Real-time control of micropollutant removal from secondary effluent by ozonation

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Abstract
Ozonation has shown to be a promising technology in removing micropollutants from wastewater effluent but current basic control strategies still result in sub-optimal ozone dosing. This work aimed at applying novel, yet simple, surrogate models (based on delta UVA254), to assess the micropollutant removal on pilot-scale as a proof-of-concept. Different events and fluctuations in effluent conditions (e.g. due to rain or dry weather) were taken into account. During this variable conditions, by alternating the ozone dosed based on the required delta UVA254, a good agreement was seen between predicted and achieved removals for a broad range of micropollutants. Fouling of the online UV-VIS sensors also seemed to be depending on the type of sensor and the effluent quality.

Keywords
ozonation; pilot-scale, UV-VIS, online control strategy, micropollutants

INTRODUCTION

Ozonation for municipal waste water effluent has shown to be a promising technology for micropollutant (MP) removal (Oneby et al. 2011, Gerrity & Snyder 2011) but the basic control strategies currently applied (e.g. flow based) result in sub-optimal ozone dosing. Optimal dosing lowers operational costs but also minimizes by-product formation. Additionally, MP analyses are time, cost and labour intensive which enhances the need for complementary more readily available (online) and less expensive surrogate measurement techniques. The potential value of simple surrogate models, e.g. correlating the removal of UV absorption at 254 nm (UVA_{254}) to MP removal, has been recognized and novel empirical models have been suggested based on lab-scale experiments (Chys et al., 2015). However, significant research is still required to further scale-up and validate these models prior to full-scale application. For example, the effect of weather conditions and temporal variations on these correlations need further elaboration. Moreover, also other approaches gain interest to increase the robustness of the models. For example the use of fluorescence spectroscopy can be an added value as it could provide a more detailed view of the complete effluent matrix (Chys et al., 2015).

This work aimed at applying the developed correlations at pilot-scale as a proof-of-concept but also to investigate/evaluate the behavior when certain events/effluent variations occur. Monitoring such behavior over several weeks/months will lead to new insights for wider application of these control strategies.

MATERIALS AND METHODS

A pilot-scale ozone reactor (up to 600 l/h) was installed at a 54,000 I.E. municipal wastewater treatment plant. Secondary effluent was fed to the ozone reactor and several on-line sensors (UV-VIS, pH, conductivity, …) were used for both effluent quality monitoring as for controlling the applied ozone dosage. Additionally, samples were taken to verify the online measurements but also for only offline available measurements such as fluorescence, instant ozone demand, alkalinity, etc. Different experimental periods were applied in which the set-point varied between 25 and 40% of UVA_{254} removal (difference before and after ozone addition). Ozone dosing at pilot-scale was adjusted as such that the required UVA_{254} decrease was obtained. Based on the lab-scale settings it was expected that these settings would result in respectively a minimal removal of 30 to 70% of low ozone reactive MPs and 90 to 100% of highly ozone reactive MPs.

RESULTS AND DISCUSSION

Performance of on-line UV-VIS sensors

Online UV-VIS measurements showed a small difference with offline UV-VIS measurements for control samples (Figure 1). This could induce an underestimation of the removal as well as the fouling of the online sensors. Nevertheless, a good agreement between online and lab-measurements is seen.

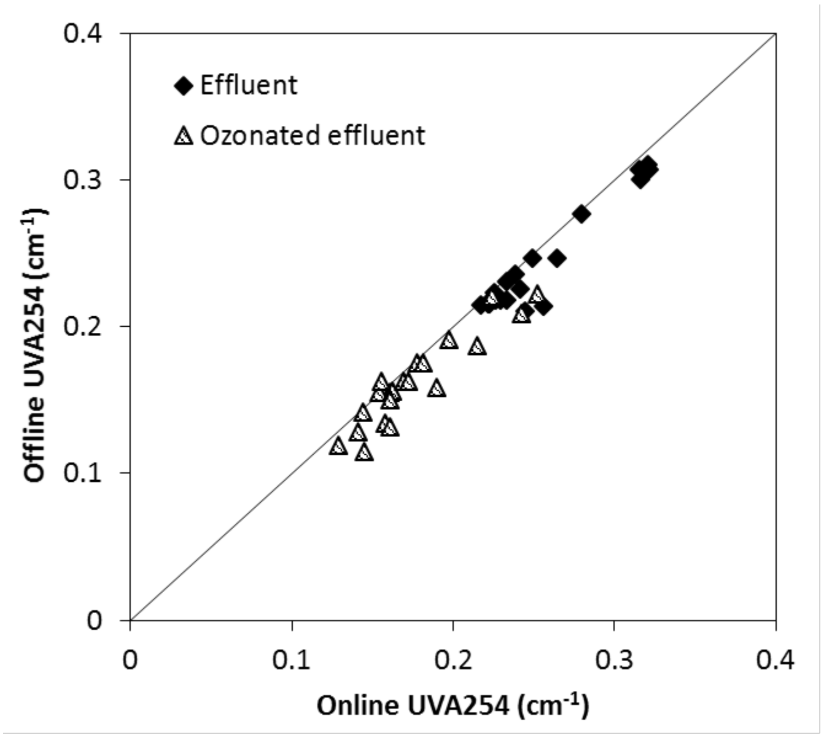

Figure 1: Comparison of online UVA254 measurements with offline sampled effluent, before and after ozonation at pilot-scale.

Prediction of pilot-scale performance

An empirical model correlating the removal of UV absorption at 254 nm (UVA_{254}) to MP removal was developed based on lab-scale experiments (Figure 2; Chys et al., 2015). These models take into account the ozone reactivity of different micropollutants. Based on this model it is expected that the applied experimental settings (25 and 40% of UVA_{254} removal) would result in respectively a minimal removal of 30 to 70% of low ozone reactive MPs and 90 to 100% of good ozone reactive MPs.

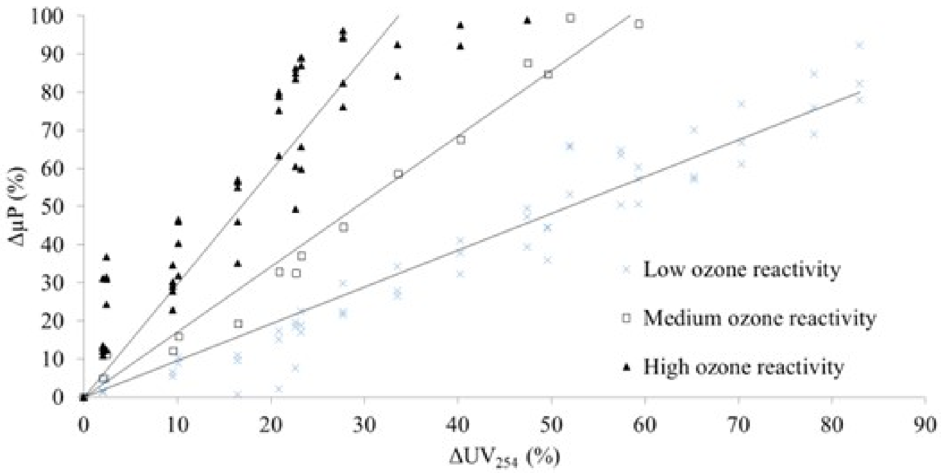

Figure 2: Correlation between delta UVA_{254} with different classes (good reactivity: e.g. diclofenac; medium reactivity: e.g. ciprofloxacin; no reactivity: flumequine) of pharmaceuticals based on their ozone reactivity

Pilot scale results

The pilot scale results showed a very good agreement between the predicted and achieved micropollutant removal. Using a set-point of 40% of ΔUVA254 resulted in very good removal, as expected, of all micropollutants. Consequently, the used control mechanisms are further evaluated mainly using the results at a set-point of 25% ΔUVA254. Based on these results, a small underestimation was seen for low and medium reactive components (Figure 3). Due to the practical aspect of the experiments, minimal fouling of the online sensors occurred during experimental trials. Therefore, the required ozone dosing to reach a removal of 25% ΔUVA254 was slightly over-estimated by the used control mechanism, leading to a higher removal of micropollutants. Applying an overdose of ozone will result in higher energy and oxygen costs. Nevertheless, a small underestimation of the micropollutant removal can be preferred to be sure that possible discharge limits are reached at any time.

Related to the highly ozone reactive components (diclofenac, levofloxacin and trimethoprim), complete removal would be expected at the imposed set-points at all times (Chys et al. 2015). Nevertheless, an average removal of approximately 90% was reached for all. It should be noted however, that all experiments were performed using real waste water effluents for the WWTP, having real occurring micropollutant concentrations. As the experiments occurred at these very low concentrations (within range of 1 µg L^{-1} to ≥ 20 ng L^{-1}), it can be expected that the limit of detection of the used measurement method will have a great influence.

Nevertheless, the presented results are of high value for full-scale applications. UVA_{254} measurements shows a great potential to serve as key input for further on-line control strategies. However, further processing and evaluation of other set-points under variable conditions will be necessary to have a broad applicable and universal strategy.

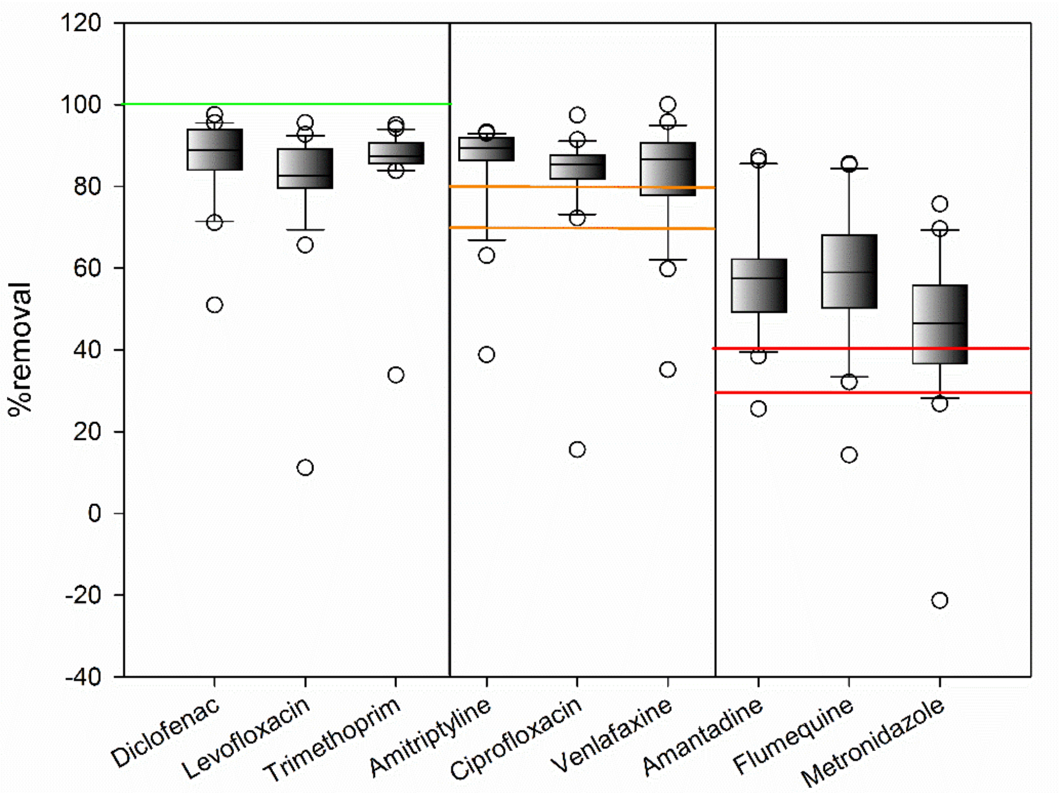

Figure 2: Achieved removal (n = 22) for 9 selected pharmaceuticals divided in three classes related with their ozone affinity (from left to right: good, medium and low ozone affinity). The colored lines indicate the predicted removal according to the used models and the applied set-point (25% delta UVA254)

CONCLUSION

The presented results are of high value for full-scale applications. Measuring UVA_{254} shows a great potential to serve as key input for further on-line control strategies. However, further processing and evaluation of other set-points under variable conditions will be necessary to have a broad applicable and universal strategy.

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