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Organic Micropollutants Removal through Performic Acid-UV Photolysis: kinetics and wastewater matrix influence

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Summary

Performic acid (PFA) is an emerging disinfection oxidant increasingly used in wastewater treatment. This study investigated the effectiveness of PFA activated by UV-C photolysis for the removal of 6 pharmaceutical compounds. Compared to PFA alone, PFA/UV was found to be more efficient, with pseudo-first-order rate constants of the pharmaceutical compounds varying between $4.76 \pm 0.32 \times 10^{-3}$ and $1.14 \pm 0.46 \text{ min}^{-1}$, with CBZ being the least reactive and DCF the most reactive compound. Comparison between PFA/UV and $\text{H}_2\text{O}_2/\text{UV}$ processes revealed that the PFA/UV process was more efficient in removing pharmaceutical compounds due to the production of specific reactive radicals during the process and not only OH° radicals. In addition, the reactivity of furosemide was found to be highly influenced by these specific radicals, rather than OH° radicals, as demonstrated by its rate constant being 15 times higher in the PFA/UV process compared to $\text{H}_2\text{O}_2/\text{UV}$. The removal of pharmaceuticals in treated wastewater effluent resulted in a removal rate ranging from 30% to 60%, with DCF being the most effectively removed compound, as expected due to its high pseudo-first-order rate constant in phosphate buffer solution.

Keywords: organic peracid, reactive oxygen species, advanced oxidation processes, kinetic rate constants, wastewater

Introduction

Performic acid (PFA) is an emerging disinfectant used to remove pathogenic microorganisms. Its use in wastewater (WW) treatment has increased over the past decade due to its high performance in removing fecal contamination indicators (*E.coli* and enterococcus) in domestic and combined sewer overflow reservoirs, compared to other oxidants such as peracetic acid and chlorine (Chhetri et al., 2017; Ragazzo et al., 2020; Rocher & Azimi, 2021). PFA has also been found effective against antibiotic-resistant bacteria (Campo et al., 2020) and has gained popularity due to its low production of disinfection by-products (DBPs), such as halogenated DBPs and N-nitrosamines, compared to ozone and chlorine under typical water treatment conditions ($< 10 \text{ mg/L}$) (Dell'Erba et al., 2007; Rocher & Azimi, 2021).

Despite its effectiveness for disinfection in WW, little attention has been given to its ability to remove organic micropollutants (OMPs) present in WW. Laboratory tests conducted by Luukkonen et al. (2015) using Bisphenol A spiked in deionized water at 60 mg/L and oxidized with 20 mg/L of PFA resulted in no degradation after 1 hour of reaction. In a pilot test conducted by Gagnon et al. (2008), PFA was used to remove 8 organic compounds (clofibric acid, ibuprofen, naproxen, triclosan, carbamazepine, diclofenac, salicylic acid, and 2-hydroxy-ibuprofen) from primary-treated WW. After 18 minutes of reaction time with a PFA dose of 6 mg/L , less than 8% of removal was observed for all compounds. Additionally, a full-scale experiment conducted previously found that PFA had a poor oxidation power with organic compounds present in WW, such as phenols at PFA doses of $0.7\text{-}1.4 \text{ mg/L}$ and reaction times of 14-30 min, or with hormones such as estrone at doses of $2\text{-}20 \text{ mg/L}$ within 30 min of reaction (Ragazzo et al., 2020). The poor removal rates of OMPs by

PFA led to the development of an advanced oxidation process (AOP) based on the coupling between PFA and UV photolysis, which has been previously explored for peracetic acid (Cai et al., 2017) in order to improve the removal of refractory OMPs. This novel AOP is based on the potential production of organic radicals. The objectives of this study were to (1) evaluate the efficiency of PFA/UV for the removal of OMPs, and (2) evaluate the influence of wastewater matrix on the removal of OMPs.

Materials and methods

The PFA solution was prepared using a method previously developed, which involved catalyzing the reaction between formic acid and hydrogen peroxide (H_2O_2) with the addition of sulfuric acid (Nihemaiti et al., 2022). The obtained PFA stock solution was periodically checked for PFA and residual H_2O_2 concentration using iodometric titration methods (Rocher & Azimi, 2021), and was found to be $19.2 \pm 1.2\%$ and $19.5 \pm 1.4\%$ in mass, respectively. The kinetics of 6 pharmaceutical compounds were investigated using PFA/UV through a self-made collimated beam apparatus with UV-C lamps emitting at a maximum of 254 nm. The studied OMPs were lidocaine (LID), furosemide (FUR), diclofenac (DCF), acetaminophen (ACT), sulfamethoxazole (SMX), and carbamazepine (CBZ). Individual oxidation experiments were conducted by spiking $1 \mu\text{M}$ of each OMP in 100 mL of phosphate buffer solution (PBS, 10 mM, pH 7.0). To achieve an initial concentration of $500 \mu\text{M}$ of PFA, a precise volume of the stock solution was added to the beaker containing each OMP of interest, and the solution was immediately placed under the UV-C lamp for irradiation (in less than 5 seconds after PFA addition) to initiate the reaction. As PFA solutions always contain a significant amount of residual H_2O_2 concentration, and $\text{H}_2\text{O}_2/\text{UV}$ is a well-known Advanced Oxidation process (AOP) due to its generation of OH^\bullet radicals, control experiments were conducted to assess the contribution of the background H_2O_2 concentration. These experiments involved replacing PFA with pure H_2O_2 at the same concentration as in the PFA solution. To stop the reaction at each UV dose interval, 1.5 mL of the sample was withdrawn and injected into an amber vial containing excess $\text{Na}_2\text{S}_2\text{O}_3$, then stored at 4°C before analysis by high-performance liquid chromatography coupled to a diode array detection. The removal of 6 OMPs by PFA/UV was also evaluated in treated biological WW effluent collected from the Seine Amont wastewater treatment plant by spiking $1 \mu\text{g/L}$ of the 6 OMPs (in addition to their initial concentrations in the WW effluent). After 1 hour, the reaction was stopped, and the sample was extracted and analyzed by high-resolution mass spectrometry. The experiments were performed in duplicate or more.

Results and discussion

Preliminary experiments (data not shown) indicated that PFA reactivity was low with the 6 studied OMPs in phosphate buffer solution (PBS) (Nabintu Kajoka et al., 2023, under review). The most reactive compounds were found to be LID and FUR, with pseudo-first-order kinetic rate constants (k_{obs}) of $6.71 \pm 0.41 \times 10^{-2}$ and $1.19 \pm 0.51 \times 10^{-2} \text{ min}^{-1}$, respectively. A similar k_{obs} ($5.33 \pm 0.72 \text{ min}^{-1}$ with 20 mg/L of PFA) was previously observed for LID under the same conditions (10 mM PBS at pH 7.0) (Nihemaiti et al., 2022). The remaining OMPs reacted with PFA, with k_{obs} ranging from $2.12 \pm 0.32 \times 10^{-4} \text{ min}^{-1}$ for CBZ to $4.00 \pm 0.73 \times 10^{-3} \text{ min}^{-1}$ for SMX. Compared to PFA alone, the PFA/UV process increased the reactivity of the OMPs from 20 to 300 times, except for LID, where the reactivity only doubled. This high reactivity is likely due to the reactive radicals produced by the PFA/UV process, such as OH^\bullet and carbon-centered radicals. Preliminary experiments conducted to indirectly identify OH^\bullet radicals through the oxidation of parachlorobenzoic acid (data not shown) revealed that the $\text{H}_2\text{O}_2/\text{UV}$ coexisting in the PFA/UV process is the unique source of the produced OH^\bullet radicals. Experiments conducted by replacing PFA with pure H_2O_2 at the same concentration as that contained in the PFA solution (30.34 mg/L of H_2O_2) revealed that LID, SMX, DCF, and ACT were more degraded (≈ 3 to 4 times) by PFA/UV than $\text{H}_2\text{O}_2/\text{UV}$, and up to 15 times more for FUR. These results indicate that, in addition to OH^\bullet radicals produced by $\text{H}_2\text{O}_2/\text{UV}$, other reactive species are present in the PFA/UV system and are responsible for the higher degradation observed in PFA/UV for the listed OMPs. The reactivity of CBZ (the most recalcitrant OMP) with PFA/UV was similar to that with $\text{H}_2\text{O}_2/\text{UV}$, indicating that its

slightly higher degradation by PFA/UV compared to PFA alone was only due to the presence of OH° radicals and that other radicals had no effect on its degradation.

The reactivity of OMPs observed in PBS was confirmed by experiments conducted with treated WW. The removal of OMPs varied from $\approx 30\%$ to 60% , with the exception of CBZ, which was only eliminated at a rate of 7% . DCF showed the highest removal rate and was the most reactive compound based on pseudo-first-order rate constants (Table 1). Based on k_{obs} , which resulted in the total elimination of OMPs except CBZ in PBS in less than 10 minutes of reaction with 31 mg/L of PFA, high removal rates were expected in real treated WW. However, the low removal of some compounds, such as ACT (28%) can be attributed to some competition effects with WW constituents.

Table 1. Pseudo-first-order rate constants (k_{obs} , min^{-1}) of pharmaceutical compounds under PFA/UV and $\text{H}_2\text{O}_2/\text{UV}$. Experimental conditions: $[\text{pharmaceutical}]_0 = 1 \mu\text{M}$ in 10 mM of PBS at $\text{pH } 7.0$, $[\text{PFA}]_0 = 500 \mu\text{M}$, $[\text{H}_2\text{O}_2]_0 = \mu\text{M}$, UV fluence = $5.0 \pm 0.1 \text{ W/m}^2$.

Compounds	$k_{\text{PFA/UV}}$ (min^{-1})	$k_{\text{H}_2\text{O}_2/\text{UV}}$ (min^{-1})
Lidocaine	$(1.17 \pm 0.12) \times 10^{-1}$	$(2.64 \pm 0.47) \times 10^{-2}$
Furosemide	$(3.76 \pm 0.9) \times 10^{-1}$	$(2.52 \pm 0.17) \times 10^{-2}$
Sulfamethoxazole	$(3.33 \pm 0.47) \times 10^{-1}$	$(1.14 \pm 0.18) \times 10^{-1}$
Diclofenac	$(1.14 \pm 0.46) \times 10^0$	$(3.30 \pm 0.42) \times 10^{-1}$
Acetaminophen	$(3.49 \pm 0.32) \times 10^{-1}$	$(9.40 \pm 1.68) \times 10^{-2}$
Carbamazepine	$(4.76 \pm 0.32) \times 10^{-3}$	$(4.09 \pm 0.18) \times 10^{-3}$

Conclusions

In this study, PFA was activated by UV-C photolysis to generate OH° and organic radicals for the removal of 6 pharmaceutical compounds. The pseudo-first-order rate constants of the 6 pharmaceutical compounds varied between $4.76 \pm 0.32 \times 10^{-3} \text{ min}^{-1}$ for CBZ and $1.14 \pm 0.46 \times 10^0 \text{ min}^{-1}$ for DCF. The comparison between PFA/UV and $\text{H}_2\text{O}_2/\text{UV}$ processes revealed that, apart from OH° radicals, other reactive species were present in the PFA/UV system and contributed to the removal of the pharmaceutical compounds, especially FUR, which was the most impacted. This finding suggests the advantage of using PFA/UV process over the known process $\text{H}_2\text{O}_2/\text{UV}$ or PFA alone. The removal of pharmaceutical compounds in treated WW resulted in a removal rate ranging from 30% to 60% , with DCF the most removed compound as expected from its high rate constant.

The identification of individual species of radicals produced by PFA/UV is currently investigated and their contribution to OMP degradation will be estimated and presented.

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