UV-VIS spectral analysis as process tool to assess ozone reactivity for secondary effluent

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Keywords: ozonation; on-line UV-VIS; micropollutants; effluent organic matter

INTRODUCTION

Due to upcoming (European) legislation, operators of municipal wastewater treatment plants (MWWTPs) are preparing for plant upgrades with advanced technologies to remove organic micropollutants (MPs) from secondary effluent. Ozonation has shown to be a promising technology for MP removal (Oneby et al. 2011, Gerrity & Snyder 2011) but the basic control strategies currently applied (e.g. constant dose, flow based) prevent cost-effective operation due to sub-optimal ozone dosing. Additionally, MP analyses are time, cost and labour intensive which enhances the need for more readily available (online) and less expensive measurement techniques (e.g. UV-VIS). Although the potential value of simple surrogate models, correlating the removal of UV_{254} absorbance (UVA_{254}) to MP removal, has been indicated (Bahr et al. 2007, Wert et al. 2009, Dickenson et al. 2009, Audenaert et al. 2013) significant research is still required to further establish and validate this type of surrogate models. Furthermore, multi-wavelength (i.e. full UV-VIS spectrum) approaches are scarcely used while the robustness and predictive power of such models might potentially be higher.
This work aimed to assess real-time UV-VIS spectra to quantify the degradation kinetics of ozone and effluent organic matter (EfOM). These insights can potentially be the basis for further research towards the use of these spectra in on-line monitoring strategies to obtain a fast pre-assessment of MP removal during ozonation of secondary MWWTP effluent.

METHODS

Secondary effluent was collected from the WWTP in Harelbeke (Belgium) operated by Aquafin. After collection, but prior to any experimentation, effluent samples were passed through a rapid sand filter to remove suspended solids. Subsequently, batch ozonation experiments were conducted by adding specific amounts of freshly prepared ozone stock solution to the effluent samples. The ozone concentration of the stock solution (± 100 ppm O_3) was determined using the indigo method (Bader & Hoigne, 1981). The effluent used was collected on two different dates and experiments were performed at different temperatures (10 & 20 °C) to assess the influence on the reaction mechanisms. In total 8 experiments were conducted, relating to different effluent samples, initial ozone doses and temperatures. Online and offline UV-VIS spectra (200-800 nm) were recorded and remaining ozone concentrations at different time intervals (ranging from 20 s until 30 min) were analyzed.

RESULTS AND DISCUSSION

An assessment was made of the reactivity of ozone towards the effluent organic matter based on the method developed by Puxty et al. (2006). For this, only an online UV-VIS profile was used. The decay of the remaining ozone concentration and EfOM is represented by two differential equations, given below. The evolution of UVA_{254} is presented in Figure 1.

$$\delta C_{O3}/_{\delta t} = -k_{O3}.C_{O3}.C_{EfOM} \qquad \delta C_{EfOM}/_{\delta t} = -k_{O3}.\gamma_{EfOM}.C_{O3}.C_{EfOM}$$

with C_{O3} = ozone concentration; C_{EfOM} = effluent organic matter concentration; k_{O3} = reaction rate of ozone; γ_{EfOM} = yield factor of EfOM

A unity spectrum for EfOM (200–800 nm; relative to UVA_{254} = 1 cm^{-1}) is retrieved from the online UV-VIS measurements before dosage. A unity spectrum for ozone (200-800 nm; related to 1 mg l^{-1}) was readily available. Multiplying the unity spectrum with the concentrations retrieved by the differential equations above, a full spectrum is determined at each time interval. Both spectra can thus be used to determine a composed UV-VIS spectrum in time, containing both the absorption by ozone and EfOM itself. Detailed explanation about this general calculation procedure can be found in Puxty et al. (2006). By minimizing the error between the calculated spectrum and the actual measured spectrum, k_{O3} and γ_{EfOM} were estimated. The goodness-of-fit between experimental and simulated values was quantified by calculating the Theil's inequality coefficient (TIC) according to Audenaert et al. (2010).
Using the online UV-VIS measurements (e.g. Figure 2 with a measurement frequency of 1 s^{-1}) of in total eight different experimental runs, a single value of k_{O3} and one for γ_{EfOM} could be estimated. This resulted to a good agreement (all individual TIC values < 0.3) between the measured and calculated UV-VIS spectrum (200-800 nm) for all eight experiments, independent of variations in sample conditions (Figure 3). A comparison between the modeled and measured profile at e.g. 254 nm is displayed in Figure 1. Determining the goodness-of-fit between the offline measured ozone concentration and the estimated concentration showed an overall TIC of 0.22 (< 0.3), indicating a good agreement with the independent measured values (see e.g. Figure 4).

CONCLUSION

UV-VIS measurements show great potential to be key input for control strategies of effluent ozonation processes. Current research already indicated the relationship between UVA_{254} removal and micropollutant removal. The usage of the complete UV-VIS profile, used in the presented model, can be the start of a further development towards a reliable control strategy for ozonation of secondary effluent treatment. A profound linking with micropollutant removal, possibly using some data-driven modeling (e.g. PCA), is of great importance.

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FIGURES

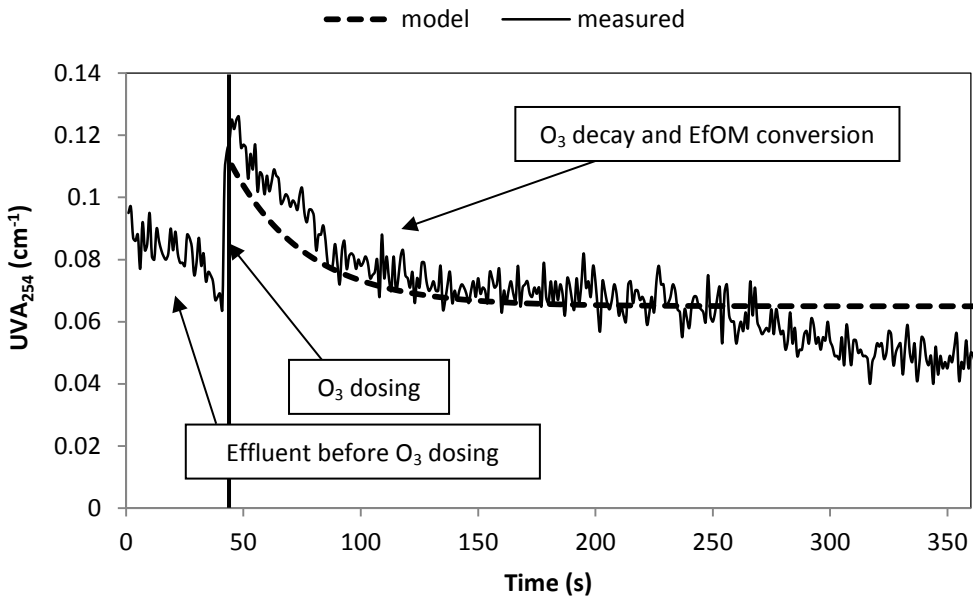

Figure 1: Lay-out of measured changes in UVA_{254} before and during the first 6 minutes of reaction time after ozone dosing (± 5 mg O_3/L; T = 10 °C) compared to the modeled profile

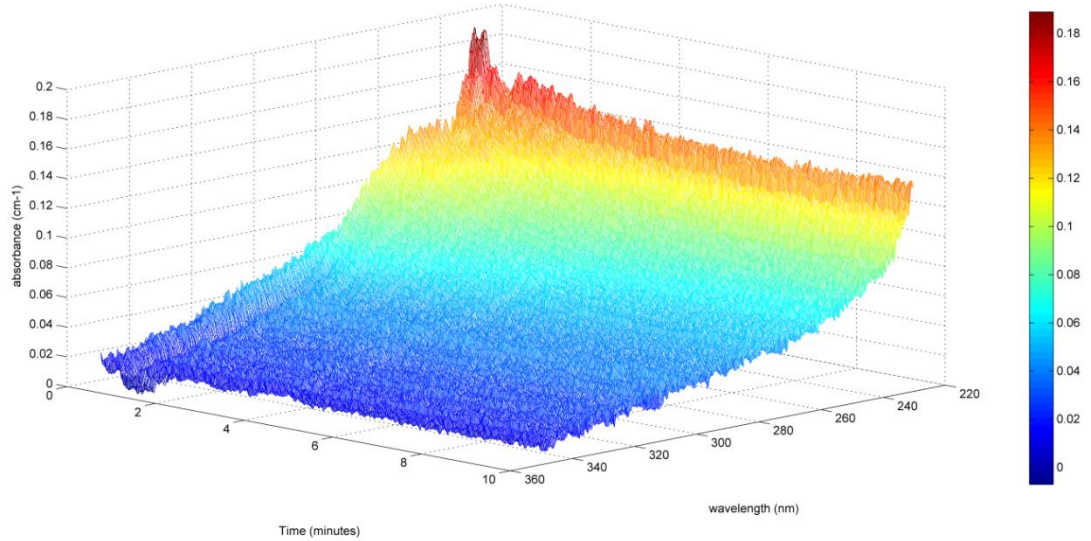

Figure 2: Online UV-VIS profile during the first 10 minutes of reaction time after ozone dosing (± 9 mg O_3/L; T = 10 °C)

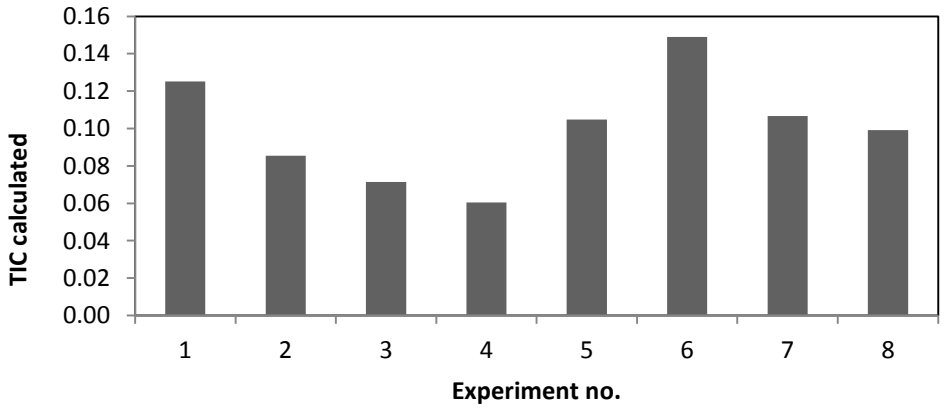

Figure 3: Goodness-of-fit (TIC) for the modeled UV-VIS spectra of 8 different experiments

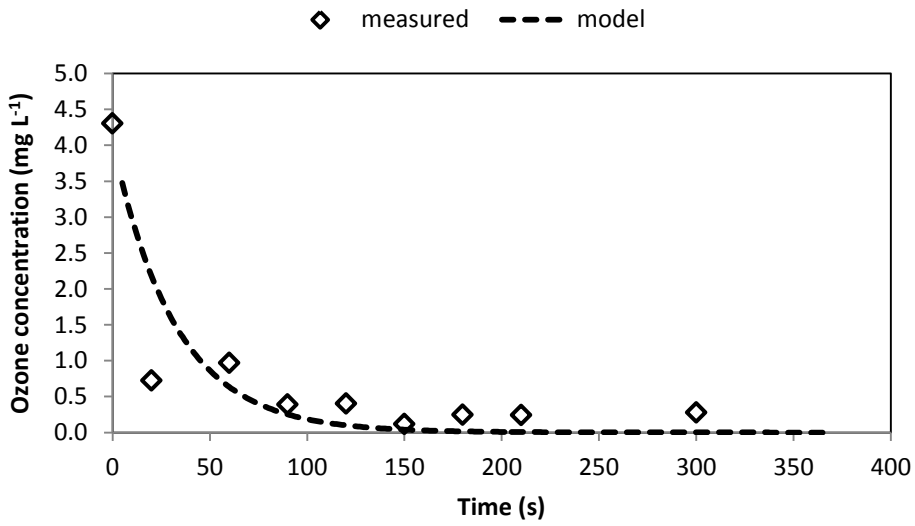

Figure 4: Comparison between measured and modeled ozone concentrations (± 5 mg O_3/L; T = 10 °C)