

# Photolytic ozonation as promising alternative AOP using UV-LEDs



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## Introduction

- Advanced oxidation processes (AOPs, Figure 1) are essential technologies for removing trace organic chemicals (TOCs) during (waste)water treatment or in water reuse schemes.
- In contrary to other processes, by applying AOPs, TOCs are destroyed within the water stream, instead of shifting them to a different medium or stream.
- Within the EU co-funded research project PRISTINE [1] a holistic approach for water treatment eliminating TOCs from different water streams is researched.
- A detailed comparison between the conventional H<sub>2</sub>O<sub>2</sub>-UV AOP and the combination of O<sub>3</sub> with UV, photolytic ozonation (O<sub>3</sub>-UV), concerning TOCs elimination is performed.
- Whereas for the H<sub>2</sub>O<sub>2</sub>-UV AOP, radicals are formed with a high quantum yield, O<sub>3</sub>-UV benefits from a higher molar absorption coefficient [2].

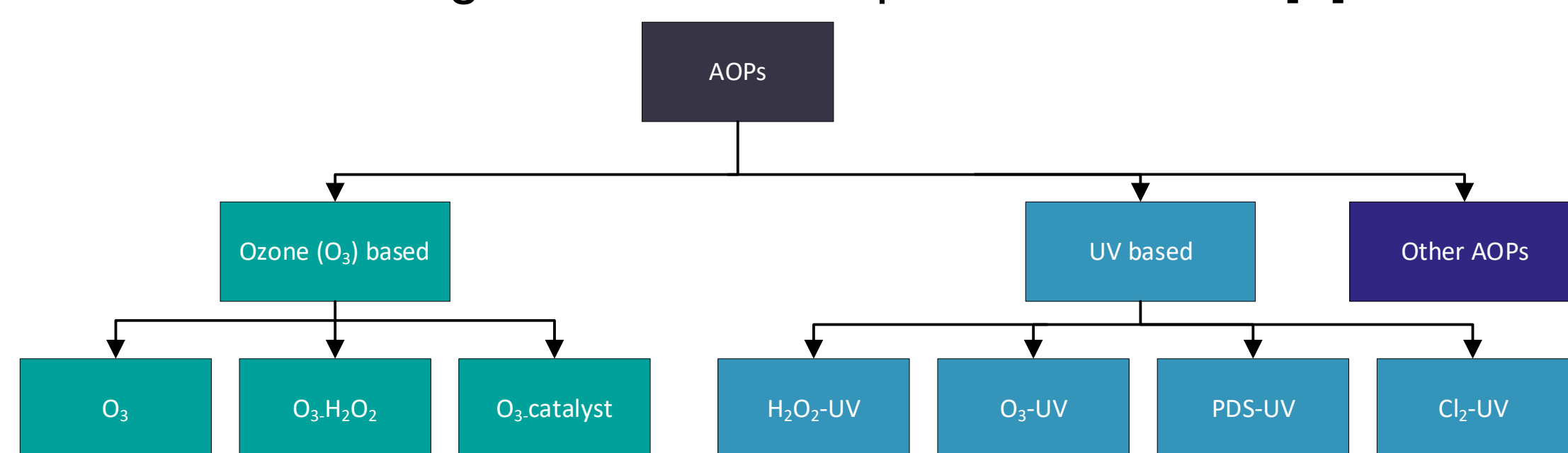


Figure 1: Overview of advanced oxidation processes (AOPs).

## Materials and methods

- 1 m<sup>3</sup>/h feed.
- Pilot scale UV-LED reactor built of 16 LED arrays.
- O<sub>3</sub> introduced before the UV reactor using a venturi-injector (Figure 2).
- O<sub>3</sub> generated from oxygen by using a GSO30 (Xylem, Germany).
- Dissolved O<sub>3</sub> concentration determined using the indigo method.
- Local tap or an artificial water matrix (deionized water, 0.15 mM tert-Butyl alcohol and 0.7 mg/L Br<sub>2</sub>, buffered with phosphate at a pH of 7.8) as feed.
- Approximately 56 µg/L para-chlorobenzoic acid (p-CBA) spiked as model compound.
- Remaining O<sub>3</sub> quenched directly after taking samples.



Figure 2: Picture of the advanced oxidation process (AOP) pilot and schematic process.

## Results and discussion

- O<sub>3</sub> introduced (with 8 and 4 g/m<sup>3</sup>) to the system fed with tap water and different numbers of LED arrays turned on. For both, applied O<sub>3</sub> dosages, O<sub>3</sub> could be effectively degraded using the UV-LED reactor (Figure 3).
- Experiments with p-CBA as model compound were performed using the artificial water and an O<sub>3</sub> dosage of 8 g/m<sup>3</sup> (Figure 4). In the experiments with UV, 7 LED arrays were turned on and a test with 10 mg/L H<sub>2</sub>O<sub>2</sub> was performed as benchmark.
- When introducing only O<sub>3</sub>, the logarithmic reduction value (LRV) of p-CBA was low (0.2) as expected by the low-rate constant of O<sub>3</sub> with p-CBA [3] and O<sub>3</sub> being quenched after sampling.
- For the UV-O<sub>3</sub> AOP a LRV for p-CBA of 1.5 was observed, being three times higher than for the H<sub>2</sub>O<sub>2</sub>-UV combination (0.5) with the same number of LEDs turned on.
- The reason for the observed higher LRV removal might be explained when calculating the radical formation based on the equations analogous to [4]:

$$r_{OH} = \ln(10) \Phi_{OH} \epsilon_{Oxi} [Oxi] E'_{P,eff}$$

$r_{OH}$  = the radical formation rate,  $\Phi_{OH}$  = the quantum yield for (photolytic) hydroxy radical formation,  $\epsilon_{Oxi}$  = molar absorption coefficient of the used oxidant,  $[Oxi]$  = the concentration of the used oxidant and  $E'_{P,eff}$  = the effective photon fluence

- $\Phi_{OH}$  for O<sub>3</sub>-UV is only 1/10 compared to  $\Phi_{OH}$  for H<sub>2</sub>O<sub>2</sub>-UV [2].
- Contrarily,  $\epsilon_{Oxi}$  for O<sub>3</sub>-UV is more than 100 times higher than for H<sub>2</sub>O<sub>2</sub>-UV [2].
- The radical formation rate further depends on the used concentration of the oxidant and the effective photon fluence.
- The effective photon fluence for the O<sub>3</sub>-UV might significantly be influenced by the oxidant itself and the utilized water matrix.

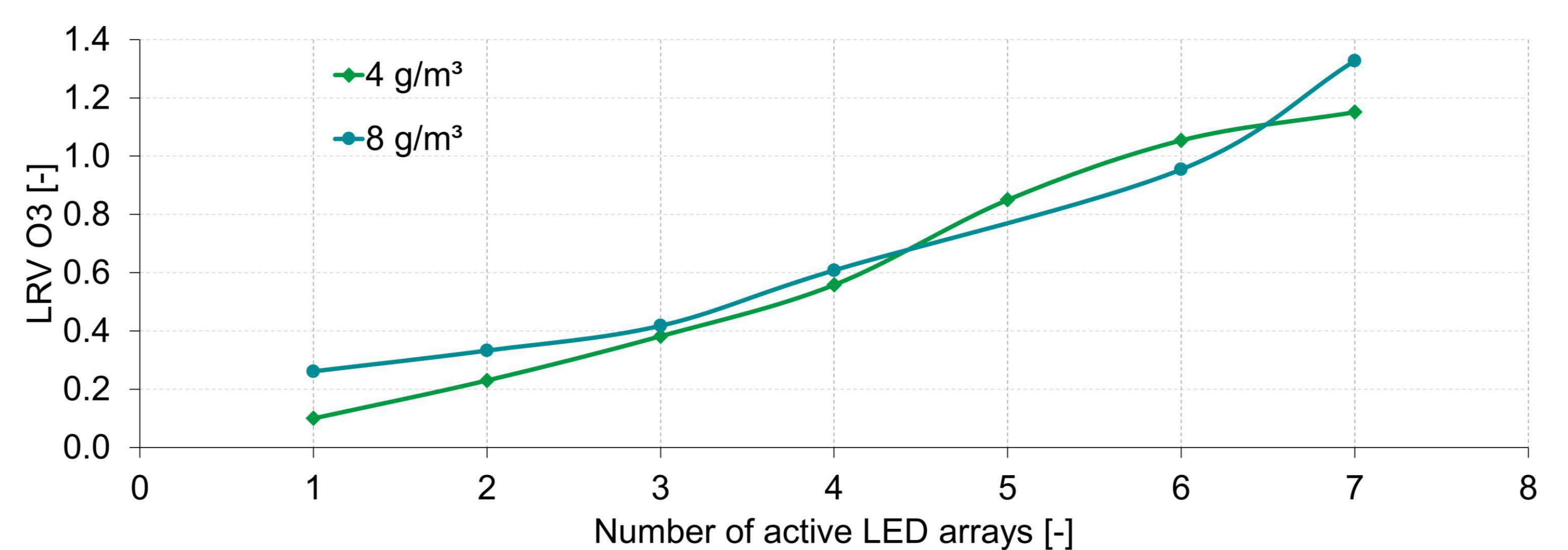


Figure 3: Logarithmic reduction values (LRV) of O<sub>3</sub> over the number of active LED arrays for 4 g/m<sup>3</sup> and 8 g/m<sup>3</sup> of introduced O<sub>3</sub> with tap water at a pH=7.4-7.7.

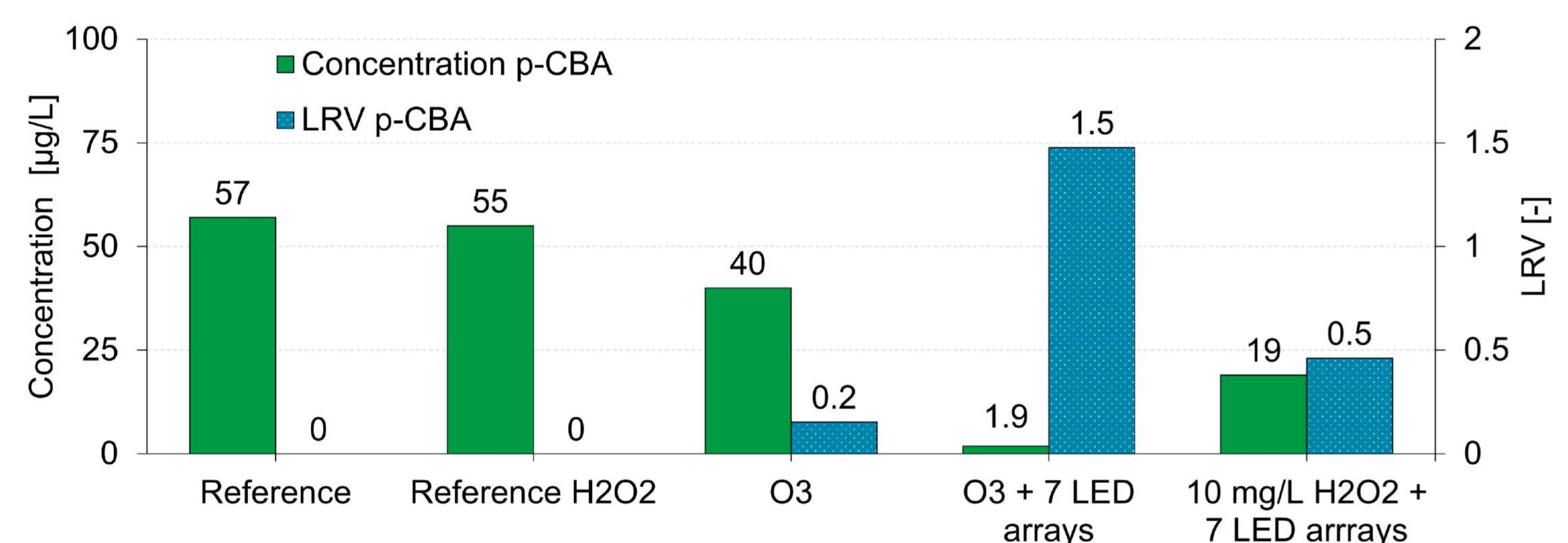


Figure 4: Results for p-CBA degradation for the artificial water matrix (0.15 mM tert-Butyl alcohol, 0.7 mg/L Br<sub>2</sub>, buffered at pH = 7.8, UVT = 96%) for 8 g/m<sup>3</sup> O<sub>3</sub> introduced or 10 mg/L H<sub>2</sub>O<sub>2</sub> added; LRV = Logarithmic reduction value.

## Conclusions

Based on the experimental results, photolytic ozonation seems to be a promising alternative to H<sub>2</sub>O<sub>2</sub>-UV when working with UV-LEDs. Amongst others, the higher LRV of p-CBA might be explained by the higher molar absorption coefficient of O<sub>3</sub>. Nevertheless, effective fluence is influenced by the absorbance of the water matrix and the oxidant applied. A cost comparison for the different AOP systems is under evaluation.

## References

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