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Hydroxyl radical generation in the photo-Fenton process: Effects of carboxylic acids on iron redox cycling

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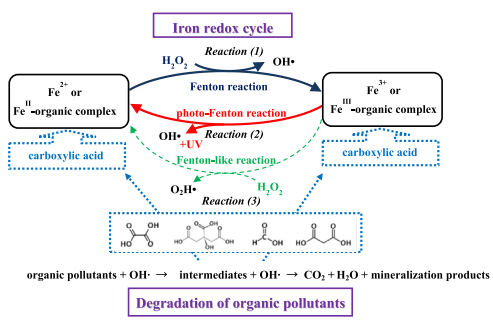
HIGHLIGHTS

- OH radical generation in the photo-Fenton process was discussed.
- Effects of carboxylic acids on iron redox cycling were examined.
- Oxalic acid and citric acid accelerated the iron redox cycle and the OH radical generation.
- Malonic acid inhibited the iron redox and the OH radical generation.
- A kinetic model reasonably simulated the OH radical generation and iron redox cycle.

GRAPHICAL ABSTRACT



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ABSTRACT

From the viewpoint of iron redox cycle promoting OH radical generation in the photo-Fenton process, effects of carboxylic acids formed in the proceeding of the degradation of organic pollutants on the photo-Fenton reactions were discussed. To elucidate the contributions of carboxylic acids forming complexes with iron ions to the photo-Fenton process, the Fenton reaction, the photo-Fenton reaction and the Fenton-like reaction composing the photo-Fenton process were individually examined. A kinetic model simulating the dynamic behaviors of iron redox cycle and OH radical generation was developed to quantify the contributions of carboxylic acids, i.e., citric acid, formic acid, malonic acid and oxalic acid. The Fe^{II}–oxalic acid complex and Fe^{II}–citric acid complex accelerated the rate of iron redox cycle or OH radical generation in the Fenton reaction by 18% and 8%, respectively. The additions of formic acid and malonic acid slightly affected the OH radical generation rate by the Fenton reaction. The photo-Fenton reaction, which is the controlling-step of the photo-Fenton process, was enhanced by oxalic acid and citric acid but largely suppressed by malonic acid. The effect of formic acid on the photo-Fenton reaction was insignificant. These results in the photo-Fenton reaction could be explained by considering the changes in the UV light absorbance with formed Fe^{III}–carboxylic acid complexes. The effects of carboxylic acids on the Fenton-like reaction were little. In the photo-Fenton process, the additions of oxalic acid and citric acid accelerated the iron redox cycle and as a result the OH radical generation by 26% and 11%, respectively. Formic acid insignificantly affected the iron redox cycle and the addition of malonic acid decelerated the iron redox and OH radical generation by approximately 39%.

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1. Introduction

In advanced oxidation processes (AOPs) exhibiting great potential in wastewater treatment, the generation of highly reactive OH radical (OH·) is the critical step since it oxidizes most organic

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molecules quickly and non-selectively and mineralizes them into carbon dioxide, water and mineralization products [1,2]. It should be noted that the complete mineralization of pollutants cannot be sometimes achieved by AOPs but the partial decomposition of non-biodegradable organic pollutants can lead to biodegradable intermediates.

The photo-Fenton oxidative degradation process is one of promising AOPs to remove organic pollutants in wastewater by OH radicals. In the photo-Fenton process, OH radicals are generated by the reactions of Fe ions with hydrogen peroxide and/or light energy [3–5]. In other words, the efficiency of the photo-Fenton oxidative degradation process is controlled by the iron redox cycle consisting of three reactions, i.e., the Fenton reaction, the photo-Fenton reaction and the Fenton-like reaction (Fig. 1). The OH radical generation characterizing the photo-Fenton process is largely dominated by the rates of iron redox cycling between the +2 and +3 oxidation states [4]. Organic ligands often accelerate or decelerate the photo-Fenton process. For example, carboxylic acids are frequently formed as intermediates in the degradation of organic pollutants by the photo-Fenton oxidative degradation process [6–9]. They will react with iron and form iron complexes (Fe^{II}–ligands and Fe^{III}–ligands), which may affect the degradation rate [10–12]. The photo-Fenton processes modified by the complexes with carboxylic acids have been also proposed [10,11].

In the Fenton reaction, the oxidation of iron generating OH radical may be represented as [10,13–15]:

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

Fe^{2+} is oxidized to produce OH radical by decomposition of H_2O_2. The formation of OH radical mainly occurs through the above reaction in the photo-Fenton process.

By the photo-Fenton reaction, the reduction of Fe^{3+} to Fe^{2+} takes place [13–17]:

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + H^{+} + OH^{\cdot} \quad (2)$$

Fe^{3+} catalyses the generation of OH radical with the UV light irradiation.

The Fenton-like reaction also reduces Fe^{3+} to Fe^{2+}:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + O_2H^{\cdot} + H^{+} \quad (3)$$

It should be noted that the oxidation potential of perhydroxyl radical ($O_2H^{\cdot}$) formed by the Fenton-like reaction is weak as compared with that of the hydroxyl radical and the influence of the Fenton-like reaction on the reduction of Fe^{3+} is less than that of the photo-Fenton reaction [5]. Other reactions also contribute the iron redox cycle and they are not considered as the main reactions in the photo-Fenton process [5,10]. The stable iron redox cycle is mainly established by the above three reactions. By iron complexes formed from iron with carboxylic acids, the above reactions organizing the iron redox cycle are modified and their reaction rates may be accelerated or decelerated as compared with their original reaction rates.

Although a number of studies have been reported on the photo-Fenton process [3,5], the photo-Fenton oxidative degradation has not been completely elucidated. The aim of the present study is to elucidate effects of carboxylic acids on the photo-Fenton oxidative degradation from the viewpoint of iron redox cycle playing a role of an engine for OH radical generation. To the best of our knowledge few systematic studies focusing on iron redox cycling in OH radical generation by the photo-Fenton process have been performed. In the degradation of organic pollutants, the photo-Fenton process produces intermediates affecting the redox cycle of iron and as a result the generation of OH radical. Some of carboxylic acids strongly increase or decrease the photo-catalytic activities of photo-Fenton reagents. Little is known about the effects of carboxylic acids on the iron redox cycle and the generation of OH radical in the photo-Fenton process. There are few studies in which the measured OH radical concentrations in the Fenton, photo-Fenton and Fenton-like reactions were used to elucidate effects of carboxylic acids on the photo-Fenton process. In this study, therefore, effects of carboxylic acids on the photo-Fenton process were examined using the results of a series of measurements for iron redox cycle and OH radical generation. By taking account of the Fenton, photo-Fenton and Fenton-like reactions organizing the photo-Fenton process as the comparison criteria, the changes in their reaction rates due to the formed iron complexes were quantified. To achieve this goal, the dynamic behaviors of iron ions and OH radical generation in the Fenton reaction, the photo-Fenton reaction and the Fenton-like reaction were separately examined. Citric acid, formic acid, malonic acid and oxalic acid, which are often formed as intermediates during

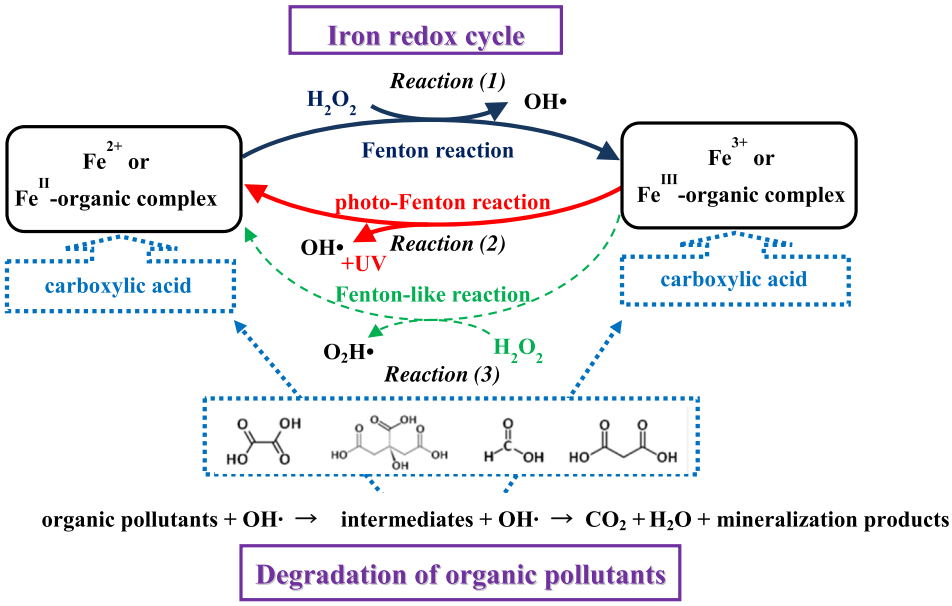

Fig. 1. Iron redox cycle and OH radical generation in the photo-Fenton oxidative degradation process. (Reaction numbers correspond to those in text.)

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