Coupling artificial neural network and fluorescence spectroscopy to control CEC removal during AOPs

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Abstract Contaminants of emerging concern (CEC) include anthropogenic compounds frequently detected in natural and engineered water systems at trace concentrations. CEC are relevant due to their high persistence and mobility and adverse effects on humans, wildlife, ecosystems. One of the main challenges is the lack of real-time monitoring systems of CEC and process parameters at wastewater treatment plants (WWTPs). In this study, fluorescence indexes and artificial neural networks (ANNs) were used to track the removal of CEC from secondary and tertiary WWTP effluents during O_3- and UV-based advanced oxidation processes operated at pilot scale. Results show that indexes served as effective surrogate parameters to monitor CEC removal within individual wastewater types. The application of an ANN model improved the correlation (R^2 = 0.87) between CEC and fluorescence indexes, highlighting the potential for fluorescence-based monitoring of CEC removal regardless of WWTP effluent type.

Keywords: Contaminants of emerging concern; real-time monitoring; advanced oxidation process; fluorescence indexes; artificial neural network.

1. Introduction

Contaminants of emerging concern (CEC) include a broad range of anthropogenic compounds (e.g., poly/perfluoroalkyl substances, pharmaceuticals, personal care products) recently identified or suspected to pose risks to human and ecosystem health even at trace levels. Conventional wastewater treatment plants (WWTPs) are not designed to remove CEC. Advanced oxidation processes (AOPs) have demonstrated high efficacy in removing a wide array of CEC. AOPs rely on reactive oxidative species like ozone (O_3) and hydroxyl radicals (·OH), produced by the decomposition of O_3 and H_2O_2 in water, often enhanced by ultraviolet (UV) irradiation. AOP optimisation requires real-time monitoring of CEC removal and process conditions (e.g., flow rate, oxidant dose, exposure time). Standard analytical techniques are expensive and time-intensive, limiting routine use. Fluorescence spectroscopy measures the intensity of the radiation emitted by fluorophores when excited by incident light. Dissolved organic matter (DOM) in water contains diverse fluorophores. The determination of fluorescence intensity at single pairs of excitation/emission (ex/em) wavelengths is rapid, non-destructive, and possible through field deployable sensors (Marino et al., 2025). Changes in DOM fluorescence have been correlated with CEC removal by AOP, allowing fluorescence indexes to serve as indirect indicators. Artificial neural networks (ANNs) are being applied in the wastewater treatment sector for modelling, control, and optimisation tasks (Jadhav et al., 2023). Research integrating ANNs with fluorescence for monitoring CEC removal in AOP-treated wastewater is limited. This study evaluates the removal of 43 CEC in real secondary and tertiary WWTP effluents using O_3- and UV-based AOPs and assesses fluorescence index changes as predictors of removal efficiency. Fluorescence-based ANN was developed and applied to effectively predict CEC removals from dissimilar wastewaters and different AOP schemes.

2. Materials and methods

The experimental activity was carried out in a wastewater reuse facility (WWRF) located in the Apulian region (Italy) which produces reclaimed water from the effluent of a close municipal WWTP. The WWRF operates a full-scale tertiary treatment consisting of coagulation, sedimentation, and disinfection. Additionally, the WWRF includes a pilot-scale (up to 8 m^3/h) AOP treatment consisting of O_3/H_2O_2 unit (0-12 mg/L), UV lamp (53-305 mJ/cm^2) and lamella clarifier. Three different wastewaters (WWs) were used: WW-A is the tertiary WWRF effluent stored in an environmental buffer (artificial lake), WW-B is the secondary WWTP effluent, WW-C is the tertiary WWRF effluent. WW-A and WW-B were subjected to the pilot-scale AOP under varying oxidant doses. WW-C was subjected to the O_3/H_2O_2 treatment unit at different O_3:H_2O_2 ratios. A total of 43 CEC were identified in the influent WWs through liquid chromatography coupled with high-resolution mass spectrometry. Fluorescence intensities of five ex/em pairs (i.e., I_i, i=1-5) were measured using a Shimadzu RF-5301 spectrometer. Feedforward three-layer (input, hidden, and output) networks were developed. Datasets were randomly divided into 50% training, 25% validation, and 25% testing sets and network performances were evaluated through the mean squared error function.

3. Results and discussion

For each WWs and AOPs, the larger the oxidant dose the higher the CEC removal. High O_3-reactive CEC (e.g., carbamazepine, diclofenac, and trimethoprim) exhibited high to moderate removal efficiencies regardless of O_3 doses. For lower O_3-reactive CEC, ·OH contributed for their degradation. Given the low UV doses applied, only high photo-susceptible CEC (e.g., diuron) were affected by the UV stage. Other CEC exhibited moderate (e.g., atenolol) to high (e.g., sucralose) recalcitrance to AOPs. The largest decreases in fluorescence were determined for protein/tryptophan-like indexes (I_2 225/340 nm and I_4, 275/345 nm) followed by humic- and fulvic-like compounds (I_5 345/440 nm and I_3 245/440 nm). Matrix effects were observed by comparing either CEC and fluorescence removals between WW-A and WW-B: the latter experienced greater removals due to scavenging effects of inorganic species (chloride, nitrite) more largely present in WW-A. Linear regression analyses were conducted on datasets A, B, and C. When correlating individual CEC with single I_i (i=1-5) (normalised values), some high R^2 were determined. For instance, atenolol and trimethoprim strongly correlated (R^2=0.84-0.93) with I_i (i=1-5) in WW-A, R^2=0.88 for caffeine-I_5 in WW-B, and I_5 had R^2 ranging from 0.59 to 0.95 for all CEC of WW-C. Even stronger correlations were found when considering individual CEC and combinations of indexes (e.g., I_3-I_4-I_5). However, when encompassing data of CEC common to all the WWs the correlations were weaker. To improve an ANN model was developed to predict CEC removal (output) through I_3-I_4-I_5 (input). The obtained strong correlation (R^2 = 0.87) (Fig. 1) suggests the chance of developing a 'universal' fluorescence-based ANN model for the monitoring of CEC removal.

4. Conclusion

This study proved that CEC removal by AOP can be effectively monitored through fluorescence measurements. Strong linear regressions were determined for individual CEC and I_i (i=1-5) indexes, while correlations weakened when encompassing CEC from dissimilar WWs. The developed ANN model demonstrated the capability to predict the overall removal of 3 CEC (common to all the tested WWs) treated by different O_3-based AOP schemes.

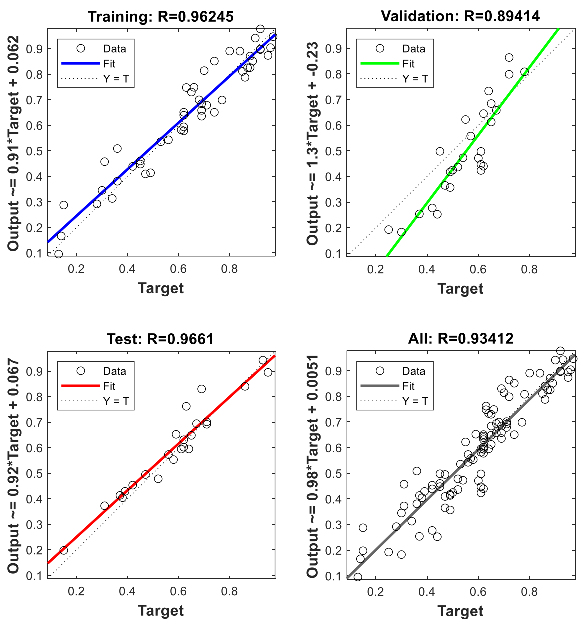

Figure 1. ANN model for predicting CEC

References

Jadhav, A.R., Pathak, P.D., Raut, R.Y., 2023. Water and wastewater quality prediction: current trends and challenges in the implementation of artificial neural network. Environ Monit Assess 195, 321.

Marino, L., Gagliano, E., Santoro, D., Roccaro, P., 2025. Fluorescence sensor enabled control of contaminants of emerging concern in reclaimed wastewater using ozone-based treatment processes. Water Research 268, 122616.

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