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UVA photolysis of bromine for emerging contaminant removal in water

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Highlights:

- **HOBr and OBr^- are photolyzed by UVA_{365} radiation with an innate quantum yield of 0.082 and 0.014 mole $Einstein^{-1}$.**
- **The modified kinetic model enables the prediction of radical concentrations and emerging contaminant removal in the UVA/bromine AOP.**
- **The UVA_{365}/bromine AOP generated $BrO^•$, $Br_2^{•-}$, $Br^•$, and $HO^•$ at a concentration of ~10^{-13}, ~10^{-13}, ~10^{-14}, and ~10^{-14} M**

Keywords: Advanced oxidation process; UVA; bromine

INTRODUCTION

Ultraviolet (UV)-based advanced oxidation processes (AOPs) are gaining popularity for degrading emerging contaminants in water and wastewater treatment. Enabling energy-efficient UV sources (e.g., UVA-LEDs and solar light) for emerging contaminant removal would make the UV-AOPs more sustainable in the context of the United Nations' Sustainable Development Goals and carbon neutrality. We herein propose a sustainable AOP based on the bromine photolysis by UVA radiation sources.

Bromine (HOBr/OBr^-) is commonly used as an alternative disinfectant to free chlorine in small-scale water and wastewater systems, such as swimming pools, ships, and oil and gas platforms (World Health Organization, 2018). The UV photolysis of bromine generates $HO^•$, $Br^•$, $Br_2^{•-}$, and $BrO^•$, and their contributions to emerging contaminant removal have been demonstrated in systems using low-pressure UV lamps that emit light at 254 nm (Guo et al., 2023). Given the high absorption of UVA radiation by bromine (332 M^{-1} cm^{-1} for OBr^- at 329 nm) (Fig. 1), we hypothesized that bromine could be photolyzed by UVA radiation to produce radicals for emerging contaminant degradation in water. In small water systems with high access to solar light (consisting of 4.5% UVA), introducing the UVA/bromine AOP to these systems would reduce the energy consumption for emerging contaminant removal.

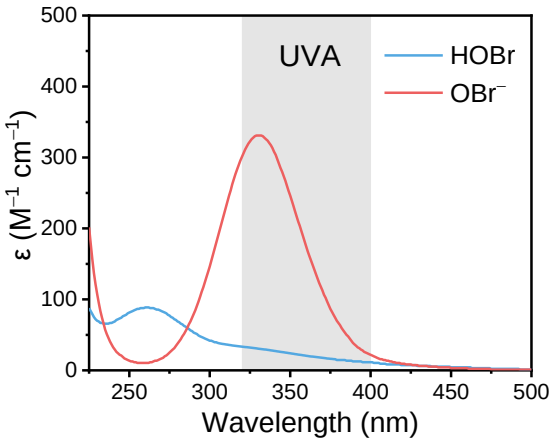

Fig. 1. The molar absorption coefficients (ε) of free bromine and bromamines.

METHODOLOGY

The photochemical experiments were conducted using a UV-LED device that emitted light at 365 nm, with an incident fluence rate (E_0) of 2.76 mW cm^{-2}. To determine the quantum yields of HOBr and OBr$^-$ photolysis, a test solution of 20 mL was dosed with 20-μM bromine and exposed to UVA radiation at 365 nm at pH 6.0 and 11.0 (adjusted by phosphate buffer and NaOH solution, respectively). Samples were collected at predetermined time intervals and analyzed for residual bromine concentration. To determine the removal of the selected micropollutant, carbamazepine (CBZ), in the UVA$_{365}$/bromine AOP, tests were conducted in a similar manner, except that the test solution was dosed with 2-μM CBZ beside bromine and buffered at pH 8.0 by phosphate buffer. Samples were collected for CBZ analysis.

The concentrations of bromine, radicals, and CBZ in the UVA/bromine process were simulated by a kinetic model using Kintecus software (Version 4.55). The kinetic model was established by Guo et al. (Guo et al., 2023) and further modified in this study.

RESULTS AND CONCLUSIONS

To estimate the innate quantum yields of HOBr and OBr$^-$ photolysis at 365 nm, the bromine decay upon UVA$_{365}$ irradiation was determined at pH 6.0 and 11.0, respectively (Fig. 2). The fitting of bromine decay was then conducted using the modified model by setting the bromine photolysis rate as the only variable in the simulation. The fitted fluence-based pseudo-first-order rate constants for HOBr and OBr$^-$ photolysis were 1.08 × 10^{-6} and 1.32 × 10^{-6} m^2 J^{-1}, respectively. With the molar absorption coefficients of HOBr (19 M^{-1} cm^{-1}) and OBr$^-$ (142 M^{-1} cm^{-1}) at 365 nm, the innate quantum yields (Φ_{inn}) of HOBr and OBr$^-$ at 365 nm were calculated to be 0.082 and 0.014 mole Einstein^{-1}, respectively. Using the Φ_{inn}, the concentrations of HO$^\bullet$, Br$^\bullet$, Br$_2^{\bullet-}$, and BrO$^\bullet$ and the removal of CBZ in the UVA$_{365}$/bromine AOP at pH 8.0 were predicted by the modified model (Fig. 3). The modified model was validated by comparing with the experimental results. The simulated CBZ removal agreed with the experimentally determined removal (Fig.

3b), with all relative errors smaller than 10%. As shown in Fig. 3a, the model-predicted concentrations of $HO^{\bullet}$, $Br^{\bullet}$, $Br_2^{\bullet-}$, and $BrO^{\bullet}$ were 1.4×10^{-14}, 1.8×10^{-14}, 1.3×10^{-13}, and 7.7×10^{-13} M, respectively, in the UVA_{365}/bromine AOP at pH 8.0. CBZ was removed by 17% at pH 8.0 and a UV fluence of 1656 mJ cm^{-2} (Fig. 3b). $HO^{\bullet}$ and $Br^{\bullet}$ dominated the CBZ degradation, accounting for 43% and 52% of the overall removal, respectively. Based on the pseudo-first-order degradation rate of CBZ, ~90% removal is expected at a fluence of 20000 mJ cm^{-2}, which is a typical UV dosage in water treatment with solar light (Wang et al., 2019).

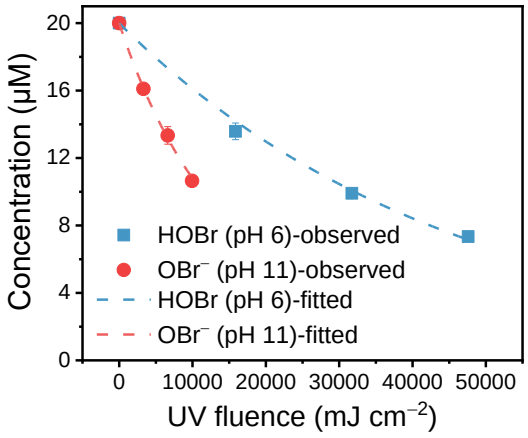

Fig. 2. The observed and fitted HOBr and OBr^- decay upon UVA irradiation at 365 nm.

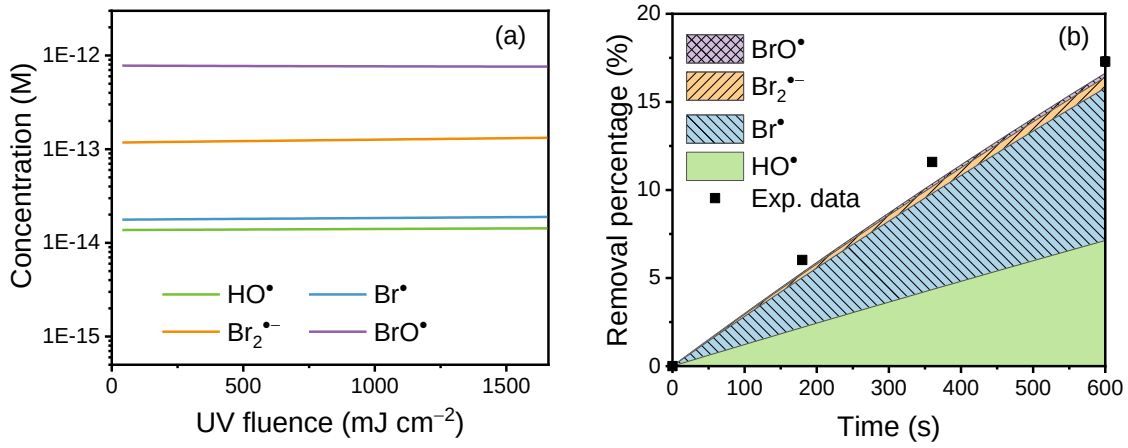

Fig. 3. The radical concentrations (a) and CBZ degradation (b) in the UVA_{365}/bromine AOP. Conditions: $[bromine]_0$ = 20 μM and pH = 8.0.

In summary, bromine can be photolyzed by UVA radiation to produce radicals for emerging contaminant removal in small water and wastewater systems (e.g., swimming pools). The kinetic model modified in this study enables the simulation of radical generation and emerging contaminant removal in the UVA/bromine AOP under different environmental and operational conditions.

ACKNOWLEDGMENTS

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