Journal of Environmental Chemical Engineering 2 (2014) 1275–1280

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Fenton–Cu^{2+} system for phenol mineralization

Jun Maekawa[a], Kazuhiro Mae[b], Hiroyuki Nakagawa[a,*]

[a] *Environment Preservation Research Center, Kyoto University, Yoshida-Honmachi, Sakyo-ku, Kyoto 606-8501, Japan*
[b] *Department of Chemical Engineering, Kyoto University, Kyoto Daigaku Katsura, Nishikyo-ku, Kyoto 615-8510, Japan*

ARTICLE INFO

Article history:
Received 5 March 2014
Accepted 13 May 2014

Keywords:
Fenton oxidation
Copper ions
Oxalic acid
Mineralization
Phenol

ABSTRACT

In this study, Cu(II) ions along with Fenton reagent were used to enhance the mineralization of phenol in the water and a significant catalytic activity of Cu(II) ions on the mineralization of phenol was observed. At 0.1 and 1.0 mM initial concentrations of Fe(II) and Cu(II) ions, respectively, 94% phenol, on a carbon basis, was mineralized under dark conditions, whereas about 60% of total organic carbon remained in the water in the absence of Cu(II) ions. Oxalic acid was found to be degraded and mineralized in the presence of both Cu(II) ions and reducing intermediates. This is supported by experiments using hydroquinone, which is one of the reducing intermediates formed during the degradation of phenol by Fenton oxidation. The Fe(III) ions coordinated to oxalic acids are reduced to Fe(II) ions in the presence of both Cu(II) ions and hydroquinone. These results suggest that Cu(II) ions catalyze the reduction of Fe(III) ions by the reducing intermediates resulting in enhanced phenol mineralization by Fenton reagent. The addition of Cu(II) ions was also found to be effective for enhancing mineralization of 4-nitrophenol, Orange II, 2,4-dichlorophenoxyacetic acid, and bisphenol A.

Introduction

Fenton oxidation, a homogeneous oxidation process using a mixture of hydrogen peroxide (H_2O_2) and ferrous ions (Fe(II)) in an acidic medium, has shown great potential to treat wastewater containing organic pollutants because (i) iron is an abundant and nontoxic element and (ii) H_2O_2 is easy to handle and environmentally safe [1]. Therefore, in the last decade, Fenton oxidation has been adopted in wastewater treatment processes, and a variety of refractory organics could be effectively degraded through Fenton oxidation [2–5].

The mechanism for Fenton oxidation mainly includes the following reactions [2,6,7]:

$$\mathrm{Fe(II)} + H_2O_2 \rightarrow \mathrm{Fe(III)} + HO^{\bullet} + OH^- \quad k_1 = 70\ \mathrm{M^{-1}\,s^{-1}} \tag{1}$$

$$\mathrm{Fe(III)} + H_2O_2 \rightarrow \mathrm{Fe(II)} + HO_2^{\bullet} + H^+ \quad k_2 = 0.001 - 0.01\ \mathrm{M^{-1}\,s^{-1}} \tag{2}$$

In this process, hydroxyl radicals ($HO^{\bullet}$), a strong oxidant ($E^{\circ} = 2.87$ V vs. NHE), are produced from the reaction of H_2O_2 with Fe(II), as shown in Eq. (1). Hydroxyl radicals react rapidly and nonselectively with a wide range of organic pollutants and convert them to CO_2, H_2O, and inorganic ions in a process, known as mineralization. The regeneration of Fe(III) to Fe(II) ions through the reduction by H_2O_2 is also accompanied in this reaction system, as shown in Eq. (2). Therefore, as long as H_2O_2 is available, the redox cycle between Fe(II) and Fe(III) ions is maintained, thus continuously forming hydroxyl radicals.

The major drawback of Fenton oxidation, which restricts its application to wastewater treatment, is the precipitation of iron hydroxide, which has to be treated further. The reduction of Fe(III) to Fe(II) by H_2O_2 expressed as Eq. (2) is very slow; therefore, a large amount of Fe(II) ions has to be supplied for complete degradation of organic pollutants. Another drawback is that the mineralization of organic pollutants is very likely to stagnate before the completion, indicating that further treatment is necessary. For phenol oxidative degradation, catechol and hydroquinone are produced as primary aromatic intermediates [8]. These intermediates are responsible for dark color observed in the solution [9] and reduce Fe(III) to Fe(II) to continue Fenton reaction, resulting in further degradation [10,11]. Zazo et al. performed phenol degradation by Fenton reagent under various conditions and quantified aromatic intermediates and short-chain organic acids [12]. They reported that 35–70% of organic intermediates remained in the water on the carbon basis and much unknown intermediates, which were assumed to be the intermediates between phenol and short-chain organic acids, were produced in low Fe(II) concentration. This is because Fe(III) cannot be reduced by forming stable Fe(III) complex with organic ligands such as oxalic acid, which is refractory for Fenton oxidation. We presented that oxalic acid significantly suppressed the reduction of Fe(III) and the yield of oxalic acid was dependent on the initial Fe(II) concentration [13]. To overcome these problems, catalytic acceleration of the reduction of Fe(III) ions is important because the pollutant degradation can then be achieved with the supply of a small amount of Fe(II) ions, resulting in no precipitation of iron hydroxide. Furthermore, iron ions can be reused in

---

[*] Corresponding author.
E-mail address: hiroyuki@cheme.kyoto-u.ac.jp (H. Nakagawa).

2213-3437/$ - see front matter
http://dx.doi.org/10.1016/j.jece.2014.05.009

Fenton process because they can be recovered by use of adsorbents such as chelate resins.

Researchers have studied the reduction rate of Fe(III) ions by coexisting compounds other than H_2O_2 and its derivatives. Chen et al. [14] added hydroxylamine, a widely used inorganic reducing agent, and concluded that the redox cycle of Fe(III)/Fe(II) ions could be accelerated, to yield nitrogen and nitrogen oxides as the reduction products. As for the industrial scale process, a homogeneous mixture of iron and copper salts is used as catalyst of wet oxidation with hydrogen peroxide in OHP® process. This technology is based on Fenton reaction and the process is operated at 110–120 °C.

In this study, we focus on Cu(II) ions to enhance the mineralization of phenol through Fenton oxidation by the acceleration of the redox cycle of Fe(III)/Fe(II) ions at room temperature. Cu(II) ions can be recovered simultaneously with iron ions by chelate resins for heavy metals. We further examine the effect on the mineralization under various conditions to achieve higher degree of mineralization. The formation of oxalic acid is also examined to understand the mineralization of phenol. Finally, this method is applied to other organic pollutants and the effect on the mineralization is examined.

Materials and methods

Chemicals

All the chemicals were purchased from Wako Pure Chemical Industries. Phenol, 4-nitrophenol (4-NP), 4,4′-isopropylidenediphenol (bisphenol A; BPA), Orange II (OGII), and 2,4-dichlorophenoxyacetic acid (2,4-D) were used as organic pollutants. Aqueous solutions of copper and iron sulfates (0.25 M) were prepared and used as the source of metal ions.

Procedure

A 300 mL glass beaker with a magnetic stirrer was used as the reactor. 250 mL of a 100 or 50 mg L^{-1} solution of each organic pollutant was prepared, the pH was adjusted to 3.0 using 0.1 M H_2SO_4 solution, and a specified amount of 0.25 M solution of metal ions was added. Next, a specified amount of H_2O_2 solution (15 wt.%) was added to initiate the reaction. The experiment was carried out at room temperature (23 ± 2 °C) in a dark room to avoid the effect of light. The initial concentrations of metal ions were varied from 0.0 to 1.0 mM. Initial concentration of hydrogen peroxide was 20 mM, which is excessive amount for complete mineralization, in all experiments to examine the effect of the amount of Fe(II) and Cu(II) dosed, although optimum amount of hydrogen peroxide should be supplied in the actual process.

Analysis

The treated water was analyzed immediately. The concentrations of H_2O_2, Fe(II), and Fe(III) ions were determined by colorimetric methods using a UV-Visible spectrophotometer (UVmini-1240, Shimadzu). The iodide method was used to analyze H_2O_2 at $\lambda = 350$ nm [15]. The bathophenanthroline disulfonic acid method was used to analyze Fe(II) at $\lambda = 534$ nm [16]. For the analysis of Fe(III) ions, hydroxylamine chloride was used for the reduction of Fe(III) to Fe(II) ions prior to applying the bathophenanthroline disulfonic acid method. The total organic carbon (TOC) concentration, which was estimated from the difference of the concentrations of total carbon and inorganic carbon, was measured using a TOC analyzer (TOC-V_{CSH}, Shimadzu). The quantitative measurement of organic acids was carried out by using a non-suppressor-type ion chromatography system equipped with a Shim-pack IC-A1 column (100 mm long). An aqueous solution of phthalic acid (2.5 mM) and tris(hydroxymethyl)aminomethane (2.4 mM) were used as the mobile phase at a flow rate of 1.5 mL min^{-1} under isocratic conditions. Prior to the analysis, a solid-phase extraction was performed to remove the Fe(III) ions from the oxalic acids because Fe(III) ions interfere with the quantitative analysis of oxalic acids. This technique can remove Fe(III) ions from water, leaving whole oxalic anions. Validity of this method was confirmed by analyzing various concentrations of oxalic acid with Fe(III), presented in supplementary material of Ref. [13].

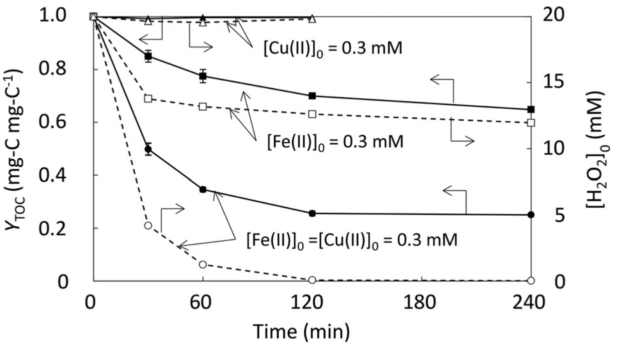

Fig. 1. The changes in TOC yield and H_2O_2 concentration as a function of time for the degradation of 100 mg L^{-1} phenol by Fenton reagent and Cu(II) ions at $[H_2O_2]_0 = 20$ mM. Values are $m \pm$ SD.

Results and discussion

The effect of copper ions on the mineralization of phenol

Fig. 1 shows the change in the TOC yield and H_2O_2 concentration, respectively, as a function of time, during the degradation of 100 mg L^{-1} phenol when Cu(II) ions were added along with Fenton reagent. The initial concentrations of Fe(II) ions, $[Fe(II)]_0$, and Cu(II) ions, $[Cu(II)]_0$, were 0.3 mM. When only the Fenton reagent was added, the TOC yield and H_2O_2 concentration were almost unchanged after 120 min although it significantly decreased during the initial stage. The TOC yield and H_2O_2 concentration at 240 min were 0.65 mg-C mg-C^{-1} and 12 mM, respectively. Under this condition, the reduction of Fe(III) was strongly suppressed by the oxalic acid produced during the phenol degradation, and therefore, a negligible amount of H_2O_2 was consumed after 120 min [13].

When Cu(II) was added along with Fenton reagent, a significant enhancement in the phenol mineralization was observed. The TOC yield significantly decreased to 0.50 mg-C mg-C^{-1} in 30 min and was down to 0.26 mg-C mg-C^{-1} at 120 min. The consumption of H_2O_2 was also accelerated and almost all the H_2O_2 was consumed at 120 min in the presence of Cu(II) ions. TOC yield after 120 min was not reduced at all even when additional H_2O_2 was added to obtain a concentration of 20 mM at 120 min. This result means that the reason why the mineralization does not proceed is not the depletion in H_2O_2. Therefore, it is assumed that Fe(III) cannot be reduced to Fe(II) due to the coordination with oxalic acid also under this condition. To examine the reaction between Cu(II) and H_2O_2, phenol was treated in the absence of Fe(II). TOC concentration did not decrease at all and the minimal amount of H_2O_2 was consumed as shown in Fig. 1. These results clearly indicate that Cu(II) ions accelerate Fenton oxidation resulting in a significant enhancement in the phenol mineralization. Therefore, Cu(II) ions exhibit significant catalytic activity on the mineralization of phenol through Fenton oxidation. As for the toxicity of Cu, permitted daily exposure (PDE) is estimated to 2.5 mg day^{-1}, which is the same value as that of Mn, by European Medicines Agency. Environmental Protection Agency set 1.3 mg L^{-1} as the maximum contaminant level of copper in drinking water. Most of copper ions in the treated water can be recovered by the adsorbent such as chelate resin; thus contamination of discharged water in low concentration