Water Purification by Using Microplasma Treatment

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Abstract. Dielectric barrier discharge microplasma generated at the surface of water is proposed as a solution for water treatment. It is an economical and an ecological technology for water treatment due to its generation at atmospheric pressure and low discharge voltage. Microplasma electrodes were placed at small distance above the water thus active species and radicals were flown by the gas towards the water surface and furthermore reacted with the target to be decomposed. Indigo carmine was chosen as the target to be decomposed by the effect of active species and radicals generated between the electrodes. Air, oxygen, nitrogen and argon were used as discharge gases. Measurement of absorbance showed the decomposition of indigo carmine by microplasma treatment. Active species and radicals of oxygen origin so called ROS (reactive oxidative species) were considered to be the main factor in indigo carmine decomposition. The decomposition rate increased with the increase of the treatment time as shown by the spectrophotometer analysis. Discharge voltage also influenced the decomposition process.

1. Introduction

Water pollution which caused by the industrial development is a problem of modern society. Conventional water treatment technologies are using chemicals, which makes the process expensive [1]. Nonthermal plasma found applicability in various field such as sterilization [2], cancer cell control [3], surface treatment [4], air treatment [5] and biomedical applications [6] due to high performance and low cost [7-9]. There are many plasma types for water treatment such as regional treatment by plasma jet [10-11], pulsed discharge in bubbling water [12-14] and pulse corona discharge using high voltage [15-17]. Needle-plate structure is often used due to the electric field concentration [18] however these methods need expensive and large device to supply the high voltage. The required voltage is in kilovolts order thus also safety is a concern. When considering the implementation of the technology, a small power supply will be required. [19-20].

Plasma discharge could generate various active species, radicals and ions [21]. Ozone, which is a one of the strong oxidizing agent, is used to destroy pollutant that are resistant to other chemical treatment [22]. However persistent substances such as DMSO (dimethyl sulfoxide) cannot be decomposed by ozone [23]. These substances could be decomposed by various active species. Thus plasma is an efficient method to be applied as the water treatment technology.

Our purpose is to apply the water treatment technology by microplasma. Microplasma which is a dielectric barrier discharge at atmospheric pressure could generate active species and radicals at relatively low discharge voltage. In this research, as the microplasma electrodes, a pair of perforated metallic plates covered with a dielectric layer, were used to generate microplasma. Electrodes were placed at small distance above the water and gas passed through the holes of electrode thus flowing towards the surface the water. As the treatment target, indigo carmine diluted in water was used as the
organic compound to be decomposed by microplasma treatment. Indigo carmine used in food industry was used as the target to be decomposed and furthermore to evaluate the effect of microplasma treatment.

2. Microplasma electrode and mechanism of water treatment

![Figure 1](image1.png)

**Figure 1.** Mechanism of water treatment by microplasma. Whole size of the electrode was 60 mm, diameter of the hole was 2.0 mm and flow rate was 10 L/min. BaTiO$_3$ was used as the dielectric barrier and its thickness was 100 µm. Electrodes were placed above the water at a distance of about 5 mm. Active species could be generated such as O$_3$s and O$_3$p between electrodes that affected and decomposed the organic compounds[24].

Figure 1 shows the schematic of microplasma electrode and mechanism of water treatment. It is difficult to generate microplasma in water due to the high electric conductivity at low discharge voltage. Electrodes were placed above the water to generate microplasma in gas phase. Microplasma electrodes were perforated metallic plates covered with a dielectric layer and faced together at small discharge gap of about 100 µm using a spacer. Only a low discharge voltage which is the one feature of the microplasma, was required due to the narrow discharge gap. The spacer also blocked the gas flow to establish the discharge area. When the voltage was applied between electrodes, microplasma was generated. Discharge voltage depends on the discharge gap and carrier gas. The various active species and radicals generated by microplasma between the electrodes were supplied to the water surface by the carrier gas and reacted to decompose the indigo carmine solution. The distance between the electrode and water surface was about 5 mm and the transit-time for the active species to reach the water surface was about 0.25 ms. Thus allowing that active species and radicals such as O$_3$ to reach the target to be decomposed. The total amount of the indigo carmine was 200 mL.

3. Experimental setup

![Figure 2](image2.png)

**Figure 2.** Experimental setup used for the water treatment by microplasma. AC power supply, four types of carrier gas and indigo carmine were used in this experiment. A Spectrum photometer, ozone monitor and ESR (electron spin resonance analyzer) were used as the evaluation methods.

Figure 2 shows the experimental setup for the water treatment by using microplasma. The carrier gases were supplied in case of the air from an air pump and in case of N$_2$, Ar and O$_2$ from gas cylinders. Experiments were carried out at atmospheric pressure at a gas flow rate of 10 L/min. The
indigo carmine solution which had concentration of 10 mg/L was used as the treatment sample. Active species generated by microplasma could react with the target liquid. The water pump placed under the treatment container had the role to assure a continuous flow of water under the electrodes for a uniform treatment of indigo carmine. The water depth beneath the electrodes was about 10 mm as shown in figure 1, small enough to react with the active species generated by the microplasma treatment. A UV-VIS(UV-3100PC, SHIMADZU) was used to measure the absorbance of the liquid and furthermore estimate its organic composition. The ozone concentration in gas phase and liquid phase were analyzed by the gas phase ozone monitor (SOZ-3300, SEKI ELECTRONICS) and the liquid phase ozone monitor (PL-620A, EBARA JITSUGYO), respectively. Ozone concentration is an important factor to consider the water treatment. The ESR(electron spin resonance analyzer)(EMX plus, BRUKER) was used to analyze the radicals dissolved in water by microplasma discharge.

A neon transformer was used as an AC power supply to generate microplasma [25]. Figure 3(a), (b) shows the waveform of the discharge voltage and corresponding discharge current during discharge.

These values contained the voltage drop with the dielectric material.

![Figure 3(a). Discharge voltage and corresponding discharge current waveforms. Discharge voltage was about 1.00 kV.](image1)

![Figure 3(b). This is the short width waveform during discharge. The current peak value was about 150 mA at 25 kHz.](image2)

4. Result and Discussion

4.1 Observation of indigo carmine absorbance

![Figure 4. The analysis of absorbance using spectrum photometer. Continuous line corresponds to the non-treated liquid and two dashed lines correspond to the treated liquid. Two absorption peaks of indigo carmine were decreased by microplasma treatment. The decomposition rate increased with the treatment time. Discharge voltage was 1.0 kV, the carrier gas was air.](image3)

The absorbance values of indigo carmine solution versus treatment time are shown in figure 4. The peaks at 610 nm and 290 nm were corresponded to the absorption peaks of indigo carmine’s organic compound [26]. Peaks’ height decreased after microplasma treatment suggesting that the organic compound of the indigo carmine solution was decomposed during microplasma treatment by the various active species.

In gas phase, this reaction was occurred during discharge [27].

\[
O + O_2 + M \rightarrow O_3 + M
\]
In water these active species were generated during discharge via reactions (2), (3) and (4) [28]. Because air was used as carrier gas O and e could reach the water and promote chemical reactions.

\[
O^· + H_2O \rightarrow \cdot OH + OH^+ \quad (2)
\]

\[
e^· + H_2O \rightarrow \cdot OH + H^+ e^- \quad (3)
\]

\[
\cdot OH + OH \rightarrow H_2O_2 \quad (4)
\]

Among these active species and radicals, OH and O3 could play an important role in the decomposition process of indigo carmine [29].

![Chemical composition of the indigo carmine and its decomposition process.](image)

**Figure 5.** Chemical composition of the indigo carmine and its decomposition process. Left structure corresponding to indigo carmine, right to isatin sulfonic acid. The double bond could be broken by the active species and radicals generated by microplasma [30].

The chemical reaction and structural formula of indigo carmine is shown in figure 5. Indigo carmine has H type chromophoric group, therefore absorbs the visible light of a specific wavelength and gives its colour blue [31]. Indigo carmine has the H type chromophoric group to take on the blue color. The indigo carmine was changed to the isatin sulfonic acid after breaking the H type chromophoric group by the active species and radicals generated microplasma [32]. The double bond of indigo carmine could be broken by microplasma.

4.2 Decomposition rates of indigo carmine for various carrier gases.

![Decomposition rate](image)

**Figure 6.** The decomposition rate of indigo carmine for various carrier gases. Oxygen was the most efficient for decomposing indigo carmine. Opposed to the oxygen and air, when using argon and nitrogen the decomposition rates were lower because of the absence of oxygen. Discharge voltage was 1.0 kV

Figure 6. shows the decomposition rates for various carrier gases. Decomposition rate was calculated under the initial and after the treatment value of absorbance as shown in the formula (5). Decomposition rates of the indigo carmine solution by the argon and nitrogen gases were lower because of the absence of the oxygen. Air and oxygen were higher due to the active species of oxygen origin.

\[
\text{Decomposition rate} = \frac{(\text{Initial absorbance}) - (\text{After treated absorbance})}{\text{(Initial absorbance)}} \times 100 \quad [\%] \quad (5)
\]

4.3 Ozone concentration in gas phase

Ozone concentration generated from microplasma discharge is shown in figure 7. Air was used as the carrier gas and flow rate was set at 10 L/min. For measuring the dissolved ozone concentration in liquid, treatment time was 10 min. and treatment volume was 200 mL of distilled water. The ozone concentration in gas phase and liquid phase increased with the increase of the discharge voltage. However total ozone generated in gas phase could not be dissolved in liquid phase. About 0.5-2.2% of the total ozone generated in gas phase was dissolved in water. This ozone also affected to decomposition process of the organic compound contained in indigo carmine.
Figure 7. Ozone concentration versus discharge voltage measured in gas phase and liquid phase by microplasma. The ozone concentration increased with the increase of the discharge voltage. Treatment time was set at 10 min. and water temperature was 26°C.

4.4 Radical analysis by the ESR method
Figure 8 shows the result of the ESR analysis which detected the dissolved OH radical generated by microplasma in water. In this analysis, spin trap agent 5,5-dimethyl-1-pyrroline N-oxide (DMPO) was used due to the short-lived radical of OH radical in liquid phase [33]. The four peaks shown in figure 8 correspond to the OH radical peaks generated by microplasma and detected by the spin trap agent [34]. OH radical could be effective factor to decompose the indigo carmine due to its oxidation process [35].

5. Conclusions
Microplasma could be used as an economical and ecological technology. Water treatment using microplasma was carried out and the following conclusions were obtained:
1. Indigo carmine was decomposed after microplasma treatment and decomposition rate increased with the treatment time.
2. The presence of OH radical could be one of the main factor to decompose indigo carmine. It was dissolved in the water as confirmed by using the ESR.
3. About 0.5-2.2% of the ozone generated in gas phase was dissolved in water at the room temperature.
4. Active species of oxygen origin could be considered as the main factors in indigo carmine decomposition as demonstrated by higher decomposition rates obtained with microplasma generated in oxygen and air.

6. Reference
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