

Effect of various oxidants in a photocatalysis/filtration system for the treatment of contaminants

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Abstract This study was conducted to investigate the effect of a photocatalysis/oxidant system for the treatment of humic acid and hazardous heavy metals in aqueous solutions. Hydrogen peroxide, ozone, and potassium peroxodisulfate were tested as oxidants. The effect of oxidant concentration was conducted with a pH of 7, a UV intensity of 64 W, and a TiO₂ dosage of 0.3 g L⁻¹. The oxidant addition in the UV/TiO₂ system enhanced the degradation efficiency of humic acid and hazardous heavy metals compared to no addition of an oxidant. The addition of oxidants over the amounts of H₂O₂ 50 mg L⁻¹, O₃ 20 g m⁻³, and K₂S₂O₈ 50 mg L⁻¹ inhibits the system efficiency. The negative effect of higher oxidant concentrations likely results from OH radical quenching caused by the excess oxidant. Therefore, the optimal dosages of oxidants such as a hydrogen peroxide, ozone, and potassium peroxodisulfate were found to be 50 mg L⁻¹, 20 g m⁻³, and 50 mg L⁻¹, respectively. The degradation efficiency of UV/TiO₂/oxidant systems for the removal of humic acid and hazardous heavy metals was much greater in the UV/TiO₂/H₂O₂ system using H₂O₂ as an oxidant.

Keywords Photocatalysis · Ozone · Titanium oxide · Persulfate · Hydrogen peroxide

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Introduction

TiO₂ photocatalytic degradation is an emerging technology which is able to effectively degrade various organic contaminants. Recently, further efforts have been made to study the TiO₂-mediated photodegradation of humic acid, which is one of a group of disinfection by-products (DBPs), including the trihalomethanes (THM), which may result due to the reaction of chlorine. In addition, it is well known that humic substances possess a significant capacity to dissolve complex species such as metal ions and to interact with mineral surfaces [1, 2].

Photocatalysis using UV along with a suspended TiO₂ catalyst is believed to have the advantage of better control in terms of producing hydroxyl radicals while avoiding or minimizing the formation of potentially toxic DBPs [3–5]. However, the UV/TiO₂ process suffers from a relatively low apparent quantum yield due to the rapid recombination of photogenerated electrons and holes. In order to match the criteria for eventual applications in environmental decontamination, improvements in the system efficiency are essential. In irradiated TiO₂ suspensions, oxygen on the TiO₂ surface provides a natural sink for the photogenerated electrons. OH radicals form via the oxidation of TiO₂ surface-sorbed H₂O or hydroxyl ions by the surviving holes. The introduction of a more effective electron acceptor than oxygen may be beneficial. The addition of inorganic oxidants, such as BrO₃⁻, O₃, H₂O₂, IO₄⁻, and S₂O₈²⁻, in TiO₂ photocatalysis has been explored [6].

Many researchers reported similar rate-enhancing effects for added inorganic oxidants, i.e., H₂O₂, IO₄⁻, and S₂O₈²⁻. Other studies have claimed that hydrogen peroxide is able to significantly improve the initial reaction rates of photocatalysis of a variety of organic compounds [7–9]. Meanwhile, negative effects on the TiO₂ photocatalysis at a high H₂O₂ concentration were also reported [10].

The objective of this study is to investigate the effects of a photocatalysis/oxidant system for the treatment of humic acid and hazardous heavy metals in aqueous solutions.

Materials and methods

A schematic of the experimental system for the photo-redox is shown in Fig. 1. The working volume of the photocatalytic reactor was 3.1 L. Illumination was generally provided by a 16-W × 4 germicidal lamp with a maximum light intensity output of 254 nm.

The TiO₂ powder P-25 Degussa (80% anatase and 20% rutile) was used in the experiments. Hydrogen peroxide (30%, reagent grade, Japan) was obtained from Showa Chemical Co. Potassium peroxodisulfate (K₂S₂O₈, extra pure reagent grade, Japan) was used as provided by the Kanto Chemical Co. Humic acid was provided by Aldrich (USA). Stock humic acid solution (1,000 mg L⁻¹) was prepared according to a previously outlined procedure [11]. The initial concentration of humic acid was chosen to be 20 mg L⁻¹. The humic acid content, expressed in terms of COD_{Cr} and the color, was measured with the models HS 3100 (Humas Co., Ltd., Korea) and DR 2010 (Hach Company, USA), respectively. A mixed solution of hazardous heavy

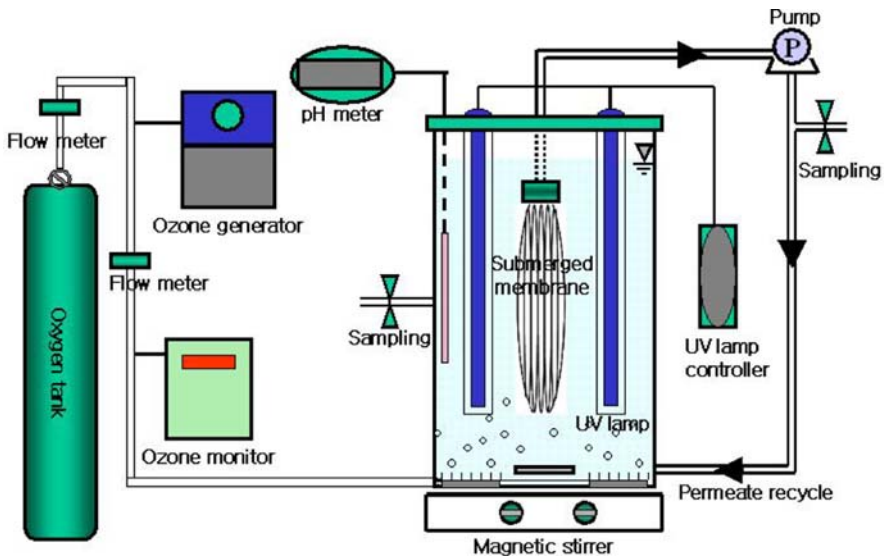


Fig. 1 A schematic of the photocatalysis/oxidant system

metals containing Cu and Cr was prepared using analytical grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Showa Chemical Co., Ltd., Japan) and $\text{K}_2\text{Cr}_2\text{O}_7$ (Deajung Chemicals and Metals Co., Ltd., Korea), respectively. Concentrations of Cu and Cr of 20 mg L^{-1} were used in all experiments. The Cu and Cr concentrations were analyzed with an AA Analyst 100 atomic absorption spectrophotometer (PerkinElmer Inc., USA), and were 324.8 and 357.9 nm, respectively. The ozone produced from the ozone generator was directed into the photocatalytic reactor with a concentration of $10\text{--}30 \text{ g m}^{-3}$. The ozone output was obtained by adjusting the voltage of the ozone generator (Model Lab-1, Ozone Tech, Korea).

Results and discussion

Effect of hydrogen peroxide

Experiments were conducted to evaluate the effect of H_2O_2 on the removal of humic acid and hazardous heavy metals in UV/ TiO_2 . The effect of H_2O_2 concentration on the removal of humic acid and hazardous heavy metals is shown in Fig. 2. In Fig. 2a, the removal efficiency for humic acid and hazardous heavy metals increases rapidly with an increase in the H_2O_2 concentration up to 50 mg L^{-1} . However, the addition of H_2O_2 over 50 mg L^{-1} inhibits the system efficiency. The negative effect of higher concentrations of H_2O_2 is thought to result from OH radical quenching by the excess H_2O_2 . Figure 2b shows the removal of humic acid and hazardous heavy metals in each of unit process. The illumination of UV to the TiO_2 resulted in a faster degradation compared to that of TiO_2 by itself; it was, however, slower than that of UV/ TiO_2 with a concentration of 50 mg l^{-1} of H_2O_2 .

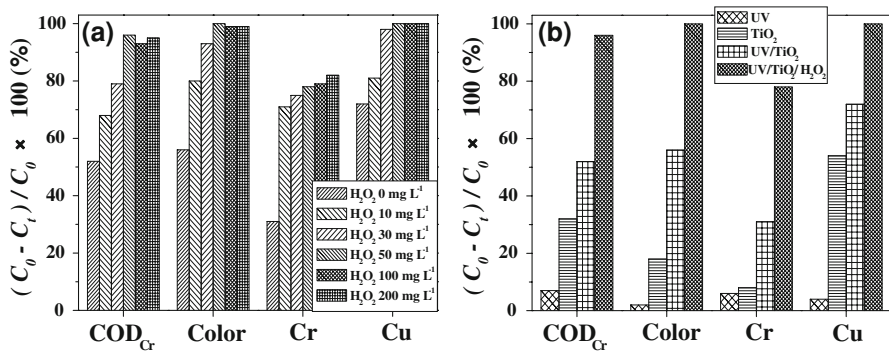


Fig. 2a, b Comparison of the removal efficiency of: **a** hydrogen peroxide concentration and **b** each unit process. Conditions: contact time 100 min, TiO₂ dosage 0.3 g L⁻¹, pH 7, temperature 20°C, humic acid 20 mg L⁻¹, heavy metals 20 mg L⁻¹, UV intensity 64 W

Effect of ozone

Figure 3 shows the effect of ozone addition on the removal efficiency of humic acid and hazardous heavy metals. The removal efficiency of humic acid and hazardous heavy metals increased with ozone concentrations ranging from 10 to 30 g m⁻³, as shown Fig. 3a. However, the removal efficiency of humic acid and hazardous heavy metals with a concentration of ozone over 20 g m⁻³ was reduced. This may be ascribed to scavenge by OH radicals caused by excessive ozone or by the attenuation of UV irradiation available to the photocatalyst. Thus, at higher ozone dosages, reactants such as humic acid are not sufficient for reactions with OH radicals, and the entire reaction efficiency is reduced. The removal efficiency of the UV/TiO₂ system is much smaller than that of the UV/TiO₂/O₃ system (see Fig. 3b). Accordingly, the addition of ozone as an oxidant increases the removal efficiency of humic acid and hazardous heavy metals due to the production of OH radicals.

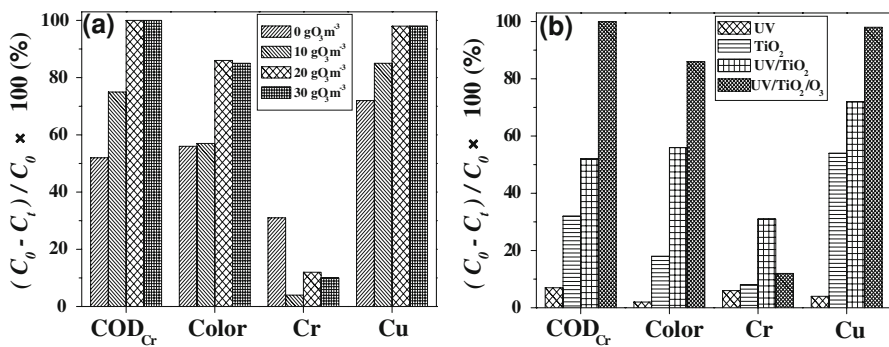


Fig. 3a, b Comparison of the removal efficiency of: **a** ozone concentration and **b** each unit process. Conditions: contact time 100 min, TiO₂ dosage 0.3 g L⁻¹, pH 7, temperature 20°C, humic acid 20 mg L⁻¹, heavy metals 20 mg L⁻¹, UV intensity 64 W

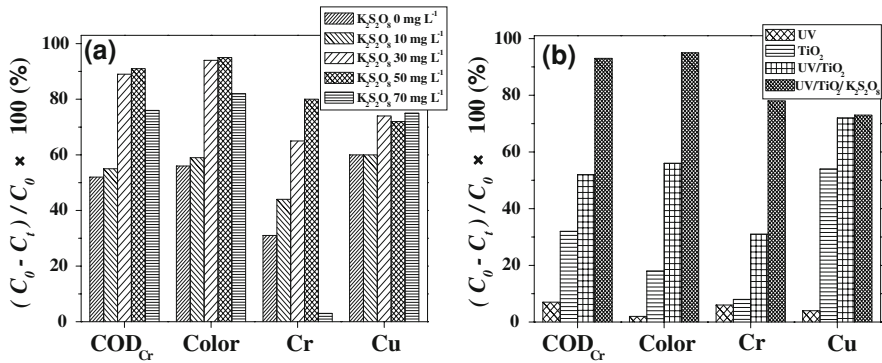


Fig. 4a, b Comparison of the removal efficiency of: **a** potassium peroxodisulfate concentration and **b** each unit process. Conditions: contact time 100 min, TiO₂ dosage 0.3 g L⁻¹, pH 7, temperature 20°C, humic acid 20 mg L⁻¹, heavy metals 20 mg L⁻¹, UV intensity 64 W

Effect of potassium peroxodisulfate

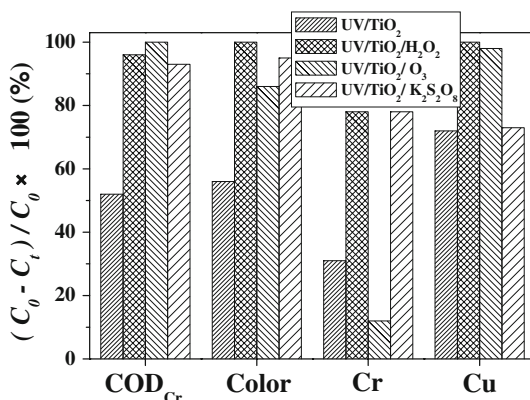
The effect of potassium peroxodisulfate (K₂S₂O₈) addition on the TiO₂ photocatalysis of humic acid and hazardous heavy metals is illustrated in Fig. 4. After a reaction time of 100 min, the removal efficiency of humic acid and hazardous heavy metals increases with the increase of K₂S₂O₈ concentration from 10 to 50 mg L⁻¹. However, K₂S₂O₈ concentration over 50 mg L⁻¹ reduces the removal efficiency of humic acid and hazardous heavy metals, as shown Fig. 4a. In Fig. 4b, the addition of K₂S₂O₈ to the UV/TiO₂ system resulted in much higher degradation compared to that of degradation without the addition of K₂S₂O₈. The potassium peroxodisulfate can generate a SO₄⁻ radical both thermally and photolytically in aqueous solutions. The SO₄⁻ radical then reacts with H₂O for OH radicals. SO₄⁻ and OH radicals produced are responsible for the rapid photodegradation of humic acid and hazardous heavy metals. In addition, the SO₄⁻ radical is a stronger electron scavenger than oxygen and is expected to improve the TiO₂ photocatalysis efficiency.

Comparison of the removal efficiency of each oxidant

Figure 5 compares the degradation efficiency of humic acid and hazardous heavy metals in the optimal conditions of the UV/TiO₂ and UV/TiO₂/oxidant systems. The oxidant concentration on the optimal conditions was H₂O₂ 50 mg L⁻¹, O₃ 20 g m⁻³, and K₂S₂O₈ 50 mg L⁻¹, respectively. The addition of oxidant into the UV/TiO₂ system resulted in a much higher degradation efficiency of humic acid and hazardous heavy metals compared to the degradation without the addition of an oxidant. As these oxidants increase the effect of UV/TiO₂ in the degradation of organic substrates by capturing the electrons ejected from TiO₂, the probability of recombination of electrons and holes will decrease. The degradation efficiency of UV/TiO₂/oxidant processes for the removal of humic acid and hazardous heavy metals was much greater in the case of the UV/TiO₂/H₂O₂ system using H₂O₂ as an

Fig. 5 Comparison of the removal efficiency of humic acid and hazardous heavy metals on each unit process.

Conditions: contact time 100 min, TiO_2 0.3 g L^{-1} , pH 7, temperature 20°C , humic acid 20 mg L^{-1} , heavy metals 20 mg L^{-1} , UV intensity 64 W , H_2O_2 50 mg L^{-1} , O_3 20 g m^{-3} , $\text{K}_2\text{S}_2\text{O}_8$ 50 mg L^{-1}



oxidant. This may be ascribed to the production of a greater amount of OH radicals in the UV/TiO₂/H₂O₂ system compared to the production in other systems.

Conclusions

This study investigated the degradation of humic acid and hazardous heavy metals on UV/TiO₂/oxidant systems. The addition of oxidants such as a hydrogen peroxide, ozone, and potassium peroxodisulfate in the UV/TiO₂ system was shown to increase the degradation efficiency for the removal of humic acid and hazardous heavy metals. The optimal concentration of oxidants was H₂O₂ 50 mg L^{-1} , O₃ 20 g m^{-3} , and K₂S₂O₈ 50 mg L^{-1} , respectively. The degradation efficiency of UV/TiO₂/oxidant systems was much greater in the case of an UV/TiO₂/H₂O₂ system due to the production of a greater amount of OH radicals. Therefore, the UV/TiO₂/H₂O₂ system using hydrogen peroxide as an oxidant is recommended by us as the most promising process for the removal of humic acid and hazardous heavy metals.

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