Developing monitoring and control strategies for emerging contaminant removal from wastewater using ozonation

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Introduction
Ozonation is an effective technology to remove contaminants of emerging concern (CECs, e.g. pharmaceuticals) from wastewater. However, due to a lack of adequate control strategies, current installations dose ozone suboptimally. This increases operational costs and may enhance formation of potentially toxic by-products. Furthermore, quantitative CEC measurements need advanced methods and expensive equipment, are time consuming, and can only be performed offline. Developing reliable, user friendly and real-time monitoring strategies to facilitate process control was the aim of this project. Lab-scale tests were performed to develop these strategies, while pilot-scale tests were started up to test the strategies at a real wastewater treatment plant.

Materials and Methods
Detailed empirical models for real-time prediction of CEC removal were developed at lab-scale using effluent from a 120,000 PE municipal wastewater treatment plant. Effluent samples were taken over a two month period to consider variations in effluent composition. Twenty different ozone doses were added to the individual samples (up to 15 mg O₃ L⁻¹) after addition of 9 pharmaceuticals with different reactivity towards ozone (1-10 µg/l). Spiking was performed to allow accurate determination of the pharmaceuticals, even at higher ozone doses. Before and after ozonation, pharmaceuticals were analysed with solid-phase extraction followed by liquid chromatography high-resolution mass spectrometry (UHPLC-Orbitrap MS, QExactive™) and UV-visible (UV-VIS) and fluorescence spectra were recorded. The spectroscopic techniques were selected as they can provide real-time information on the effluent composition. PARAllel Factor Analysis (PARAFAC) was applied to the raw fluorescence data in order to decompose the complex excitation-emission matrices into 5 distinct fluorescence compounds (FCs).

Results & Conclusion
The removal of the 9 pharmaceuticals was strongly correlated to both the reduction of UV-VIS and fluorescence signals. For every compound, a clear relationship could be obtained that was consistent throughout the sampling campaign. For pharmaceuticals that react fast with ozone, complete removal corresponded to a reduction of about 20% in UV signal (254 nm wavelength). For slower reacting substances, complete removal corresponded to higher reductions in UV₂⁵⁴ (50%) as more ozone was needed. The 5 FCs (FC1-5) reacted differently. FC1 was most susceptible to ozone attack. Complete removal of slow and fast reacting substances corresponded to a 40-50% and a 70-80% reduction of FC1, respectively. Relationships for fast reacting pharmaceuticals were typically almost linear until complete removal while those for slow reacting substances behaved exponentially prior to deflection. The shape of the models obtained was hence related to the reactivity towards ozone: e.g. a good correlation was obtained between literature reported rate constants (describing the reactions between ozone and the individual pharmaceuticals) and the shape and slope of the curves.
Unique and consistent correlation models for different pharmaceuticals were developed. Both UV-VIS and fluorescence could be used as surrogates for CECs removal during ozonation which is very promising for full-scale operation. The relations obtained are now tested at pilot-scale for real-time monitoring of CEC removal and control of the ozone dose.

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