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Elimination of 4-chlorophenol in aqueous solution by the bimetallic Al–Fe/O_2 at normal temperature and pressure

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HIGHLIGHTS

- The Al–Fe/O_2 process exhibited higher removal efficiency of 4-CP.
- The degradation pathway of 4-CP in Al–Fe/O_2 may only follow 4-chlorocatechol pathway.
- Fenton reaction occurred within Fe and H_2O_2 generated by the reaction of Al and O_2.
- EDTA significantly enhanced the degradation of 4-CP.
- The degradation pathway of 4-CP may contain hydroquinone pathway in Al–Fe/O_2 + EDTA.

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ABSTRACT

Oxidative degradation of 4-chlorophenol in aqueous solution at normal temperature and pressure by the bimetallic Al–Fe/O_2 was investigated. The proposed main mechanism, verified by the addition of methanol and benzoic acid as ·OH scavenger and the detection of para-hydroxybenzoic acid, involves the in situ generation of H_2O_2 by the electron transfer from ZVAl to O_2, and the Fenton reaction occurring within ZVI and H_2O_2. The effects of initial pH, concentration of 4-chlorophenol and ethylenediaminetetraacetic acid, Fe^0 content and Al–Fe loading were investigated. The results showed that the bimetallic Al–Fe/O_2 process exhibited higher reactivity than ZVAl/O_2 and ZVI/O_2 process and the 50 mg L^{-1} of 4-CP could be completely degraded in 2 h with the 100:1 mass ratio of Al and Fe. EDTA significantly enhanced the degradation of 4-CP with the optimized 1:1 mass ratio of Al and Fe while its appropriate initial concentration needed to be optimized. The degradation pathway of 4-CP in Al–Fe/O_2 may only follow 4-chlorocatechol pathway, while it may contain hydroquinone pathway in Al–Fe/O_2 + EDTA.

1. Introduction

Chlorophenols are a particular group of priority toxic pollutants listed respectively in the Clean Water Act [1] by US EPA and the European Decision 2455/2001/EC [2]. They have been widely used as disinfectants, paints and leather preservatives, as well as insecticides. They can also be generated in waste incineration. As a result, they can be found in water and soil, and aggravate environmental pollution problems [2]. However, most of them are highly toxic and difficult to be removed from the environment by conventional biological treatment process [3].

Over the past few decades, advanced oxidation processes (AOPs), especially the Fenton reaction, have received increasing attention for their significant effectiveness on destruction of various recalcitrant organic pollutants [4,5] because the produced reactive oxygen species (ROS, e.g., hydroxyl radical) exhibit high oxidation potential.

$$Fe^{2+} + H_2O_2 \rightarrow {}^{\cdot}OH + OH^- + Fe^{3+} \quad (1)$$

However, AOPs usually require chemical oxidants (H_2O_2 or ozone) and/or high energy input (UV light, Ultrasound or Microwave). It requires high amounts of oxidant and/or large residence time involving high operating costs to completely degrade the pollutants [1,6,7]. From an economical point of view, the use of O_2 as a precursor of ROS is highly desirable in AOPs. The activation of O_2 to ROS is enabled by photochemical processes (e.g., vacuum UV photolysis) and electrical discharge [8,9].

Though, the corrosion of Fe^0 by O_2 can lead to the oxidation of organic compounds, the oxidant yield is too low for application. That may attribute to the increase of aqueous solution pH and the formation of iron hydroxide precipitates during the corrosion process [10,11].

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O_2 \quad (2)$$

$$Fe^0 + H_2O_2 \rightarrow Fe^{2+} + 2OH^- \quad (3)$$

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In order to improve the yield of ROS, several scholars added chelating agent (e.g., EDTA, polyoxometalate anions or metalloporphyrins) to oxygen-containing solution of zero-valent iron. However, it may cause new pollution if the additive is too more to be degraded simultaneously [12–17]. Therefore, some scholars proposed other environmentally friendly agents to overcome this shortcoming. According to Rastogi et al. [18], Huang et al. [19] and Klamerth et al. [20], as the isomer of EDTA, ethylenediamine-N,N′-disuccinic acid (EDDS) could also improve the yield of ROS. And it would not pollute the environment or increase toxicity.

Compared with ZVI, zero-valent aluminum (ZVAl) could provide a greater thermodynamic driving force for electron transfer on the facile transfer of electrons to O_2 [21]. The generation of ROS through ZVAl-induced electron transfer to O_2 has been reported by Lien and Wilkin [22]. And Bokare and Choi also reported the oxidative degradation of 4-CP using ZVAl in the presence of dissolved oxygen [23]. However, it needed more than 5 h to completely degrade 100 μM 4-CP. That may attribute to the low reaction rate of Eq. (7) compared with Fenton reaction (Eq. (1)) [23,24].

$$\mathrm{Al^0} \rightarrow \mathrm{Al^{3+}} + 3e^- \quad E^{\ominus}(\mathrm{Al^{3+}/Al}) = -1.66\ \mathrm{V} \tag{4}$$

$$\mathrm{O_2} + \mathrm{H^+} + e^- \rightarrow \mathrm{HO_2^{\cdot}} \tag{5}$$

$$2\mathrm{HO_2^{\cdot}} \rightarrow \mathrm{H_2O_2} + \mathrm{O_2} \tag{6}$$

$$\mathrm{Al^0} + 3\mathrm{H_2O_2} \rightarrow \mathrm{Al^{3+}} + 3\ {}^{\cdot}\mathrm{OH} + 3\mathrm{OH^-} \tag{7}$$

The bimetallic process is one of the focuses in recent years. It was invented to enhance the reactivity of single metal and overcome some shortcomings on the operation [25]. Some refractory organics, such as nitrobenzene [26], trichloroethylene, tetrachloroethylene and carbon tetrachloride [27], could be effectively reduced by this process. According to Ma and Zhang [28], a small amount of Cu was added directly to a conventional Fe^0 reactor. And the efficiency of the electrode reactions was increased by the high potential difference between Fe and Cu. Therefore, some refractory organics could be reduced directly on the surface of Cu. According to Agarwal et al. [29,30], the polychlorinatedbiphenyls and 2-chlorobiphenyl could be dechlorinated by the bimetallic Pd–Mg process. And bimetallic Pb–Fe could also be applied to dechlorinate hexachlorobenzene in a short time [31]. However, there was little report about the application of bimetallic process in AOPs. Liu et al. reported that EDTA could be degraded in 3 h by the bimetallic Fe–Cu/O_2 process [25].

This work reported the degradation of 4-CP at normal temperature and pressure by the bimetallic Al–Fe/O_2 process without any external energy and additional H_2O_2. The Fe^0 in this process was used to spontaneously generate the Fe^{2+} which could accelerate the generation of ROS (e.g., $^{\cdot}OH$) (Eq. (1)) by the corrosion reaction. Therefore, the higher oxidation efficiency of bimetallic Al–Fe/O_2 process was obtained compared with ZVAl/O_2 system. The effects of initial pH, initial concentration of 4-chlorophenol (4-CP) and EDTA, Fe content and Al–Fe loading were investigated. The main oxidation mechanism, which was verified by the addition of methanol and benzoic acid (BA) as $^{\cdot}OH$ scavenger and the detection of para-hydroxybenzoic acid (p-HBA), involves: (A) electron transfer from ZVAl to O_2 and in situ production of H_2O_2 and $^{\cdot}OH$, (B) the Fenton reaction occurring within Fe^0 and H_2O_2, and (C) EDTA enhanced in situ production of H_2O_2 and $^{\cdot}OH$. Moreover, the degradation pathway of 4-CP in Al–Fe/O_2 system was analyzed by the verification of reaction intermediates and Cl^- concentration. And the influence of EDTA on the degradation pathway was also investigated.

2. Experimental

2.1. Chemicals

All the chemicals were of analytical grade and used without further purification except the methanol (Fisher, HPLC grade) and 1.000 g L^{-1} Cl^- standard solution (Shanghai Institute of Measurement and Testing Technology, China). They were purchased from China National Pharmaceutical Group Corporation. All aqueous solutions were prepared with ultra-pure water (Millipore Milli-Q system, resistivity > 18.2 MΩ). 4-CP solution or the mixture of 4-CP and BA was prepared by dissolving 4-CP and BA in ultra-pure water. The molecule structure of 4-CP is shown in Fig. 1. The initial pH was adjusted by H_2SO_4 and NaOH. The granular Fe^0 (99%) was less than 100 mesh (0.15 mm). The granular Al^0 (99%) was 200 mesh.

2.2. Experimental procedures

2.2.1. Preparation of bimetallic Al–Fe powder

As a typical procedure, 200 g of Fe^0/Al^0 was washed with 500 mL of 1% HCl (volume percentage) for 3 min in a 2 L glass beaker equipped with HJ-6 magnetic stirring apparatus (Changzhou Guohua, China), and purged with deoxygened-ultra-pure water to neutral. Thereafter, the freshly prepared metallic powder was spread in a thin layer on a filter paper and dried at room temperature in argon atmosphere for 24 h (100 mL min^{-1}). The dried powder was then collected and stored in refrigerator for subsequent use [32].

2.2.2. Oxidative degradation reaction

The degradation experiments were conducted in a series of 200 mL glass beakers equipped with HJ-6 magnetic stirrer (Changzhou Guohua Electric Appliance Co., Ltd.), at room temperature (20 ± 2 °C). Simulated wastewater containing 4-CP or other organic substance (e.g., EDTA/BA) of 100 mL was oxygen saturated through continuous stirring at least 30 min then, the experiments started by adding Al–Fe powder. The beakers were open to the air to prevent the depletion of dissolved oxygen during the reaction. At the given reaction time intervals, samples was taken out and filtered using 0.45 μm hydrophilic polyethersulfone (PES) syringe filters (Shanghai ANPEL Scientific Instrument Co., Ltd.). The filtrate was then withdrawn for the assay of TOC, 4-CP and EDTA.

2.2.3. The verification of chlorine substituted intermediates

The verification experiments were conducted in a series of 50 mL polyethylene centrifuge tubes equipped with XW-80A vortex mixer (Changzhou Guohua Electric Appliance Co., Ltd.) at room temperature (20 ± 2 °C). Simulated wastewater containing 4-CP or EDTA and 4-CP of 1 mL was oxygen saturated through continuous stirring at least 30 min then, the experiments started by adding Al–Fe powder at optimum initial parameters. The tubes were open to the air to prevent the depletion of dissolved oxygen during the reaction. The filtrate was withdrawn in given time for the analysis of chlorine substituted intermediates and Cl^-. After 3 h reaction, all of the Al–Fe powder in the two systems was respectively dissolved by 4 M H_2SO_4. This solution was then withdrawn for the assay of total Cl^-.

2.3. Analytical methods

Surface morphologies of the bimetal powder were observed using a JSM-6360LV scanning electron microscope (JEOL, Japan). X-ray powder diffraction (XRD) patterns were obtained on a D8 ADVANCE X-ray diffractometer (Bruker, Germany).

Quantitative analysis of 4-CP, EDTA, intermediates(except Iminodiacetate, Formate and Acetate) and p-HBA was performed respectively with high performance liquid chromatography on a