Removal of Pharmaceutical Residues Using Ozonation as Intermediate Process Step at Linköping WWTP, Sweden

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Introduction

Pharmaceutical residues and other priority and emerging substances pass through most wastewater treatment plants (WWTPs) and end up in recipients posing a risk to ecosystems. Traditional treatment processes will have to be complemented in order to remove targeted substances. Ozone treatment is one of the most promising techniques but some of the metabolites created might be more or less toxic, which proposes a proper handling of this potential risk.

Tekniska verken (Linköping, Sweden) and IVL Swedish Environmental Research Institute have tested ozonation as basis for the design, implementation and operation of a future full-scale plant at the Linköping WWTP. The target was an efficient removal of priority substances to concentrations so low that no risk to the recipient is posed.

The tested solution consisted of an ozonation step between the bio-sedimentation and post-denitrification processes. This setup may have the advantage that potential toxic oxidation products from the ozonation process could be reduced.

Materials and Methods

A pilot plant of the intended process configuration was operated on-site and ozone doses of 1.8 - 23.1 mg O_3/L (at 10 mg DOC/L) were investigated at a water flow of about 1.5 m^3/h.

Analyses included 42 pharmaceuticals, other organic priority compounds, bacteria, antibacterial resistance and a number of different toxicity tests including micro algae (green algae) and macro algae (red seaweeds), crustaceans (Nitocra), estrogen activity (YES test) and AMES genotoxicity tests (TA98, TA100, YG7108).

Activity tests in the MBBR system as well as nitrogen, phosphorus and organic carbon analyses complemented the study.

Results

Table 1. Priority list of pharmaceuticals with a risk EC/PNEC ≥ 0.01 at an applied ozone dose of 5 mg O_3/L.

	Substance	EC (µg/L)	NOEC (µg/L)	Safety factor	Dilution in recipient	EC/ PNEC
HR	Oxazepam	0.10	1.8	1 000	27	2.0
MR	Metoprolol	0.25	1.0	50	27	0.5
MR	Estrone	<0.023	0.008	100	27	0.13
LR	Etinylestradiol	<0.158	0.00003	10	27	0.07
LR	Estradiol	<0.146	0.0004	10	27	0.05
LR	Ciprofloxacin	0.009	0.1	10	27	0.03
LR	Fluoxetin	0.002	0.029	10	27	0.03
LR	Levonorgestrel	<0.432	0.0008	10	27	0.03
LR	Trimetoprim	0.001	0.29	100	27	0.01
LR	Ibuprofen	0.14	10	10	27	0.01

HR - High risk; MR – Moderate risk; LR - Low risk
EC - Environmental Concentration; NOEC - No Effect Concentration; PNEC - Predicted No Effect Concentration = $\frac{NOEC * Average\ dilution}{Safety\ factor}$

At a dose of 5 mg O_3/L only one substance remained with a high risk and two with a moderate risk. Tests showed that slightly increased doses would imply only low risk classification of all substances. Also other investigated substances were not negatively affected by the intermediate oxidation step.

All ecotoxicological tests showed no indication of negative effects in the effluent water discharged into the recipient for the tested ozone doses. Bacteria could be significantly reduced and the performance of the whole process was very good during the test period of 6 months.

Different control strategies using easily measurable parameters that can be measured continuously by on-line probes were tested and evaluated.

Conclusions

The pilot studies show that intermediate ozonation can be a feasible option for the efficient removal of pharmaceutical substances. The described process setup further implies minimum risks for harmful effects in the recipient due to a biological post-treatment before final discharge. A dose of ozone of 0.5-0.8 mg O_3/mg DOC (5 – 8 mg O_3/L) was required to remove identified priority substances below the level of risk of adverse effects, except for a substance that is barely above risk ratio. Adverse effects or operational problems caused by ozonation could not be identified in the final effluent or on the following biological process.

Based on these results, the planning for the full-scale implementation of the treatment system was initiated in 2015.