Advanced oxidation processes for emerging contaminants removal in wastewater and opportunities for water reuse

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Introduction:

- Advanced Oxidation Processes (AOPs) are effective in treating drinking water and wastewater by generating Reactive Oxygen Species (ROS) like hydroxyl radicals (•OH, O_3, •O_2), which oxidize and mineralize micropollutants. They are particularly useful for degrading hard-to-remove micropollutants which are found at low concentrations.
- Amongst AOPs, those based on ozone showed high efficiency in treating water.
- Electro-peroxone process (EPP), which combines ozone and hydrogen peroxide produced in an electrochemical cell has particularly been found very effective, but several factors influence its efficiency:

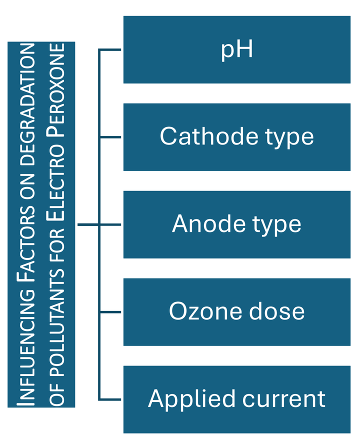
•pH levels: The process is most efficient at neutral to alkaline pH, with pH 7.5 showing nearly complete mineralization of emerging contaminants such as pharmaceuticals.

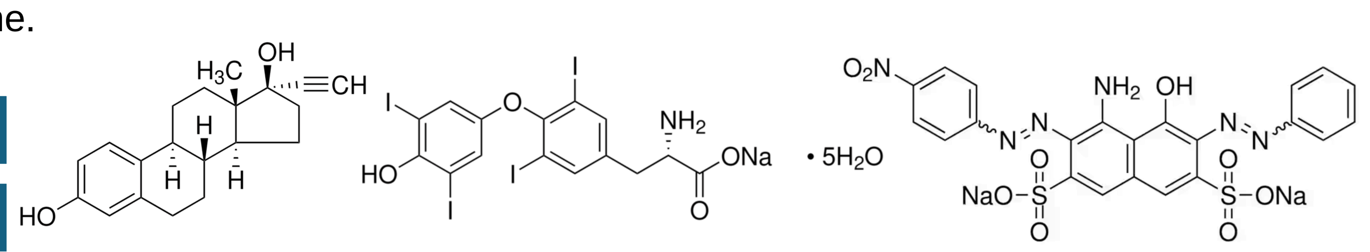
•Ozone dosage: Higher ozone levels enhance micropollutant removal, with exposure to ozone and hydroxyl radicals increasing linearly.

•Applied electrical current: While crucial for pollutant degradation, excessive current reduces efficiency due to ozone solubility limits and hydroxyl radical scavenging by excess H_2O_2.

•Cathode type: Carbon-based cathodes outperform metal ones in H_2O_2 production and process efficiency.

•Anode material: Has minimal impact on degradation rates, particularly for contaminants like oxalic acid and 1,4-dioxane.





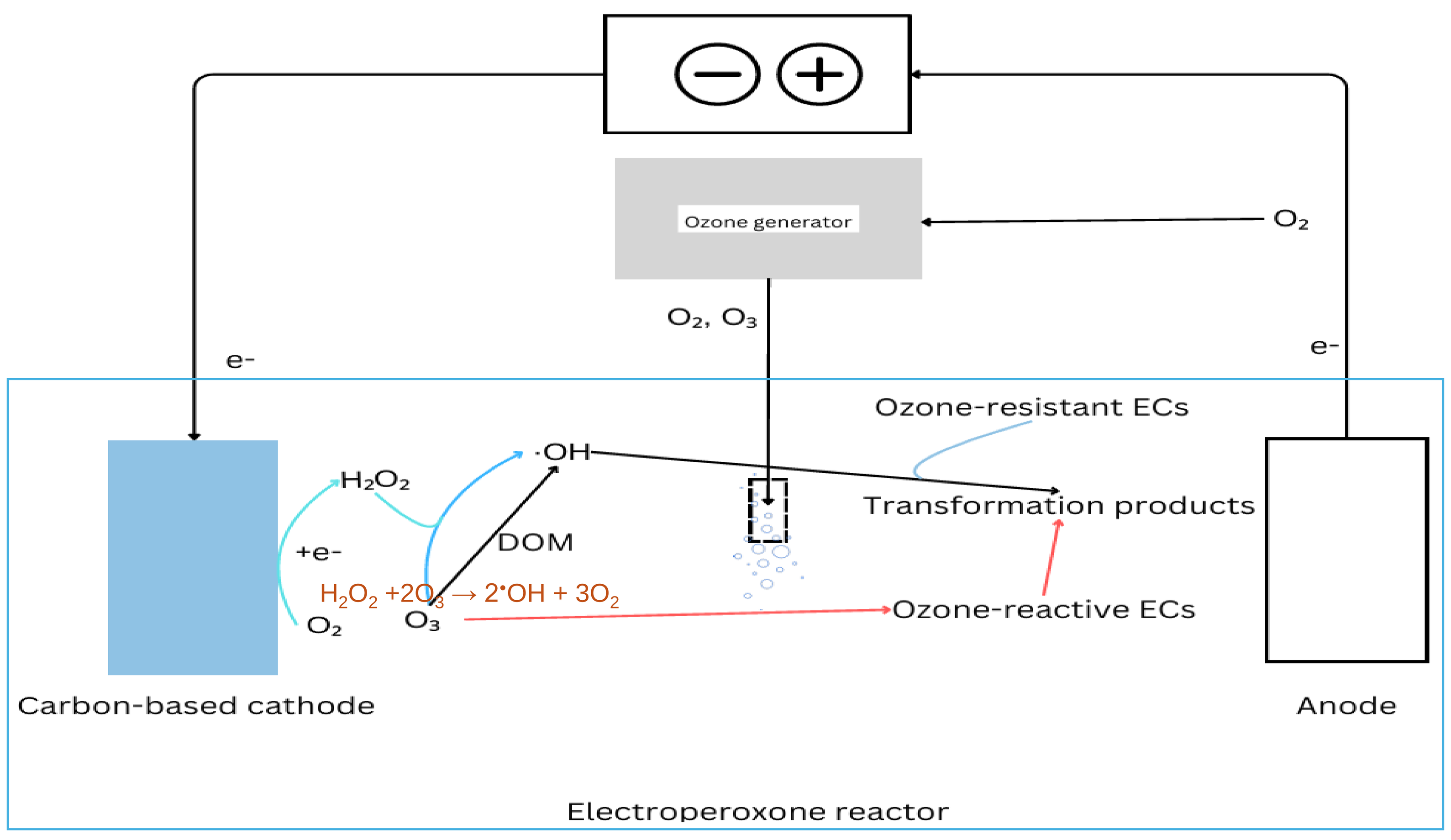
Ethinyl Estradiol   L-Thyroxine sodium salt pentahydrate   naphthol blue black

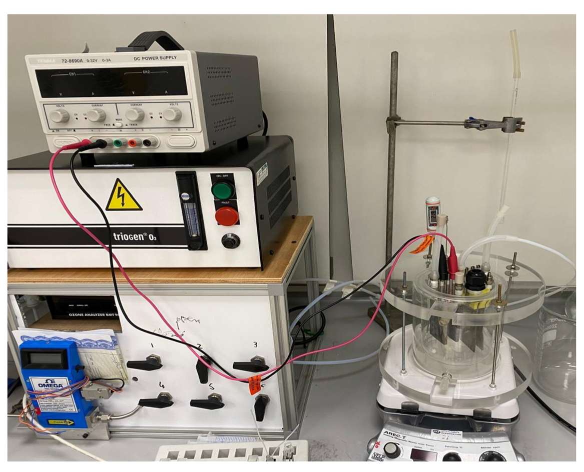
Objectives:

The aim of this investigation is to evaluate the efficiency of ozone-based AOPs including EPP in degrading emerging contaminants in water and to assess the potential for water reuse through circular water initiatives.

Methodology:

Several experiments will be conducted to degrade selected pharmaceuticals and antimicrobial substances, using ozone-based AOPs including peroxone and electro peroxone. The performance of these AOPs will be evaluated based on their kinetics, by-products formation, reactive species, gas/liquid mass transfer. The water will be characterized using a range of techniques, including COD, TOC, BOD, spectroscopy, HPLC/UV/MSMS, and GC/MS.





Results and discussion:

- Mass transfer was studied for the ozonation of DI water at different pHs using different types of acids to mimic real wastewaters. The experiments were run using oxygen flowrate of 500 mL/min and ozone concentration of 48 g/m³ NTP. The results showed that inorganic acids were more stable and did not alter the ozone mass transfer coefficient, however organic acids (e.g. acetic acid) increased the observed mass transfer coefficient due to their reaction with ozone (Fig. 1). In general ozone was found to be more stable at low pH (Fig. 2).
- EPP was evaluated for naphthol blue black (10 mg/L), as a model pollutant, with electrolyte 0.05 M Na_2SO_4, at voltage 10 V and current around 660 mA was done using carbon cathode and titanium anode. The ozone gas concentration was 25 g/m³ NTP at flow rate 500 mL/min. The results showed a rapid degradation of naphthol blue black using the EPP process (Fig. 3&4).

$$C_{AL} = \frac{K_L a \times C^*_{AL}}{K_L a + k_d}\left(1 - \exp\left(-\left(k_L a + k_d\right)t\right)\right)$$

Model O_3 mass transfer

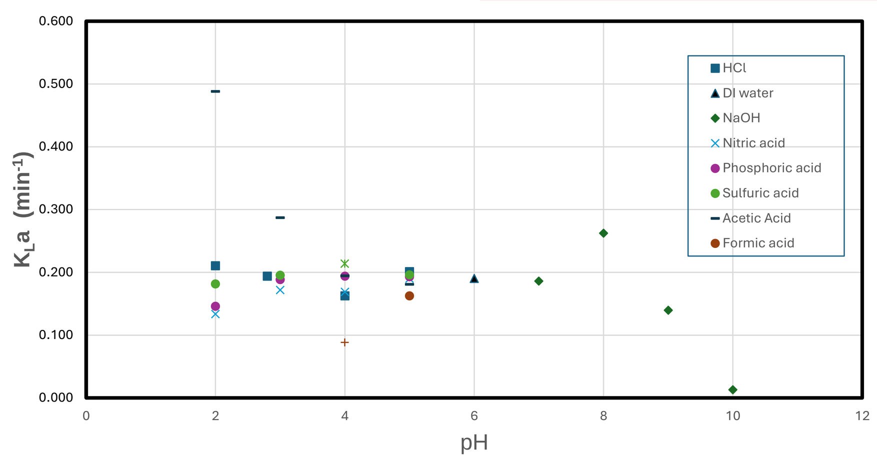


Figure 1: *K_La at different pH for acids and NaOH*

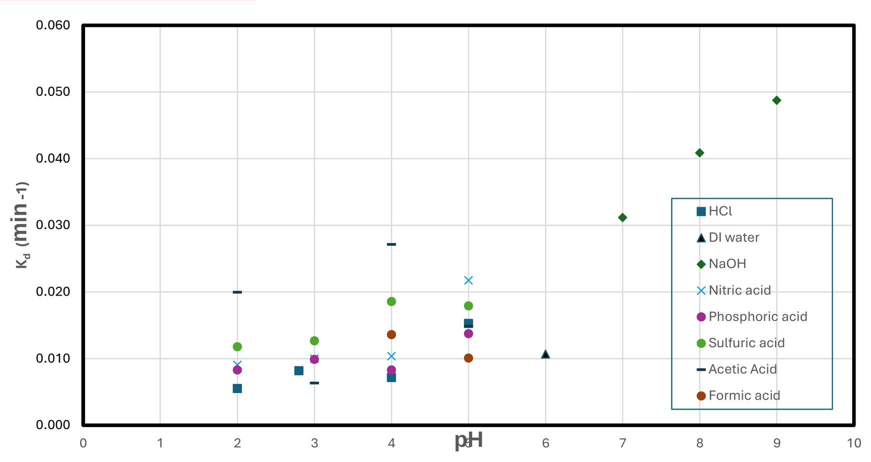


Figure 2: *K_d at different pH for acids and NaOH*

Table 1: *Average K_La (min^{-1}) of different acid and NaOH*

Type of aqueous medium	Average K_La (min^{-1})	pH
DI water	0.190	6
Base	-	
NaOH	0.196	7 to 9
Inorganic acids	-	
HCl	0.192	2 to 5
Sulfuric acid	0.180	2 to 5
phosphoric acid	0.180	2 to 5
nitric acid	0.166	2 to 5
Organic acids	-	
Acetic acid	0.288	2 to 5
Formic acid	0.125	4 to 5

Table 2: *Average K_d (min^{-1}) of different acid and NaOH*

	Average K_d (min-1)	pH
DI water	0.011	6
Base	-	
NaOH	0.040	7 to 9
Inorganic acids	-	
HCl	0.009	2 to 5
Sulfuric acid	0.015	2 to 5
phosphoric acid	0.010	2 to 5
nitric acid	0.013	2 to 5
Organic acids	-	
Acetic acid	0.017	2 to 5
Formic acid	0.012	4 to 5

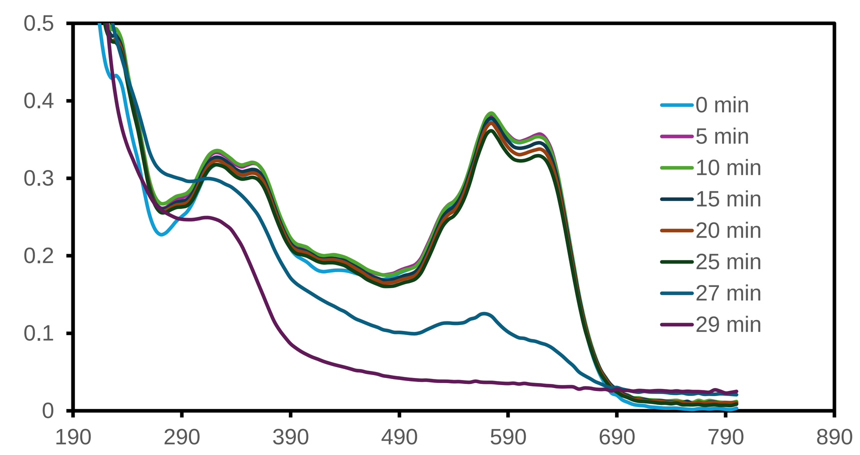


Figure 3: Spectra of electrolysis of naphthol blue black 10 mg/L

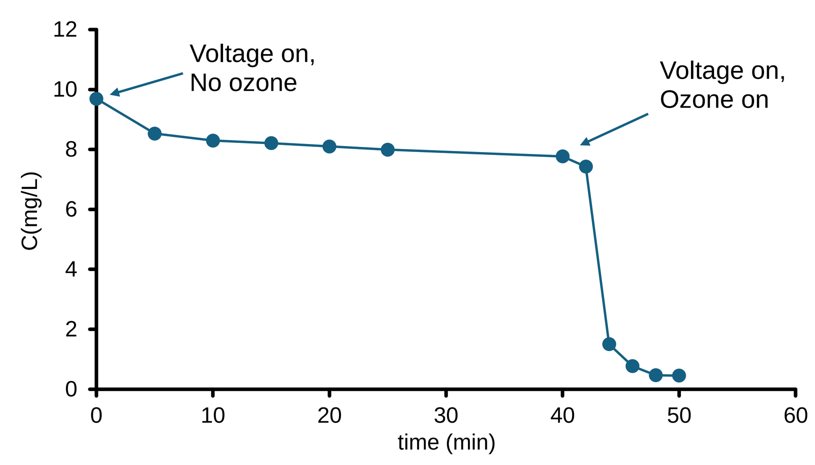


Figure 4: EPP for naphthol blue black degradation (voltage = 8V)

Conclusions:

- AOPs show excellent performance for treating emerging contaminants
- Further research is on going to optimise the technology
- This research will contribute to the development of sustainable and efficient technologies for the treatment and reuse of water and help to address challenges associated with water scarcity and pollution.

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