AOX removal from industrial wastewaters using Advanced Oxidation Processes: assessment of a combined chemical-biological oxidation

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Introduction and problem description

AOX = Adsorbable Halogenated Organic Compounds (Group parameter)
= Hazardous / toxic organic pollutants
= Source: mostly industrial production

→ Decreasing discharge limits (EU water framework directive 2000/60/EC)

AOX + AOP (O_3, H_2O_2/UV, O_3/UV Fe(II)/H_2O_2)→ Degradation products
(Parilti et al., Perez et al.,Kusic et al.)

AOPs increase the biodegradability of waste water streams
(Van Aken et al., Ballesteros et al., Guo et al.)

Presence of halogenated ions (Cl^-, Br^-,…) jeopardises the use of AOPs
(Baycan et al., Sniegowski et al.)

Introduction and problem description

Industrial waste water: halogenated compounds (AOX) ↔ matrix compounds (COD)

$$AOX + oxidant \xrightarrow{k_1} degradation\ products$$

$$COD + oxidant \xrightarrow{k_2} degradation\ products$$

→ Selective AOX degradation is requested
→ Reaction order might change during experiments (especially with O_3)
→ Oxidant dose is a key parameter for removal efficiency

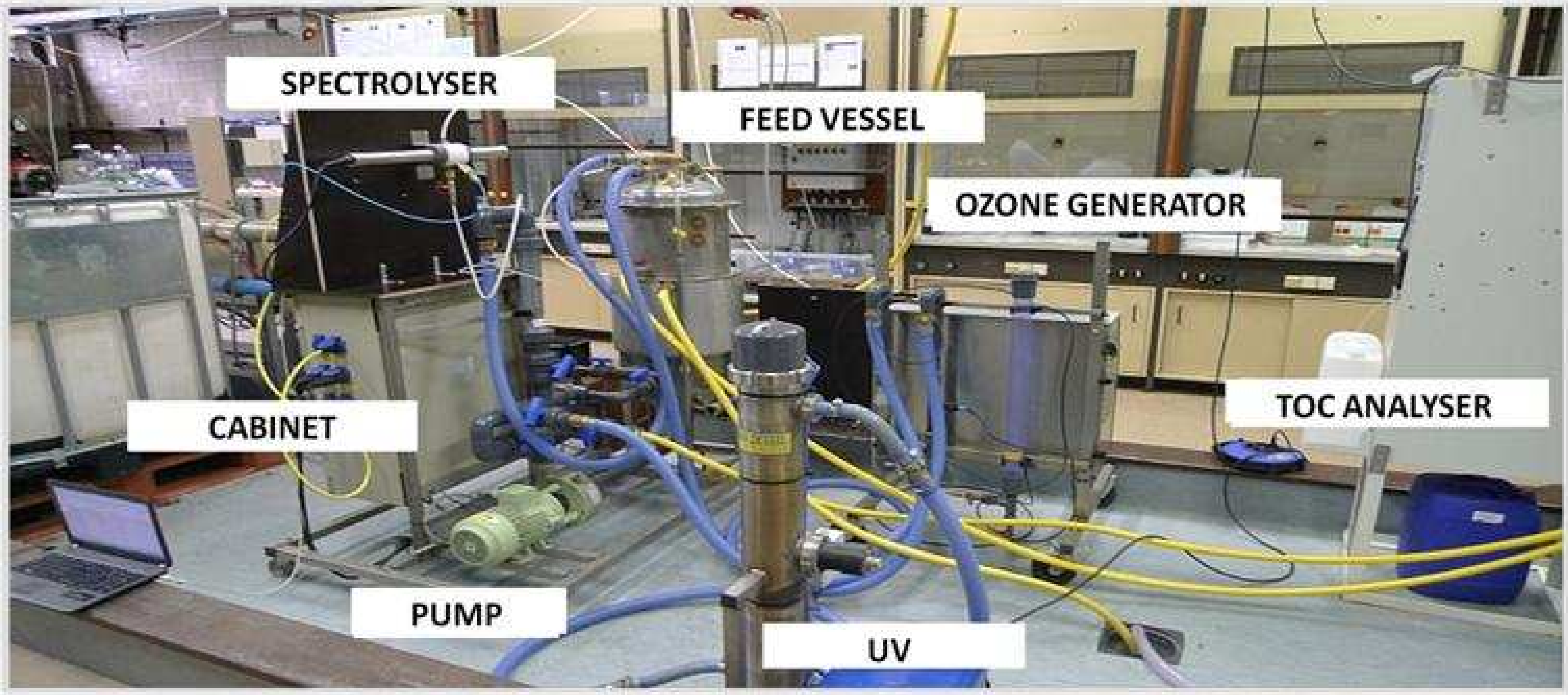
Potential of a combined chemical and biological oxidation for removal of AOX in industrial waste waters?

Sensitivity of AOX removal on operational parameters?

Methods and materials

100% Ozone : 16 g O_3/h
100% UV: 2000 W
100% H_2O_2: 2 mg H_2O_2 / mg COD

Pilot scale plant : Volume 50 L
Medium pressure Hg lamp, Philips
$[Fe^{2+}]/[H_2O_2]$ ratio of 1/100 ww



Methods and materials

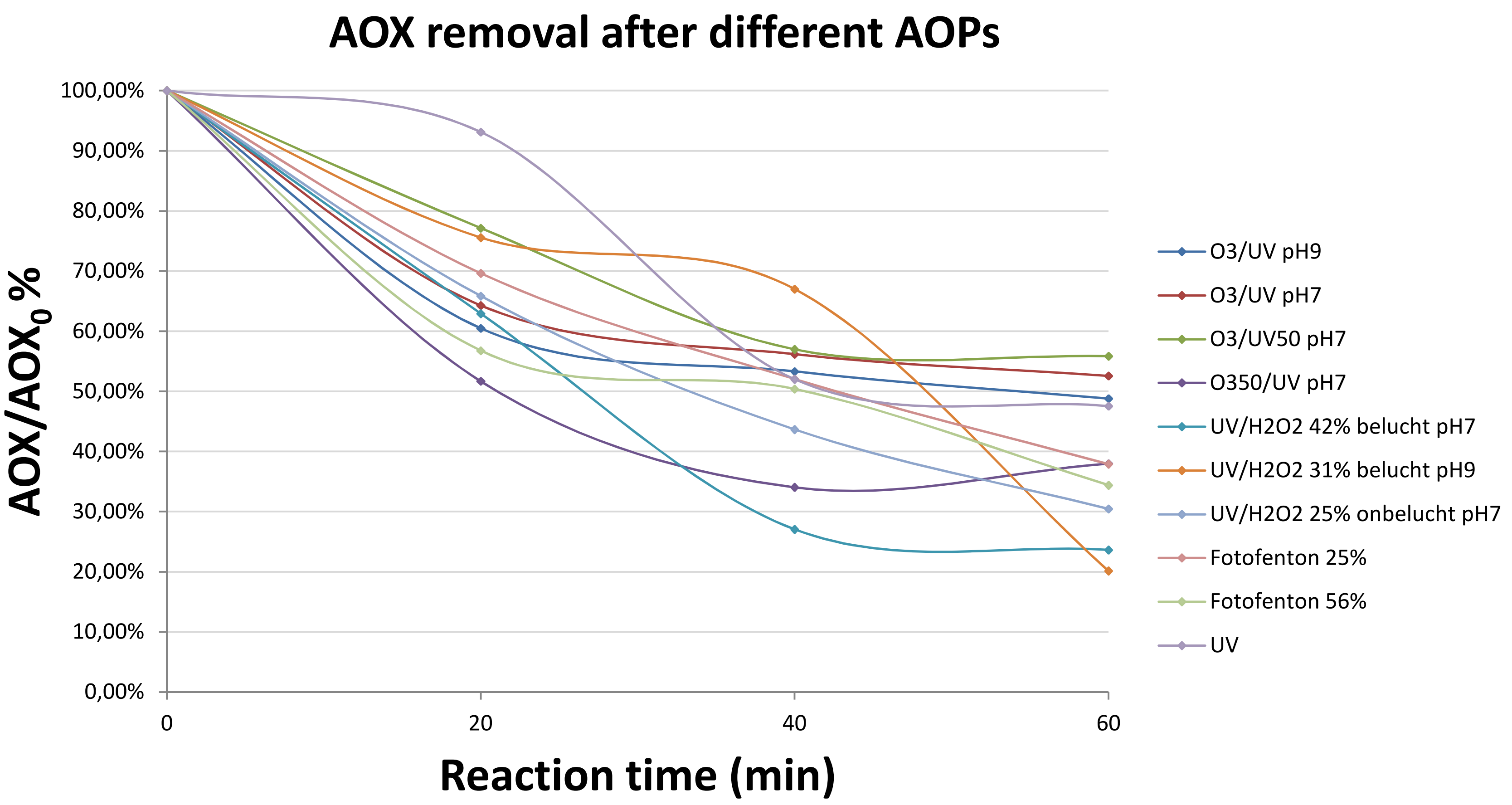
	Sample 1	*Sample 2*	*Sample 3*
Chloride (mg/l)	*750*	*650*	*1500*
AOX (µg Cl/l) (discharge limit)	1500 (400)	*5000 (400)*	*10000 (1000)*
pH	*7,8*	*7,9*	*8*

Different halogenated compounds, Batch production (Samples 1 and 2)

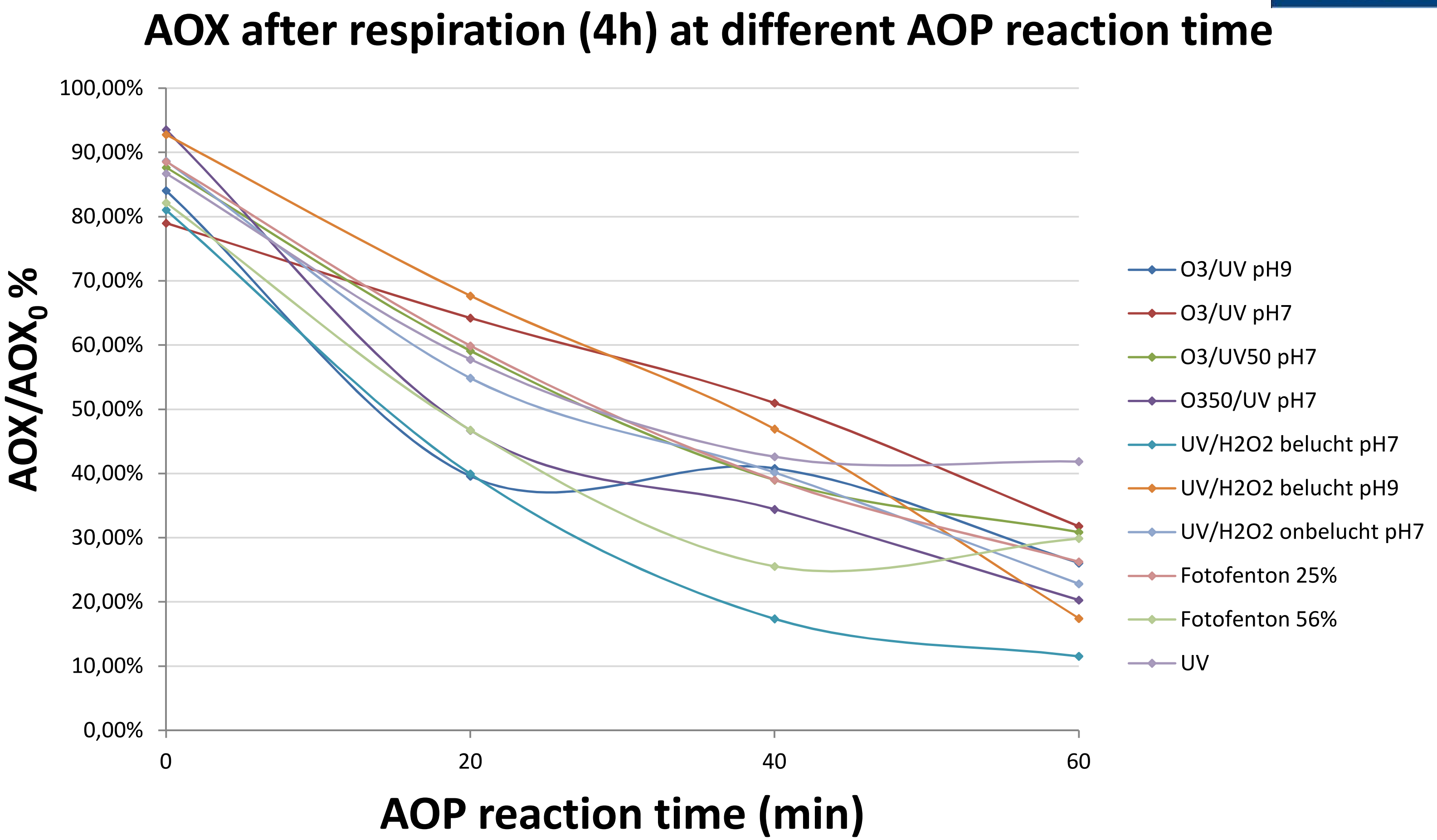
Specific compound (Sample 3)

- Biological oxidation (4h): Respirometry experiments using 500 ml waste water and 300 ml communal WWTP activated sludge (300 ml), periodically aerated.
- AOX measurements according WAC/IV/B/011 protocol, ThermoFischer Scientific 3000 systems TN/TS/TX (SphiNCX)
- Nanocolor® COD reactor and Nanocolor® 500 D colorimeter from Machery Nagel

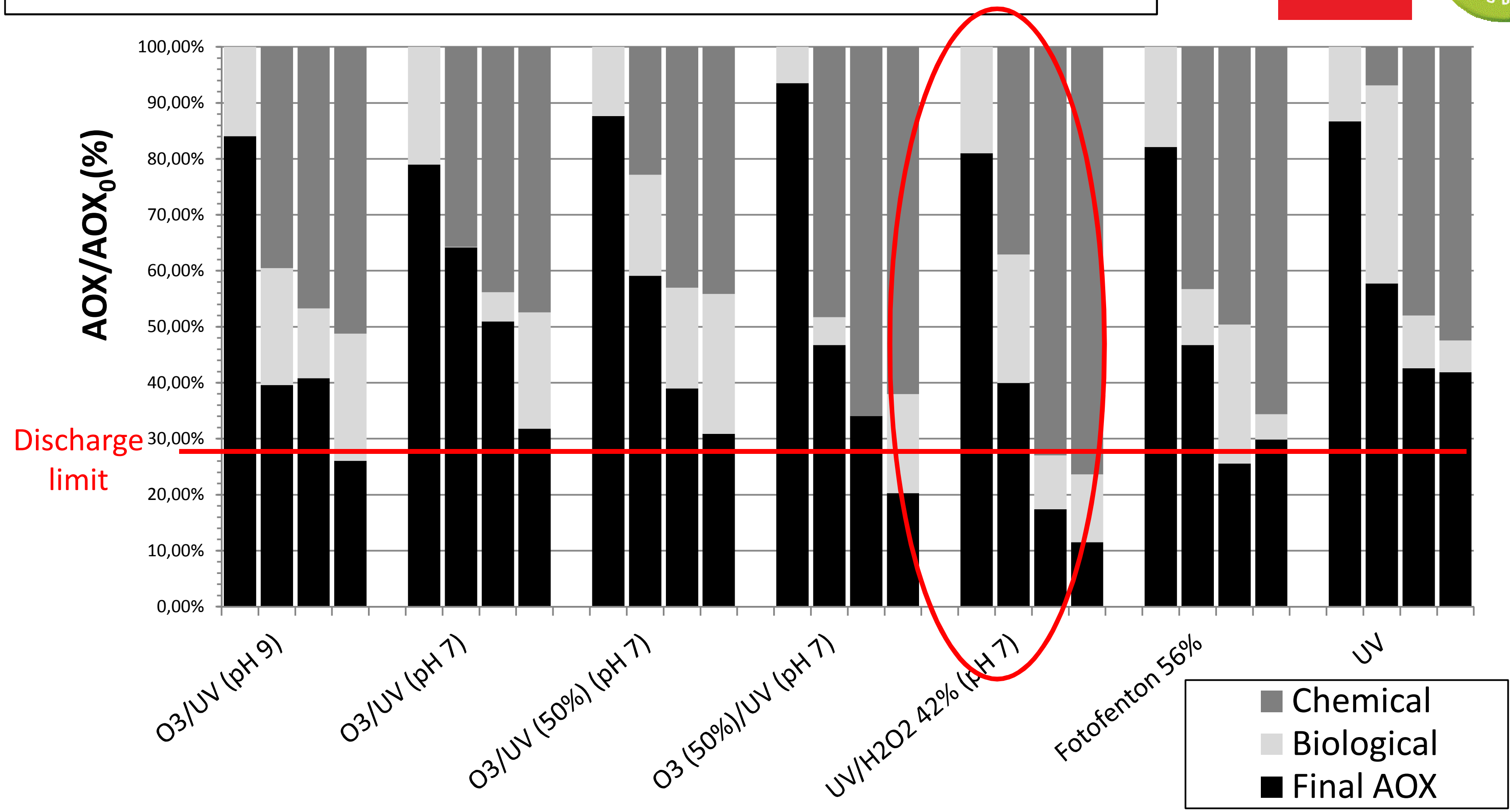
Results waste water I



Results waste water I



Results: waste water I



- Biological oxidation of the original wastewater : ± 20%.
- Ozone based techniques: 50 % removal after 60 minutes, more biodegradable than H_2O_2 based techniques
- UV alone: 50% AOX, slightly biodegradable

Results: Selectivity coefficient

For H_2O_2-based experiments no selectivity parameter is reported
Varying H_2O_2 results in similar AOX and COD removal efficiencies.

Technique	AOX_0	AOX_f	COD_0	COD_f	Overall selectivity *S(AOX/COD)*
O_3/UV pH 9	1647	804	206	184	4.9
O_3/UV pH 7	1700	894	184	102	1.1
O_3/UV(50%), pH 7	1517	847	177	94	0.9
O_3 (50%)/UV, pH 7	1660	631	170	93	1.4

- Ozone based AOP can selectively degrade AOX towards COD
- Selectivity: O_3(50%)/UV > O_3/UV > O_3/UV(50%)

→ lower ozone concentration with respect to UV intensity is recommended

- Increasing the pH to 9 enhances the selectivity for AOX removal

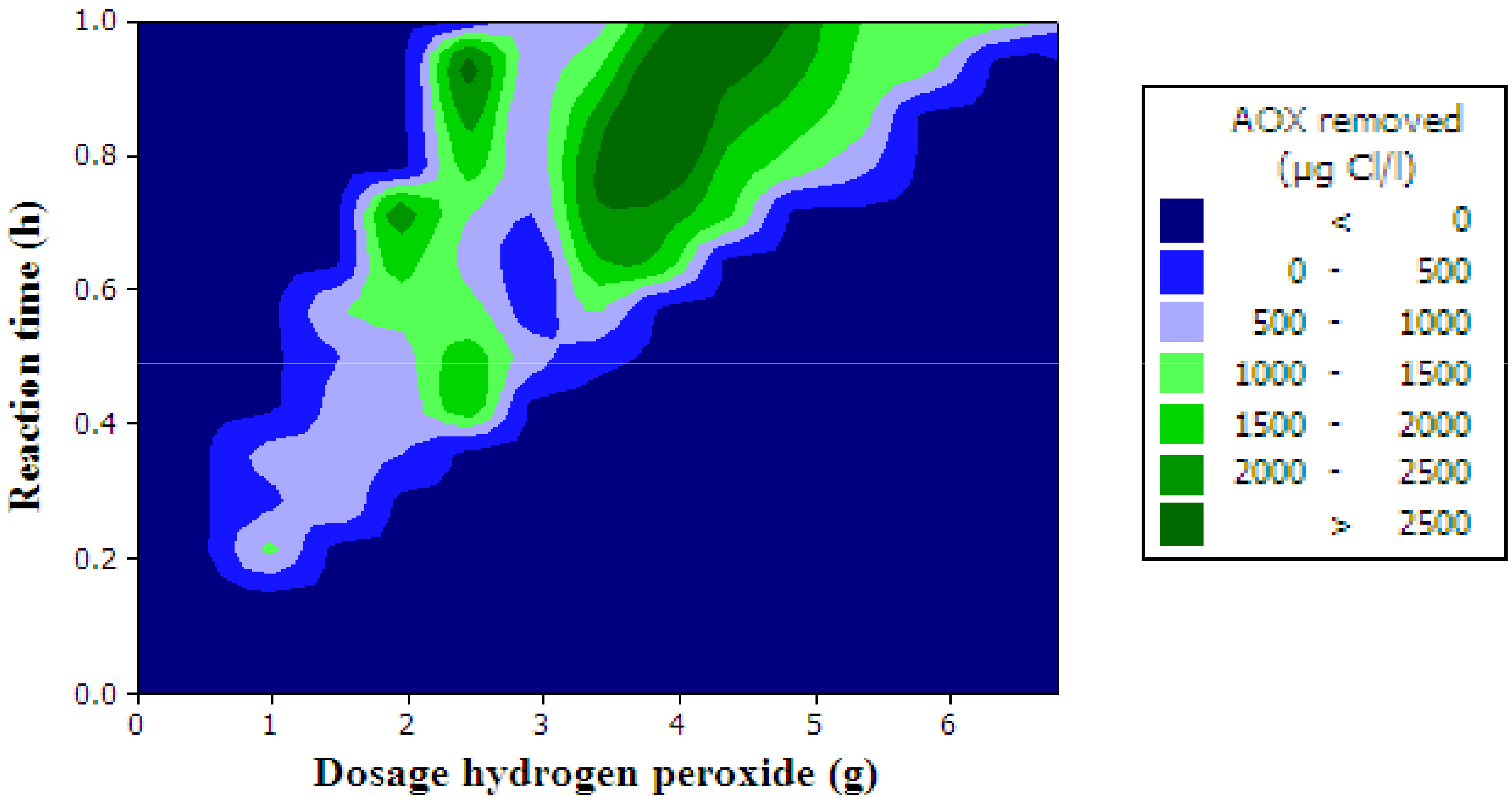
Results: Effect of UV intensity and H_2O_2 dose

UV intensity (kW)	Oxidant + dose (g/h)	AOX_0 (µg Cl/l)	AOX (µg Cl/l) after AOP (60 min)	AOX (µg Cl/l) after biological oxidation (4 h)
0.25	H_2O_2 /6.79	4130	4401	3382
0.5	H_2O_2 /6.79	4110	3835	2835
0.5	H_2O_2 /3.4	4908	4106	3388
2.0	H_2O_2 /6.79	5493	4572	3358
2.0	H_2O_2 /4.53	4640	1707	1658
2.0	H_2O_2 /2.5	5355	2506	1880
1.0	H_2O_2 /6.79	5283	3357	2358
2.0	O_3/ 16	4438	4748	2205

- O_3/UV at pH 7 leads to an increase in (biodegradable) AOX
- H_2O_2-based techniques: high UV intensity and intermediate H_2O_2 dosage is requested.
- Variable effluent concentrations demand strict monitoring as the discharge limit is not reached within 60 minutes reaction time (+ biodegradation) due to high initial AOX level

Results: Sensitivity of operational parameters

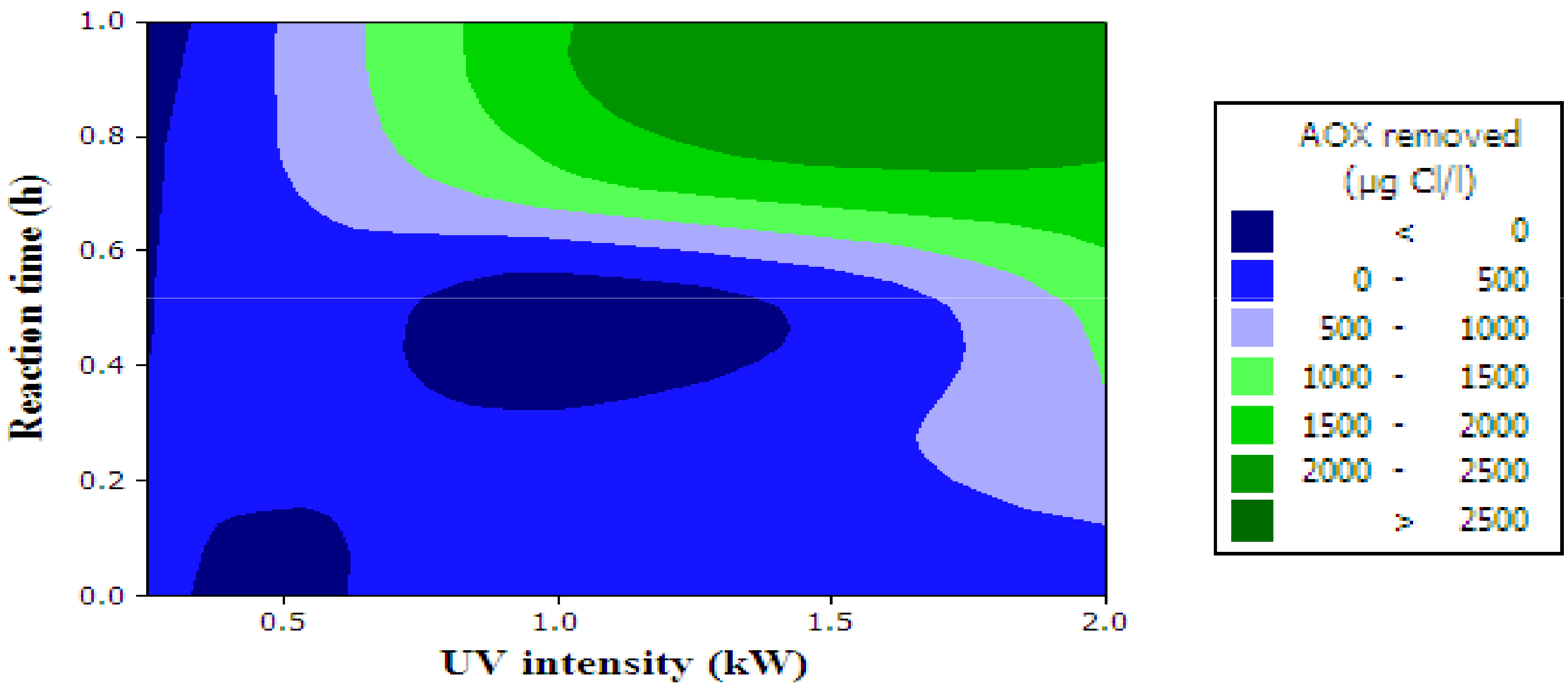
AOX removal by UV/H_2O_2 at pH 7



- Reaction time and H_2O_2 dose should be balanced in order to avoid AOX formation.
- Optimal: H_2O_2 dosage of 3-4.5 g corresponding with a reaction time of 50-60 min.

Results: Sensitivity of operational parameters

AOX removal by UV/H_2O_2 at pH 7



- Best results: UV power between 1 - 2 kW
- Optimal combination of reaction time and UV intensity is crucial!

Conclusions

- AOX can be significantly reduced in industrial wastewater by a combined chemical-biological treatment. Monitoring is crucial with variable effluent composition.
- Oxidant concentration is a key parameter for selective degradation of AOX towards COD
- For O_3/UV, lowering the ratio of O_3 dosage to UV intensity leads to a better selectivity for AOX.
- O_3-based AOPs remove less AOX than H_2O_2-based AOPs but increases the biological degradable fraction more.
- Reaction time, H_2O_2 dose and UV intensity needs to balanced for optimal AOX removal.

Acknowledgment & questions

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