

Influence of Fenton oxidation on soil organic matter and its sorption and desorption of pyrene

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Abstract

The influences of Fenton oxidation on the content and composition of soil organic matter (SOM) and the consequent change of its sorption and desorption of pyrene were investigated using three soil samples. The results showed that both the content and the composition of the SOM changed, with total SOM content decreasing. The content of humic acid (HA) was reduced, while the content of humin did not change significantly, however the content of fulvic acid (FA) had a tendency to increase. Correlation analysis of soil–water distribution coefficient (K_d) and different parts of the SOM reveals that humin and HA are the key factors controlling the sorption of pyrene. Organic carbon normalized K_d (K_{OC}) varied to different extents after Fenton oxidation due to the change of SOM composition. The reduction of K_{OC} is significant in Soils 1 and 2 where large part of HA was reduced to FA, whose sorption ability is low. The change of K_{OC} by oxidation in Soil 3 is not so significant due to that the percentage of humin and HA in Soil 3 did not change greatly after oxidation. Desorption was hysteretic in all cases, and humin percentage was found to be the key factor on the extent of desorption hysteresis. Oxidation made desorption more hysteretic due to the elevated proportion of humin.

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1. Introduction

Sorption and desorption are two important processes that influence the amount of hydrophobic organic contaminants (HOCs) retained by soils. Understanding of the sorption and desorption of HOCs is very important in predicting their behavior, and therefore their fate and risk in the environment. Soil–water distribution coefficient (K_d , L/kg) is usually used to describe the extent to which a compound is associated with the solid phase at equilibrium [1]:

$$K_d = \frac{C_S}{C_W} \quad (1)$$

where C_S is the concentration of HOCs in solid phase (mg/kg) and C_W is the concentration of HOCs in aqueous phase (mg/L). K_d value of a given compound has been found to positively cor-

relate with the content of soil organic matter (SOM) [2]. Hence, organic carbon normalized distribution coefficient (K_{OC}) was defined to express the sorption ability based on the unit mass of SOM:

$$K_{OC} = \frac{K_d}{f_{OC}} \quad (2)$$

where f_{OC} is the content of organic carbon in soils. f_{OC} was acquired by dividing SOM content with 1.724, according to Liu et al. [3], for SOM usually contains 50–60% organic carbon. K_{OC} value of a given HOC should be similar among different soils if K_d correlates linearly with the SOM content [2,4]. However, latter researches [5,6] have found that K_{OC} value of a given HOC shows variation between different humic substances. For example, Gerstl [6] found that the difference of K_{OC} value of atrazine is over 100 times in different soils, using data from numerous research groups. This indicates that not only the quantity, but also the composition and structure of the SOM have an influence on K_d , and the variation in K_{OC} might primarily reflect the difference in chemical structure of the SOM.

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Moreover, it has recently been found that desorption of HOCs from soils are hysteretic in many cases [7–9]; that is, desorption isotherm deviates markedly from the corresponding sorption isotherm, indicating that sorption of HOCs in soils is not completely reversible. In general, desorption isotherm often has higher capacity than its respective sorption isotherm, and hence K_d measured in desorption is greater than the K_d measured in sorption at a constant equilibrium C_w . Huang et al. [9] have defined a hysteresis index to express the extent of desorption hysteresis:

$$\text{hysteresis index} = \frac{q_e^d - q_e^s}{q_e^s} \Big|_{T, C_e^w} \quad (3)$$

where q_e^d and q_e^s are solid-phase solute concentrations for the sorption and desorption experiments, respectively, and the subscripts T and C_e^w specify constant conditions of temperature and residual solution phase concentration at equilibrium, respectively. This hysteretic or resistant desorption phenomenon is practically important because the increased K_d of desorption corresponds to a lowered chemical activity and bioavailability of the adsorbed chemical at a fixed sorption equilibrium condition [10].

Polycyclic aromatic hydrocarbons (PAHs) are an important class of widespread persistent organic pollutants (POPs) due to incomplete combustion of fossil fuel and some natural processes. PAHs have received increased attention in recent years in soil pollution and remediation studies because some of these compounds are highly carcinogenic or mutagenic. Traditionally, biological processes have been considered to be the most economical and simple option to treat these pollutants. However, this technique is not always feasible due to their high chemical stability and low bioavailability caused by irreversible sorption in soils [11].

In situ chemical oxidation (ISCO) has shown to be a promising alternative to remediate soils and groundwaters contaminated by HOCs. Fenton reaction, which uses H_2O_2 as oxidant and ferrous ions as catalyst to generate hydroxyl radical ($\bullet OH$), is a promising technology due to its high efficiency and low cost [12].

SOM has been found to consume and compete for the oxidant during Fenton oxidation reaction, and as a result, the content and structure of the SOM might vary after Fenton oxidation [13]. The variation in the content and structure of the SOM can strongly influence its sorption and desorption for HOCs. Although it has been well documented that SOM predominantly controls the sorption and desorption of PAHs and other HOCs in soils and sediments [14,15], the role of its composition in determining the sorption and desorption of HOCs requires further corroboration. Besides, there are very limited studies regarding the change of SOM and the following effects on sorption and desorption characteristic to HOCs after ISCO, such as Fenton oxidation.

The objectives of this study were to measure the change of the content and composition of SOM due to Fenton oxidation, and to study the sorption and desorption of pyrene using three different types of soil samples before and after treatment by Fenton oxidation.

2. Materials and methods

2.1. Soil samples

Clean soils were sampled from the surface horizon of Shangqiu County, Henan Province; Garden of Nankai University and Xiqing County, Tianjin of China, which are named Soils 1–3, respectively. Their characteristics are shown in Table 1. Background levels of pyrene and other 16 prior PAHs (recommended by US EPA) have been checked using Soxhlet extraction, and none was found.

The soil samples were air-dried, passed through a 2-mm sieve and stored in closed containers in dry place under the dark at room temperature in order to prevent photo-oxidation of SOM that may change the major soil characteristics prior to use. The content of SOM was determined by potassium dichromate–outside heating method [3] after removing the visible plant residues, where the content of SOM is calculated based on the loss of potassium dichromate after superfluous potassium dichromate with soil sample is heated in a 170–180 °C oil bath for 10 min. Fulvic acid (FA) is SOM fraction that soluble in acids and bases, whereas humic acid (HA) is SOM fraction that soluble in bases, but not in acids. To obtain HA and FA extracts, the soil were heated in solution containing 0.1 M $Na_4P_2O_7$ and 0.1 M NaOH for 1 h in a 100 °C water bath. After separation of solid and aqueous phase by centrifugation, the supernatant was acidified to pH of 1.5 with 6 M HCl to obtain HA precipitation. Fraction that remains soluble in the acidic solution is FA, and humin is the insoluble material that remains after HA and FA extractions. The content of HA and FA then can be measured using the sequential extracts by the same method as that of SOM after vaporizing the water, and the content of humin can be achieved by subtraction of the content of HA and FA from the content of the total SOM. pH was measured in a 1:1 (w/w) soil– $CaCl_2$ water suspension. Grain-size distribution was determined by densimeter method. The infra-red (IR) spectra of HA of Soil 3 before and after oxidation were observed using a Shimadzu Perkin 2 Elmer 1725 X type spectrometer in KBr pellets.

2.2. Chemicals

Pyrene of 98% purity was purchased from Aldrich Chemical Company, Inc. Pyrene stock solution (1 g/L) was prepared

Table 1
Selected properties of the tested soils

	No.		
	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
Texture type	Loamy sand	Sandy loam	Loamy sand

in HPLC-grade methanol. Test solution was aqueous solution containing 0.01 mol/L CaCl_2 and 200 mg/L NaN_3 in order to poise certain ionic strength and to prevent microbial activity, respectively. H_2O_2 and ferrous sulfate were of analytical grade. Acetonitrile used for the mobile phase of HPLC analysis was of HPLC grade.

2.3. Treatment of the soils by Fenton oxidation

Soil samples were treated in a 1:1 slurry of oxidation solution containing 0.2 mol/L Fe^{2+} and specific amount of H_2O_2 . The optimum amount of H_2O_2 was determined by a preliminary experiment. pH of the reaction system was not adjusted, and the pH of soils after oxidation decreased insignificantly (less than 0.5 pH unit). After 12 h of oxidation, the soils were washed with deionized water five times to remove any residual H_2O_2 and Fe^{2+} . Then the soils were dried at 105 °C, passed through a 2-mm sieve and stored in closed containers at room temperature prior to use. No residual H_2O_2 in the treated soils was detected. The quantity of SOM was measured using the same method above after oxidation.

2.4. Sorption

Batch sorption experiments were conducted in 10 mL round-bottom glass tubes. One gram of the soil samples (before and after oxidation) was mixed with 10 mL of test solution, then specific amount of pyrene stock solution was added to start the sorption. Initial concentration of pyrene in the test solution for sorption experiments ranged from 3 and 1.8 mg/L for Soil 1, 4.6 and 2.2 mg/L for Soil 2, 16 and 12 mg/L for Soil 3 before and after oxidation, respectively. Each isotherm was measured using five concentrations. The carrier solvent (methanol < 1%) was assumed to have no effect on the interactions between sorbate and sorbent [16]. The tubes were capped with Teflon septum and shaken under 165 rpm in an air bath at 25 ± 1 °C for 48 h. Kinetic studies showed that sorption equilibrium could be achieved in 40 h or less. After equilibrium, the tubes were centrifuged (HERLE Z323 Centrifuge, MA, Germany) at 3500 rpm for 20 min. After centrifugation, the supernatants were analyzed directly by HPLC. The experiments were conducted in duplicate. Blank samples indicated that pyrene loss due to the sorption to reactor walls and volatilization was less than 8%.

2.5. Desorption experiments

Desorption experiments were initiated immediately after sorption studies for all the soil samples using initial concentration of 2.4 and 1.0 mg/kg for Soil 1, 2.9 and 1.7 mg/kg for Soil 2, 12.4 and 12.2 mg/kg for Soil 3 before and after oxidation, respectively. Successive desorptions were conducted by sequential refreshment (5–7 times) of the test solution [17]. Each desorption was conducted for 48 h, then the tubes were centrifuged at 3500 rpm for 20 min and the supernatant was aspirated out and analyzed by HPLC. Desorption experiments were conducted in duplicate.

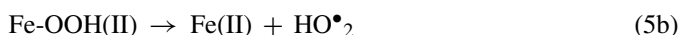
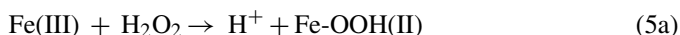
2.6. HPLC analysis

The HPLC system was SCL-10AVP (Shimadzu, Japan) system equipped with a programmable fluorescence detector. A reverse-phase column (VP-ODS Kromasil C₁₈, 150 mm × 4.6 mm × 5 μm) was employed under the ambient temperature. Mobile phase containing 85% acetonitrile and 15% water (Milli-Q) flew at 1.0 mL/min and the injection volume was 20 μL. The fluorescence detection was achieved at an excitation wavelength of 260 nm and an emission wavelength of 373 nm. The amount of pyrene was determined with external pyrene standards. The amount of sorbed pyrene was calculated by quantifying the loss of pyrene in solutions.

3. Results and discussion

3.1. Effects of H_2O_2 dose on the degradation of SOM

H_2O_2 plays as oxidizing agent in Fenton reagent. Fenton oxidation is shown by Eqs. (4)–(5b) [18], and SOM can be degraded by $\bullet\text{OH}$:



In order to choose an optimum H_2O_2 dose, the soil samples were treated with different dose of H_2O_2 . It was found that the reduction of SOM in Soil 1 increased with the dose of H_2O_2 (Fig. 1). The removal percentage of the SOM reached approximately 22.4% when H_2O_2 was 2.5 mol/L. However, when H_2O_2 was continually elevated to 3 mol/L, the removal of SOM did not increase much significantly. The results of the other two soils are similar with that of Soil 1 (data not listed). Gates and Siegrist [13] also reported a partial oxidation of SOM during Fenton oxidation. We think that SOM becomes more and more difficult to be oxidized with the proceeding of oxidation due to its high heterogeneity. Humic, which is composed of lignin, polysaccharides, mineralbound lipids, kerogen and black carbon, etc., is expected to be more difficult to be oxidized than those with small molecules, such as HA and FA. Therefore, elevating the

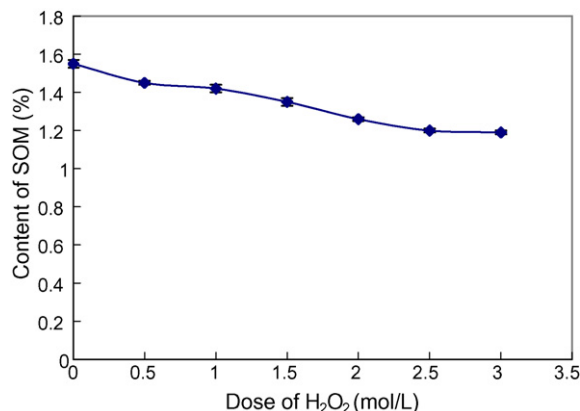


Fig. 1. Effect of H_2O_2 dose on SOM degradation in Soil 1.

Table 2
Content (%) of total SOM and different fractions before (BO) and after (AO) oxidation

Soil	HA	FA	Humin	SOM
1 BO	0.75	0.24	0.56	1.55
1 AO	0.10	0.54	0.54	1.18
2 BO	0.80	0.22	0.84	1.86
2 AO	0.12	0.63	0.74	1.49
3 BO	1.24	1.22	2.74	5.20
3 AO	0.27	1.05	2.78	4.10

amount of H_2O_2 to 3 mol/L, the removal efficiency of SOM did not increase significantly, and H_2O_2 dose of 2.5 mol/L was chosen for the following experiments in this study.

3.2. Change of SOM content and composition after oxidation

As has been pointed out above, humic substances are highly heterogeneous mixtures of macromolecules with molecular weights ranging from a few hundred to several hundred thousand Daltons [19]. Depending upon their extractability in dilute base and acid solutions, three humic fractions: FA, HA and humin, were further defined operationally. Due to their different structure, sorption ability of the different SOM fractions for HOCs is quite different [20]. Hence, the change of the three fractions as well as the total content of the SOM after oxidation was determined (Table 2).

Content of the total SOM decreased significantly after oxidation, with SOM content changing from 1.55 to 1.18%, 1.82 to 1.49% and 5.20 to 4.10% for Soils 1–3, respectively. Among the three fractions of the SOM, HA was reduced most significantly, while the content of humin did not change significantly. FA had a tendency to increase after oxidation except for Soil 3, whose FA content decreased to a little extent. HA is macromolecular acid that can be degraded by Fenton oxidation. The infra-red (IR) spectra of HA of Soil 3 before and after oxidation were compared (Fig. 2). It can be seen that the spectra of the HA changed greatly after oxidation. Bands at $3700\text{--}3200\text{ cm}^{-1}$,

which represents phenolic O–H stretching, dose not changed significantly, whereas bands at $1720\text{--}1700\text{ cm}^{-1}$, which represents carboxylic C=O stretching, and bands at $1250\text{--}1200$ and at $1100\text{--}1000\text{ cm}^{-1}$, which correspond to the antisymmetric and symmetric stretching of C–O ether bonds, appear decreased after oxidation. These results indicate that HA structure did change by Fenton oxidation, and similar results have been reported by Schnitzer and Khan [21]. Humin is a complex matter containing lignin, polysaccharides, mineralbound lipids, kerogen and black carbon etc. These kinds of matters are highly stable and difficult to change, and hence the variation of humin is insignificant under the condition of this study. The molecule of FA is smaller than that of HA, and treatment with Fenton oxidation can change it partly to CO_2 . The elevation of FA is thought to be due to the incomplete degradation of HA. Hence, not only the content but also the composition of the SOM changed after Fenton oxidation.

3.3. Sorption isotherms

Pyrene sorption isotherms in the three soils before and after oxidation are shown in Fig. 3, and the data were checked by three isotherm models (linear, Freundlich, Langmuir), and our data fitted in with Freundlich pattern (Eq. (6)) best, as indicated by the high regression coefficients (Table 3):

$$\log C_S = \log K_F + n \log C_W \quad (6)$$

where C_S is the sorbed concentration (mg/kg), C_W the equilibrium concentration of the sorbate (mg/L) in aqueous phase, K_F the Freundlich coefficient and n is a constant representing non-linearity. The K_F values (Table 3) show that pyrene was adsorbed most strongly in Soil 3, followed by Soils 2 and 1 in a decreasing order, being in the same order with that of the SOM content. Similar results of the effect of organic matter on the sorption of naphthalene have been reported [17].

Soil–water distribution coefficients (K_d) were calculated at the equilibrium concentration of $60\text{ }\mu\text{g/L}$ (Table 3), as an example. K_d in the three soils decreased after the oxidation due to the reduction of SOM content. Correlation analysis between K_d value and different fractions of the SOM reveals that humin and HA jointly controlled the sorption of pyrene, and among which, humin is the key factor (Table 4).

Moreover, K_{OC} of the three soils varied to different extents (Table 3) after oxidation due to the variation of SOM composition after oxidation. The decrease of K_{OC} was great in Soils 1 and 2, whereas the change of K_{OC} by oxidation in Soil 3 was not so significant. It has been reported that for HOCs sorption, humin bears stronger ability than HA, which is stronger than FA [21]. Similarly, Kang and Xing [5] reported that the K_{OC} value of phenanthrene sorption was larger in humin than that in HA. Hence, we can explain why K_{OC} in Soils 1 and 2 reduced significantly after oxidation by that relatively large amount of HA was changed to FA in Soils 1 and 2 (Table 2), whose sorption ability is low. Percentages of the sum of humin and HA decreased from 84.5 to 54.2%, and 88.2 to 57.7% for Soils 1 and 2 after oxidation, respectively. Therefore it is easy to accept that the sorption ability of unit mass of the SOM for these two soils decreased

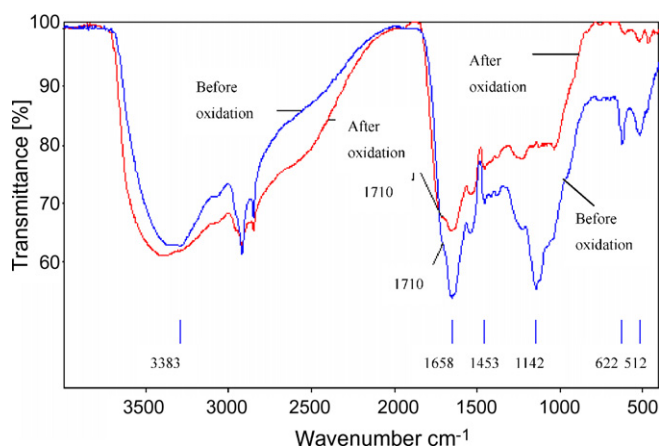


Fig. 2. IR spectra of HA of Soil 3 before and after oxidation.

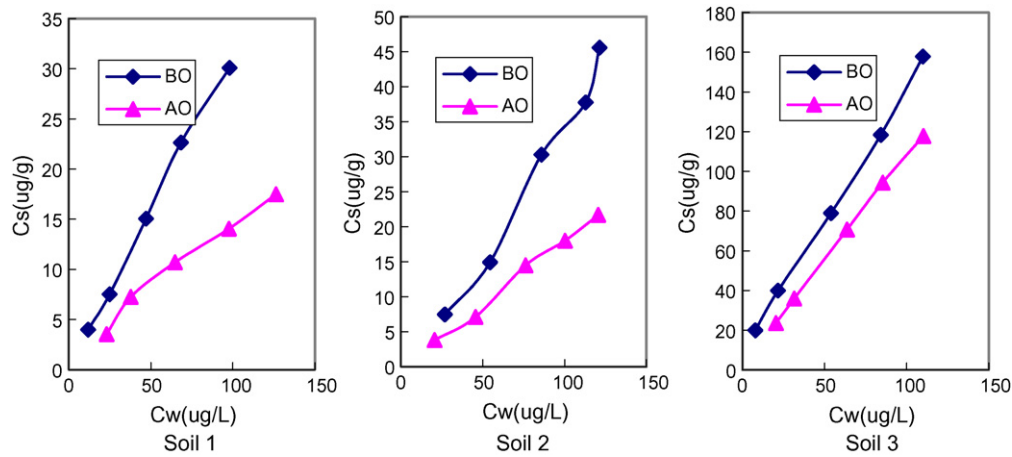


Fig. 3. Pyrene sorption isotherm curves in the three soils before oxidation (BO) and after oxidation (AO).

Table 3
Sorption Freundlich isotherms, K_d and K_{OC} of pyrene in different soils before (BO) and after oxidation (AO)

Soil	Freundlich regression equation	R^2	K_d ($60 \mu\text{g/L}$) ^a	K_{OC} ($60 \mu\text{g/L}$) ^a
1 BO	$\log C_S = 0.98 \log C_W + 2.47$	0.997	3.16×10^2	3.51×10^4
1 AO	$\log C_S = 0.89 \log C_W + 2.07$	0.972	1.57×10^2	2.12×10^4
2 BO	$\log C_S = 1.07 \log C_W + 2.62$	0.972	3.40×10^2	3.24×10^4
2 AO	$\log C_S = 1.01 \log C_W + 2.26$	0.989	1.77×10^2	2.06×10^4
3 BO	$\log C_S = 0.77 \log C_W + 2.90$	0.995	1.53×10^3	5.06×10^4
3 AO	$\log C_S = 0.95 \log C_W + 2.99$	0.999	1.11×10^3	4.67×10^4

C_S : mg/kg; C_W : mg/L; K_F : L/kg.

^a K_d and K_{OC} were obtained at equilibrium concentration of $60 \mu\text{g/L}$.

after oxidation. Whereas, in Soil 3, the content of both HA and FA decreased, while the content of humin did not change. As a result, percentage of humin and HA decreased only to a little extent (76.5–74.4%), which led to a not significant reduction of K_{OC} in Soil 3.

3.4. Desorption hysteresis

Desorption data were achieved by successive refreshment experiment, and are compared with the corresponding sorption isotherms in Fig. 4 in order to disclose the irreversibility of sorption. Desorption isotherms fitted in with Freundlich pattern well (Table 5). It can be seen that desorption data of pyrene deviate from the corresponding isotherms to different extents, and desorption were hysteretic in all cases. Such differences may be caused by several factors, including changes in solution composition, loss of pyrene due to degradation, and irreversible binding to soils [22]. Under the condition of this paper, the change of solution and degradation of pyrene is not plausible, so the key factor is irreversible binding.

Hysteresis index (HI) at two equilibrium solution concentration (C_e^w), 30 and $60 \mu\text{g/L}$, were calculated to observe the

Table 4
Linear correlation analysis of K_d with different parts of SOM

SOM fractions	FA	HA	Humin	Humin + HA
Correlation coefficient (R^2)	0.6886	0.3346	0.9243	0.9785

deviation extent of desorption from sorption at different equilibrium concentration. q_e^s and q_e^d in Eq. (3) were acquired using the corresponding sorption (Table 3) and desorption isotherms (Table 5), and then HI were calculated for each samples (Table 5) according to Eq. (3). The HI values varied greatly among the different soils with HI being the greatest in Soil 3. It has been pointed out that HOCs sorbed in humin fractions in soils would be more difficult to release than that in FA and HA [23]. This is because that FA and HA are of relatively loose and amorphous structures that can be swollen by water molecules and become more flexible to allow the adsorbed molecules to diffuse rapidly in and out. In contrast, humin is of relatively condensed, rigid three-dimensional structures, which is difficult for the sorbed molecules to diffuse out again. Correlation analysis of the HI value with the percentage of different parts of SOM (Table 6) shows that the HI value is linearly correlated with the percentage

Table 5
Desorption Freundlich isotherms and HI values of pyrene by different soils

Soil	Desorption Freundlich isotherm	R^2	HI value	
			$30 \mu\text{g/L}$	$60 \mu\text{g/L}$
1 BO	$\log C_S = 0.73 \log C_W + 2.23$	0.967	0.37	0.15
1 AO	$\log C_S = 0.79 \log C_W + 2.01$	0.947	0.27	0.18
2 BO	$\log C_S = 0.71 \log C_W + 2.23$	0.945	0.48	0.14
2 AO	$\log C_S = 0.43 \log C_W + 1.69$	0.971	1.09	0.39
3 BO	$\log C_S = 0.051 \log C_W + 2.14$	0.978	1.17	0.32
3 AO	$\log C_S = 0.055 \log C_W + 2.14$	0.877	2.34	0.78

C_S : mg/kg; C_W : mg/L; K_F : L/kg.

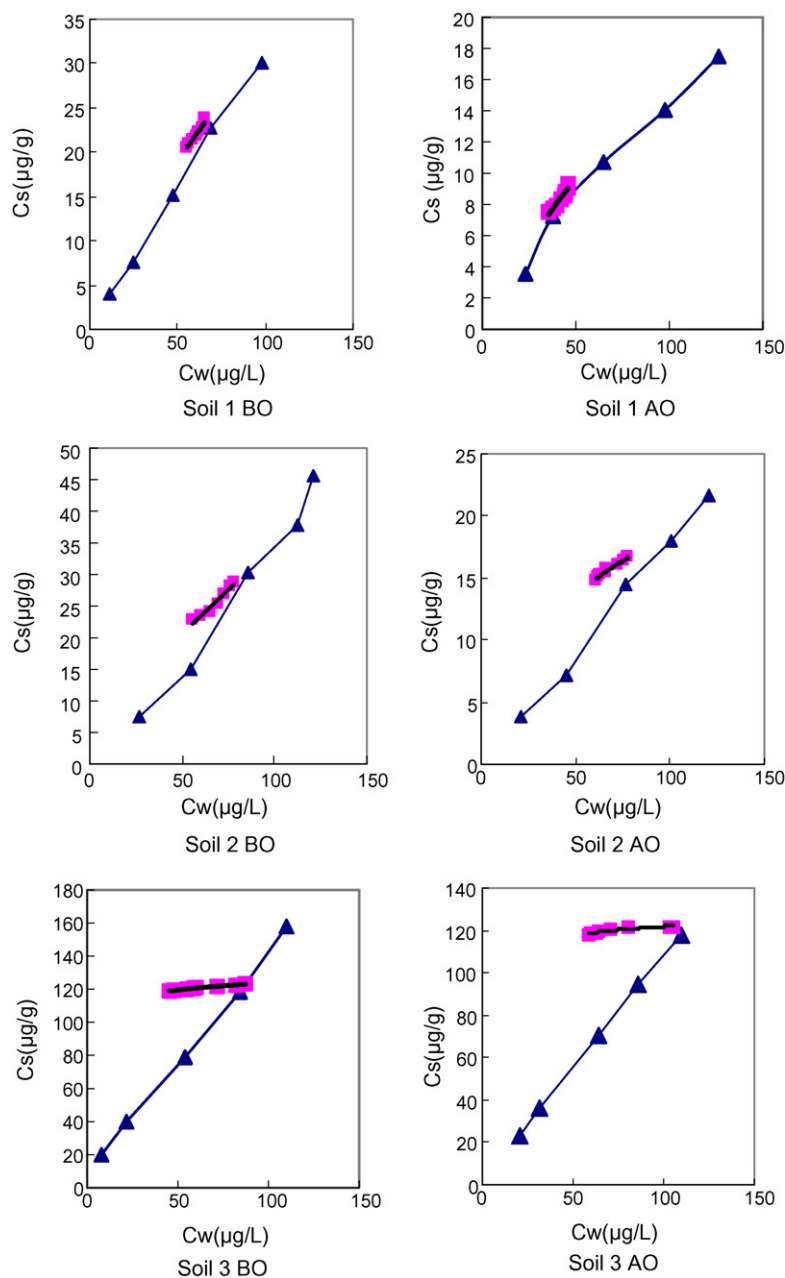


Fig. 4. Sorption (filled triangle symbols) and desorption (filled square symbols) isotherms of pyrene.

of humin, and correlation relationship dose not exist for other fractions of the SOM. Hence, humin is the key structural reason for the hysteresis of desorption, and the difference of HI value in Soils 1–3 can be attributed to the difference of the humin percentage in SOM. The highest humin percentage led to the highest HI in Soil 3.

Table 6
Linear correlation analysis of HI with different parts of SOM

Equilibrium solution concentration ($\mu\text{g/L}$)	Correlation coefficient (R^2)			
	FA	HA	Humin	Humin + HA
30	8×10^{-4}	0.2878	0.8817	1×10^{-4}
60	0.0214	0.4025	0.8714	0.0215

HI values were smaller at higher equilibrium concentration than those at the lower concentration for all the three soils (Table 5). For example, for Soil 3 after oxidation, HI is 2.34 and 0.78 at equilibrium concentration of 30 and 60 $\mu\text{g/L}$, respectively. This is in consistent with our expectancy, and is attributed to that there are only a limited high energy sites in SOM matrix that HOCs could be associated tightly and resist desorption. The proportion of pyrene molecules combined with these sites was higher at lower concentration. At higher concentration, the limited high-energy sites (resistant fraction) were saturated and the proportion of resistant fraction would be lower, thus, larger part behave to be easily desorbed, which led to a reduced HI.

After oxidation, the value of HI became higher. For example, at 60 $\mu\text{g/L}$ of equilibrium concentration, HI in Soil 3 increased

to over two times of that before oxidation. This is because that humin, which is the key structure for irreversible sorption, kept unchanged during oxidation. Humin percentage in the total SOM increased from 36.1 to 45.8%, 45.2 to 49.7, and 52.6 to 67.8% for Soils 1–3 after oxidation, respectively, which made them more accessible to pyrene.

4. Conclusion

Fenton oxidation cannot only decrease the content of total SOM but also change its composition. Totally, under the condition of this study, humin did not change significantly, and HA and FA were degraded greatly. However, due to the incomplete decomposition of HA, FA content increased in some cases. Soil–water distribution coefficient (K_d) did not linearly correlate with the content of total SOM, which could be reflected by the variety of K_{OC} . Correlation analysis discovers that humin together with HA are the key factors determining sorption ability. After oxidation, the decrease of K_{OC} is significant in Soils 1 and 2, whose percentage of humin and HA, decreased remarkably by oxidation. K_{OC} in Soil 3 did not change significantly due to an almost unchanged percentage of the sum of humin and HA.

Pyrene desorption was hysteretic in all cases. We found that humin with rigid structure is the main structural reason for desorption hysteresis. As has been expected, desorption hysteresis is much more significant at the lower concentration. This is because the proportion, of which pyrene can be associated with desorption-resistant sites, is higher at lower concentration. Oxidation led to an increase of HI in most cases, due to the elevation of the proportion of humin.

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