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Synergetic degradation of Acid Orange 7 (AO7) dye by DBD plasma and persulfate

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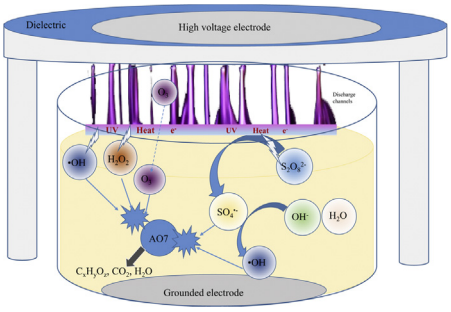
HIGHLIGHTS

- Effect of persulfate on AO7 degradation by DBD plasma was studied.
- Persulfate greatly improved the decolorization and mineralization of AO7.
- Enhanced degradation of AO7 is attributed to SO_4^{-}· and ·OH.
- Possible degradation pathways of AO7 was tentatively given.

GRAPHICAL ABSTRACT



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ABSTRACT

The synergetic degradation performance of Acid Orange 7 (AO7) by dielectric barrier discharge plasma (DBDP) and persulfate (PS) was examined. Addition of PS in AO7 solution hardly degraded any AO7 in 50 min, but when DBDP was initiated over the solution surface, PS greatly enhanced the decolorization efficiency of AO7, and the improvement efficacy depended on the addition dosage of PS, the applied voltage, the air discharge gap and the gas discharge atmosphere. An increase in AO7 decolorization efficiency of 60% was obtained for AO7 solution of 5 mg/L at a PS addition dosage of 100:1 (molar ratio of PS to AO7) and a discharge power of 3.6 W, correspondingly, the decolorization rate of AO7 was accelerated by 6.7 times. The improvement on AO7 degradation mainly attributes to the enhanced production of sulfate radical (SO_4^{-}·) and hydroxyl radicals (·OH) which are produced from the activated PS by DBD plasma. The activators of PS were tentatively speculated as the UV irradiation and heat released in discharge channels, and hydrated electrons may also play a role in the activation process of PS. The intermediates identified by GC–MS and the TOC measurement show that addition of PS into AO7 solution had little effect on the degradation pathways of AO7, but greatly improved the mineralization of AO7, which was mainly due to the increased production of SO_4^{-}· and ·OH.

1. Introduction

Together with the development of industrialization, the quality of many water bodies has deteriorated due to the input of untreated or not fully treated industrial wastewater. The toxic chemical compounds in wastewater greatly endanger the living organisms in water body and the drinking water safety of human beings. At present the activated sludge process is the most widely used biological process for both domestic and industrial wastewater [1], however, toxic or recalcitrant organic substances discharged by chemical industries are commonly resistant to biological treatment [2].

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Electric discharges in air or directly in water were studied as an efficient method to generate reactive species for degrading aqueous organic pollutants [3], and the biodegradability of wastewater was improved after discharge plasma treatment [4]. The main reactive species produced by electric discharge in air is ozone, while electric discharge in water or over water surface can in situ produce many kinds of physical and chemical effects such as UV irradiation, shockwave, local high temperature, and reactive oxygen species (ROS) including ·OH, ·H, O_3 and H_2O_2 [5–7]. The ROS, especially ·OH, is very strong to attack organic molecules, even the organics containing aromatic rings. However, direct photolysis and thermalysis of organics by DBD plasma hardly happen owing to the low UV irradiation dosage and temperature elevation.

Chemical oxidation pre-treatment is also efficient for improving the biodegradability of wastewater by converting refractory organics into biodegradable byproducts [7]. Persulfate (PS) is a strong oxidant with a redox potential (E_0^{Θ} = +2.01 V) similar to O_3 (E_0^{Θ} = +2.07 V), which was commonly used as an in situ chemical oxidation (ISCO) reagent for remediation of contaminated groundwater, soils. [8]. More importantly, PS can be dissociated into a stronger oxidative species, sulfate radical anions (SO_4^{-}·). The redox potential (E_0^{Θ} = 2.5–3.1 V) of SO_4^{-}· is comparable to another well-known strong oxidative radical, ·OH (E_0^{Θ} = 1.89–2.72 V), but the half-life of SO_4^{-}· (30–40 μs) is far longer than that of ·OH (10^{-3} μs) [9].

Heat or microwave heating [10–12], UV light [13,14], transition metals [15–17], base [18], or other methods [19–21] have been used to activate PS to produce SO_4^{-}· for degradation of organic compounds in water. In addition, Kitagawa et al. [22] studied to decompose perfluoro compounds (PFOS) by combining plasma and persulfate treatments, in which 99% PFOS were firstly degraded by plasma, and then the residue PFOS and byproducts with short carbon chains were further degraded by a persulfate-added hot-water treatment. In this paper addition of PS in AO7 solution for enhancing the degradation of Acid Orange 7 (AO7) dye by DBDP was studied. It is expected that DBD plasma can activate PS to produce SO_4^{-}· because DBD plasma also emits UV irradiation, heat in the process of electric discharge. Effect of PS on the degradation of AO7 by DBDP was studied according to the addition dosage of PS, the applied voltage, the gas discharge gap, the gas discharge atmosphere. Moreover, the degradation pathways of AO7 and possible activation mechanism of PS by DBDP were also tentatively analyzed.

2. Materials and methods

2.1. Materials

Except that AO7 dye (>97%) was purchased from Tianjing Heowns Biochemical Technology Co., China, all of other chemicals including the sodium hydroxide (>96%), sulphuric acid (95–98%), potassium persulfate (>99.5%), potassium titanium (IV) oxalate (>98.5%), sodium indigotin disulfonate (>96%), potassium dihydrogen phosphate (>99%), potassium iodide (>99%), sodium hyposulfite (>99%) and ethyl acetate were purchased from Sinopharm Chemical Reagent Co., China. Except that ethyl acetate for extracting the intermediates for GC–MS analysis is chromatographic pure, all other chemicals are analytically pure and used as received without any purification.

2.2. DBD reactor and discharge power measurement

Fig. S1 shows the experimental system for AO7 degradation. The DBD reactor is a water vessel with parallel high-voltage electrode and grounded electrode, and AO7 solution was put in the water vessel for plasma treatment. Both the high-voltage electrode and the ground electrode in DBD reactor are round stainless steel plates with a dimension of 77 mm in diameter and 1 mm in thickness, and a round glass plate with a dimension of 130 mm in diameter and 2 mm in thickness is used as the insulation dielectric. The high-voltage electrode is put on a glass dielectric over the dye solution surface; the ground electrode is placed on the floor of the water vessel. The air gap between the solution surface and the glass dielectric can be changed between 2 mm and 8 mm. The DBD reactor is powered by a 50 Hz AC power supply, and the voltage was monitored by a digital oscilloscope (Tektronix TDS2014, USA) through a high-voltage probe (Tektronix P6015A, USA) as well as the current was measured by monitoring the voltage across a sampling resistance (100 Ω) through a voltage probe (Tektronix P2220, USA). The discharge power was calculated by Q-V Lissajous figure. The optical emission spectrum (OES) of discharge plasma was measured by an optical emission spectrograph (Princeton SP2750, USA).

2.3. AO7 degradation

200 mL AO7 dye solution prepared with deionized water (<1.5 μS/cm) was put in the DBD reactor for discharge plasma treatment. Potassium persulfate was added into AO7 solution according to the molar ratio of PS to AO7 changing from 20:1 to 140:1. The pH value (changing from 2.5 to 10.8) of AO7 solution was adjusted using 0.05 M sodium hydroxide solutions and 0.05 M H_2SO_4. The AO7 solution was sampled every 10 min for analyzing the change in its concentration and the decolorization efficiency of AO7 was calculated according to Eq. (1).

$$\text{Decolorization efficiency}/\% = \left(1 - \frac{C}{C_0}\right) \times 100 \quad (1)$$

Decolorization kinetic constant of AO7 is obtained according to the logarithmic concentration change of AO7 vs. time.

2.4. Analytic methods

The AO7 concentration was determined through spectrophotometric method by a spectrophotometer (Shimadzu U2800, Japan) at a wavelength of 485 nm. Solution conductivity was measured using an electrical conductivity meter (Hanna EC215, Italy). The pH value of AO7 solution was measured by a pH meter (Sartorius PB10, Germany). Aqueous H_2O_2 was measured by potassium titanium (IV) oxalate method in which the H_2O_2 concentration was obtained through monitoring the absorbance of a yellow-orange titanium (IV)-peroxide complex at a wavelength of 400 nm by a spectrophotometer (Shimadzu U2800, Japan) [23]. O_3 in air was determined by iodometric titration method, in which gas stream at the reactor outlet was sampled and absorbed into KI solution and a standard solution of $Na_2S_2O_8$ was used to titrate the absorption liquid for determining the concentration of O_3 in air [24], and NOx in air was measured by a flue gas analyzer (Testo 350, Germany). O_3 in solution was measured by indigo disulphonate spectrophotometry similar to that in [25]. The degradation intermediates of AO7 were analyzed by GC–MS (Agilent 7000B, USA). The mineralization of AO7 was analyzed through a TOC analyzer (Jena TOC multi NC 2100s TOC/TN, Germany).

3. Results and discussion

3.1. Effect of initial concentration of AO7

Figs. 1 and S2 present the AO7 degradation (C/C_0) and degradation kinetic constant with and without (w/wo) PS under different initial concentrations of AO7, respectively. It was found that AO7

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