Far-UVC photolysis of peracetic acid for micropollutant degradation in water

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Highlights:

· PAA and PAA^- photolyzed by UV_{222} radiation with an innate quantum yield of 0.78 and 0.57 $Einstein^{-1}$.

· The UV_{222}/PAA AOP generates $CH_3C(O)O^•$, $CH_3C(O)OO^•$, and $HO^•$ at a concentration of $\sim 10^{-11}$, $\sim 10^{-10}$, and $\sim 10^{-13}$ M.

· The fluence-based concentration of $HO^•$ in the UV_{222}/PAA AOP was one order of magnitude higher than that in the UV_{254}/PAA AOP.

Keywords: Advanced oxidation process; Ultraviolet; Peracetic acid (PAA)

INTRODUCTION

UV-based advanced oxidation processes (UV-AOPs) combining UV irradiation with an oxidant precursor (e.g., H_2O_2) to generate reactive species are promising technologies for micropollutant abatement in water treatment. Peracetic acid (PAA) is an emerging disinfectant and oxidant for wastewater treatment, including some small systems (e.g., industrial effluent and ballast water) (Ao et al., 2021). Compared to the UV/H_2O_2 AOP, the UV/PAA AOP has several advantages: 1) it generates both hydroxyl radicals ($HO^•$) and carbon-centered radicals (e.g., $CH_3C(O)O^•$) which complement each other for micropollutant degradation (Luukkonen and Pehkonen, 2017); 2) the O-O bond dissociation energy is lower in PAA (170 kJ/mol) than in H_2O_2 (210 kJ/mol), resulting in easier activation of PAA than H_2O_2 by UV radiation.

Recent studies found enhanced performance of the UV-AOP (e.g., UV/H_2O_2 AOP) when switching the UV radiation source from conventional low-pressure UV (UV_{254}) to far-UVC (UV_{222}). We herein propose a UV_{222}/PAA AOP, taking advantage of the 10-fold higher absorption of PAA at 222 nm than 254 nm (Fig. 1 (a)). Given the higher PAA absorption, UV_{222} photolysis of PAA is hypothesized to generate higher concentrations of radicals for more efficient micropollutant degradation than UV_{254}, which would reduce the energy consumption and contribute to the

carbon neutrality of small water and wastewater systems (e.g., industrial effluent and ballast water treatment).

METHODOLOGY

PAA stock solution (23% w/w PAA, 10% w/w H_2O_2) was prepared through the reaction between acetic acid and H_2O_2 under the catalysis of H_2SO_4. The photochemical experiments were conducted using a KrCl* excimer lamp that emitted light at 222 nm, with an incident fluence rate (E_0) of 0.18 mW cm^{-2} and four monochromatic low-pressure mercury UVC lamps emitting light at around 254 nm (UV$_{254}$). To determine the quantum yields of PAA and PAA$^-$ photolysis, a test solution of 20 mL was dosed with 100-μM PAA and exposed to UV radiation at 222 nm at pH 6.0 and 10.0 (adjusted by phosphate buffer and NaOH solution, respectively). Samples were collected at predetermined time intervals and analyzed for residual PAA concentrations. To determine the concentrations of the hydroxyl radical (HO$^•$), acetic acid radical (CH$_3$C(O)O$^•$), and peracetic acid radical (CH$_3$C(O)OO$^•$) in the system, nitrobenzene (NB), bisphenol A (BPA), and phenol were selected as probe compounds. The degradation experiments of three probe compounds were conducted at pH 7.0 upon UV$_{222}$ and UV$_{254}$ radiation. The 20-mL test solution was dosed with 2 μM of each probe compound and 100 μM of PAA. At predetermined time intervals, samples were collected and analyzed to determine the degradation rate constants of the three probe compounds by the UV$_{222}$/PAA and the UV$_{254}$/PAA processes Radical concentrations at UV$_{222}$ were then calculated from the probe compound degradation based on competition kinetics (Fig. 2). The concentrations of radicals that were generated in the UV/PAA process were determined using competition kinetics based on the degradation rate constants of the selected compounds (Huang et al., 2023). All tests were conducted in duplicate.

The concentrations of PAA in the UV/PAA AOP were simulated by a kinetic model using Kintecus software (Version 4.55). The kinetic model was established by Zhang et al. (2020) and further modified in this study.

RESULTS AND CONCLUSIONS

The molar absorption coefficients of PAA and PAA$^-$ were 50.17 and 1208.69 M^{-1} cm^{-1} at 222 nm, and 3.18 and 110.85 M^{-1} cm^{-1} at 254 nm, respectively (Fig. 1 (a)). Using the PAA photolysis experiment data and modified model by setting the photolysis rate as the only variable in the simulation, the fitted fluence-based pseudo-first-order rate constants for PAA and PAA$^-$ photolysis were determined. With the molar absorption coefficients, the innate quantum yields of PAA and PAA$^-$ at 222 nm were calculated to be 0.78 and 0.57, respectively.

According to Fig. 1 (b), the apparent pseudo first order rate constant of the degradation of NB, phenol, and BPA in the UV$_{222}$/PAA process was 2.5×10^{-4} s^{-1}, 8.4×10^{-4} s^{-1}, and 1.0×10^{-4} s^{-1} respectively. The radical concentrations were then calculated by using these data.

As shown in Fig. 1 (c), [HO$^•$]$_{SS}$/E$_0$, [CH3C(O)O$^•$]$_{SS}$/E$_0$, and [CH3C(O)OO$^•$]$_{SS}$/E$_0$ at UV$_{222}$ were 2.2×10^{-13}, 1.3×10^{-11}, and 1.4×10^{-10} M cm^2 mW^{-1}, respectively. [HO$^•$]$_{SS}$/E$_0$ was about one order of magnitude higher than in the UV$_{254}$/PAA AOP (i.e., 3.4×10^{-14} M cm^2 mW^{-1}). The higher

concentration of HO$^\bullet$ in the UV$_{222}$/AOP might be attributed to the higher absorption at 222 nm and comparable quantum yields at these two wavelengths (i.e., 0.78 and 0.86 for PAA at 222 nm and 254 nm). CH$_3$C(O)O$^\bullet$ was undetectable in the UV$_{254}$/PAA AOP. Given the higher rate constant of HO$^\bullet$ with probe compounds (three to four orders of magnitude higher than carbon-centered radicals), though its concentration was three orders of magnitude lower than carbon-centered radicals, it played the dominant role in the AOP (Cai et al., 2017; Sun et al., 2018; Zhang and Huang, 2020). Combining this and the higher concentration of HO$^\bullet$, the UV$_{222}$/PAA AOP could have a higher efficiency in removing micropollutants than the UV$_{254}$/PAA AOP.
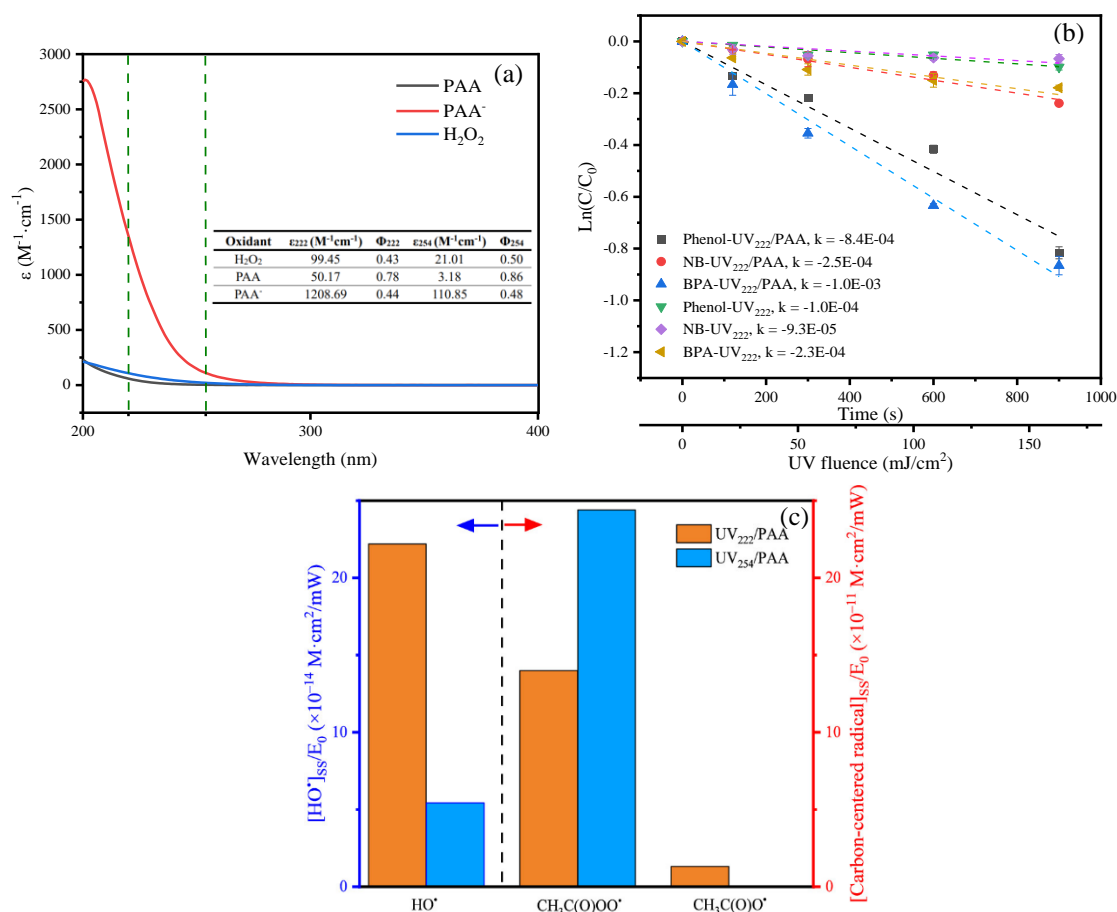

Fig. 1 (a) The molar absorption coefficients (ε) and innate quantum yields (Φ) of PAA, PAA$^-$, and H$_2$O$_2$ at UV$_{222}$ and UV$_{254}$. (b) The degradation of probe compounds in the UV$_{222}$/PAA AOP. Conditions: [NB]$_0$ = [phenol]$_0$ = [BPA]$_0$ = 2 µM, [PAA]$_0$ = 100 µM, pH = 7.0. (c) The radical concentrations normalized by fluence rates in the UV/PAA systems.

To sum up, UV$_{222}$ can photolyze PAA more efficiently than UV$_{254}$, thereby forming higher concentrations of radicals for micropollutant degradation. The performance of the UV$_{222}$/PAA AOP in removing emerging contaminants in tap water will be evaluated in the future, to assess its application in point-of-use (POU) water treatment.

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