



Rapid degradation of methyl orange using hybrid advanced oxidation process and its synergistic effect



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ABSTRACT

An advanced oxidation process system to remove residual azo dye in water, called microwave-assisted UV (MDEL)/TiO₂/K₂S₂O₈ hybrid system, was developed and evaluated. The combinations of the component techniques led to increased decomposition rate constants, which are higher than the sum of each component technique. In particular, the decomposition rate constant obtained using the MDEL/TiO₂/K₂S₂O₈ hybrid system, which was the highest obtained in this study, was about 1.5 times larger than the sum of the rate constant obtained using the MDEL/K₂S₂O₈ system and that obtained using the MDEL/TiO₂ system.

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Introduction

Azo dyes have been widely used in a variety of industrial applications because of their chemical stability and versatility. They are characterized by one or more azo bonds (–N=N–) associated with aromatic structure. Due to its high stability, however, the degradation of azo dyes in nature is very difficult and residual azo dyes create environmental pollution problems [1–5]. Various techniques have been adopted to decompose residual azo dyes: biodegradation [6], sorption [7], membrane filtration [8], and electrochemical and oxidative degradation [9]. These processes, however, usually require long residence time and often produce secondary pollutants.

Advanced oxidation process (AOP) is an advanced technology used to degrade persistent organic pollutants. In an AOP, radical species with high oxidizing power and sterilizing action, such as OH radicals, are generated as intermediate products, which oxidize organic pollutants [10].

TiO₂ is one of the representative catalysts that are most widely used in photochemical catalytic processes, such as energy conversion processes and degradation of organic water and air pollutants [11]. TiO₂ photocatalyst has also long been applied to AOP processes [12]. TiO₂ is typically used in powder form. The powder catalysts, however, often form aggregates when the concentration is high. In addition, it is difficult to separate them after the photochemical reaction. Thin TiO₂ film synthesized by the sol-gel method [13], the sputter method [14], or the chemical vapor deposition (CVD) method [15] is considered as an alternative form retaining high photochemical activity. In particular, the CVD method is regarded as a promising way to generate high-quality thin films with well-controlled composition and low defect density over large surface area [16,17].

Persulfate oxidation is one of the AOPs developed recently. Persulfate (S₂O₈²⁻) is one of the strongest oxidants existing in aqueous solution. Its electric potential is higher (2.01 V) than that of H₂O₂ (1.76 V) [18]. The main advantages of persulfate are ease of storage and transport, high stability, high solubility in water, and low price [19]. Due to its high efficiency and general feasibility, persulfate oxidation has received significant attention [20]. However, its application is limited thus far because of relatively

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low reactivity [21,22]. Efforts have been made to reduce the activation energy and promote the reaction, e.g., application of microwave (MW), ultraviolet (UV), or transition metal ions, to produce strong oxidant species, known as sulfate free radical ($\text{SO}_4^{\cdot-}$, $E^0 = 2.60$ V), from persulfate anion ($\text{S}_2\text{O}_8^{2-}$) [23–26].

A hybrid AOP to remove residual azo dye in water, called microwave-assisted UV/TiO₂/persulfate oxidation process, was developed and evaluated experimentally in this study. Methyl orange ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$, referred to MO hereafter) was used as a model azo dye species. The effects of various parameters, e.g., MW power and $\text{K}_2\text{S}_2\text{O}_8$ dosage, on the degradation efficiency of MO were examined.

Experimental

High-purity grade MO was purchased from Daejung Chemicals & Metals Co., Ltd. Double distilled water was used to make MO aqueous solution. 1500 mL of the aqueous MO solution with the initial concentration of 8.72×10^{-2} M was circulated into the quartz reactor tube (230 mm length, 40 mm diameter) with a flow rate of 500 cm³/min. The MO decomposition rate was calculated as a function of irradiation time from the MO concentration decay. The MO concentration was determined by measuring the absorbance at 465 nm using a spectrophotometer (UV-1601, Shimadzu). Potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$, referred to PP hereafter) was purchased from Daejung Chemicals & Metals.

TiO₂ film with anatase crystal structure was synthesized using a low pressure metal organic CVD method. Titanium tetraisopropoxide ($\text{Ti}(\text{OC}_3\text{H}_7)_4$, referred to TTIP hereafter) was used as the precursor. Detailed information of the reactor was given elsewhere [15,16]. Argon gas was passed through a bubbler containing liquid TTIP, heated to 323 K, to carry TTIP vapor to the reactor. The gas was diluted further with argon and oxygen at the reactor tube inlet. The CVD conditions used for the preparation of TiO₂ films were as follows: total flow rate of gas fed to the reactor of 1500 sccm, oxygen gas flow rate 750 sccm, argon gas flow rate 750 sccm, operating pressure of 1 Torr. The flow rates of argon and oxygen were controlled by mass flow controllers. The system was evacuated by a rotary oil vacuum pump and the operating pressure was measured by a pressure transducer at the reactor tube outlet. The source gas was led to a liquid nitrogen trap, while the reactor was heated to a desired temperature before the film

growth or was cooled down to room temperature after the film growth. Photocatalyst balls were prepared by depositing TiO₂ film on alumina balls (Nikkato, HD-11, $\Phi 8$ mm). Fig. 2 shows the FESEM images of TiO₂ films grown at 773 K formed on the alumina ball surface prepared by CVD method. Fig. 2a shows a low-magnification image of broken photocatalyst alumina ball, whereas Fig. 2b shows the high-magnification cross section image of alumina ball coated by TiO₂ film. The thickness of TiO₂ film coated on the alumina ball was 1.19 μm . This TiO₂ film image shows packed columnar crystals. In our previous paper [15], we reported that the XRD analysis of the TiO₂ films grown at 773 K indicated anatase type crystal structure. Characterization of the grown film by energy-dispersive X-ray spectrum (EDX), X-photoelectron spectroscopy (XPS) and FT-IR indicated that the purity of the film was good.

The degradation rate was evaluated from the change in the MO concentration at the reactor outlet, determined by measuring the absorbance at 465 nm using a spectrophotometer (UV-1601, Shimadzu). The following calibration formula was obtained by measuring the absorbance at different concentrations and applying the least square method to the data:

$$\text{Abs.} = (22.714 \times \text{conc. of MO}) + 0.0167 \quad (1)$$

The concentrations of degradation reaction intermediates were also measured using gas chromatograph-mass spectrometer (GC/MS, QP 2000, Shimadzu) equipped with a fused silica capillary column (ID 0.25 mm, length 30 m) to study the degradation pathways. GC/MS (QP 2000, Shimadzu) equipped with a fused silica capillary column (ID 0.25 mm, length 30 m) was used in this study. Samples were extracted using dichloromethane. Temperature was increased at a rate of 3.4 K/min from 80 K (after maintaining for 3 min) to 573 K. In every experiment, the MO solution was allowed to circulate for 10 min before applying the MW power.

Fig. 1 shows the schematic of the MW/UV/TiO₂/PP hybrid photo-catalyst system used in this study. MW was irradiated from an MW system manufactured by Korea Microwave Instrument, consisting of an MW generator (frequency, 2.45 GHz; maximal power, 1 kW), a three-stub tuner, a power monitor, and a reaction cavity. The MO aqueous solution containing TiO₂ photocatalyst balls was irradiated by the MW (actual power used, 300–500 W) delivered through a copper wave-guide. The MW radiation was

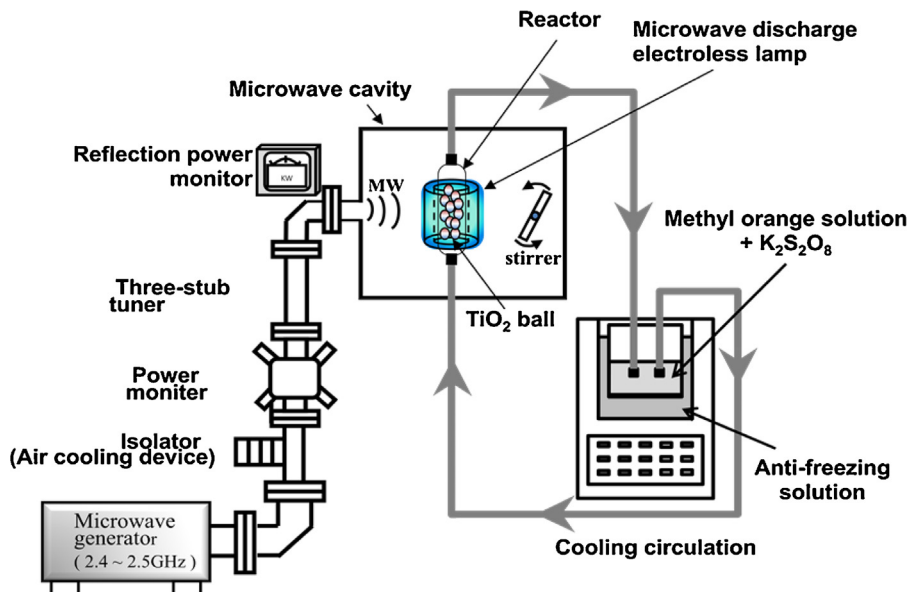


Fig. 1. Schematic of the experimental apparatus used in this study.

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