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# Novel iron bound to soil organic matter catalyzes $H_2O_2$ to oxidize long-chain alkanes effectively in soil

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## HIGHLIGHTS

- Putting forward a new and efficient catalytic method.
- The oxidation mechanism of the long-chain alkanes in the Fe-SOM Fenton system is proposed.
- Effective oxidation achieved in Fe-SOM system of long-chain alkanes in soil was not limited by short lifespan of ·OH.

## ARTICLE INFO

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## ABSTRACT

In order to explore the removal mechanism of long-chain alkanes in the Fenton system with iron bound to soil organic matter (Fe-SOM), this study carried out 16 groups of experiments to compare the oxidation efficiency of the long-chain alkanes in the Fenton system with Fe-SOM and with typical Fe (Fe unbound to SOM) (total petroleum hydrocarbon (TPH) concentration was 9068 mg/kg). The results showed that the long-chain alkanes removal ($C_{21}$-$C_{30}$) in the Fenton system with Fe-SOM was up to 361–380 mg/kg (73%–77%), which was 1.6 times higher than that achieved in the Fenton system with typical Fe. The highest removal efficiency of the long-chain alkanes was for $C_{27}$, i.e., up to 77%, which indicated that the long-chain alkanes in soil could be removed with a high efficiency in the Fenton system with Fe-SOM. Compared with Fenton system with typical Fe, Fenton system with Fe-SOM can achieve a higher removal efficiency of the long-chain alkanes and a lower residual concentration of long-chain alkanes in aqueous phase. In this system, the $H_2O_2$ decomposition is rapid, and the existence of the hydroxyl radicals (·OH) is short. The results indicated that the long-chain alkanes oxidation in Fe-SOM system is different from the indirect oxidation in a typical Fe system. This non-indirect oxidation with Fe-SOM was not limited by the short existence of the ·OH, and these were the reasons for highly efficient oxidation of the sorbed long–chain alkanes in soil.

## 1. Introduction

The Fe-catalyzing $H_2O_2$, also known as the Fenton oxidation process, has become one of the most common techniques used for *in situ* chemical oxidation (ISCO). It is also a promising technology to solve the increasingly serious problem of petroleum-contaminated soil [1–4]. The Fenton oxidation process can degrade large quantities of total petroleum hydrocarbon (TPH), benzol hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) [5–7]. The generation of hydroxyl radicals (·OH) is the key aspect of the Fenton oxidation process [8]. The ·OH has a high oxidation potential (2.80 V), and it can oxidize organic pollutants into non-toxic, easily degradable small molecules, carbon dioxide and inorganic salts without producing secondary pollution [5,6]. The oxidation reactions can rapidly and effectively remove crude oil [9]. Thus, the Fenton oxidation process is a high-cost but simple and easy to be operated oxidation process that is used for a number of environmental applications, including the pretreatment of industrial wastewater, treatment of water containing dilute concentrations of xenobiotics, and remediation of soils and groundwater [9–11]. The Fenton process has been increasingly used for a wide range of applications in recent years [12,13].

However, longer-chain or heavy alkanes are less prone to adsorb to soil organic matter (SOM) in natural weathering processes, including volatilization, biodegradation and dissolution [14,15]. In general, long-chain alkanes in a solid soil phase are oxidized before they desorb into the aqueous phase, which is a traditional, indirect oxidation process

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[16,17]. Because ·OH has a short lifetime in aqueous phases [18–20], it often disappears before the long-chain alkanes desorb from the solid phase, which greatly reduces the removal efficiency of long-chain alkanes by oxidation. Presently, there are two main methods used to solve the above problems, i.e., extending the lifespan of the free radicals in solution and increasing the removal efficiency of long-chain alkanes.

In the first method, $H_2O_2$ is stabilized by adding other chemicals, including $KH_2PO_4$ [21,22], chelating agents, citric acid [1], chitosan (Cs) [23], hydroquinone [24] and humic acid (HA), or by using an $Fe^{3+}$ [25] complex and $Fe^{3+}$ as catalysts at an acidic pH. This method can extend the lifespan of ·OH in the aqueous phase. For the second method, several studies [26,27] have indicated that the hydroperoxyl free radical ($HO_2\cdot$), superoxide radical ($O_2\cdot^-$), and non-radical hydroperoxide ion ($HO_2^-$) which are produced by adding high concentrations of hydrogen peroxide, as well as surfactants and solid iron instead of dissolved iron, can accelerate the desorption of TPH and improve the oxidation of crude oil. These methods have improved the oxidation of chlorophenols, olefins, PAHs and benzene, toluene, and xylene (BTX) [28], but they have limited the oxidation of long-chain alkanes in petroleum-contaminated soil. These long-chain alkanes do not enter the aqueous phase before ·OH disappears due to their strong hydrophobicity and slow desorption.

To overcome the above problems, our previous research [29] discovered that the Fenton system with iron bound to soil organic matter (Fe-SOM) produced a large number of ·OH in the solid soil phase, which significantly enhanced the oxidation efficiency of crude oil. However, whether the ·OH generated in this process can enhance the oxidation of long-chain alkanes and the removal mechanism of long-chain alkanes remain unclear. In generally, oxidation of long-chain alkanes occurred with a given number of ·OH. In this process, indirect oxidation of long-chain alkanes requires that the alkanes were first desorbed into the aqueous phase and then oxidized [30]. Therefore, the indirect oxidation of long-chain alkanes requires long lifespan of ·OH, and it cannot occur when the lifespan of ·OH is short. Non-indirect oxidation has also been observed [30], but has not been well studied. Fe-SOM is a promising catalyst for the Fenton reaction. Whether the indirect or non-indirect oxidation of long-chain alkanes occurs in Fe-SOM system is unclear, and no previous studies have focused on this topic. The primary aim of this study is to explore the removal mechanism of long-chain alkanes in the Fe-SOM system. Therefore, 16 groups of experiments were carried out to compare the oxidation efficiency in the Fenton system with Fe-SOM and the Fenton system with typical Fe (Fe unbound to SOM) in soil, and analyze the decomposition characteristics of $H_2O_2$, the lifespan of ·OH, and the oxidation and desorption of long-chain alkanes in the two Fenton systems.

## 2. Materials and methods

### 2.1. Reagents

Liquid hydrogen peroxide (30% by weight) was purchased from Paini Reagent Company (Zhengzhou, China). Citric acid ($C_6H_8O_7$, analytical grade) was purchased from the National Medicine Group Chemical Reagent Factory (Beijing, China). Ferrous sulfate ($FeSO_4{\cdot}7H_2O$, analytical grade) was purchased from the Guang Hua Chemical Reagent Factory (Guangdong, China). Methylene dichloride ($CH_2Cl_2$, HPLC grade), sodium hydroxide (NaOH, analytical grade) and hydrochloric acid (HCl, analytical grade) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). Chitosan (Cs, analytical grade) was purchased from Lanji Biotechnology Co., Ltd. (Shanghai, China). Humic acid (HA), 5,5-dimethyl-1-pyrroline N-oxide (DMPO, 98% purity) and saturated alkanes standard ($C_7$-$C_{30}$, 99% purity) were purchased from Sigma Aldrich in the USA.

### 2.2. Characteristics of the soil materials and crude oil samples

The soil used to prepare Fe-SOM was collected from Xi'an, Shaanxi Province, China (S1) [29]. This background soil S1 contains C—O bond. The soil used to prepare the typical Fe was collected from Yan'an, Shaanxi Province, China (S2) [29]. This background soil S2 did not contain C—O bond. The other characteristics of the soil materials (S1 and S2) are shown in Table 1. The soil materials were sieved through a 2 mm mesh to remove impurities, homogenized with a rotary shaker (12.5 rpm, 48 h), and then preserved airtight in a freezer at −4°C.

Crude oil was collected from an oil well in Yan'an, China, and stored at room temperature (22 ± 2 °C). The most common aliphatic components were n-alkanes with carbon numbers between 11 and 30, shorter-chain molecules ($C_{11}$-$C_{15}$) comprising 21.3%, short-chain molecules ($C_{16}$-$C_{20}$) comprising 22.9%, long-chain molecules ($C_{21}$-$C_{25}$) comprising 24.2% and longer-chain molecules ($C_{26}$-$C_{30}$) comprising 31.6% of the oil. Thus, the crude oil was primarily composed of long-chain molecules.

### 2.3. Experimental methods

#### 2.3.1. Iron transformation

To investigate the oxidation characteristics and mechanisms of long-chain alkanes in the Fe-SOM system using oil-contaminated soils, seven concentrations of Fe-SOM and typical Fe were prepared for the next oxidation experiments.

*2.3.1.1. Preparation of Fe-SOM.* The Fe-SOM preparation followed the modified method from our previous study [23]. To improve the Fe-SOM content, seven different ratios of HA: Cs (0:0, 0:2, 2:0, 2:1, 2:3, 1:2 and 3:2 (w/w)) were added to sieved background soil S1.

Exactly 20 g of sieved background soil S1 with C—O was weighed to a 500 mL flask. Then, 40 mL of 5.8 mol/L citric acid-$FeSO_4$ and 21.6 mL of 30% $H_2O_2$ (900 mmol/L) [31] were added, and the final volume of the reaction solution was 240 mL via the addition of demineralized water. The pH was adjusted to 7.2 with 5 mol/L NaOH [26]. Dissolved iron was easily transformed into SOM with the application of $H_2O_2$. Subsequently, Fe-SOM was formed when the transformed iron was bound to SOM in the solid phase. The process of $Fe^{2+}$ transfer to the solid phase was completed when the $Fe^{2+}$ concentration was unchanged in the solution. After the reaction, the supernatant was centrifuged and discarded. Next, ultra-pure water (18.2 MΩ/cm, ELGA, UK) was used to wash the sample several times to completely remove the $Fe^{2+}$. The soil samples were then freeze-dried (FD-1D-50; Beijing Boyikang). After drying, the content and components of Fe-SOM were determined. The Fe-SOM was ready for the oxidation experiments.

*2.3.1.2. Preparation of typical Fe.* The typical Fe was prepared similar to Fe-SOM, except soil S2 was used, which does not contain C—O bond. That means, there is no bound between the SOM and Fe. Seven ratios of HA: Cs were used, identical to those used in the Fe-SOM preparation. In addition, 20 g of soil material S2 was used in 500 mL flasks. The same amounts as used before, 40 mL of 5.8 mol/L citric acid-$FeSO_4$ and 21.6 mL of 30% $H_2O_2$ (900 mmol/L) [31], were added, and the final volume of the reaction solution was 240 mL by the addition of demineralized water. The pH was adjusted to 7.2 with 5 mol/L NaOH [26]. After the reaction, the supernatant was centrifuged and discarded. Next, ultra-pure water (18.2 MΩ/cm, ELGA, UK) was used to wash the sample several times to completely remove the $Fe^{2+}$. The soil samples were then freeze-dried (FD-1D-50; Beijing Boyikang). After drying, the content and components of the typical Fe were determined. The typical Fe was ready for the oxidation experiments.

#### 2.3.2. Oxidation of long-chain alkanes in soil samples using Fe-SOM to catalyze $H_2O_2$

To investigate the effects of the Fe-SOM-catalyzing $H_2O_2$ on the