Degradation behavior of effluent organic matter and comparison of different oxidation processes during ozonation, UVC/H$_2$O$_2$ and UVC/persulfate revealed by fluorescence analysis

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This paper reports a new insight into the evolution of Effluent organic matters (EfOM) during ozonation and advanced oxidation process (AOPs), such as UV/H$_2$O$_2$ and UV/PS, revealed by fluorescence-PARAFAC. EfOM posed risks to receiving aquatic environments due to the complex compositions [1]. Based on previous reports, ozonation and advanced oxidation processes showed excellent performance during organic micropollutants removal and biotoxicity reduction. The principal reactions during ozonation and AOPs were shown in Table 1. However, it was lack of knowledge on evolution of EfOM during ozonation and AOP. Fluorescence coupled with PARAFAC was a useful tool to trace the EfOM [2]. So this study introduced a new insight into the EfOM transformation and oxidant kinetics during different oxidation processes.

Methods

All experiments were performed under batch test. DOC was determined using a TOC -VCPH analyser. UV absorbance was measured with a UV-VISIBLE Spectrophotometer. Fluorescence EEMs were created using a fluorescence Spectrophotometer. PARAFAC was modeled with DOMfluor Toolbox.

Results and Discussion

The water quality of secondary effluent was shown in Table 2. Four components were identified based on fluorescence-PARAFAC, including three humic-like substances (C1，C2 and C4) and a tryptophan-like substances (C3) (Fig. 1). C1, C2 and C4were related to the humic-like substances, and C3 was related to protein-like substances. These components were commonly found in secondary effluent [2]. The degradation of UV$_{254}$, DOC and PARAFAC components during all processes fitted well with pseudo-first-order kinetic. The degradation of PARAFAC components during ozonation was faster than that during AOP. With higher oxidants dosage, indicators removal rates and oxidants decline rates were both increased. This made a new insight into the use of oxidants during AOP.

Conclusion

Fluorescence components were more sensitive indicators than UV$_{254}$ and DOC in indicating the evolution of EfOM. Ozonation was an outstanding pretreatment process for AOP for its higher apparent reaction rate with fluorescence indicators. Moreover, efficiencies of ozonation and AOP could be observed by monitoring the change of fluorescence components, thus controlling the oxidants dosage dynamically.

Table 1. Principal reactions in this study

	Reaction
ozonation	$O_3 + OH^- \rightarrow HO_2^- + O_2$
	$O_3 + HO_2^- \rightarrow HO\cdot + O_2^{\cdot-} + O_2$
	$O_3 + O_2^{\cdot-} \rightarrow O_3^{\cdot-} + O_2$
	$O_3^{\cdot-} + H^+ \rightarrow HO_3\cdot$
	$HO_3\cdot \rightarrow HO\cdot + O_2$
	$O_3 + NOM \rightarrow products$
UV/H_2O_2	$H_2O_2 + h\nu \rightarrow 2HO\cdot$
	$EfOM + HO \rightarrow products$
	$HCO_3^- + HO \rightarrow CO_3^{\cdot-} + H_2O$
	$NH_3/HO\cdot$
UV/PS	$(S_2O_8)^{2-} + h\nu \rightarrow 2SO_4^{\cdot-}$
	$SO_4^{\cdot-} + H_2O \rightarrow HO\cdot + SO_4^{2-} + H^+$
	$NOM + SO_4^{\cdot-} \rightarrow products$
	$HCO_3^- + SO_4^{\cdot-} \rightarrow HCO_3\cdot + SO_4^{2-}$

Table 2 Water quality of secondary effluent

UV_{254} (cm^{-1})	DOC (mg/L)	Ammonia (mg/L)	pH
0.16	8.78	4.3	7.7

C1 (QSU)	C2 (QSU)	C3 (QSU)	C4 (QSU)
64.43	57.03	101.16	46.97

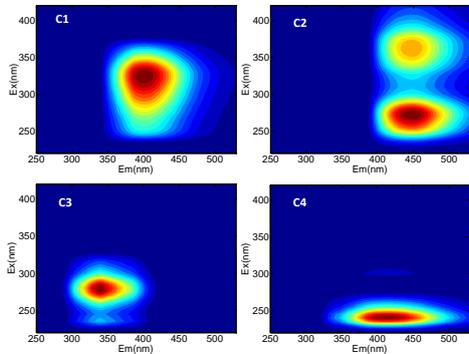| Alkalinity (mg/L as CaCO$_3$)	Conductivity (μS/cm)
106.4	108.2

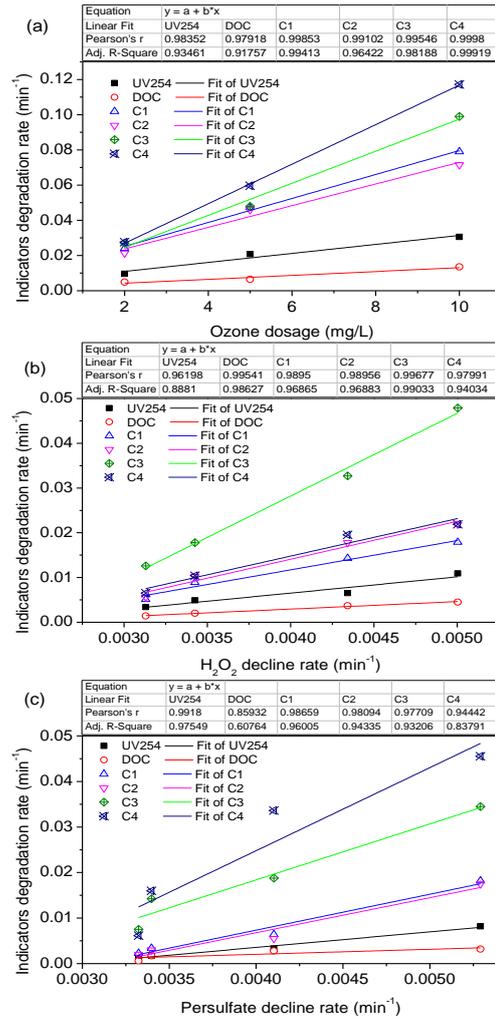Fig. 1 Fluorescence components identified by PARAFAC

Fig. 2 Degradation rates versus ozone dosage or oxidants decline rates during ozonation and AOP

REFERENCES:

[1] I. Michael-Kordatou, C. Michael, X. Duan, X. He, D. D. Dionysiou, M. A. Mills, D. Fatta-Kassinos, Dissolved effluent organic matter: Characteristics and potential implications in wastewater treatment and reuse applications, Water Res. 77 (2015) 213-248.

[2] D. D. Phong, J. Hur, Non-catalytic and catalytic degradation of effluent dissolved organic matter under UVA-and UVC-irradiation tracked by advanced spectroscopic tools, Water Res. 105 (2016) 199-208.