19th International Conference on Environmental Science and Technology

CEST 2025

Kos, Greece, 3 to 6 September 2025

Removal of organic micropollutants by quaternary treatments controlled by optical sensors

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Abstract. Advanced oxidation processes (AOPs) are widely applied to degrade persistent organic pollutants. In view of new stringent regulations on organic micropollutants, the real-time monitoring of AOPs became crucial to fulfil the high quality standards over time. A fluorescence sensor was employed to investigate the real-time monitoring of ozone and UV doses during AOPs designed to remove organic micropollutants from wastewater. Based on fluorescence data obtained in real-time with the sensor, accurate predictive models of UV and ozone doses were developed for two different tertiary wastewater effluents. This approach shows how fluorescence sensors can be used to optimize AOPs in real-time in terms of efficiency, chemicals and energy consumption.

Keywords: Contaminants of emerging concern (CEC), endocrine disrupting chemicals, pharmaceuticals, PFAS, wastewater.

1. Introduction

By 2045, all wastewater treatment plants serving over 150,000 population equivalents (p.e.) must implement quaternary treatment to remove a broad spectrum of micropollutants, including pharmaceuticals, personal care products, microplastics, and PFAS (per- and polyfluoroalkyl substances). Plants serving over 10,000 p.e. may also be required to adopt this treatment based on risk assessments. In particular, European Directive (2024/3019) mandates a minimum 80% removal efficiency for at least six indicator substances, such as diclofenac, carbamazepine, and venlafaxine. As a result, the importance of real-time control of AOP effectiveness has grown significantly where rapid responses to operational changes are essential. Controlling key parameters, such as ozone and UV doses in real-time plays a pivotal role in optimizing AOP efficiency, minimizing the risk of insufficient CEC degradation, and mitigating by-product generation (Deniere et al., 2021). Effective ozone dosing strategies must account for temporal variations in EfOM load and reactivity. Similarly, determining the actual UV dose delivered to target compounds can be challenging, as it often deviates from predictions due to fluctuating water quality. Fluorescence spectroscopy has emerged as a rapid, sensitive, and cost-efficient method for characterizing organic matter and monitoring CEC removal in WWTPs (Korshin et al., 2018). However, its potential for real-time AOP optimization remains largely unexplored. This study addresses this gap by introducing an innovative real-time AOP control method utilizing an online tryptophan-like fluorescence sensor.

2. Materials and methods

Experimental investigations were conducted under relevant environmental conditions using a pilot-scale system installed downstream of two different wastewater reuse facilities. Processes tested included O_3, O_3/H_2O_2, UV, and UV/H_2O_2. Ozone doses ranged between 2 and 9 mg/L, UV doses between 150 and 1600 mJ/cm², and H2O2 doses between 4 and 9 mg/L. details about the experimental procedures can be found in prior publications (Marino et al., 2024; 2025).

3. Results and discussion

The sensor provided real-time feedback on treatment performance, detecting rapid water quality changes due to adjustments in operational parameters (e.g., flowrate, UV dose) on the two wastewaters (WW-1, WW-2) tested. For instance, Figure 1 shows the real-time fluorescence data recorded by the sensor during O_3 based AOPs in WW-2 (Marino et al., 2025). Correlation models were developed between real-time fluorescence data and applied theoretical doses. Strong correlations were observed for ozone dose predictions ($R^2 = 0.94$) in both WW-1 and WW-2 and for UV dose predictions ($R^2 > 0.96$) in WW-1 (Figure 2). These results demonstrate the novel effective application of fluorescence sensors as real-time control tools for UV and O_3 doses in AOPs. This optimization approach has the potential to reduce chemical and energy consumption, lower by-product formation, and enhance overall process efficiency. The findings of this study pave the way for the development of advanced real-time monitoring systems that can adapt to dynamic water quality conditions, leading to cost savings and a reduced environmental footprint for quaternary treatments.

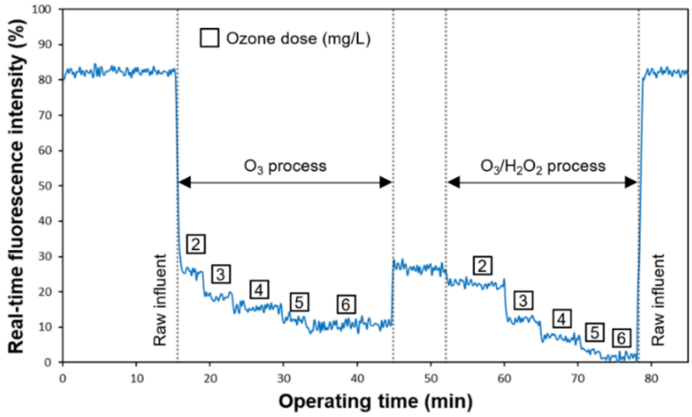

Figure 1. Real-time fluorescence trends recorded by the sensor during O_3 in WW-2 (Marino et al., 2025).

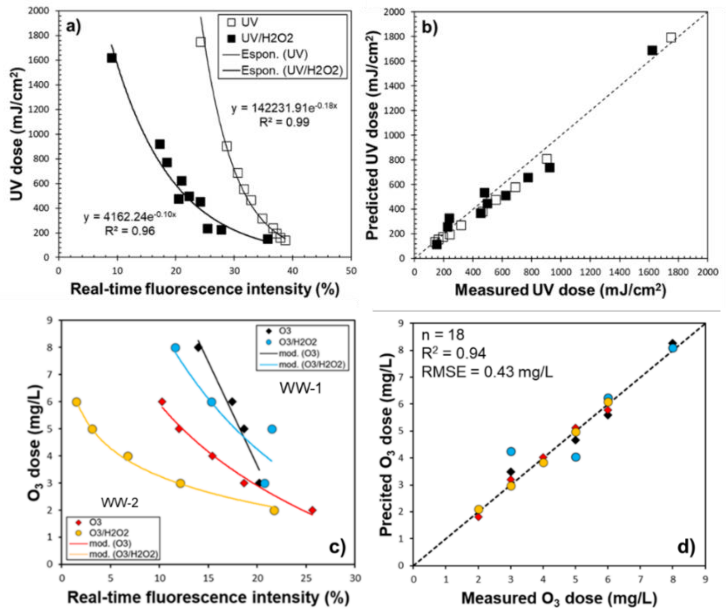

Figure 2. Correlation models for UV dose (a, b) and ozone dose (c, d) prediction (Marino et al., 2024; 2025).

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Acknowledgements

This study was partially supported by the European Union (NextGeneration EU), through the MUR-PNRR project SAMOTHRACE (ECS00000022).