PhD Thesis abstract

Contribution to performance characterization and kinetic modelling of micropollutants abatement in water and wastewater by ozone-based oxidation processes

Candidate: Alberto Cruz Alcalde
Supervisors: Carme Sans Mazón
Santiago Esplugas Vidal

Department of Chemical Engineering and Analytical Chemistry, Faculty of Chemistry, University of Barcelona

The increasing water scarcity is gradually forcing a switch from the classical wastewater management paradigm to a circular view in which wastewater is regarded as a precious resource and advanced tertiary treatments are required in order to make the most of it. But regardless of whether the final effluent is discharged or reused, there is a concerning aspect of wastewater pollution that still remain unregulated: the need of removing the so called micropollutants, especially those classified as priority substances and contaminants of emerging concern. If the aquatic environment is wanted to be preserved and safe water reuse practices established, these potentially harmful substances must be removed from wastewater.

Ozonation is nowadays a mature and competent technology for enhanced wastewater treatment. The combination of ozone, a strong and selective oxidant, with the even powerful and unselective hydroxyl radical, formed through ozone decomposition, is effective in the abatement of a number of organic compounds. However, there are still some points to be addressed for a more efficient application of ozone-based processes to wastewater treatment and reclamation.

Among micropollutants potentially present in wastewater effluents, there are several compounds that react very slowly with ozone. They are known as ozone-resistant micropollutants. If a high quality water is wanted to be obtained, these substances should

be also removed from the effluent. In addition, modelling the abatement of micropollutants during wastewater ozonation is essential for process simulation, optimization and real-time control. To make this possible, performance characterization in terms of oxidation efficiency is required, as well as some kinetic information regarding the abatement of micropollutants. The first can be addressed by using normalizing parameters allowing the estimation, for instance, of hydroxyl radical availability as a function of the consumed ozone, or any other parameter whose measurement during the process is simple. The most accurate way of obtaining kinetic data of micropollutants oxidation is conducting individual studies on this chemicals degradation by ozone and hydroxyl radicals. Through these ones and some complementary tests, valuable data regarding the mechanisms of degradation and the potential ecotoxicological effects of formed transformation products can also be obtained.

This thesis was divided in two parts: first, individual batch ozonation studies of selected priority and emerging concern micropollutants were conducted. Particularly, the pesticides methiocarb, acetamiprid and dichlorvos were selected for that work. The second part consisted of the application of single ozonation and the combination of ozone and hydrogen peroxide (*i.e.*, peroxone process) was tested in the removal of ozone-refractory micropollutants from actual municipal wastewater effluents. The latter was done through semi-batch ozonation experiments. The objectives were, on one hand, obtaining kinetic, mechanistic and toxicological data of some priority/emerging concern chemicals. On the other, ozonation studies with real effluent samples were performed with the aim of exploring the removal of ozone-recalcitrant chemicals and potential strategies for the modelling and real-time control of this process. In addition, improvement strategies for peroxone process application were investigated.

Different kinetics were observed for pesticides reaction with ozone, being acetamiprid the most recalcitrant compound. In addition, toxicity of some of the pesticides transformation products was revealed, especially in the case of methiocarb degradation. Regarding ozone-based processes application to actual wastewater effluents, the removal of model ozone-recalcitrant compounds was found difficult, concluding that ozone doses higher than those corresponding to the immediate ozone demand value were required for a more effective abatement of these substances, regardless of the process employed. In the case of the peroxone process application, dosing hydrogen peroxide simultaneously to ozone bubbling was found to potentially entail important energy savings related to oxidants use. The oxidation performance of ozone-based processes and thus the abatement of ozone-refractory compounds could be effectively modelled using kinetic parameters, the monitoring of water quality parameters and empirical relationships obtained for each effluent. Furthermore, side reactions of involved oxidants with effluent organic compounds was found to increase the content in small and oxidized organic compounds in all cases. In the case of effluents containing suspended solids, ozone application also caused a net increase in the dissolved organic load.