

Abstract

The presence of organic micropollutants in wastewater imposes a problem to the water treatment industry. Such persistent compounds enter the sewer system after domestic or medical use, and are inefficiently removed by traditional wastewater treatment technologies and subsequently discharged into the aquatic environment.

Chemical oxidation using ozone has been proven as an effective treatment process for a wide spectrum of micropollutants during bench-, pilot- and full-scale experiments in both wastewater and drinking water. However, a major disadvantage of ozonation is the formation of transformation products (TPs) instead of a full mineralization of parent compounds. Although there is still an overall lack of information regarding their toxicity, bioaccumulation, or occurrence, many of these compounds are suspected to have potential effects on humans and other species.

A proper sample preparation method is required to enrich a wide range of micropollutants from water samples for a subsequent use in chemical analysis as well as toxicological evaluation. Solid phase extraction (SPE) has become the most common sample preparation technique in environmental analysis.

In the first stage of research, the performance of several commercial SPE materials belonging to three different groups: reversed-phase, mixed-mode anion exchanger and mixed-mode cation exchanger, was evaluated. Eight parent compounds and seventeen ozonated TPs with different physicochemical properties were extracted from pure water samples. Different pH values, washing and elution solvents were tested to optimize the procedure. Recoveries $\geq 91\%$ were obtained by combining mixed-mode strong anion and cation exchangers in tandem without pH adjustment.

A liquid chromatography-tandem mass spectrometry (LC-MS/MS) method was developed to analyze the compounds of interest using the optimized SPE procedure. Full validation followed by trace determination of target compounds in different water matrices was performed. Consequently, recoveries between 90 and 110%, Linearity (> 0.99), method quantification limits (MQL's) at low ng/L-range and low matrix effect (ME) were achieved.

In the second stage of the study, suspect screening approach was used to examine the presence of structurally diverse organic compounds and their ozonated TPs in environmental water samples without reference standards. The suspect list was assembled after an extensive search to include 245 candidates reported from laboratory experiments in literature. The analytical procedure was therefore optimized by combining liquid chromatography-quadrupole-time-of-flight-mass spectrometry (LC-Q-TOF-MS) based on the use of accurate mass with the optimized SPE method exhibiting broad enrichment efficiency. The relative concentration levels of the suspects were determined and compared according to their peak areas in several advanced wastewater samples at different treatment levels and the final receiving water. Mass accuracy < 5 ppm, isotopic score $\geq 80\%$ and peak height > 1000 counts were obtained for all detected suspects. In addition, a plausible matching was shown between the retention times of TPs relative to parent compounds and the available values from literatures. The results showed that the studied wastewater treatment plant was efficient to degrade partially or completely organic micropollutants and the formed TPs after advanced treatment.

The future focus will be to study the occurrence and toxicological relevance of various compound classes and TPs in different aquatic environments using the improved SPE procedure. Additionally, further confirmation of suspect screening data will be beneficial.