



Elimination of 4-chlorophenol in aqueous solution by the bimetallic Al-Fe/O₂ at normal temperature and pressure

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HIGHLIGHTS

- The Al-Fe/O₂ process exhibited higher removal efficiency of 4-CP.
- The degradation pathway of 4-CP in Al-Fe/O₂ may only follow 4-chlorocatechol pathway.
- Fenton reaction occurred within Fe and H₂O₂ generated by the reaction of Al and O₂.
- EDTA significantly enhanced the degradation of 4-CP.
- The degradation pathway of 4-CP may contain hydroquinone pathway in Al-Fe/O₂ + EDTA.

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ABSTRACT

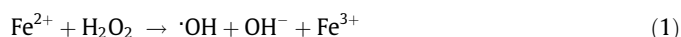
Oxidative degradation of 4-chlorophenol in aqueous solution at normal temperature and pressure by the bimetallic Al-Fe/O₂ was investigated. The proposed main mechanism, verified by the addition of methanol and benzoic acid as ·OH scavenger and the detection of para-hydroxybenzoic acid, involves the in situ generation of H₂O₂ by the electron transfer from ZVAl to O₂, and the Fenton reaction occurring within ZVI and H₂O₂. The effects of initial pH, concentration of 4-chlorophenol and ethylenediaminetetraacetic acid, Fe⁰ content and Al-Fe loading were investigated. The results showed that the bimetallic Al-Fe/O₂ process exhibited higher reactivity than ZVAl/O₂ and ZVI/O₂ 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/O₂ may only follow 4-chlorocatechol pathway, while it may contain hydroquinone pathway in Al-Fe/O₂ + EDTA.

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1. Introduction

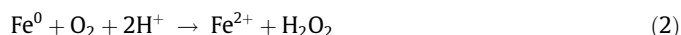
Chlorophenols are a particular group of priority toxic pollutants listed respectively in the Clean Water Act [1] by US EPA and the European Decision 2455/2001/EC [2]. They have been widely used as disinfectants, paints and leather preservatives, as well as insecticides. They can also be generated in 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.



However, AOPs usually require chemical oxidants (H₂O₂ 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 O₂ as a precursor of ROS is highly desirable in AOPs. The activation of O₂ to ROS is enabled by photochemical processes (e.g., vacuum UV photolysis) and electrical discharge [8,9].

Though, the corrosion of Fe⁰ by O₂ 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].

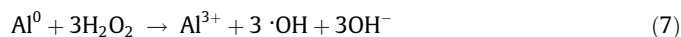
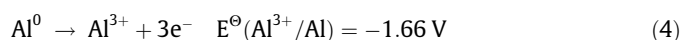


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In order to improve the yield of ROS, several scholars added chelating agent (e.g., EDTA, polyoxometalate anions or metalloporphyrins) to oxygen-containing solution of zero-valent iron. However, it may cause new pollution if the additive is too more 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 Klammer 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 O₂ [21]. The generation of ROS through ZVAL-induced electron transfer to O₂ 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].



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 Fe⁰ 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 polychlorinated biphenyls 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/O₂ process [25].

This work reported the degradation of 4-CP at normal temperature and pressure by the bimetallic Al–Fe/O₂ process without any external energy and additional H₂O₂. The Fe⁰ in this process was used to spontaneously generate the Fe²⁺ which could accelerate the generation of ROS (e.g., ·OH) (Eq. (1)) by the corrosion reaction. Therefore, the higher oxidation efficiency of bimetallic Al–Fe/O₂ process was obtained compared with ZVAL/O₂ 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 ·OH scavenger and the detection of para-hydroxybenzoic acid (p-HBA), involves: (A) electron transfer from ZVAL to O₂ and in situ production of H₂O₂ and ·OH, (B) the Fenton reaction occurring within Fe⁰ and H₂O₂, and (C) EDTA enhanced in situ production of H₂O₂ and ·OH. Moreover, the degradation pathway of 4-CP in Al–Fe/O₂ 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 H₂SO₄ and NaOH. The granular Fe⁰ (99%) was less than 100 mesh (0.15 mm). The granular Al⁰ (99%) was 200 mesh.

2.2. Experimental procedures

2.2.1. Preparation of bimetallic Al–Fe powder

As a typical procedure, 200 g of Fe⁰/Al⁰ 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 deoxygenated-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 H₂SO₄. 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 Imidodiacetate, Formate and Acetate) and p-HBA was performed respectively with high performance liquid chromatography on a

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