Production of hydroxyl radical and hydrogen peroxide by different types of plasma in contact with water

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Abstract: Hydroxyl radical and hydrogen peroxide are key species in the decomposition processes of persistent organic compounds using plasmas in contact with water. In this study, the production pathways of hydroxyl radical and hydrogen peroxide with two types of plasma in contact with water, namely Ar plasma generated over a water surface and diaphragm discharge plasma have been investigated.

1. Introduction

Treatment of wastewater containing organic compounds is one of the key issues in the protection of water resources. Although ozone (O_3) treatment has come into practical use, it is difficult to decompose persistent organic compounds such as acetic acid because the oxidation potential of O_3 is not sufficient. Hydroxyl radical (•OH) has a higher oxidation potential than that of many well-known oxidants. Thus, advanced oxidation processes (AOPs) using •OH have been studied extensively [1] and many kinds of plasma processes have been investigated as AOPs.

•OH has considerably high reaction rates and mainly converts to hydrogen peroxide (H_2O_2) by self-quenching in a short period. H_2O_2 can reproduce •OH through liquid-phase reactions with O_3, which is often referred to as a peroxone process. It was confirmed that a combined process of plasma in contact with water with O_3 aeration can achieve high energy efficiency and decomposition rate in decomposition of persistent organic compounds [2]. In this plasma/ozone combination process, the total energy efficiency can be further improved by improving the production efficiency of H_2O_2 by the plasma. In this study, the production pathways of hydroxyl radical and hydrogen peroxide with two types of plasma in contact with water, namely Ar plasma generated over a water surface and diaphragm discharge plasma have been investigated.

2. Methods

The details of Ar plasma generated over a solution are described in [3]. A metal disk with 84 needles is fixed to an acrylic cylindrical container. The acrylic container has one open end and is placed over a Petri dish that contains a solution (20 mL). The open end of the container is in contact with the solution, and Ar gas is fed into the container at a flow rate of 100 sccm. The gap distance between the needle tips and the solution surface is 1 mm. A grounded metal plate is placed at the bottom of the solution. Filamentary plasma channels are generated between the needle tips and the solution surface by applying a pulsed positive voltage to the needles.

The details of diaphragm discharge plasma are described in [4]. The reactor is mainly made of acrylic plates. One side of the reactor has a quartz window to observe optical emissions from the UV region. We prepared 20 mS/cm of a conductive solution by dissolving 20 g of sodium sulfate in 1 L of pure water and filling the reactor with the solution. An acrylic wall with a ceramic plate is used to separate the solution. The ceramic separation has ten holes with diameters of 0.3 mm where the electrical current is forced to flow. When bipolar high voltage pulses are applied to the reactor, the electrical current in the hole becomes high and vaporizes the solution around the hole. The vaporization forms H_2O bubbles, and diaphragm discharge plasma is generated in the bubbles.

3. Results and Discussion

The H_2O_2 production efficiency was decreased with increasing the input power to the Ar plasma generated over a solution. A numerical simulation revealed that •OH in a gas phase is mainly produced by a dissociation of H_2O by metastable Ar atoms [3]. Gas-phase H_2O_2 is produced by the self-quenching of •OH and diffuses into the solution. The contribution of direct generation of •OH in the solution will be investigated in the future.

On the other hand, the H_2O_2 production efficiency was improved with increasing the input power to the diaphragm discharge plasma. Here, the main pathway to produce gas-phase •OH is thermal dissociation of H_2O with a relatively high temperature inside the plasma [4]. Then, gas-phase H_2O_2 produced by self-quenching of •OH diffuses in to the solution.

4. Conclusion

In a diaphragm discharge plasma, •OH is mainly produced by thermal dissociation of H_2O, and the •OH is the main source of H_2O_2. The production efficiency could be increased by increasing the input power, which is suitable to achieve high production rate of H_2O_2 with a small reactor footprint.

Acknowledgement
This work was partially supported by JSPS KAKENHI Grant Number JP23H01393 and JP23K26088.

References
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