



# **Ozonation and UV/hydrogen peroxide treatment of natural water and secondary wastewater effluent: experimental study and mathematical modelling**

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## Summary

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Multiple factors impose severe stress on the global water system and urban water supplies. These factors include worldwide population growth in general and in water scarce areas in particular, depletion of groundwater resources, uneven geographical spread of water resources and increasing water consumption per capita. Additionally, the occurrence of emerging contaminants such as endocrine disruptors (EDCs), pharmaceuticals and personal care products (PPCPs) is a potential risk for both the environment and human health.

Hence, the interest in advanced water and wastewater treatment systems in view of water reuse and the removal of these harmful compounds is significantly increasing. Oxidation processes, and especially ozonation and ultraviolet (UV) irradiation in combination with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) have found to be effective in this context. The UV/ $\text{H}_2\text{O}_2$  process is generally called an advanced oxidation process (AOP) as it relies on the production of the reactive hydroxyl radical ( $\text{HO}^\bullet$ ). The main advantage that these processes hold over other techniques is that target pollutants are (partially) destroyed, rather than transferred to another phase which is the case during e.g. adsorption or membrane filtration processes.

Despite the current interest and rapidly growing number of applications, the design and operation of ozone and UV/ $\text{H}_2\text{O}_2$  processes for advanced water and wastewater treatment still have to be optimized. In this context, mathematical models can be of great value as they allow for prediction of process efficiency at different operational and water quality conditions and, hence, allow for virtually testing a multitude of scenarios before actual implementation in practice. However, despite extensive research on the reactions taking place during oxidation, the chemical complexity of the processes currently impedes modelling efforts. The presence of dissolved organic matter (DOM) is the main reason for the system complexity associated with “real water” oxidation. This knowledge gap has to be filled in order to enable optimal process design and operation and hence, cost effective advanced water treatment.

In this PhD dissertation, ozonation and UV/ $\text{H}_2\text{O}_2$  treatment of surface water and secondary treated municipal wastewater were studied. Lab-scale or full-scale reactors were used for experimenting and to calibrate and validate mechanistic models with an emphasis on conversion of DOM. As such, a combination of practical experimentation and mathematical modelling at various operational and water quality conditions was the major scientific contribution of the work performed during this study. Research was performed at both lab- and full-scale.

A full-scale ozone reactor for drinking water treatment ( $60,000 \text{ m}^3 \text{ d}^{-1}$  treatment capacity) was modelled using a kinetic model consisting of a limited set of equations. The model including key processes such as ozone decomposition, organic carbon removal, disinfection and

bromate formation was implemented in the modelling platform WEST and calibrated using historical data collected over a period of 300 d. The absorption coefficient at 254 nm ( $UV_{254}$ ) was used as a surrogate for DOM. The predicting performance was verified with a goodness-of-fit test and key parameters were determined through a local sensitivity analysis. Furthermore, different scenario analyses were conducted to study the system's behaviour at different operational conditions. Model parameters involving  $UV_{254}$  (both rate constants and stoichiometric coefficients) strongly affected model output. Some parameters with respect to bromate and bacteria showed to be only, but to a large extent, sensitive to their associated concentrations. The model was able to describe the operation of the full-scale ozone reactor, although further data collection for extensive model validation is necessary.

A more complex kinetic ozone decomposition model was used to study the impact of DOM on ozone and  $HO^\bullet$  concentrations. Local and global sensitivity analyses were used to determine the most important elementary reactions and to understand the reaction mechanism. Only seven of the twenty-eight first and second order rate constants showed to impact ozone and  $HO^\bullet$  concentrations. Processes involving  $HO^\bullet$  scavenging by inorganic carbon were of minor importance. Mass-transfer related parameters  $k_L a$  and ozone saturation concentration ( $[O_3^*]$ ) were of major importance in all cases. Hence, it is of extreme importance that these parameters are determined with high accuracy. It was shown that the aqueous ozone concentration is extremely sensitive to parameters involving DOM at very low scavenger concentrations implying that impurities should always be considered in models, even in ultrapure water systems. Due to the limited importance of many of the parameters, simplification of the elementary radical scheme should be considered. On the other hand, a model extension with regard to reactions involving DOM should be performed in order to improve the applicability of mechanistic ozonation models.

Multiple mechanistic models describing the  $UV/H_2O_2$  process have been proposed in literature. One of them was used to predict the behaviour of a full-scale reactor treating secondary treated wastewater. The model was calibrated and validated with non-synthetic influent using different operational conditions. A local sensitivity analysis was conducted to determine the most important operational and chemical model parameters. The hydrogen peroxide concentration, absorption coefficient at 310 nm ( $UV_{310}$ , as a surrogate for natural organic matter) and pH could be satisfactorily predicted during model validation using an independent data set. It was demonstrated that real-time calibration is an option at less controllable full-scale conditions. The reactivity of  $UV_{310}$  towards hydroxyl radicals did not show significant variations over time suggesting no need for frequent recalibration. Parameters that determine the initiation step, i.e. photolysis of hydrogen peroxide, exerted a large impact on most of the variables. Some reaction rate constants were also of importance, but nine kinetic constants did show absolutely no influence to one of the variables. Parameters related to UV shielding by DOM were of main importance. Hydrogen peroxide concentration was classified as a non-sensitive variable, in contrast to the concentration of a micropollutant which showed to be very to extremely influential to many of the parameters. UV absorption proved to be a valuable DOM surrogate to be included in models.

Based on the above findings, research was conducted to assess the impact of (advanced) oxidation on the properties of DOM. Conversions of effluent organic matter (EfOM) were experimentally examined using two different oxidation techniques: ozonation and UV/H<sub>2</sub>O<sub>2</sub> treatment. Multiple surrogates for EfOM related to its concentration, polarity, biodegradability, molecular size and spectral properties were used to study the oxidant induced conversions. Spectral calculations as differential absorbance spectra (DAS) and absorbance slope indexes (ASIs) proved to be useful to unravel mechanistic differences between ozone and HO<sup>•</sup> induced transformation of EfOM. DAS and ASIs behaved totally different in the presence or absence of ozone. Effluent ozonation inherently led to significant HO<sup>•</sup> production and as a result of changing EfOM properties, the HO<sup>•</sup> production yield increased as function of ozone dose. During the UV based process, pseudo steady-state behaviour of the HO<sup>•</sup> concentration was observed. The HO<sup>•</sup> production during ozonation was strongly correlated to UV<sub>254</sub>. Further, the pH extremely impacted ozone decomposition. Most likely, the degree of dissociation of EfOM controlled its reactivity towards ozone. The ozone decomposition constant ( $k'_{app}$ ) rapidly decreased as function of ozone dose following a power function. Both processes had similar effects on oxygen demand, dissolved organic carbon (DOC), polarity and biodegradability. EfOM was converted to compounds with an increased oxidation state, decreased hydrophobicity and higher biodegradability.

Finally, the above mentioned lab-scale UV/H<sub>2</sub>O<sub>2</sub> system for secondary effluent oxidation was modelled using two slightly different kinetic UV/H<sub>2</sub>O<sub>2</sub> models. The models were successfully calibrated but only poor predictions of effluent organic matter conversion and HO<sup>•</sup> exposure could be obtained during model validation. This was not the case for hydrogen peroxide decay, which could be satisfactorily predicted. The modelling exercise was severely impeded by complex and variable the character of EfOM. Model-based description of secondary effluent treatment was found to be much more difficult compared to the modelling of natural water oxidation. More research should be conducted to extend the model in order to predict UV/H<sub>2</sub>O<sub>2</sub> treatment of secondary treated municipal effluent. Alternatively, possible extensions of semi-empirical concepts should be investigated.

Throughout this PhD thesis, several issues that were found valuable to be covered by future research could be defined. First, model structures should be extended in order to achieve more accurate predictions of oxidant production and consumption rates. In this context, the use of suitable surrogates for DOM is of vital importance. Second, more studies on oxidation of real, multicomponent water matrixes building upon those described in this work are needed to increase the level of understanding on the complex mechanisms that are occurring. These studies should be conducted using lab-, pilot- and full-scale reactors. Third, more information is needed on the integration of oxidation processes in a treatment train consisting of multiple unit processes. In this way, the interactions between each step can be assessed.