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Ferrous–tetrapolyphosphate complex induced dioxygen activation for toxic organic pollutants degradation

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ABSTRACT

In this study, we demonstrate that ferrous–tetrapolyphosphate complex could activate dioxygen to produce reactive oxygen species for highly efficient aerobic degradation of toxic organic pollutants at room temperature and pressure. Cyclic voltammogram study revealed the chelation of ferrous ions with tetrapolyphosphate could significantly reduce the redox potential of Fe^{3+}/Fe^{2+} to efficiently activate molecular oxygen in air. The dioxygen activation ability of ferrous–tetrapolyphosphate complex was found to be related to its concentration and pH value in the solution. The mechanism of dioxygen activation induced by ferrous–tetrapolyphosphate complex and the degradation pathway of sodium pentachlorophenol were studied in detail. We also found that a kind of dissimilatory iron-reducing bacterium could reduce ferric-tetrapolyphosphate to ferrous–tetrapolyphosphate under anaerobic conditions and therefore regenerate the deactivated ferrous–tetrapolyphosphate/air system. This study provides a novel green oxidation method for environmental pollutant control and remediation.

1. Introduction

The development of green oxidation technology is vital to eliminate toxic organic pollutants without secondary pollution. The typical feature of green oxidation technology is the utilization of green oxidants and environmental friendly catalysts/additives. Dioxygen is the most green, abundant, and economic oxidant. However, at ambient conditions dioxygen molecule is at a ground triplet state according to Hund's rule and singlet–triplet transitions in dioxygen molecule is spin-forbidden, so dioxygen could not oxidize organics directly because of the singlet ground state of organics [1,2]. It is well known that some enzymes or artificial metal complexes could efficiently activate dioxygen to produce various reactive oxygen species for organics oxidation [3–7]. Unfortunately, these enzymes and artificial metal complexes are not desirable for the oxidation of environmental pollutants because of their poor stability and/or high cost. It is therefore of great significance to develop efficient but low cost methods to activate dioxygen to degrade toxic organic pollutants.

Iron is the fourth most common element in the Earth's crust, which involves in biological free radical oxidations through the reaction of Fe^{2+} with O_2 [8,9]. However, yields of reactive oxygen species generated in Fe^{2+}/O_2 system are too low to be applied for environmental pollutant control and remediation. It is known that the chelation of ferrous ions with suitable ligands could efficiently reduce the electrode potential of Fe^{3+}/Fe^{2+}, which benefits for dioxygen reduction to generate more reactive oxygen species [10]. Ethylenediaminetetraacetic acid (EDTA) is a well-known organic ligand to chelate ferrous ions to improve the oxidation efficiency of Fe^{2+}/O_2 system [11]. However, in view of environmental oxidation application, EDTA possesses two disadvantages as follow. One is that EDTA would consume reactive oxygen species produced in the system leading to low oxidation efficiency of target pollutants. The other is that simultaneous decomposition of EDTA would decrease the yield of reactive oxygen species [12]. Therefore, it is of great importance but a challenge to seek an inorganic ligand with low cost and nontoxicity for dioxygen activation and subsequent aerobic oxidation of toxic organic pollutants.

It was known that polyphosphate chelators could enhance the autooxidation of Fe^{2+} to generate more hydroxyl radicals during the investigation on the effect of hydroxyl radicals in biological system [13]. As a widely used food additives, tetrapolyphosphate is relatively safe and low-cost for environmental application. Herein we demonstrate that tetrapolyphosphate (TPP) could decrease the redox potential of Fe^{3+}/Fe^{2+} more effective than EDTA (Fig. 1) and the resulting ferrous–tetrapolyphosphate (Fe(II)–TPP) complex could rapidly oxidize organic pollutants for the first time. We systematically measure reactive oxygen species generated in this novel ferrous ions/tetrapolyphosphate/air (FTA) system and propose a possible dioxygen activation mechanism induced by Fe(II)–TPP complex.

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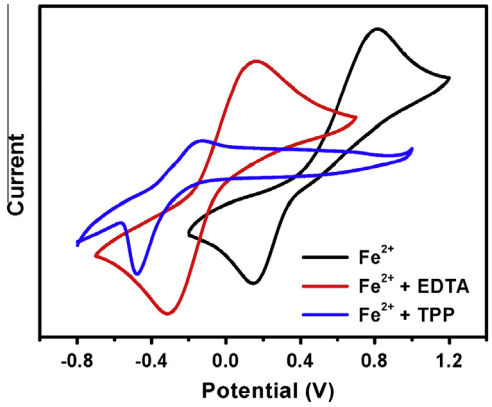

Fig. 1. CV curves of Fe^{2+} ions, Fe^{2+} ions and EDTA ligand, Fe^{2+} ions and TPP ligand. Three electrode system, electrolyte Na_2SO_4 0.5 mol/L, scan rate 5 mV/s. The concentrations of ferrous ion, EDTA, tetrapolyphosphate were 10, 50 and 50 mmol/L, respectively.

In homogeneous oxidation system like Fenton (Fe^{2+}/H_2O_2) and ferrous auto-oxidation (Fe^{2+}/O_2) reactions, the recycle of iron is crucial to avoid the exhaustion of Fe^{2+} [14,15]. It is known that iron-reducing bacteria could reduce Fe^{3+} to Fe^{2+} under anaerobic conditions [15,16]. We also demonstrate that *Shewanella putrefaciens* 200 (SP200), a kind of dissimilatory iron-reducing bacteria could regenerate the inactive FTA system to realize the iron recycle in this study.

2. Experimental section

2.1. Degradation experiment

All of experiments were carried out at room temperature and pressure. The stock tetrapolyphosphate solution was prepared by dissolving tetrapolyphosphate acid in deionized water and adjusting pH value to 6.9 ± 0.1 with NaOH and HCl solutions. Target pollutants (rhodamine B, eosin B or sodium pentachlorophenol) were mixed with the stock tetrapolyphosphate aqueous solution before adding any other reagents, the initial pH value was about 7.2. Commercially available ferrous ammonium sulfate (Tianjin Kermel Chemical Reagent Co., Ltd., China) was then added to initiate the degradation reaction with bubbling air of 1.5 L/min in flow speed. The typical concentration of ferrous ion and tetrapolyphosphate were 10 and 50 mmol/L, respectively. Sample aliquots were extracted at predetermined intervals for analysis. Initial concentrations of target pollutants (C_0) were the concentration of sample aliquots without the addition of ferrous salt. The concentrations of rhodamine B (RhB), and eosin B were measured immediately to prevent the further reaction after extracting samples. For sodium pentachlorophenol (NaPCP), ethanol was added to the extracted sample to quench the reaction for the subsequent high pressure liquid chromatography (HPLC) measurement. The initial concentrations of RhB, eosin B and NaPCP were 5, 5, and 10 mg/L, respectively.

2.2. TOC measurement

20 mg/L NaPCP was chose to study the mineralization of organic pollutants in the FTA system. The initial concentrations of ferrous and tetrapolyphosphate ions were 5 and 15 mmol/L, respectively. The solution was saturated with dissolved dioxgen of about 250 μmol/L in concentration. The degradation experiment was conducted in 50-mL conical flask sealed with butyl-rubber stoppers to prevent the fast exhaustion of ferrous ions by air. The reaction mixtures were quenched with HCl.

2.3. Analytical methods

The concentration of NaPCP was determined by HPLC (LC-20AT, Shimadzu), an Agilent TC-C18 reverse phase column was used. The injection volume is 10 μL, the eluent was 0.75% (w/w) acetic acid (20%) and methanol (80%), flow rate was 0.8 mL/min, and UV detector was set at 214 nm. RhB and eosin B concentrations were determined with a UV–Visible spectrophotometer (UV-2550, Shimadzu) at a wavelength of 553 nm and 476 nm, respectively. The total organic carbon (TOC) measurements were measured with a Shimadzu TOC-V analyzer.

The possible degradation intermediates were determined using gas chromatography–mass spectrometry (GC–MS) (Agilent 7890–5975). For pre-treatment, 20 mL of samples were acidified to pH < 2 with HCl solution and then extracted with 20 mL dichloromethane for 3 times. The combined extracts were dried with anhydrous sodium sulfate and the dichloromethane was removed under vacuum. The residue was re-dissolved in 1 mL acetone for detection. 1.0 μL of final sample was automatically injected into GC equipped with HP-5MS column with splitless mode. The oven temperature was held at 50 °C for 3 min, then elevated to 200 °C at 10 °C/min, from 200 to 270 °C at 20 °C/min, and finally held at 290 °C/min for 2 min.

A modified 1,10-phenanthroline method was used to determine the concentration of ferrous ions [17]. Samples were added to 1 mL of 1,10-phenanthroline (2 g/L) in a 1 cm quartz cell, water was added to make the final volume of 3 mL. The absorbance was measured at λ = 510 nm, which is the maximal adsorption of Fe(II)-1,10-phenanthroline complex. When the total iron concentration was measured, hydroxylamine hydrochloride was utilized as the reductant.

Coumarin-3-carboxylic acid (3-CCA) was used as the fluorescent probe for hydroxyl radicals' detection [18]. 7-hydroxy-coumarin-3-carboxylic acid (7-OHCCA), which is the fluorescent product of the reaction of 3-CCA with ·OH, has a strong fluorescent emission around 448 nm when excited at 400 nm. The concentration of 3-CCA used for the measurement of ·OH was 2 mmol/L. Fluorescence measurement in this study was conducted on a FluoroMax-P spectrophotometer.

The concentration of H_2O_2 was determined by a (p-hydroxyphenyl) acetic acid (POHPAA) fluorescence method [19]. 50 μL of fluorescence reagent was reacted with 2 mL of sample for 10 min, 1 mL of 0.1 mol/L NaOH solution was then added to maintain the reaction solution at pH 10.0 or higher. The fluorescence reagent contains that 2.7 mg of (p-hydroxyphenyl) acetic acid and 1 mg of horseradish peroxidase in 10 mL of 8.2 g/L potassium hydrogen phthalate buffer solution. This reagent should be stored below 4 °C.

Cyclic voltammetry was conducted using a CHI-600C electrochemical workstation employing a three electrode system. Platinum electrode, saturated calomel electrode and glassy carbon electrode were used as the counter, reference and working electrodes, respectively. The electrolyte used in this study was Na_2SO_4 (0.5 mol/L). The scan rate was 5 mV/s.

Electron spin resonance (ESR) spectra of the radicals were recorded on a Bruker EPR A300 spectrometer employing 5, 5-dimethyl-l-pyrroline-N-oxide (DMPO) as the radical trapper. Resonance Raman spectrum was measured on a Renishaw invia system with a 532 nm laser.

2.4. Fe(III)–TPP reduction and Fe(II)–TPP reusability test

The microbial Fe(III)–TPP reduction experiments were performed with using *S. putrefaciens* 200 (SP200) as the model iron reducing bacterium [20,21]. SP200 was grown aerobically in nutrient broth at 30 °C. Then the cells were harvested at exponential