



Hydroxyl radical concentration profile in photo-Fenton oxidation process: Generation and consumption of hydroxyl radicals during the discoloration of azo-dye Orange II

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ABSTRACT

Dynamic behaviors of hydroxyl (OH) radical generation and consumption in photo-Fenton oxidation process were investigated by measuring OH radical concentration during the discoloration of azo-dye Orange II. The effects of operating parameters for photo-Fenton discoloration, i.e. dosages of H₂O₂ and Fe, initial dye concentration, solution pH and UV irradiation, on the generation and consumption of OH radicals playing the main role in advanced oxidation processes were extensively studied. The scavenger probe or trapping technique in which coumarin is scavenger of OH radical was applied to estimate OH radical concentration in the photoreactor during the photo-Fenton discoloration process. The OH radical generation was enhanced with increasing the dosages of Fenton reagents, H₂O₂ and Fe. At the initial stage of photo-Fenton discoloration of Orange II, the OH radical concentration rapidly increased (Phase-I) and the OH radical concentration decreased after reaching of OH radical concentration at maximum value (Phase-II). The decrease in OH radical concentration started when the complete discoloration of Orange II was nearly achieved and the H₂O₂ concentration became rather low. The dynamic behavior of OH radical concentration during the discoloration of Orange II was found to be strongly linked with the change in H₂O₂ concentration. The generation of OH radical was maximum at solution pH of 3.0 and decreased with an increase of solution pH. The OH radical generation rate in the Fenton Process was rather slower than that in the photo-Fenton process.

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1. Introduction

Advanced oxidation processes (AOPs) being based on the generation of powerful oxidizing species have shown great potential in water and wastewater treatment (Parsons, 2004). The hydroxyl radical ($\cdot\text{OH}$) is a strong oxidant that reacts rapidly and non-selectively with most electron-rich sites of organic contaminants (e.g., Lee and Yoon, 2004; Maciel et al., 2004; Xiao et al., 2008; Zimbron and Reardon, 2009). Reactions involving the highly reactive hydroxyl radical characterize the AOPs. Since OH radical potentially leads to complete mineralization of contaminants, a number of studies have been conducted to elucidate its quantitative role on degradation of contaminants in AOPs (Parsons, 2004). Several methods have been developed to measure hydroxyl radical concentrations in liquid and they are classified into the direct detection methods and the indirect detection methods. One of the direct methods is based on the electron paramagnetic

resonance technique in which transitions of unpaired electrons such as free radicals are measured in a magnetic field (Kim and Metcalfe, 2007; Luo et al., 2009). Although this method has been frequently used because of its sensitivity and selectivity in the detection of the hydroxyl radical, it requires an expensive instrument system and a skillful technique. The scavenger probe or trapping technique in which scavengers such as coumarin and benzene trap hydroxyl radicals is an indirect detection method and has been widely applied (Derbalah et al., 2004; Louit et al., 2005; Czili and Horvath, 2008; Ciotti et al., 2009). Since the lifetime of hydroxyl radical is very short ($\sim 10^{-9}$ s), the techniques used to measure hydroxyl radical concentrations have often obliged to be indirect.

The photo-Fenton and Fenton processes are well-known examples of AOPs. They are strongly attributed to the oxidation power of OH radical formed due to the decomposition of hydrogen peroxide catalyzed by ferric ion and have been increasingly used in the treatment of contaminated water (Tokumura et al., 2006a,b; Pouloupoulos et al., 2008; Sun et al., 2008).

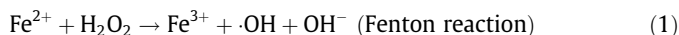
In the photo-Fenton degradation process which combines UV light and Fenton reagents, H₂O₂ is converted to hydroxyl radical in a catalytic cycle with Fe ions acting as catalyst (Kang et al., 2000; Parsons, 2004; Duesterber et al., 2008; Huang et al., 2008). Firstly,

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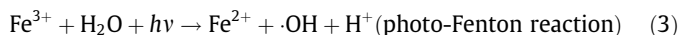
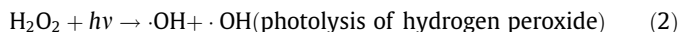
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the hydroxyl radical is generated due to iron catalyzed decomposition of hydrogen peroxide as:



The formation of OH radical also occurs by the following reactions:



Reaction (3) in which Fe(III) catalyzes the generation of $\cdot\text{OH}$ with the irradiation of UV light is followed by Reaction (1) and iron cycle between Fe(II) and Fe(III) occurs. Hydroxyl radicals generated in Reactions (1)–(3) can react with target organic contaminants and lead to the complete mineralization of them. The oxidative attack of OH radicals plays a vital role in degradation of organic contaminants in wastewater.

Although the concentration of powerful oxidizing OH radicals controls the rate of oxidation in AOPs, there are few studies concerned with the concentration profiles of OH radical formed during photo-Fenton degradation processes.

We have investigated the influence of various operating parameters on the OH radical generation and consumption during the photo-Fenton discoloration of azo-dye Orange II. Orange II chosen as a model dye in this study is a typical non-biodegradable azo-dye. The change of OH radical concentrations has been measured during the Orange II discoloration process using a trapping reaction with coumarin. Effects of operating parameters such as initial dye concentration, Fe dosage, H_2O_2 dosage, solution pH and UV light on the rates of OH radical generation and consumption have been quantitatively discussed.

2. Experimental

2.1. Degradation of Azo-dye Orange II

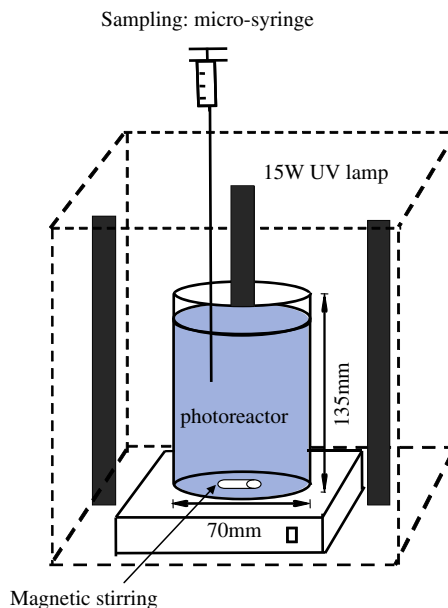
Photo-Fenton discoloration of Orange II in water was examined using an external light irradiation type photoreactor (Fig. 1a). Experiments were carried out in a Pyrex glass cylindrical photoreactor. Its working volume was 300 mL. The photoreactor was mounted on a magnetic stirrer and complete mixing of the reagent (H_2O_2 and Fe ion) through the photoreactor was achieved by vigorous magnetic stirring. All experiments were conducted at room temperature. The solution pH was initially adjusted to the optimum pH for Fenton and photo-Fenton reactions of 3.0 except as otherwise specified by addition of H_2SO_4 or NaOH. The UV light irradiation sources were three 15 W near-UV fluorescent lamps (Sankyo Electronics, Co., Japan) having the radiation peak at 352 nm. The distance between the photoreactor surface and the lamps which were parallel to the photoreactor axis was 0.025 m. Samples from the liquid phase were withdrawn at predetermined time intervals using a micro-syringe.

A UV–Vis spectrophotometer (U-1100, Hitachi Co., Japan) was used to determine the absorbance of Orange II at a wavelength of 486 nm. The TOC (total organic carbon) of the samples was measured using a TOC analyzer (TOC-VE, Shimadzu, Co., Japan).

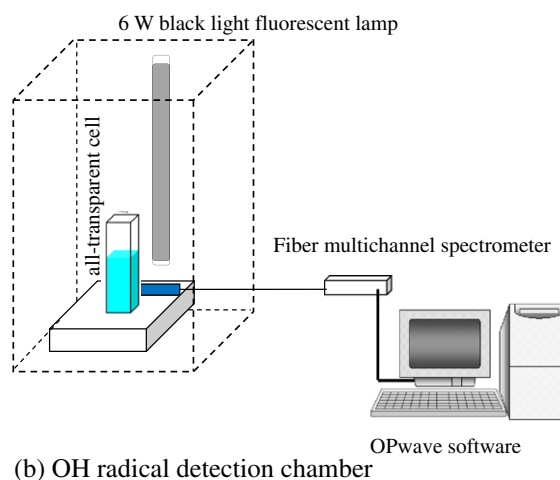
The concentration of H_2O_2 was measured by the glucose oxidase method (Tokumura et al., 2006a,b). The 1,10-phenanthroline method (Tokumura et al., 2006a,b) was used to measure the concentrations of total Fe ion and Fe^{2+} ion.

2.2. Detection of hydroxyl radicals

The direct detection of OH radical in situ (i.e., in the photoreactor where photo-Fenton discoloration of Orange II is conducted) is



(a) Photoreactor for photo-Fenton discoloration of Orange II



(b) OH radical detection chamber

Fig. 1. Schematic of experimental setups for photo-Fenton discoloration of Orange II. (a) Photoreactor for photo-Fenton discoloration of Orange II. (b) OH radical detection chamber. (c) Typical fluorescence spectra of 7-hydroxycoumarin in the sample solution withdrawn from the photoreactor at different sampling times, i.e. 5, 30, 60, 90 and 120 min.

extremely difficult due to very short lifetime and high reactivity of OH radical (Louit et al., 2005). Therefore, several indirect OH radical detection techniques have been developed (Derbalah et al., 2004; Louit et al., 2005; Czili and Horvath, 2008; Ciotti et al., 2009). In this study, coumarin was used as a probe or scavenger for hydroxyl radical quantitation. Coumarin reacts directly with OH radical to produce the highly fluorescent compound, 7-hydroxycoumarin (Louit et al., 2005; Czili and Horvath, 2008). In general, the concentration of hydroxyl radicals in in situ samples is very low and their generation and disappearance almost instantaneously occur (Jen et al., 1998). Therefore, all hydroxyl radicals generated in the photoreactor cannot be trapped by coumarin molecules. Only for the degradation of OH radical scavengers, the measurement of OH radical concentration in the reactor is possible. In the case of the degradation of pollutants except OH radical scavengers, however, the addition of OH radical scavenger into the reaction system significantly changes the OH radical behavior. Since, furthermore, the OH radical concentration in the withdrawn

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