,  $63.0 \pm 2.0\%$ , and  $42.3 \pm 2.5\%$ , for Soils 1, 2, and 3, respectively. However, the oxidation efficiencies in samples aged for 60 and 180 days did not differ significantly from those of samples aged for 30 days. The aging period may have allowed some of the pyrene that had originally combined with the “easily accessible sites” to transfer to the “difficultly accessible sites”, where the availability of the molecule to the oxidation reaction is lower. This process is called sequestration, and it is believed that sequestration is a natural process in soils that reduces the availability of HOCs to biodegradation and other reactions (Alexander, 2000).

The mechanism of sequestration has been proposed to result from slow diffusion of HOCs within the nanopores of organic–mineral complexes or the compact structure of SOM (Pignatello and Xing, 1996). Many authors have concluded that interactions between SOM and HOCs occurs as a two-step process, in which sequestration begins with partitioning of the HOC molecules into the HA and FA fractions (which have amorphous structures), followed by diffusion into the humin–mineral fraction, which has a rigid net structure (Huang et al., 2003; Pignatello and Xing, 1996). The release of HOC molecules that have combined with the HA and FA fractions is believed to be relatively easy, whereas the release of those that have combined with the humin fraction is more difficult (Sun and Yan, 2007). Nam and Kim (2002) studied the distribution of phenanthrene in different SOM fractions, and found that more than 90% of the initial amount was found in the humin–mineral fraction regardless of the aging period. The recovery of phenanthrene from the HA and FA fractions is about 11% after 1 day of aging in soil samples, and decreased with the increasing contact time.

Moreover, Alexander (2000) pointed out that there are many pores or voids with diameter of 0.3–1.0 nm in soil aggregates, and this size range is similar to the range for the molecular size of HOCs. Malekani et al. (1997) demonstrated that the high porosity in humin–mineral complexes mainly comes from humin, not from the mineral surfaces. The molecular volume of pyrene is  $0.186 \text{ nm}^3$  (Brion and

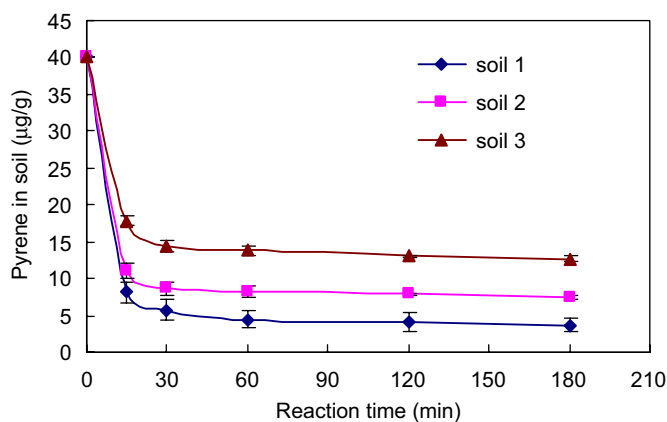


Fig. 3. Pyrene degradation dynamics in different soils under optimal conditions for Fenton oxidation (in a 1:5 slurry with 200 mM  $\text{H}_2\text{O}_2$  plus 20 mM  $\text{FeSO}_4$  at pH 3).

Table 2  
Integration of solid-state  $^{13}\text{C}$  NMR spectra and aliphaticity (the ratio of the sum of aliphatic to aromatic carbons) for three HA and three humin samples<sup>a</sup>

Sample	Distribution (%) of chemical shift (ppm)				Aliphatic C (%)	Aromatic C (%)	Aliphaticity
	0–60	60–108	108–160	160–190			
HA 1	56.8	11.8	10.1	21.3	68.6	10.1	6.79
Humin 1	16.6	47.3	36.1	—	63.9	36.1	1.77
HA 2	44.4	16.8	19.9	18.9	61.2	19.9	3.08
Humin 2	7.0	55.9	37.0	—	62.9	37.0	1.7
HA 3	59.3	8.1	17.8	14.8	67.4	17.8	3.79
Humin 3	4.6	60.1	35.3	—	64.7	35.3	1.83

<sup>a</sup>Aliphatic C represents the total aliphatic carbon region (0–108 ppm); aromatic C represents the total aromatic carbon region (108–160 ppm); aliphaticity represents the ratio aliphatic C (0–108 ppm)/aromatic C (108–160 ppm).

Table 3  
Correlation coefficients ( $R^2$ ) for the relationship between pyrene degradation in the three soils and their SOM parameters

Total SOM	HA	Humin	HA + humin	Aromatic carbon in (HA + humin) (%)
–0.890	–0.900	–0.915	–0.912	–0.955

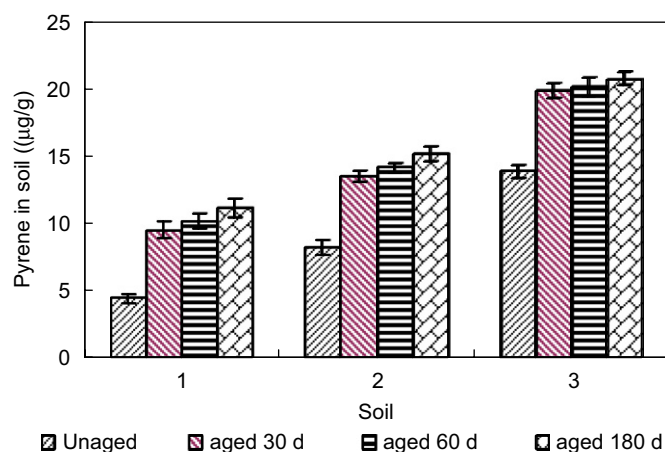


Fig. 4. Effect of contact time (aging) on the efficiency of pyrene degradation by Fenton oxidation in different soils (30-min reaction time in a 1:5 slurry with 200 mM  $\text{H}_2\text{O}_2$  and 20 mM  $\text{Fe}^{2+}$ ).

Pelletier, 2005), which is similar to the size of the soil pores. Hence, it is plausible to hypothesize that molecules trapped in micropores or nanopores are less available than those found in relatively larger macropores (i.e., pores that are larger compared with the size of the pollutant molecule). Hence, the smaller pores in SOM and in soil minerals can serve as sequestration sites for HOCs.

#### 3.4. Comparison of pyrene desorption and degradation

Desorption dynamics were assessed for six pyrene-contaminated soils (three soils, with unaged and 30-days-

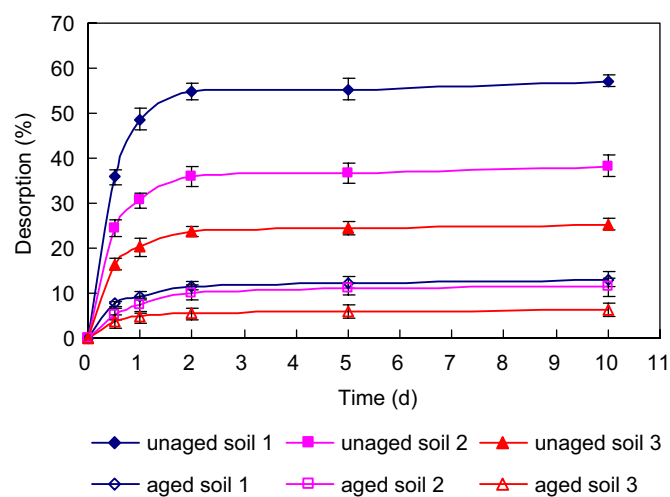


Fig. 5. Desorption percentages of sorbed pyrene in 30 days-aged and unaged samples of the three soils using desorption assisted by Tenax beads.

aged samples for each; Fig. 5). Pyrene desorbed quickly within the first day, but after 2 days, desorption seemed to cease, and a steady-state was achieved in all the six samples. These results demonstrate that pyrene quickly became adsorbed to the soils and subsequently resisted desorption, with desorption percentages of only 54.7%, 35.9%, and 23.7% for unaged Soils 1, 2, and 3, respectively. The desorption percentages of the aged soils were much lower, with the corresponding values of 13.12%, 11.34%, and 6.25%. On the other hand, pyrene degradation by Fenton oxidation was completed in 0.5 h, resulting in about 65–89% degradation of the parent compound. This seems to indicate that Fenton reaction can oxidize pyrene sorbed to soil particles. However, there may be other explanations. First, SOM content was reduced during the Fenton reaction due to the oxidation, and this would release many of the sorbed pyrene molecules. In our previous study, we found that Fenton oxidation reduced the SOM content of the same three soils from 1.55% to 1.28%, from 1.82% to 1.49%, and from 5.20% to 4.10% for Soils 1, 2, and 3, respectively (Sun and Yan, 2007). Moreover, the Fenton reaction can generate both oxidant

and reductant species, and it has been proposed that the reductant species have the potential to enhance desorption of sorbed HOCs (Watts et al., 1999, 2002). Therefore, a vigorous Fenton reaction may provide a complex reaction matrix that can change the content and structure of the SOM, and as a result, the combination states of the contaminant. Although the Fenton oxidation percentage for pyrene is higher than its desorption percentage, oxidation still depends strongly on the pyrene's combination state in the soil. As was discussed above, oxidation efficiency differed greatly among the three soils due to their different SOM contents and structures. Furthermore, oxidation decreased further after aging, presumably as a result of sequestration at less accessible sites.

#### 4. Conclusions

An optimum molar ratio of 10:1 for the oxidant ( $\text{H}_2\text{O}_2$ ) and the catalyst ( $\text{Fe}^{2+}$ ) existed for the degradation of pyrene in soils by Fenton oxidation. Increasing the dosage of the oxidant or the catalyst separately, causing a deviation from this optimum ratio, decreased the oxidation efficiency. Pyrene degradation varied greatly among the three soils, with values of  $88.9 \pm 2.7\%$ ,  $79.4 \pm 2.1\%$ , and  $65.4 \pm 2.0\%$  for Soils 1, 2, and 3, respectively. The degradation percentage was influenced by the content and structure of the SOM, and the aromatic carbon content was the key factor controlling oxidation efficiency. That is, pyrene molecules combined with the aromatic carbon fraction of the SOM, whose structure is believed to be compact and rigid, were much less accessible to Fenton oxidation. Pyrene degradation had decreased after 30 days of aging, reaching values of  $74.7 \pm 3.1\%$ ,  $63.0 \pm 2.0\%$ , and  $42.3 \pm 2.5\%$  for Soils 1, 2, and 3, respectively. This is because during aging, more pyrene molecules became trapped in less accessible sites. Fenton oxidation was largely complete by 30 min, whereas desorption only occurred at rates of 54.7%, 35.9%, and 23.7% for unaged Soils 1, 2, and 3, and these values are considerably lower than the corresponding degradation percentage. Though Fenton oxidation is strongly influenced by the combination state of the pollutant molecules in soils, the reaction can change the combination state of the HOCs by reducing SOM content and enhancing desorption of the HOCs by reductant species.

#### Acknowledgments

The authors thank the Ministry of Science and Technology of China (2004cb-418504) and the National Foundation of Natural Science (40273036) of China for their financial support.

#### References

Alexander, M., 2000. Aging, bioavailability, and overestimation of risk from environmental pollutants. *Environmental Science and Technology* 34, 4259–4264.

- Bogan, B.W., Trbovic, V., 2003. Effect of sequestration on PAH degradability with Fenton's reagent: roles of total organic carbon, humin, and soil porosity. *Journal of Hazardous Material B* 100, 285–300.
- Brion, D., Pelletier, E., 2005. Modelling PAHs adsorption and sequestration in freshwater and marine sediments. *Chemosphere* 61, 867–876.
- Chiou, C.T., Kile, D.E., Ruthereord, D.W., 2000. Sorption of selected organic compounds from water to a peat soil and its humic-acid and humin fractions: potential sources of the sorption nonlinearity. *Environmental Science and Technology* 34, 1254–1258.
- Conrad, A.U., Comber, S.D., Simkiss, K., 2002. Pyrene bioavailability; effect of sediment–chemical contact time on routes of uptake in an oligochaete worm. *Chemosphere* 49, 447–454.
- Gates-Anderson, D.D., Siegrist, R.L., Cline, S.R., 2001. Comparison of potassium permanganate and hydrogen peroxide as chemical oxidants for organically contaminated soils. *Journal Environmental Engineering* 127, 337–347.
- Goi, A., Trapido, M., 2004. Degradation of polycyclic aromatic hydrocarbons in soil: the Fenton reagent versus ozonation. *Environmental Technology* 25, 155–164.
- Harkey, G.A., Van Hoof, P.L., Landrum, P.F., 1995. Bioavailability of polycyclic aromatic hydrocarbons from a historically contaminated sediment core. *Environmental Science and Technology* 14, 1551–1560.
- Huang, W.L., Peng, P.A., Yua, Z.Q., Fu, J.M., 2003. Effects of organic matter heterogeneity on sorption and desorption of organic contaminants by soils and sediments. *Review Applied Geochemistry* 18, 955–972.
- Kan, A.T., Fu, G., Tomson, M.B., 1994. Adsorption/desorption hysteresis in organic pollutants and soil/sediment interaction. *Environmental Science and Technology* 28, 859–867.
- Kang, N., Hua, I., 2005. Enhanced chemical oxidation of aromatic hydrocarbons in soil systems. *Chemosphere* 61, 909–922.
- Kang, S.H., Xing, B.S., 2005. Phenanthrene sorption to sequentially extracted soil humic acids and humins. *Environmental Science and Technology* 39, 134–140.
- Kulik, N., Goi, A., Trapido, M., Tuhkanen, T., 2005. Degradation of polycyclic aromatic hydrocarbons by combined chemical pre-oxidation and bioremediation in creosote contaminated soil. *Journal of Environmental Management* 78, 382–391.
- Laor, Y., Strom, P.F., Farmer, W.J., 1996. The effect of sorption on phenanthrene bioavailability. *Journal of Biotechnology* 51, 227–234.
- Lee, B.D., Hosomi, M., 2001. A hybrid Fenton oxidation—microbial treatment for soil highly contaminated with benz(a)anthracene. *Chemosphere* 43, 1127–1132.
- Liu, G.S., Jiang, N.H., Zhan, L.D., Liu, Z.L., 1996. *Soil Physical and Chemical Analysis Description of Soil Profiles*. China Standard Methods Press, Beijing, China (in Chinese).
- Lunar, L., Sicilia, D., Rubio, S., Pérez-Bendito, D., Nickel, U., 2000. Degradation of photographic developers by Fenton's reagent: condition optimization and kinetics for metal oxidation. *Water Research* 34, 1791–1802.
- Macleod, C.J.A., Semple, K.T., 2000. Influence of contact time on extractability and degradation of pyrene in soils. *Environmental Science and Technology* 34, 4952–4957.
- Malekani, K., Rice, J.A., Lin, J.S., 1997. The effect of sequential removal of organic matter on the surface morphology of humin. *Soil Science* 162, 333–342.
- Martinez, N.S.S., Fernández, J.F., Segura, X.F., Ferrer, A.S., 2003. Pre-oxidation of an extremely polluted industrial wastewater by the Fenton's reagent. *Journal of Hazardous Material B* 101, 315–322.
- Mueller, J.G., Middaugh, D.P., Lantz, S.E., Chapman, P.J., 1991. Biodegradation of creosote and pentachlorophenol in contaminated groundwater: chemical and biological assessment. *Applied Environmental Microbiology* 57, 1277–1285.
- Nam, K., Kim, J.Y., 2002. Role of loosely bound humic substances and humin in the bioavailability of phenanthrene aged in soil. *Environmental Pollution* 118, 427–433.
- Nam, K., Rodriguez, W., Kukor, J.J., 2001. Enhanced degradation of polycyclic aromatic hydrocarbons by biodegradation combined with a modified Fenton reaction. *Chemosphere* 45, 11–20.

- Palmroth, M.R.T., Langwaldt, J.H., Aunola, T.A., Goi, A., Puhakka, J.A., Tuhkanen, T.A., 2006. Treatment of PAH contaminated soil by combination of Fenton's reaction and biodegradation. *Journal of Chemical Technology and Biotechnology* 81, 598–607.
- Pignatello, J.J., Xing, B., 1996. Mechanisms of slow sorption of organic chemicals to natural particles. *Environmental Science and Technology* 30, 1–11.
- Quan, H.N., Teel, A.L., Watts, R.J., 2003. Effect of contaminant hydrophobicity on hydrogen peroxide dosage requirements in the Fenton-like treatment of soils. *Journal of Hazardous Material B* 102, 277–289.
- Ravelet, C., Grosset, C., Montuelle, B., Benoit-Guyod, J.L., Alary, J., 2001. Liquid chromatography study of pyrene degradation by two micromycetes in freshwater sediment. *Chemosphere* 44, 1541–1546.
- Sun, H., Li, J., 2005. Availability of pyrene in unaged and aged soils to earthworm uptake, butanol extraction and SFE. *Water, Air and Soil Pollution* 166, 353–365.
- Sun, H., Yan, Q., 2007. Influence of Fenton oxidation on soil organic matter and its sorption and desorption of pyrene. *Journal of Hazardous Material*, in press (available on line, DOI:10.1016/j.jhazmat.2006.10.005).
- Walker, A., Rodriguez-Cruz, M.S., Mitchell, M.J., 2005. Influence of ageing of residues on the availability of herbicides for leaching. *Environmental Pollution* 133, 43–51.
- Walling, C., Goosen, A., 1973. Mechanism of the ferric ion catalyzed decomposition of hydrogen peroxide. Effect of organic substrates. *Journal of American Chemical Society* 95, 2987–2991.
- Watts, R.J., Bottenberg, B.C., Hess, T.F., Jensen, M.D., Teel, A.L., 1999. Role of reductants in the enhanced desorption and transformation of chloraliphatic compounds by modified Fenton's reactions. *Environmental Science and Technology* 33, 3432–3437.
- Watts, R.J., Stanton, P.C., Howsawkung, J., Teel, A.L., 2002. Mineralization of a sorbed polycyclic aromatic hydrocarbon in two soils using catalyzed hydrogen peroxide. *Water Research* 36, 4283–4292.