

# Ozonation, advanced oxidation and hydrodynamic cavitation for removal of persistent pollutants

Čehovin M.<sup>1</sup>, Žgajnar-Gotvajn A.<sup>2</sup>

<sup>1</sup> MAK CMC Water Technology Ltd., Ljubljana, Slovenia

<sup>2</sup> University of Ljubljana, Faculty of Chemistry and Chemical Technology, Ljubljana, Slovenia

\*corresponding author: e-mail: andreja.zgajnar@fkkt.uni-lj.si

## Abstract

Ozone is commonly used in advanced oxidation processes (AOPs) in combinations with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and UV radiation (UV). Hydrodynamic cavitation (HC) has been experimentally proven to result in effects, typical of AOPs. Combinations of AOPs with O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and UV, and HC (with cavitation numbers less than 0.2, generated by various orifice plates and nozzles, with number of passes up to 12) were experimentally assessed on model water, containing organic matter. Various synthetic organic micropollutants (iohexol, diatrizoic acid and metaldehyde with concentrations of 10 µg L<sup>-1</sup>) were selected as the target compounds. At dosages of O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and UV above 2 mg L<sup>-1</sup>, 4 mg L<sup>-1</sup> and 450 mJ cm<sup>-2</sup>, respectively, herein applied HC had no beneficial effect on target pollutants removal. At lower dosages of the aforementioned oxidants, HC was able to improve the removal rate of the target pollutants by as much as 15 %. Moreover, in terms of electrical energy consumption, the hybrid process with HC was found to be as efficient per order (90 %) of removal ( $E_{EO}$ , kWh m<sup>-3</sup> order<sup>-1</sup>).

**Keywords:** Hydrodynamic cavitation, hydrogen peroxide, micropollutants, ozone

## 1. Introduction

Synthetic organic compounds resulting from various anthropogenic activities present in the environment lead to various unwanted responses of non-target organisms. Their presence in the environment is relatively new and no mechanism could be developed to adapt to them so quickly (Čehovin, 2017). These chemicals show mostly long-term effects (carcinogenicity, mutagenicity, genotoxicity, disruption of endocrine system etc.), with already very low concentrations in the range of µg L<sup>-1</sup>. Due to the presence of numerous species, their harmful effects could be multiplied by the so-called “cocktail effect”. Their persistency and bioaccumulation in the environment are of further concern, as well as the challenges of drinking and waste water treatment, because they can not be removed by traditional technologies (e.g. coagulation, flocculation, oxidation, filtration, biological treatment etc.).

Advanced oxidation processes (AOPs) have already been well-researched and practically applied for the treatment of recalcitrant natural and synthetic organic pollutants in drinking and wastewater (Gogate, 2015). They act by oxidizing chemical species in water matrix with the highly reactive and non-selective hydroxyl radicals (HO•) which are considered to be the strongest technically applicable oxidants in water treatment with the oxidation potential of 2.81 V. They are mainly generated by the combination of strong oxidants, such as ozone (O<sub>3</sub>, 2.07 V) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 1.78 V) or their combination with the UV irradiation (Sierka, 1985). To enhance treatment efficiency and to reduce material and energy inputs synergistic effects of combined treatment processes are evaluated.

Cavitation is the formation, cyclic growth and rarefaction with terminal implosive collapse of vapour bubbles in the liquid phase. It can be triggered by turbulent flows, fast moving particles, boiling, electrical discharge, laser or ultrasonic irradiation. When cavitation bubbles collapse, for a very brief time of micro- to milliseconds, extreme temperatures (up to 5000 °C inside cavitation bubble and up to 2000 °C at the bubble-liquid interface) and pressures (approx. 500-1000 bar) can exist locally. Energy released from cavitation occurrence causes mechanical and chemical changes in materials in contact (Rault-Jadhav, 2013). Therefore the effects of cavitation can be used for degradation or synthesis of chemicals in various industrial and environmental applications (Čehovin, 2017; Houas, 2001).

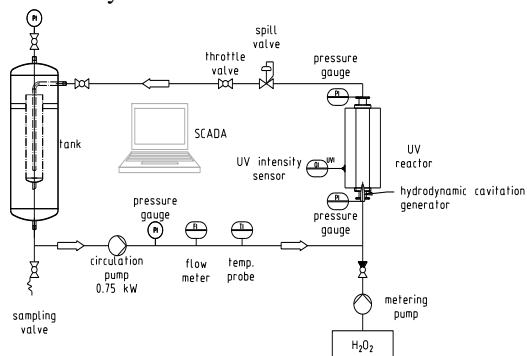
## 2. Materials and Methods

In Figure 1 experimental set-up of the oxidation system is presented. Water flow, temperature and pressures (at the entry and the exit of UV reactor) were continuously measured. The UV lamps were placed outside the quartz glass pipe with reflectors directing the photons towards the centre of the pipe and thus concentrating the UV irradiance in the zone with the highest axial velocity and distributing the UV fluence rate (Čehovin, 2017).

The intensity of cavitation phenomena is described by dimensionless cavitation number ( $C_v$ ):

$$C_v = (P_2 - P_v) / (1/2 \cdot \rho \cdot v^2) \quad (1)$$

where  $P_2$  is absolute downstream pressure (backpressure) [Pa],  $P_v$  is vapour pressure at a given temperature [Pa],  $\rho$  is water density at a given temperature [ $\text{kg m}^{-3}$ ] and  $v$  is flow velocity [ $\text{m s}^{-1}$ ] at the throat of the constriction (Sharma, 2008). Another important parameter is the number of passes (*NOP*) through the HC generator. Between 9 and 12 were used in this study.



**Figure 1.** Design of the experimental set-up.

Experiments were accomplished as described in Table 1 using dosages of  $2 \text{ mg L}^{-1}$  of  $\text{O}_3$  and concentration of synthetic micropollutants of  $10 \text{ }\mu\text{g L}^{-1}$ .

**Table 1.** Experimental conditions.

Pollutant	$\text{H}_2\text{O}_2$ [ $\text{mg L}^{-1}$ ]	UV [ $\text{mJ cm}^{-2}$ ]	<i>NOP</i> [/]
Methylene blue	5.0	500-2800	12
metaldehyde, diatrizoic acid, iohexol)	10.0	500-1900	9
	10.0	450-2700	9

### 3. Results and Discussion

To assess the energy efficiency (Table 2), electric energy per order (or 90%) of removal  $E_{\text{EO}}$  [ $\text{kWh m}^{-3} \text{ order}^{-1}$ ] of the selected evaluated parameter was calculated using the term:

$$E_{\text{EO}} = P \cdot t / (V \cdot \log ([x_0]/[x_t])) \quad (2)$$

where  $P$  [kW] is the electrical power consumption of the experimental setup, measured using the power meters,  $x_0$  is the initial value of the micropollutants concentration and  $x_t$  at experiment time  $t$  [h]. The  $P$  for the experiments without the application of HC was 0.73 kW,  $P$  for the HC-coupled experiments was 0.98 kW, including the power consumption of the UV photolytic reactor.

System with HC as a hybrid process was as energy efficient as the  $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$  AOPs alone. In the case of methylene blue removal efficiency was also increased by the application of HC (up to 18%), justifying the

additional energy input. On the other hand, micropollutants in general, and especially the contrast agents, were more efficiently removed without the application of HC (up to 15%).

**Table 2.** Electric energy per order of removal.

Experimental configuration	$E_{\text{EO}}$ [ $\text{kWh m}^{-3} \text{ order}^{-1}$ ]		
	methylene blue	metaldehyde	diatrizoic acid, iohexol
Without HC	46.2	11.0	2.4
With HC	46.6	12.0	4.0

### 4. Conclusions

The effects of the treatment by AOPs alone and those coupled with hydrodynamic cavitation on the removal of selected micropollutants were investigated. As shown by this study, coupling HC with  $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$  AOPs can be of interest for further research and it could be transferred to practical or industrial applications. The potential benefits of the HC application as a hybrid process to the applied AOPs were emphasized in the conditions of relatively (i) high UV absorbance (at  $\lambda = 254 \text{ nm}$ ) and colourization of the matrix, i.e. unfavourable conditions for the efficient fluence rate distribution in the photolytic reactor; (ii) high pollutant concentrations; (iii) low dosages of oxidants and UV; (iv) low ratio of (photo-) oxidants dosages to pollutant concentration.

### References

- Houas, A., (2001). Photocatalytic degradation pathway of methylene blue in water. *Appl Catal B Environ* **31**:145–157.
- Sierka, R.A., Amy, L.G., (1985). Catalytic Effects of Ultraviolet Light and/or Ultrasound On The Ozone Oxidation of Humic Acid and Trihalomethane Precursors. *Ozone Sci Eng* **7**:47–62.
- Gogate, P.R., Patil, P.N., (2015). Combined treatment technology based on synergism between hydrodynamic cavitation and advanced oxidation processes. *Ultrason Sonochem* **25**:60–69.
- Čehovin, M., Medic, A., Scheideler, J., Mielcke, J., Ried, A., Kompare, B., Žgajnar Gotvajn, A., (2017). Hydrodynamic cavitation in combination with the ozone, hydrogen peroxide and the UV-based advanced oxidation processes for the removal of natural organic matter from drinking water. *Ultrason Sonochem* **37**:394–404.
- Raut-Jadhav, S., Saharan, V.K., Pinjari, D., Sonawane, S., Saini, D., Pandit, A., 2013. Synergetic effect of combination of AOP's (hydrodynamic cavitation and  $\text{H}_2\text{O}_2$ ) on the degradation of neonicotinoid class of insecticide. *J Hazard Mater* **261**:139–147.
- Sharma, A., Gogate, P.R., Mahulkar, A., Pandit, A.B., (2008). Modeling of hydrodynamic cavitation reactors based on orifice plates considering hydrodynamics and chemical reactions occurring in bubble. *Chem Eng J* **143**:201–209.