



Carbonate-activated hydrogen peroxide oxidation process for azo dye decolorization: Process, kinetics, and mechanisms



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HIGHLIGHTS

- Carbonate-activated H₂O₂ oxidation was successfully applied for azo dye removal.
- Carbonate and H₂O₂ concentration positively affected CAP for AO7 removal.
- O₂^{•-} and CO₃^{•-} might be the main ROSs in the CAP oxidation process
- A possible degradation pathway of AO7 by the CAP oxidation were proposed.

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ABSTRACT

Advanced oxidation processes offer effective solutions in treating wastewater from various industries. This study is the first time to investigate the potential of carbonate-activated hydrogen peroxide (CAP) oxidation process for the removal of organic pollutant from highly alkaline wastewaters. Azo dye acid orange 7 (AO7) was selected as a model pollutant. The influences of various parameters on AO7 decolorization by the CAP oxidation were evaluated. Furthermore, the active species involved in AO7 degradation were explored using scavenger experiments and electron spin resonance analysis. Additionally, AO7 degradation products by the CAP oxidation were identified to elucidate possible transformation pathways. Results showed that the CAP oxidation had better AO7 decolorization performance compared to bicarbonate-activated hydrogen peroxide method. The AO7 decolorization efficiency augmented from $3.70 \pm 0.76\%$ to $54.27 \pm 2.65\%$ when carbonate concentration was increased from 0 to 50 mM at pH 13.0, and then changed slightly with further increasing carbonate concentration to 70 mM. It increased almost linearly from $5.95 \pm 0.32\%$ to $94.03 \pm 0.39\%$ as H₂O₂ concentration was increased from 5 to 50 mM. Moreover, trace amount of Co(II) could facilitate AO7 decolorization by the CAP reaction. Superoxide and carbonate radicals might be the main reactive oxygen species involved in the CAP process. Finally, a possible degradation pathway of AO7 by the CAP oxidation was proposed based on the identified products.

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1. Introduction

Advanced oxidation processes (AOPs) have received intensive attention for application in environmental remediation over recent decades (Ikehata and El-Din, 2004; Wols and Hofman-Caris, 2012; Oturan and Aaron, 2014). Among various AOPs, Fenton and Fenton-like technologies have been demonstrated to be effective in the treatment of a wide diversity of industrial wastewater (Neyens and

Baeyens, 2003; Bokare and Choi, 2014). However, transition metal salts or complexes are generally used as catalysts for activation of hydrogen peroxide during these processes (Duarte et al., 2009; Silva et al., 2013; Bokare and Choi, 2014; Fu et al., 2014). The leaching of those metals is inevitable and must be removed to meet the given standards before discharging the water. Moreover, a low pH condition is usually required for Fenton and Fenton-like reactions, since the catalysts (e.g., Fe²⁺ and Cu²⁺) could precipitate under high pH values. However, operating under the low pH or acidic condition requires the equipment to be fit for such corrosive exposure, which can be relatively expensive.

Recently a simple and transition-metal-free approach, i.e.,

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bicarbonate-activated hydrogen peroxide (BAP) method, has been introduced for degradation of organic pollutants in wastewater under slightly alkaline (pH 8–9) conditions (Xu et al., 2011a). This technology has been successfully adopted for oxidative removal of various pollutants such as azo dyes, aliphatic amines, aryl sulfide and chlorophenols (Richardson et al., 2000; Zhou et al., 2013; Cheng et al., 2014). In such a BAP process, bicarbonate acts as an activator of hydrogen peroxide to generate many active oxygen species (ROS) including peroxymonocarbonate, superoxide ion and singlet oxygen, which efficiently accelerate the degradation of organic pollutants.

Nevertheless, many typical wastewaters, especially the industrial ones (e.g., printing and dyeing wastewater), are characterized by relatively high alkalinity (pH > 12.0), which makes it difficult for the wastewater to be treated by traditional biological or chemical methods (Prisciandaro et al., 2005; Rao et al., 2007). The other difficulty rises from the fact that these kinds of wastewater normally contain plenty of inorganic carbon. For instance, sodium carbonate is frequently used in dyeing processes to improve dye fixation on textile products, resulting in high concentration of inorganic carbon in the dyeing wastewater (Aleboyeh et al., 2012). Inorganic carbon in these wastewaters are majorly present in the form of carbonate rather than bicarbonate due to high pH level. As direct removal of organic pollutants from these typical wastewaters without pH adjustment would be a better choice, it is important to understand the role of carbonate in the treatment process, particularly whether or not carbonate could activate hydrogen peroxide to generate ROSs for the removal of organic pollutants from highly alkaline wastewaters.

Therefore, the present study focuses on the carbonate activated hydrogen peroxide (CAP) oxidation process for the removal of pollutants. It was demonstrated for the first time that the azo dye in the highly alkaline wastewater could be efficiently decolorized by the CAP oxidation process at ambient temperature. Azo dye acid orange 7 (AO7) was chosen as a model pollutant since it is widely present in dyeing wastewaters (Singh et al., 2007). The influences of various operational parameters on AO7 decolorization by the CAP oxidation were investigated. In addition, the ROSs involved in AO7 degradation by the CAP oxidation were explored using both scavenger experiments and electron spin resonance (ESR) analysis. Furthermore, the degradation products of AO7 by the CAP oxidation were identified to elucidate the possible transformation pathways.

2. Experimental

2.1. Chemicals

NaHCO₃, H₂O₂, NaOH, CoSO₄·7H₂O, *p*-benzoquinone, ascorbic acid, methanol, and tertiary butanol were obtained from local Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). AO7 and 5,5-Dimethyl-1-pyrroline N-oxide (DMPO, 98%) were purchased from Aladdin Reagent Co. Ltd (Shanghai, China). All chemicals were used without further purification in this study.

2.2. Azo dye degradation experiments

All batch experiments were carried out in 150 mL sealed bottles kept at 25 °C with an incubator shaker (90 rpm). In typical degradation experiments, 100 mL of 0.2 mM AO7 solution containing certain amount of sodium bicarbonate was initially added into the bottle, and then the solution pH was adjusted to the desired value by NaOH. After that, though oxygen would be generated due to H₂O₂ decomposition during the reaction, the solution was still purged with nitrogen for at least 30 min to remove oxygen to ensure similar initial conditions before reaction for each

experiment. Finally, the reaction was initialized by adding H₂O₂ into the bottle, and the bottle was immediately sealed within 10 s to avoid the possible impact of air. Each degradation experiment was repeated at least three times and the result is expressed as mean value ± SD in this study. Additionally, an open system for AO7 degradation by the CAP oxidation at pH 13.0 was also conducted for comparison in this study.

We firstly compared AO7 degradation by the BAP and CAP oxidation at various initial pHs. After that, the impacts of carbonate concentration in the range of 0–70 mM and H₂O₂ amount from 0 to 50 mM on AO7 degradation by the CAP oxidation were evaluated. Finally, the effect of 10 μM Co(II) dosage on AO7 degradation by the CAP oxidation was further explored at various carbonate concentrations in this study.

For radical scavenger experiments, different radical scavengers including ascorbic acid (5 mM), methanol (1 M), tertiary butanol (1 M) and *p*-benzoquinone (1, 2 mM) were respectively added into the bottle before dosing H₂O₂ to start the reaction.

2.3. Analysis and calculations

At the given reaction time intervals, the samples taken from the bottle by injectors were adjusted to pH 7.0 by mixing it with equal volume of 100 mM phosphate buffer to exclude the impact of pH on AO7 measurement, as AO7 has two pKa of 8.2 and 11.4 with color change from amber (pH 7.2) to orange (pH 8.6) and orange (pH 10.2) to red (pH 11.8) (Zhang et al., 2014). Then the AO7 concentration was determined immediately at the characteristic λ_{max} of 484 nm using a UV–vis spectrophotometer (Cary 60, Agilent Technologies, CA, USA).

The ROSs involved in the reaction were identified by an ESR spectrometer (JES-FA200, Tokyo, Japan) at room temperature with the following parameters: center field 3242 G, sweep width 80 G, microwave frequency 9.86 G, modulation frequency 100 kHz, and microwave power 5 mW. The measurement was carried out by adding 5 μL H₂O₂ (1 M) into 1 mL mixture solution, during which a spin-trapping agent DMPO (25 mM) was pre-added before reaction and then measured by ESR spectroscopy in 10 min.

The degradation products of AO7 were identified by using a high-resolution LTQ-Orbitrap XL mass spectrometer (Thermo Fisher, CA, USA) equipped with an orthogonal geometry ESI source. Nitrogen was used as the drying (3 L min⁻¹) and nebulizing (6 psi) gas at 275 °C. The spray shield was set to 4.0 kV and the capillary cap was set to 4.5 kV. Scanning was performed from *m/z* 100 to 400 in the standard resolution mode at a scanning rate of 13 kDa s⁻¹. Samples were concentrated by three times via solid-phase extraction (SPE) before analyzed. The chemical oxygen demand (COD) was analyzed according to the standard method (APHA, 1998).

AO7 decolorization efficiency (DE) and its pseudo-first-order rate constant (*k*_{obs}) were estimated according to Eqs. (1) and (2), respectively:

$$DE (\%) = (C_0 - C_t) / C_0 \times 100 \quad (1)$$

$$\ln(C_0 - C_t) = k_{obs} \times t \quad (2)$$

where *C*₀ (mM) is the initial AO7 concentration, *C*_{*t*} (mM) is the AO7 concentration at reaction time *t* (h), and *k*_{obs} (h⁻¹) is the pseudo-first-order constant.

3. Results and discussion

3.1. AO7 decolorization by the BAP/CAP oxidation at various pHs

As shown in Fig. 1, with addition of 10 mM IC and 5 mM H₂O₂,

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