



Enhanced Fenton degradation of polychlorinated biphenyls in capacitor-oil-contaminated soil by chelating agents



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ABSTRACT

Effects of chelating agent (CA) on the removal of polychlorinated biphenyls (PCBs) from capacitor-oil-contaminated soil slurry were investigated through homogeneous Fenton treatment at natural soil pH. Among the five CAs used, promoting PCB removal by sodium pyrophosphate (SP) was the strongest, followed by the promoting effect of ethylenediamine-*N,N'*-bis(*o*-hydroxyphenyl) acetic acid (EDDHA). When the Fe²⁺ concentration was 50 mM, the optimal Fe²⁺/SP/H₂O₂ and Fe²⁺/EDDHA/H₂O₂ molar ratios were 1/1/20 and 1/0.5/20, respectively; the corresponding efficiencies of 48 h PCB degradation at 63.9 mg kg⁻¹ initial PCB concentration in soil slurry were 87.5% and 77.1%, respectively. The efficiency of H₂O₂ oxidation was significantly higher than that of Na₂S₂O₈ oxidation, regardless of activation by either Fe²⁺-SP complex or Fe²⁺-EDDHA complex. The final pH of the Fe²⁺/EDDHA/H₂O₂ system was markedly lower (2.7) than the initial soil pH (7.6), and that of the Fe²⁺/SP/H₂O₂ system was slightly lower (about 6.6) after 48 h of reaction. Electron paramagnetic resonance detection directly showed that [•]OH is the primary species involved in PCB degradation whether CA was added to the Fenton reaction system or not. The probe test revealed that PCB degradation in the Fe²⁺/SP/H₂O₂ system is mainly attributed to [•]OH and that it is ascribed to the combined actions of [•]OH and O₂^{•-} in the Fe²⁺/EDDHA/H₂O₂ system. Results of this study indicate that CA-enhanced Fenton oxidation is an effective and practical means of remediation of soil heavily contaminated with PCBs.

1. Introduction

Polychlorinated biphenyls (PCBs) are among the first 12 persistent organic pollutants listed by the Stockholm Convention. The improper disposal of discarded capacitors has resulted in serious leakage of oil containing PCBs into soils [1]. Outdated techniques for dismantling e-waste have also led to severe PCB contamination of soils in China [2]. The most polluted areas that process capacitors and e-waste in China are Guiyu in Guangdong Province and Taizhou in Zhejiang Province [3]. Furthermore, PCBs can be released from the atmosphere via dry and wet deposition and from the aquatic environment via adsorption and precipitation because of their poor volatility and hydrophobic nature. Consequently, the soil is the main pool of PCBs once they enter the environment; thus, the remediation of PCB-contaminated soils has become an urgent problem in China. The remediation technologies for PCB removal mainly include excavation and incineration [4], thermal desorption [5], microwave irradiation [6], photocatalysis [7], chemical oxidation and reduction [8], and biological treatment [9]. However, many of them have drawbacks for PCB-contaminated soil remediation.

For instance, excavation and incineration not only involve enormous cost but also yield highly toxic byproducts; the application of photocatalysis in soil remediation is restricted due to useless light irradiation under the subsurface; the high toxicity of PCBs inhibits their biodegradation efficiency. Therefore, more cost effective, in-situ applicable and sustainable alternatives become a demand for safe PCB-contaminated soil remediation.

In situ catalyzed H₂O₂ propagations (CHP), a kind of in situ chemical oxidation (ISCO), have become an effective and practical remediation technology for the removal of persistent organic pollutants [10]. Venny et al. [11] highlighted several advantages of CHP for soil remediation, including non-selected degradation ability, easy manipulation of reagents, shorter treatment time and higher oxidation ability of [•]OH with an oxidation potential (E⁰ = 2.8 V) that is higher than that of SO₄^{•-} (E⁰ = 2.6 V), ozone (E⁰ = 2.1 V) and permanganate (E⁰ = 1.68 V), and heat released from reactions for enhancing mass transfer, reaction rate and microbial activity. However, one fatal drawback of the requirement for low pH (~3.0) limits the application of the traditional Fenton (TF) process for soil remediation [12,13].

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Another drawback of TF is that H_2O_2 can be excessively rapid decomposed in the subsurface upon contact of H_2O_2 with the activators [11]. Although the application of Fe^{3+} in place of Fe^{2+} slows down the useless decomposition of H_2O_2 in soil [14], high acidity (about pH 3.0) is still necessary to prevent the precipitation of Fe^{3+} [15]. In order to avoid soil acidification, the heterogeneous Fenton reaction catalyzed by iron oxides has been carried out, which has considerable efficiency in degrading PCBs [16–18] at neutral pH. But the reaction rate in the heterogeneous Fenton system is markedly lower than that of the homogeneous Fenton system under the same acidic conditions. Furthermore, the homogeneous Fenton system is more easily manipulated during the in situ soil remediation than the heterogeneous Fenton system. Chelating agents (CAs) have been proven to maintain iron in soluble form or stabilize H_2O_2 in a homogeneous Fenton reaction at near-neutral pH. By preventing iron precipitation or by slowing down the useless decomposition of H_2O_2 , CAs can improve the oxidation efficiency and the optimal reaction pH of the TF reaction [19]. Ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) were initially used as stable iron-chelating agents in the modified Fenton (MF) processes [20,21]. However, non-biodegradable property of EDTA and NTA in soil restricts their application. In general, soil contains many natural CAs, such as humic acid and fulvic acid that are fraction of soil organic matter (SOM). Sherwood et al. [22] observed that the MF treatment using 10–15% SOM of polluted arctic soils as the only CA achieved much higher rate of diesel fuel removal than that with addition of EDTA in the polluted arctic soil slurry as CA. Low-molecular-weight organic acids have also been used as CAs, such as oxalate, succinate and citrate [23]. Citrate could remarkably promote PAH degradation in marine sediments via stabilizing Fe^{2+} in the TF process [24]. However, the concentration of natural CAs in soil is usually difficult to reach the optimal ratio of iron ions and CA. Therefore, it's necessary to find more biodegradable, environmentally friendly and highly reactive CAs to develop the application of CHP in soil remediation.

Ethylenediamine-*N,N'*-disuccinic acid (EDDS), a structural isomer of EDTA, has been used to replace EDTA because of its biodegradability and low impact on the environment. Sodium *N,N'*-bis(carboxymethyl) glutamic acid (GLDA) has an equivalent iron-chelating capability to EDTA and NTA. It is also a biodegradable CA with greater than 60% degradation rate within 28 days [25]. Ethylenediamine-*N,N'*-bis(*o*-hydroxyphenyl) acetic acid (EDDHA), one of the most efficient iron-chelating agents [26], has two phenolic groups substituting the carboxylates of EDTA, which increase the stability of the iron chelate by $> 10^{10}$ [27]. In general, EDDHA is used as an Fe fertilizer because it is biodegradable in soil [28]. An inorganic CA such as sodium pyrophosphate (SP) is more efficient than an organic CA at enhancing the oxidation efficiency of the TF reaction because inorganic CA can't react with $\cdot OH$ [29].

Although many studies of PCB degradation have been conducted in the liquid phase or in spiked contaminated soils, little information can be obtained about using Fe-complex MF treatment for actual PCB-contaminated soil. Therefore, in the present study, we used five biodegradable compounds to investigate the feasibility of iron complex MF treatment to degrade PCBs in capacitor-oil-contaminated soil slurry and to evaluate the effects of CA type and dosage on the degradation efficiency of PCBs and soil properties under different reaction conditions. These compounds comprise an inorganic CA (SP) and four organic CAs (EDDS, sodium citrate (SC), GLDA, and EDDHA). The composition and contribution of reactive species on the degradation of PCBs in the Fe-complex MF treatment were also determined in this study.

2. Materials and methods

2.1. Chemicals and materials

High-performance-liquid-chromatography-grade *n*-hexane, acetone,

Table 1
Physical and chemical characteristics of the soils used.

Parameters	Clean soil	PCBs polluted soil	Mixed soil
Location	A farmland	A landfill, Taizhou	
OM content (g/kg)	15.1	11.0	14.7
pH	7.5	6.3	7.6
CEC (cmol/kg)	20.6	20.8	21.6
ΣPCB (mg/kg)	ND ^a	739.0	63.9
Total metal concentration (mg/kg)			
Fe	3720.0	9583.3	4465.0
Cu	6.3	9.2	6.5
Mn	115.0	86.2	113.0
Ca	1005.0	162.5	818.3
Mg	1248.3	253.8	1175
Zn	16.2	15.5	16.2

^a Not detected.

methanol, and isopropanol (IPA) were obtained from Merck (Darmstadt, Germany). $FeCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, H_2O_2 (30%), $Na_2S_2O_8$, and Na_2SO_3 were obtained from National Medicines Corporation Ltd. (Beijing, China). EDDS (35% in H_2O), SC (98%), SP (99%), and 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) were purchased from Sigma-Aldrich (Shanghai, China). GLDA (45–49% in H_2O) was bought from Akzo Nobel Chemicals Corporation (Shanghai, China). EDDHA and hexachloroethane (C_2Cl_6) were purchased from J & K Scientific Ltd. (Shanghai, China). The properties of the five CAs are summarized in Table S1 (Supporting Information). The standard solution of PCBs was purchased from AccuStandard (New Haven, CT, USA). The standard solution contains 20 congeners. The systematic names and concentrations of the PCB congeners are listed in Table S2 (Supporting Information). Ultrapure water was obtained by using a Milli-Q Advantage A10 water purification system (Millipore, Bedford, MA, USA). All chemicals were used as received.

Soil that was heavily polluted with capacitor oil was collected from a transformer-filled landfill in Taizhou. PCB concentrations and soil properties are presented in Table 1. Because the total PCB concentration (739 mg kg^{-1}) in the capacitor oil contaminated soil was much higher than most actual concentrations of PCBs in e-waste or transformers recycling site in China [30–32], the raw contaminated soil was mixed with clean soil to adjust it to 63.9 mg kg^{-1} as the initial concentration of PCBs in treated soil by CA-enhanced Fenton oxidation.

2.2. Experimental procedure

Batch experiments were conducted under constant stirring at $150 \pm 5 \text{ rpm}$ and at $25 \pm 1 \text{ }^\circ\text{C}$ in 50 mL borosilicate centrifuge vials (Jiangsu, China) with Teflon-lined septa caps. PCB-contaminated soil (1.0 g) was added to 20 mL of reaction solution, which contained 10 mL Fe or Fe/CA solution and 10 mL of H_2O_2 or $Na_2S_2O_8$ solution. Fe/CA solutions were prepared by mixing appropriate volumes of freshly prepared aqueous solutions of Fe and CAs for 12 h. The Fe^{2+} /CA solutions were bubbled with N_2 gas for 10 min in order to prevent Fe^{2+} oxidation. A 10 mL activator (Fe^{2+} or Fe^{3+}) or activator/CA solution was added to attain the desired concentration, and the reaction was immediately started upon addition of 10 mL of oxidant (H_2O_2 or $Na_2S_2O_8$). Experiments were performed without adjustment pH (soil: $pH_{t=0} = 7.6 \pm 0.5$), and the pH was determined during the reaction. At a designated time, 2 M Na_2SO_3 solution was added to quench the reaction [33]. A portion of each sample was centrifuged at 3500 rpm for 15 min, the supernatant was carefully removed, and then the residual soil ($< 0.3 \text{ mL}$ water) was extracted with 10 mL of *n*-hexane/acetone (1:1 v/v) solution for 1 h at 25 C. A standard was added to the solid sample before the soil extraction to evaluate the effect of the extraction process and the average recovery of the soil extraction procedure was $92.9 \pm 9.4\%$. The soil slurry was then centrifuged at 3500 rpm for

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