# Development and perspective of plasma-based water treatment technologies for the decomposition of persistent organic compounds

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**Abstract:** Establishing economical and eco-friendly technologies for water treatment is crucial for the realisation of a sustainable society. Plasma is a promising method for decomposing persistent organic compounds (POPs). Herein, the development of plasmabased water treatment processes to improve the rate and efficiency of the decomposition of POPs, such as acetic acid, is presented.

Keywords: Plasma-based water treatment, persistent organic compounds, OH radical, ozone.

## 1. Introduction

Water pollution has become a global issue of significant concern owing to the growth in population, industry, and agriculture. Conventional water treatment technologies include coagulation, sedimentation, filtration, ozonation, and disinfection using Cl [1]. However, persistent organic compounds (POPs) that are water-soluble cannot be treated using conventional technologies. Although the use of membranes, such as reverse osmosis membranes, is effective for the removal of organic compounds, this method has some disadvantages, such as fouling, which necessitates the maintenance or replacement of the membranes. The use of OH radicals (·OH), which have high oxidation potentials, is another promising option for the treatment of POPs. The aim of such treatment is to decompose organic compounds into CO<sub>2</sub> gas and water, which is referred to as mineralisation. Water treatment processes using OH are known as advanced oxidation processes (AOPs). Various types of AOPs have been studied extensively [2],[3], including the H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>, ultraviolet (UV)/H2O2, UV/O3, photo-Fenton, and TiO2assisted photocatalytic processes.

The use of plasma in contact with water is another AOP that has been studied for several decades by many researchers and scientific committees [4]-[8]. When plasma comes into contact with water, ·OH is generated from the water molecules in the gas phase via electronimpact dissociation and reactions with radicals, excited molecules, and metastable atoms. A portion of the ·OH generated in the gas phase diffuses into water and decomposes organic compounds. In addition to the diffusion of gas-phase ·OH, direct generation mechanisms for ·OH in water via the photodissociation of water under vacuum UV irradiation and charge exchange under positive ion irradiation have been proposed. A wide range of decomposition rates and energy efficiencies have been observed in the treatment of organic compounds using various plasma reactors and experimental conditions. Herein, the basic characteristics of plasma-based water treatment technology are introduced, and an improvement of the system for decomposing POPs is presented.

## 2. Small-Scale Treatments

Experiments on acetic acid decomposition by Ar plasma generated over a solution were conducted with a solution volume of 20 mL. A trade-off between the decomposition rate and energy efficiency was observed, and a numerical simulation revealed that hydrogen peroxide  $(H_2O_2)$ generated by a self-quenching reaction of OH radicals acts as a scavenger of  $\cdot$ OH, which resulted in the trade-off. The simulation also indicated that the penetration depth of  $\cdot$ OH is extremely shallow (less than 200 nm) [9]. Such a tradeoff was also observed in different types of plasma reactors, such as plasma generated within O<sub>2</sub> and Ar gas bubbles in a 10 mL solution, as shown in Fig. 1 [8].

## 3. Large-Scale Treatments

It is possible to generate plasma within gas bubbles in parallel by inserting a ballast capacitor between the highvoltage electrode and AC power supply [10], which enables an increase in the treatment solution volume from several tens of millilitres to a litre. One litre of acetic acid solution, with an initial concentration of  $30 \text{ mg}_{\text{TOC}}/\text{L}$  (TOC: total organic carbon), was treated with twenty-one plasmas generated within the O<sub>2</sub> bubbles under different input powers. In contrast to the previous small-scale treatments, the decomposition rate and efficiency were high at a low input power with small ballast capacitances, and when the solution pH was maintained at 7.3 by adding phosphate buffer [11]. This tendency was not observed for Ar bubbles [12], as shown in Fig. 2. These results indicate that the bulk reactions generating ·OH from H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> are important in the acetic acid decomposition process, in addition to the ·OH directly generated in the plasma. It was confirmed that with a low input power, more O3 and less H2O2 are



Fig. 1. Trade-off between TOC decomposition rate and efficiency in the decomposition of acetic acid. (Modified from [8].)

generated with the plasma generated within  $O_2$  bubbles [11],[13].  $O_3$  could be effectively used to regenerate  $\cdot OH$  from  $H_2O_2$  in a large-scale treatment due to the long residence time of the bubbles in the solution.

## 4. Plasma–Ozone Combination Process

To maximise the treatment efficiency of the plasmabased water treatment process,  $H_2O_2$  was generated by a diaphragm discharge [14], whereas  $O_3$  was generated by an ozoniser using a dielectric barrier discharge and supplied to the solution as fine bubbles through a diffuser. Such plasma-ozone combination processes overcome the tradeoff between the decomposition rate and efficiency, as shown by the red symbols in Fig. 3.

#### **5. Summary and Perspectives**

Many efforts have been made to improve plasma-based water treatment processes. Thus far, a plasma-ozone combination process is a promising method for decomposing POPs in remote areas, such as offshore oil plants. Extensive research to increase the decomposition rate and energy efficiency will continue. In addition, because the treatment efficiency is strongly affected by solution pH, the behaviour of the pH in a solution containing many kinds of foreign substances should be investigated.

#### 6. References

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Fig. 2. Decomposition of acetic acid by the twenty-one plasmas generated within  $O_2$  or Ar bubbles at high or low input power.  $C_0$  and C correspond to TOC concentrations before and during treatment, respectively.

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Fig. 3. Comparison of TOC decomposition rates and efficiencies between various methods [8]. The numbers in the figure correspond to the references in [8].