

Trace organic contaminants (TrOCs) are a class of emerging pollutants, on which drinking water treatment plants are increasingly focusing on to remove from drinking water. A well-established technique for removal of TrOCs in drinking water is the use of advanced oxidation processes (AOPs), however in AOPs, halogenated organic compounds (including many TrOCs) are usually less effectively removed. This is because the carbon-halogen (C–X) bonds in these molecules are less susceptible to oxidative reactions[1,2].

An alternative to AOPs could be the use of advanced reduction processes (ARPs) to treat halogenated organic compounds. In ARPs, the goal is to produce reducing radicals (such as the hydrogen atom or hydrated electrons). These reducing radicals can react rapidly with many oxidized species, including molecules containing C–X bonds[1,2]. One example of an ARP is the sulfite/UV process, where upon UV irradiation of sulfite reducing radicals are produced. Here, removal of target compounds can in theory be induced by three processes: (1) reducing radicals (ARP), (2) UV irradiation (photolysis) and (3) chemical reduction because of sulfite.

In this study, the applicability of the sulfite/UV ARP for the removal of a broad range of TrOCs (a mixture of 27 compounds) is investigated. The main TrOC breakdown mechanisms will be discussed, as well as the effect of pH and sulfite dose on TrOC removal.

The addition of sulfite as a reducing agent, in absence of UV irradiation, did not result in TrOC breakdown of any of the 26 compounds investigated. This indicates that TrOCs are not susceptible to chemical reduction by sulfite, which can be explained by its low reduction capability[3]. Only 1 compound, diglyme, proved to be recalcitrant to all of the breakdown mechanisms under investigation. This can be explained by its molecular structure, lacking reducible functional groups, making reductive breakdown impossible. All other TrOCs showed breakdown in the ARP experiments, indicating that ARPs have a great potential for abatement of a wide range of TrOCs.

Photolysis could be attributed as being the main breakdown mechanism to 5 TrOCs. This was observed by means of a decreasing reaction rate upon addition of sulfite. Indeed, when photolysis is the major breakdown mechanism, then additional sulfite will only act as a photon competitor, reducing the available amount of photons for photolytic TrOC breakdown.

The breakdown of 11 TrOCs could be attributed to mainly ARP, of which 9 are easily broken down at pH 8 and 10, where hydrated electrons are the mainly produced reducing species, while 2 others (ibuprofen and gemfibrozil) are more easily removed at pH 6 due to hydrogen atoms.

For the remaining 9 TrOCs, the breakdown due to photolysis and ARP was very fast with complete removal within 10 minutes, making it unable to distinguish the dominant removal process.

The maximum removal efficiencies at the optimal removal conditions (determined by pH and sulfite dose) however were very high for all TrOCs, with >97% removed within 120 minutes.

These results provide a first insight in the applicability of the sulfite/UV process for a wide range of TrOCs. Further research should focus on identification of reduction products, and complementarity to other processes such as biodegradation of the reduction products (due to dehalogenation reactions taking place, which should enhance biodegradability).

References

- [1] Li, X. et al. Efficient reductive dechlorination of monochloroacetic acid by sulfite/UV process. *Environ. Sci. Technol.* 2012, 46 (13), 7342–7349.
- [2] Qu, Y. et al. Photo-reductive defluorination of perfluorooctanoic acid in water. *Water Res.* 2010, 44 (9), 2939–2947.
- [3] Liu, X. et al. Photochemical degradation of vinyl chloride with an Advanced Reduction Process (ARP) – Effects of reagents and pH. *Chem. Eng. J.* 2013, 215–216, 868–875.