

Comparative Evaluation of the Removal Characteristic of Ibuprofen by UV/H₂O₂ and UV/S₂O₈²⁻ Processes

Minhwan Kwon¹, Seonbaek Kim¹, Yejoon Yoon¹, Tae-Mun Hwang², and Joon-Wun Kang^{1,†}

¹ Department of Environmental Engineering, Yonsei University, 234, Maeji-ri, Heungeop-myeon, Wonju-si, Gangwon-do, 220-710, Republic of Korea

² Water Resources and Environmental Research Division, Korea Institute of Construction Technology, 2311, Deawha-dong, Ilsan-gu, Goyang-si, Gyeonggi-do, 411-712, Republic of Korea

[†] Corresponding author: jwk@yonsei.ac.kr

Key words: Advanced oxidation process; Hydroxyl radical; Ibuprofen; Sulfate radical

INTRODUCTION

A substantial number of pharmaceuticals are continuously being released into the environment and have been detected in various aquatic systems (Halling-Sorensen et al., 1999). Because many pharmaceuticals are resistant to conventional water-treatment processes, a more effective process to remove the pharmaceuticals is urgently needed (Kim and Tanaka, 2009).

The UV/H₂O₂ process, which is a kind of advanced oxidation processes (AOPs), is used as an alternative process due to the generation of the OH radical that has an excellent removal efficiency of the persistent organic matter. However, the potential of alternative AOPs to improve the removal efficiency or to reduce the undesired by-products is always interest. The UV/S₂O₈²⁻ process is an emerging AOP due to the generation of the SO₄⁻ radical that is known to be a very strong oxidant (redox potential of 2.43 V).

This study compared the two processes, UV/H₂O₂ and UV/S₂O₈²⁻, in terms of the radical generation, reaction mechanism, and scavenging effect in the natural and synthetic solutions. To make comparative evaluations, the model pharmaceutical compound ibuprofen (IBF) and the radical probe compound para-chlorobenzoic acid (pCBA) were used.

MATERIALS AND METHODS

UV photolysis experiments

The photo degradation experiments were carried out in a bench-scale quasi-collimated beam apparatus (Bolton and Linden, 2003) equipped with two 11 W low-pressure lamps (Philips Co., Netherlands). All test solutions were placed in a petri dish at a depth of about 0.786 cm (50 mL of each solution). A small stir bar was placed inside the Petri dish to ensure homogeneous UV exposure. The UV fluence (mW/cm²) was determined using a calibrated radiometer equipped with a 254 nm detector (UVX Radiometer, UVP Co., USA).

Analytical methods

A high performance liquid chromatography (HPLC, Gilson Inc., USA) equipped with a reverse phase column (Xbridge™ C18 5.0 μm, 4.6 mm x 250 mm), a degasser, an auto-sampler, and a UV/Vis wavelength detector was used for analysis of IBF. The mobile phase was 23% v/v A (5 mM phosphoric acid) and 77% v/v B (methanol), and the detector wavelengths were 222 nm. The concentration of H₂O₂ was measured by an H₂O₂ assay test kit (colorimetric with test strips, Merckoquant®). The molar absorption coefficients of IBF and the absorbance of solution were measured at 254 nm using a UV spectrophotometer (Cary-50, Varian).

The dissolved organic carbon (DOC) was analyzed using a TOC analyzer-TOC-V_{CPH/CPN} (Shimadzu Co., Japan). Alkalinity was measured by titration with 0.02 N H₂SO₄ to the methyl orange endpoint. The pH values were measured with a pH meter (Thermo, ORION 3 STAR, US) calibrated with pH 4, 7, and 10 buffer solutions.

RESULTS AND DISCUSSION

In the UV direct photolysis process, IBF was very slowly removed (0.00015 cm²mJ⁻¹). This is due to the low molar absorption coefficient (ϵ , 2.56 M⁻¹cm⁻¹) and the quantum yield (Φ , 0.192 mole ein⁻¹) of IBF (Wols and Hofman-Caris, 2012), which are important parameters that influence the removal efficiency of pharmaceuticals and other organic compounds during UV irradiation processes.

To observe if the removal efficiency in the UV/H₂O₂ and UV/S₂O₈²⁻ processes is enhanced compared with the UV direct photolysis process, each oxidant (H₂O₂ or S₂O₈²⁻) was initially added at levels of 0.2 mM and 2 mM before irradiation. Fig. 1 shows the removal rate constants of IBF according to the initial concentration of oxidants in the UV/H₂O₂ and UV/S₂O₈²⁻ processes. In both processes, the removal efficiency of IBF increased as the concentration of additives increased, but the increased removal rate in the UV/S₂O₈²⁻ process was significantly higher than that in the UV/H₂O₂ process. To investigate the difference in removal rates, the second-order rate constants between IBF and the OH radical and between IBF and the SO₄⁻ radical were calculated by experimental method using the following equation (e.g. [1]) (Pereira et al., 2007).

$$k_{\text{radical,IBF}} = k_{\text{radical,pCBA}} \left(\frac{\ln\left(\frac{[\text{IBF}]_T}{[\text{IBF}]_0}\right) - \ln\left(\frac{[\text{IBF}]_D}{[\text{IBF}]_0}\right)}{\ln\left(\frac{[\text{pCBA}]_T}{[\text{pCBA}]_0}\right) - \ln\left(\frac{[\text{pCBA}]_D}{[\text{pCBA}]_0}\right)} \right) \quad [1]$$

The calculated second-order rate constant between the OH radical and IBF ($k_{\text{OH,IBF}} = 5.91 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) is about five times higher than the calculated second-order rate constant between the SO₄⁻ radical and IBF ($k_{\text{SO}_4^-, \text{IBF}} = 1.15 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$), but the removal efficiency of IBF in the UV/S₂O₈²⁻ process is higher than that in the UV/H₂O₂ process. A plausible reason is that the generation yield of the SO₄⁻ radical in the UV/S₂O₈²⁻ process is higher than the yield of the OH radical in the UV/H₂O₂ process

due to higher molar absorption coefficient ($\epsilon_{\text{S}_2\text{O}_8^{2-}}$, 44 M⁻¹cm⁻¹) and quantum yield ($\Phi_{\text{S}_2\text{O}_8^{2-}}$, 1.4 mole ein⁻¹) of S₂O₈²⁻ than H₂O₂ ($\epsilon_{\text{H}_2\text{O}_2} = 19 \text{ M}^{-1}\text{cm}^{-1}$ and $\Phi_{\text{H}_2\text{O}_2} = 1.0 \text{ mole ein}^{-1}$) (Deng et al., 2013).

The shape of the removal rate increase is different for the two processes (Fig. 1). The removal rate increase in the UV/S₂O₈²⁻ process shows a linear line with the initial concentration of S₂O₈²⁻ whereas the removal rate increase in the UV/H₂O₂ process describes a parabola with the initial concentration of H₂O₂. The reason for this difference can be explained by the second-order rate constant between the additive and the generated radical ($k_{\text{OH,H}_2\text{O}_2} = 2.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$, $k_{\text{SO}_4^-, \text{S}_2\text{O}_8^{2-}} = 6.6 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$) and the rate constant of each radical-radical recombination reaction ($k_{\text{OH,OH}} = 5.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, $k_{\text{SO}_4^-, \text{SO}_4^-} = 7.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$). The high reactivity of OH radical with H₂O₂ and OH radical can lead to the decreased removal rate in excess amount of H₂O₂ condition of UV/H₂O₂ process.

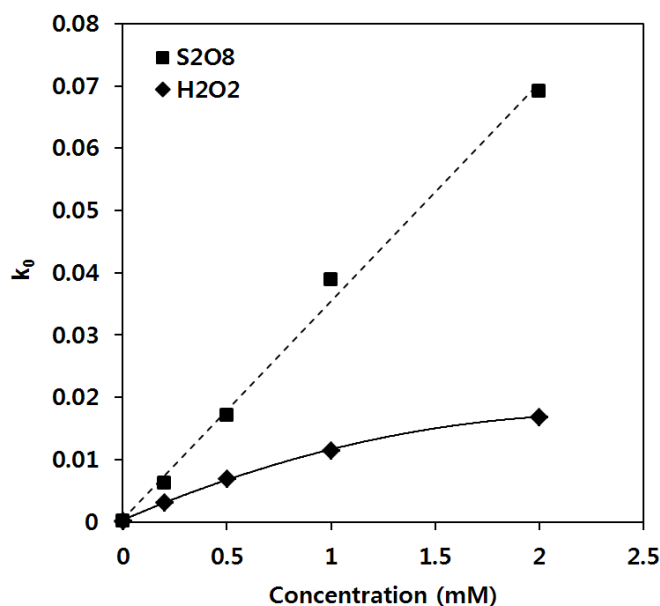


Fig.1. Effect of hydrogen peroxide (H₂O₂) and persulfate (S₂O₈²⁻) concentration on k₀ value of IBF removal by UV/H₂O₂ and UV/S₂O₈²⁻ processes ([IBF]₀ = 10 μM, UV irradiation = 0.35 mW/cm², reaction time = 600 s)

This study has shown different reaction characteristics and mechanisms between the OH radical and the SO₄⁻ radical in various water conditions that included synthetic solutions (alkalinity, pH, Cl⁻, NO₃⁻, and SO₄²⁻) and wastewater reuse plant waters (inlet water and RO treated water).

CONCLUSIONS

From this study, it appears that the UV/H₂O₂ and UV/S₂O₈²⁻ processes can effectively remove IBF. The second order rate constant of SO₄⁻ radical with IBF is lower than between OH radical and IBF, but the removal rate in the UV/S₂O₈²⁻ process is higher than the UV/H₂O₂ process from the higher production of SO₄⁻ radical than OH radical in same condition. The removal rate increase in the UV/S₂O₈²⁻ process shows a linear line with the initial concentration of S₂O₈²⁻ whereas the removal rate increase in the UV/H₂O₂ process describes a parabola curve, which meaning that excess amounts of H₂O₂ dose decrease the removal efficiency. In the scavenging test using the synthetic and natural source water, the removal rates of IBF by the two processes were different according to the conditions. These results suggest an alternative to choice an efficient UV-AOP process according to the water quality.

REFERENCES

- Bolton, J.R. and Linden, K.G. "Standardization of methods for fluence (UV dose) determination in bench-scale UV experiments", *J Environ Eng-Asce*, 129: 209-215 (2003)
- Deng, J., Shao y., Gao, N., Xia, S., Tan, C., Zhou, S., and Hu, S. "Degradation of the antiepileptic drug carbamazepine upon different UV-based advanced oxidation processes in water", *Chem Eng J*, 222;150-158 (2013)
- Halling-Sorensen, B., Nielsen, S.N., Lanzky, P.F., Ingerslev, F., Lutzhoft, H.C.H., and Jorgensen, S.E. "Occurrence, fate and effects of pharmaceutical substances in the environment - A review", *Chemosphere*, 36; 357-394 (1998)
- Kim, I., Tanaka, H. "Photodegradation characteristics of PPCPs in water with UV treatment", *Environ Int*, 35; 793-802 (2009)
- Pereira, V.J., Weinberg, H.S., Linden, K.G., and Singer, P.C. "UV degradation kinetics and modeling of pharmaceutical compounds in laboratory grade and surface water via direct and indirect photolysis at 254 nm", *Environ Sci Technol*, 41;1682-1688 (2007)
- Wols, B.A. and Hofman-Caris, C.H.M. "Review of photochemical reaction constants of organic micropollutants required for UV advanced oxidation processes in water", *Water Res*, 46;2815-2827 (2012)

Many options, one leading concept.

New intelligent multiple lamp solution for Low Pressure lamps 120 - 800W.

High efficiency, analog and digital controls and preprogrammed lamp characteristic settings for optimal lamp life.



UVineo

The best solution in UV Disinfection

Nedap Light Controls Europe | Head Office | Parallelweg 2 | 7141 DC Groenlo | The Netherlands | +31 (0)544 471888

Nedap Light Controls North America | 14A Industrial Way | Atkinson | NH 03811 | USA | +1 603.458.2089

info@nedap-lightcontrols.com | www.nedap-lightcontrols.com

 **nedap** | light controls

World leader in UV lamp drivers