Application of chemical oxidation for removal of pharmaceuticals in wastewater effluents - DTU Orbit (20/10/2019)

Application of chemical oxidation for removal of pharmaceuticals in wastewater effluents

This study was conducted to evaluate the potential of the chemical oxidation processes chlorine dioxide (ClO2) and ozone (O3) as tertiary steps in wastewater to remove traces of active pharmaceutical ingredients (APIs). Wastewater effluents of varying organic content (COD ~ 30-90 mg/L) were collected from different wastewater treatment plants in Sweden to represent different types of biological treatment. Laboratory-scale batch experiments were carried out employing different doses of ClO2 (0-20 mg/L) and O3 (0-12 mg/L) to treat biologically treated wastewater spiked with approx. 1 μg/L of each API. Analyses of the 56 APIs were carried out by liquid chromatography coupled to triple quadrupole mass spectrometry.

During ClO2 treatment, high oxidative degradation of the APIs was observed with high ClO2 dose (8-20 mg/L) while only few APIs can be oxidized with the lowest dose (0.5 mg/L ClO2). In effluent 1 (35 mg/L COD), more than half of the APIs were already oxidized at 5 mg/L ClO2 in comparison to effluent 2 (55 mg/L COD) where significant increase in API oxidation was observed after treatment with 8 mg/L ClO2. The antiphlogistic diclofenac and antidiabetic repaglinide can be easily oxidized by more than 90% with 0.5-1.25 mg/L ClO2 whereas citalopram (antidepressant) and trimetoprim (antibiotic) required 8-10 mg/L ClO2 to reach over 90% degradation. In higher COD wastewater (effluent 2), the same degree of API oxidation can be achieved but requires higher ClO2 dose. In comparison to ozonation of wastewater effluent, over 90% removal of diclofenac and repaglinide was reached but with much higher ozone dose. On the other hand in effluent 3 (51 mg/L COD), citalopram and trimetoprim can be oxidized effectively by lower O3 dose than ClO2 however, in high COD wastewater (effluent 4, 90 mg/L COD), O3 treatment dose is comparable to ClO2. Nevertheless, ozonation significantly enhanced the removal of most APIs including carbamazepine, metoprolol, flutamide, bupropion and beclomethasone. In addition, ozonation allows removal of ibuprofen at higher oxidant dose. APIs that possess the reactive electron-rich functional groups in their structure such as aniline (diclofenac) and tertiary amine (repaglinide) are easily removed during oxidation. On the other hand, the presence of electron-withdrawing functional groups such as halogens resulted in slow reactivity of the APIs to oxidation. In addition, the difference in removal of the APIs between the oxidants can be explained by the varying COD content of the wastewater effluents. This study illustrates that treatment of wastewater containing pharmaceuticals is possible with either chlorine dioxide or ozone as additional treatment depending on the target pollutant. Oxidation by-products and toxicity have to be investigated before it can be considered for application in wastewater treatment. The use of ClO2 oxidation for pharmaceutical treatment may be beneficial for small wastewater treatment plants where ozonation could be too expensive and complicated to operate.