Advanced oxidation of fluoroquinolone antibiotics in water by ozone and the peroxone process: mechanisms, kinetics and antibacterial activity

Kristof Demeestere, Bavo De Witte, Jo Dewulf, Herman Van Langenhove
Research Group EnVOC, Department of Sustainable Organic Chemistry and Technology, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653. B-9000 Ghent, Belgium. E-mail: Kristof.Demeestere@UGent.be

The release of quinolone antibiotics in WWTP effluent and surface waters may induce bacterial resistance against these and related antibiotics[1-2] and toxicity to aquatic organisms[3-4]. Since quinolones are not readily biodegradable, physical-chemical removal technologies are indispensable for their removal. This presentation highlights the main insights and conclusions that have been gained from a 5-years research[5-10] (2007-2011) on the ozone-based advanced oxidation of two antibiotics – ciprofloxacin and levofloxacin – spiked in both deionized and hospital WWTP effluent.

Ozonation of both antibiotics was investigated in a temperature controlled bubble reactor containing a water volume of 1.75 L. At pH 7 and similar conditions, levofloxacin ozonation proved to be faster than that of ciprofloxacin, with half life times of 13 and 16 min, respectively. Increasing the ozone inlet concentration (660 - 3680 ppmv) linearly increased the ciprofloxacin degradation rate, and fastest degradation occurred at the lowest initial ciprofloxacin concentration (23-136 µM). No clear trends were found as a function of temperature (6-62°C). For levofloxacin, approximately two times faster ozonation was observed at pH 10 compared to pH 3 and 7, while ciprofloxacin degradation was 25 and 10% faster at pH 3 compared to pH 7 and 10, respectively.

Based on UV and CID-HRMS analysis of ozonated samples, ten ciprofloxacin and nine levofloxacin degradation products were identified, allowing the proposal of reaction path-ways. Degradation showed to occur at (1) the piperazinyl substituent, (2) the quinolone moiety with formation of isatin analogues and (3) the quinolone moiety with formation of anthranilic acid analogues. No degradation was observed at the cyclopropyl (ciprofloxacin) or oxazinyl group (levofloxacin). Degradation at the quinolone moiety was enhanced at pH 7. Since t-butanol addition excluded the formation of isatin and anthranilic acid analogues, the necessity of radicals for formation of these products is plausible. At pH 10, deprotonation of the N4'-atom of the piperazinyl group enhanced direct ozonation at this site of the molecule. Addition of H_2O_2 to ciprofloxacin and levofloxacin ozonation experiments at pH 7 had only limited effect on quinolone degradation, ozone as well as H_2O_2 consumption, suggesting that the radical chain mechanism is of minor importance for quinolone degradation compared to direct ozonation.

In hospital WWTP effluent, sorption on suspended solids proved to be important. The largest sorption was found at pH 7 which may be linked to the relatively slow ciprofloxacin ozonation at this pH. Addition of H_2O_2 increased ciprofloxacin half life times at pH 7 from 29 min without H_2O_2 to 38 min with 1000 µM H_2O_2, probably due to competition of ciprofloxacin with H_2O_2 for ozone as well as radical species. The residual antibacterial activity against *P. fluorescens* and *E. coli* seemed mainly determined by the parent compound degradation rate. For *B. coagulans*, however, no difference in antibacterial activity reduction was observed as a function of ozonation pH although fastest ozonation was obtained at pH 10. This suggests that residual antibacterial activity against *B. coagulans* is also affected by differences in reaction products and pathway.

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