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Chapter

A Novel Wastewater Treatment Method Using Electrical Pulsed Discharge Plasma over a Water Surface

Katsuyuki Takahashi, Koichi Takaki and Naoya Satta

Abstract

Electrical pulsed discharge plasma produces various powerful oxidizing agents, such as hydroxyl radicals and ozone, which have high oxidation potential. These species play an important role in the decomposition of persistent organic compounds in wastewater. Because highly concentrated oxidants are directly produced inside the plasma, plasma realizes high-speed wastewater treatment without pretreatment of samples, such as pH adjustment. The pulsed discharge plasma generated over the water surface and inside bubbles is highlighted as a highly efficient method for plasma generation and radical supply into wastewater. In this paper, the physical and chemical properties of the discharge plasma generated over a water surface are described. The decomposition of persistent organic compounds dissolved in wastewater, such as 1,4-dioxane, formic acid, and dichloromethane, by plasma discharge is demonstrated, and their mechanisms are discussed. These persistent compounds, which have strong toxicity and stability, can be efficiently decomposed and removed quickly from solutions by plasma treatment. Furthermore, the treatment of nutrient solutions used in hydroponic systems for plant cultivation is also introduced as a novel application of plasma, and the effects of bacterial inactivation, decomposition of allelochemicals, and improvement in plant growth by plasma are demonstrated.

Keywords: plasma, wastewater, persistent compounds, advanced oxidation process, hydroxyl radical, oxidation, ozone

1. Introduction

Electrical pulsed discharge under water, an advanced oxidation process (AOP), can instantaneously produce chemically active species such as hydroxyl radicals and ozone in a nonthermal plasma [1–3]. It is well known that these species are powerful oxidizing agents that play an important role in degrading persistent organic chemical compounds and sterilizing bacteria in wastewater [4, 5]. Hydroxyl radicals can contribute to the decomposition of persistent organic pollutants, which cannot be decomposed by conventional methods because of their very high oxidation potential. Wastewater treatment using discharge plasma has several advantages over other AOPs. In the plasma system, active species are directly produced in plasma

through various reactions initiated by high-energy electron impact. These active species are directly dissolved into water, and then oxidation reactions are induced. Because only electricity-supplied metal electrodes and a high voltage power supply are needed to generate plasma, pretreatment of water, such as pH adjustment is not required for active species production, unlike other AOPs such as Fenton and ozone/hydrogen peroxide methods [6]. Plasma can also be adapted for the treatment of water, which has ultraviolet (UV) light non-transmitting properties, which is advantageous over AOPs utilizing UV light, such as photocatalytic processes and UV-hydrogen peroxide methods. In the case of plasma discharge in contact with water, the types of active species produced in plasma can vary by atmospheric gas species. The production of active species can be localized near the plasma channel. Thus, water treatment using plasma discharge can be useful in various uses. Furthermore, because the density of active species in plasma is very high, it can also be used for the treatment of highly concentrated wastewater. These characteristics of discharge plasma can make the system simple, easy to use and easy to install anywhere. Owing to these advantages, the plasma technique has attracted attention as a promising method in various fields, such as industrial and environmental wastewater treatment [4, 6, 7] and material [8], agricultural [9, 10], and medical applications [11].

In this article, characteristics of discharge plasma generated by pulsed high voltages, chemical reactions induced by plasma, and treatment of persistent organic pollutants such as 1,4-dioxane and dichloromethane dissolved in water by plasma discharges are introduced. Agricultural applications of discharge plasma in contact with water surfaces are also mentioned as a novel application.

2. Generation of pulsed discharge plasma

Plasma is one of the states of matter and consists of high-density electrons and ions produced through ionization reactions of neutral gas atoms and molecules. Ionization is initiated by an impact of high-energy electrons accelerated by a high electric field; then, the electron and ion densities rapidly increase due to an electron avalanche phenomenon, and plasma forms [12]. To generate a high electric field, a sharpened metal electrode to which a high voltage is applied is generally used. Although various kinds of voltage waveforms, such as DC and AC, are employed, a pulsed high voltage generated by a pulsed power generator is used for highly efficient plasma generation, [13, 14] especially under water. Pulsed power is a special technology used to generate a pulse voltage that has a high voltage amplitude over several tens of kV, high power over several tens of kW, short pulses on the order of nanoseconds, and high pulse frequencies over several kHz, achieved with a compact system [15].

When a pulsed high voltage is applied to pointed electrodes immersed in water, discharge plasma is generated at the tip of the electrode. One of the formation mechanisms of the discharge plasma in water using a long pulse voltage on the order of several μs is considered as follows: In the first step, the discharge is initiated in a small bubble on the electrode surface, and then it propagates into the water, as shown in **Figure 1**. The current in the high electric field region causes Joule heating and vaporization of the liquid, forming bubbles [16–18]. The electron density in the plasma directly generated under water is very high, on the order of 10^{25} m^{-3} [19], which can produce very high density chemically active species such as hydroxyl radicals and contribute to high-speed wastewater treatment. The plasma discharge under water can also produce strong shock waves with pressure on the order of several GPa. The problem with this method is that wastewaters exhibit high

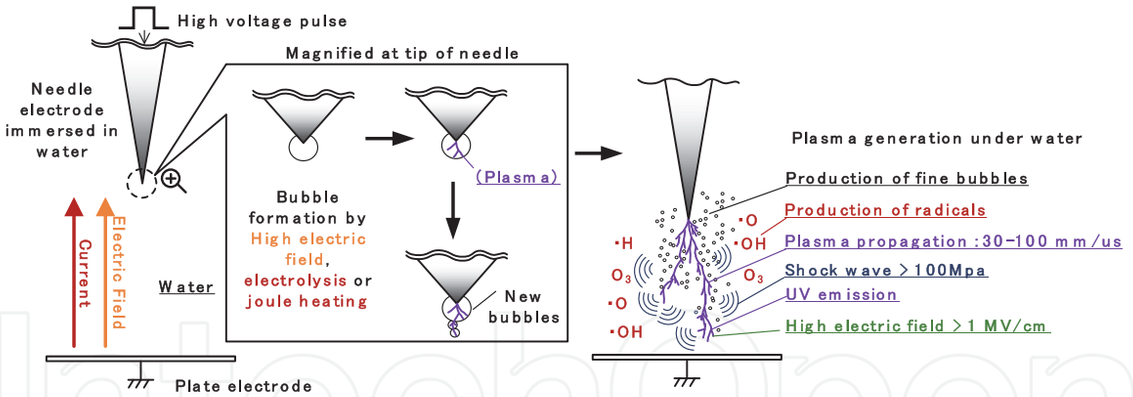


Figure 1.
Schematic illustration of discharge plasma using electrodes immersed in water.

conductivity due to the high concentration of various substances. When a voltage is applied to the electrodes immersed in water, which has high conductivity, a large current flow, and large energy are dissipated during Joule heating, which does not contribute to chemically active species production. The discharge volume decreases with increasing conductivity of the water at the same input energy. As a result, the energy efficiency for water treatment by discharge decreases to a low value under high-conductivity water conditions. Furthermore, because the breakdown strength of water is 300 MV/m and is 10 times higher than that of air (3.2 MV/m), high voltage is required to generate plasma discharges under water and to increase plasma volume. To solve this problem, methods to generate a pulsed discharge in contact with water using an electrode in the gas phase have been investigated [20–22]. Because the electrode is insulated by gas, the energy loss caused by the conductive current is significantly reduced. Plasma generation in the gas phase is much easier than that in the liquid phase, which contributes to a decrease in operating voltage and makes the system compact and light.

Various methods to generate a pulsed discharge in contact with water have been proposed [23, 24]. **Figure 2** shows schematic illustrations and photographs of

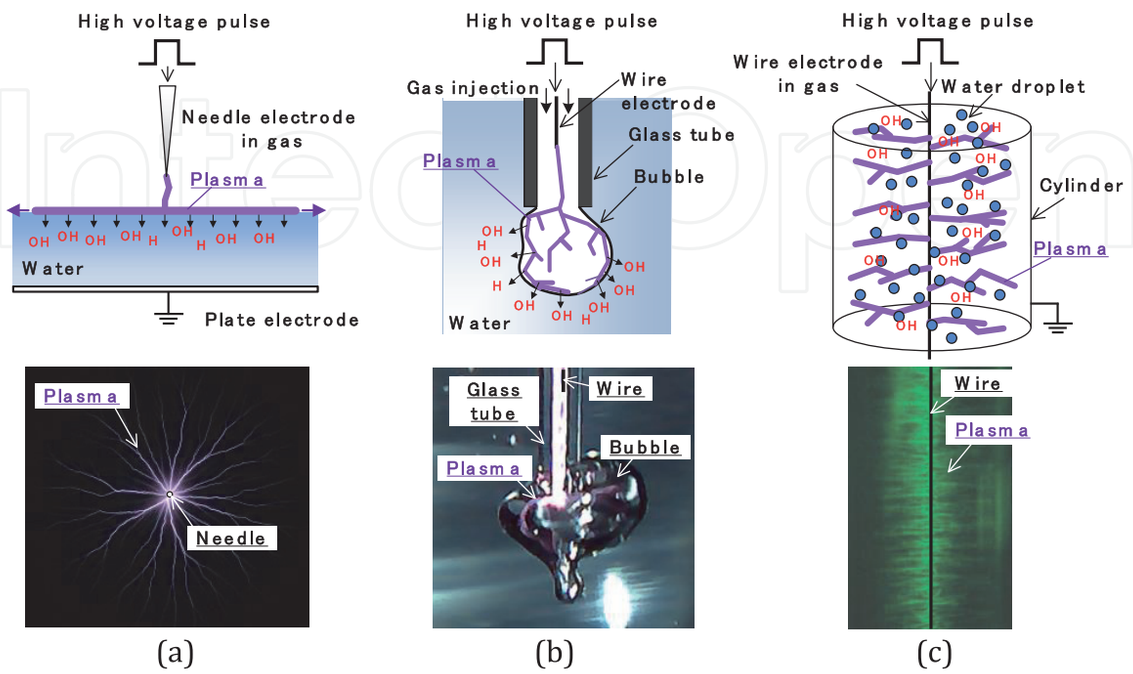


Figure 2.
Schematic illustrations and photographs of pulsed discharge in contact with water generated (a) above the stationary water surface, (b) inside the bubble, and (c) area where droplets are sprayed.

examples. The simplest method is to generate discharge that propagates and spreads over the water surface by using a high-voltage electrode placed above stationary water, [25, 26] as shown in **Figure 2(a)**. The chemical species generated in the plasma discharge are dissolved into the water and react with organic compounds in the water as described later. The discharges generated inside bubbles as shown in **Figure 2(b)**, which are produced by injecting gas into the water using a gas feed tube, have been widely investigated [23, 26–28]. This method has advantages such as a high ratio of water surface to gas volume, easy control of the gas purity and components, easy use in various fields, and automatic water circulation. The reactor can be simply constructed as shown in **Figure 3(a)** [29]. This reactor consists of a sealed glass vial for gas chromatography and glass tubes in which wire electrodes are inserted. Because the glass vial is sealed, the purity of the gas component in the reaction area in the vial can be improved. The treatment speed and volume can be increased easily by increasing the number of gas feed tubes and electrodes, as shown in **Figure 3(b)**. **Figure 3(c)** shows a reactor consisting of a separator film that has tiny pores and a high voltage wire electrode in the gas phase [20]. Multiple

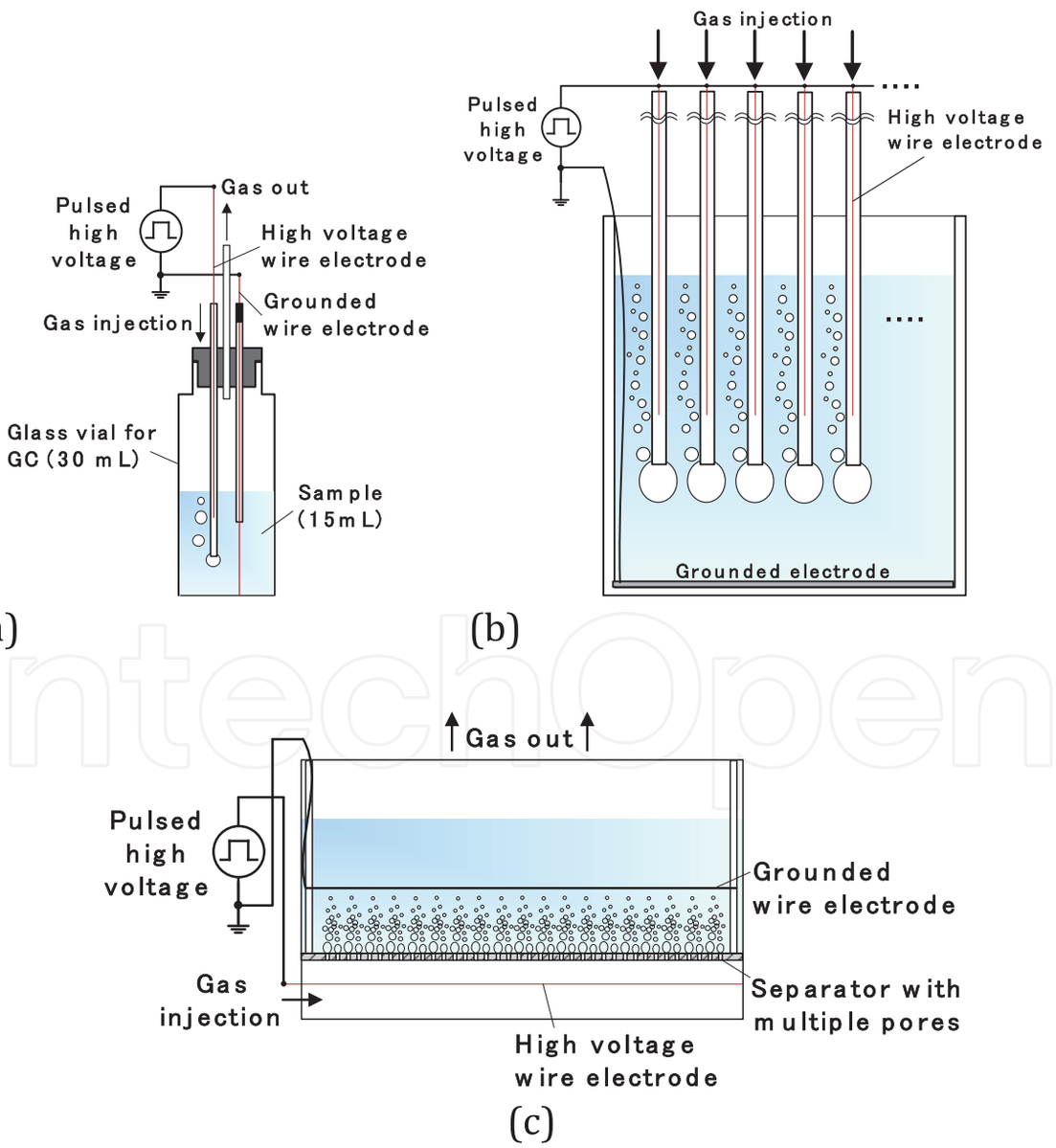


Figure 3.
A reactor used for pulsed discharge generation inside bubbles using (a) a single electrode inserted in a sealed glass vial, (b) parallel electrodes inserted in a vessel, and (c) a separator with multiple pores and a high voltage wire electrode placed in the gas phase.

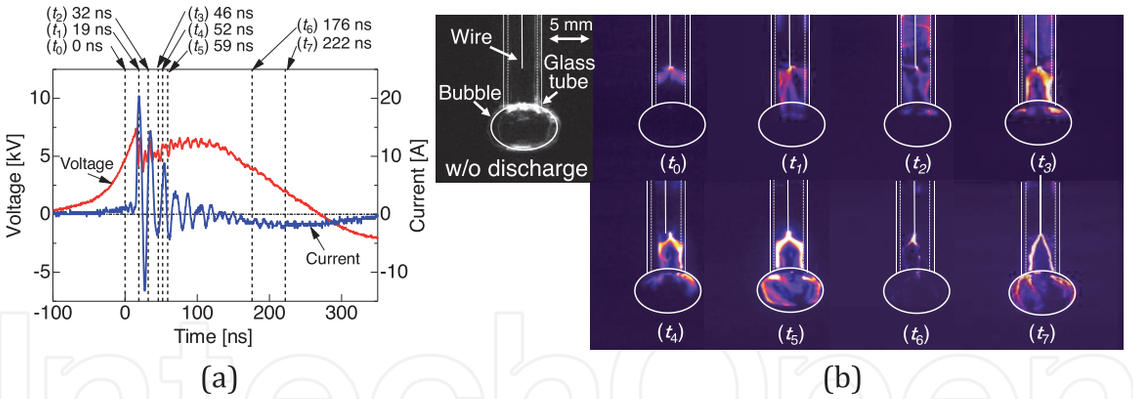


Figure 4.
(a) Typical voltage–current waveforms and (b) flaming photograph of discharge generated inside argon bubble.

discharge plasmas occur simultaneously on the wire electrode surface, which propagates into the bubbles. The separator film is used to separate the liquid phase and gas phase for insulation of the high voltage electrode. Instead of the separator and the wire electrode, ceramics with millipore needle electrodes have been used in some studies [7, 30].

When a pulsed high voltage is applied to the high-voltage electrode in the gas phase, the discharge propagates into the bubble surface from the high-voltage electrode [31, 32]. **Figure 4** shows typical voltage–current waveforms and flaming photographs of the pulsed discharge generated in an argon bubble, as shown in **Figure 2(b)** taken by using an intensified CCD camera with an exposure time of 5 ns. At time t_0, a corona discharge occurs at the tip of the electrode, and then, the discharge propagates to the tip of the glass tube along the surface of the glass at t_1 and t_2. Inside the glass tube, discharge occurs at not only the tip of the electrode but also the side of the electrode, as observed with dielectric discharges. At t_3, the discharge propagates along the bubble surface and does not travel to the bubble at t_3 to t_5. The results obtained by numerical simulation also show that a large part of the discharge inside the bubble propagates along with the bubble with similar size of bubbles [33, 34]. The propagation velocity of the discharge is 2.7–3.6 $\times$ 10^5 m/s in the Ar gas bubble [32] and 5 $\times$ 10^5 m/s on the surface of a glass tube filled with air, [31] which correspond to the surface discharge over a dielectric material under atmospheric pressure [35, 36]. When the voltage drops, the discharge disappears at t_6, but back discharge occurs again at t_7 due to the electric field formed by charges accumulated over the bubble surface.

Conductivity is the most important parameter for discharge propagation. Generally, the energy efficiency for discharge generation and propagation over a water surface is strongly affected by the conductivity of the water [32, 37]. **Figure 5** shows the equivalent circuit model [38] of (a) discharge in contact with water using the electrode system shown in **Figure 2(b)** discharge generated under water using the electrode system shown in **Figure 1**. When a breakdown occurs, switch SW_1 is turned on. The plasma impedance $Z_{P(t)}$ depends on the electron density of the plasma and changes with time during voltage application. The equivalent circuit of the water surface is expressed as the resistor R_L and capacitor C_L connected in parallel. The resistance of the resistor decreases with increasing conductivity. The discharge in contact with water propagates with the charging water surface. The decrease in resistance enhances the leakage of the accumulated charge on the surface of the bubble with decreasing conduction relaxation time, which is expressed by dividing the permittivity by the conductivity of the solution, which concentrates the discharge current and decreases the electric field. Therefore, the

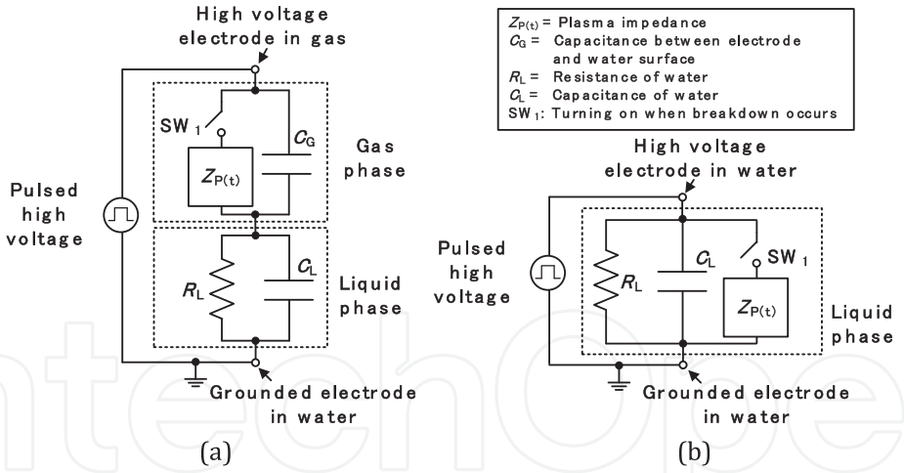


Figure 5.
Equivalent circuit model of (a) plasma contacted in water and (b) plasma generated under water.

discharge length decreases with increasing conductivity. For example, in the case of pulsed discharge generated inside a bubble as shown in **Figure 4**, the maximum discharge length decreases by 50% by increasing conductivity from 7 μS/cm to 1000 μS/cm [32].

When the electrode is placed in the gas phase and is not in contact with water, conductive current does not flow into the water without plasma generation, *i.e.*, without SW_1 turning on. On the other hand, when the electrode is placed in water, conductive current always flows into the water, which causes energy loss, and the energy efficiency for active species production decreases. This is one of the reasons that the energy efficiency of a wastewater treatment method using plasma contacted water is much higher than that using plasma directly generated under water [39]. Using this method, the energy efficiency can be improved over tens of times, especially for highly conductive wastewater treatment [39].

To reduce the influence of the conductivity, a method to generate streamer discharges into the area where droplets are sprayed using a pulsed high voltage is proposed as shown in **Figure 2(b)** [40]. This is one of the most efficient methods to supply chemical species into the water because streamer generation in the gas phase is not affected by water droplets, and the contact area between the discharge and water is large.

3. Production of chemical species by discharge plasma

In the plasma generated in the gas phase, various chemically active species such as ozone (O_3), oxygen radicals (O), and hydroxyl radicals (OH) are produced and dissolved at the water surface. Since these species have a high oxidation potential, they can contribute to wastewater treatment, *i.e.*, the decomposition of organic compounds and the inactivation of bacteria. The production reactions are initiated by the impacts of high-energy electrons on neutral molecules. Representative reactions in a gas that contains O_2, N_2, and Ar are as follows: [41–43].

$$O_2 + e\ (>8.4\ eV) \rightarrow O(^1D) + O(^3P) + e \quad (1)$$

$$O_2 + e\ (>5.58\ eV) \rightarrow O(^3P) + O(^3P) + e \quad (2)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \quad (3)$$

$$H_2O + O(^1D) \rightarrow 2OH \quad (4)$$

$$N_2 + e\ (>9.0\ eV) \rightarrow N(^4S) + N(^2D) + e \quad (5)$$

$$N(^2D) + H_2O \rightarrow OH + NH \quad (6)$$

$$N(^2D) + O2 \rightarrow NO + O(1D) \quad (7)$$

$$N(^2D) + O_2 \rightarrow NO + O(^3P) \quad (8)$$

$$Ar + e\ (>11.55\ eV) \rightarrow Ar(^3P) + e \quad (9)$$

$$Ar(^3P) + H_2O \rightarrow Ar + OH + H \quad (10)$$

$$H_2O + e\ (>7.1\ eV) \rightarrow OH + H + e \quad (11)$$

$$H_2O + e\ (>12.62\ eV) \rightarrow H_2O^+ + 2e \quad (12)$$

$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH \quad (13)$$

where (3) is a three-body recombination reaction and a neutral molecule such as O_2, N_2 or Ar is the third collision partner (M), which takes part in energy absorption, but does not react chemically. Ar, a noble gas, is generally used for highly efficient plasma generation at low cost. Because the reaction rates of (11) and (12) are not high in atmospheric nonthermal plasma, OH is mainly produced by indirect reactions such as reactions (4), (6) and (10) [44–46]. When a water surface is used as the cathode, OH is also produced under water by the bombardment of high-energy positive ions produced inside plasma, such as H_2O^+ and Ar^+, to the water surface [47, 48].

$$Ar + e\ (>15.8\ eV) \rightarrow Ar^+ + 2e \quad (14)$$

$$Ar^+ + H_2O \rightarrow H_2O^+ + Ar \quad (15)$$

$$H_2O^+ \rightarrow OH + H^+ \quad (16)$$

Figure 6 shows typical emission spectra of the discharge inside the Ar or O_2 bubble. The peaks at wavelengths of 282 and 308 nm are the $A^2\Sigma^+$ (v = 1) → $X^2\Pi$ (v = 0), and $A^2\Sigma^+$ (v = 0) → $X^2\Pi$ (v = 0) emission lines of OH, respectively. The peak at 656 nm is attributed to a Balmer H-alpha emission [32]. These peaks are strongly observed in argon gas because of its high electron density. In O_2 gas, the peak at a wavelength of 774 nm corresponds to the atomic oxygen (O) transition of

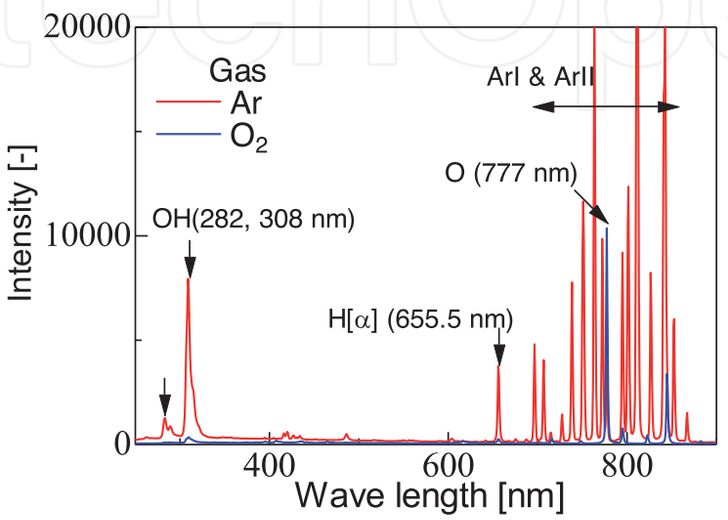


Figure 6.
Typical emission spectra of discharge inside argon or oxygen bubble.

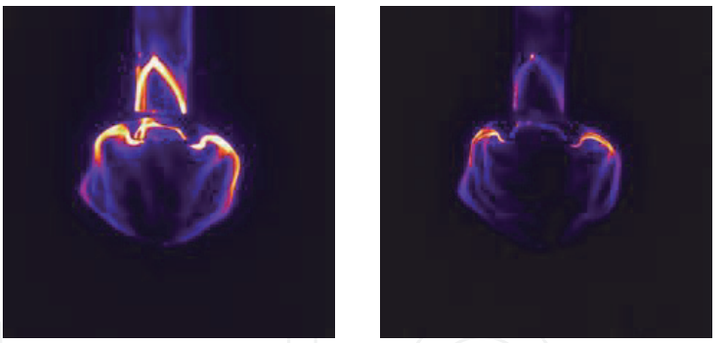


Figure 7.
Photograph of discharge inside the bubble (a) without and (b) with a bandpass filter (310 ± 10 nm).

$3p^5P\text{-}3s^5S^0$. **Figure 7** shows the photograph of discharge inside an Ar bubble taken by a high-speed intensified CCD camera with and without a bandpass filter with a bandwidth of 310 ± 10 nm, showing light emission with a wavelength corresponding to an excitation line of OH (308 nm). The photograph shows that the excitation-emission of OH with a wavelength of 308 nm is observed at the same position of the plasma channel generated along the bubble surface observed without the bandpass filter. This result shows that OH is produced inside the plasma channel.

Because these oxidants have high reactivities, they are consumed in loss reactions in both the gas and aqueous phases, which decreases the efficiency of wastewater treatment as shown in **Figure 8**. OH is well known as the most powerful oxidant and has a very short lifetime. OH is mainly lost by three-body recombination reactions, as shown in reaction (17) in the gas phase and reactions (18) and (19) in the aqueous phase [49, 50].

$$OH + OH + M \rightarrow H_2O_2 \quad (17)$$

$$OH + OH \rightarrow H_2O_2 \quad (18)$$

$$OH_) + H \rightarrow H_2O \quad (19)$$

The lifetime and diffusion constant of OH in the gas phase are on the order of 10^{-5} s and 10^{-10} m^2/s, respectively, and the diffusion length is several tens of μm [51]. The lifetime of dissolved OH is on the order of $10^{-6} \sim 10^{-7}$ s with penetration lengths on the order of $10^{-5} \sim 10^{-6}$ m [52–54]. **Figure 9** shows the hydrogen peroxide (H_2O_2) concentration produced by the OH recombination reaction, as

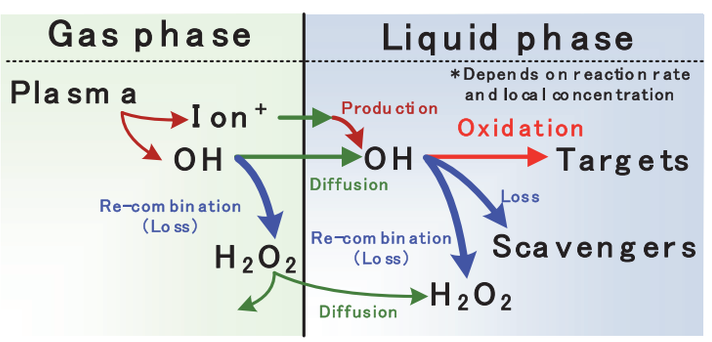


Figure 8.
Schematic illustrations of reactions of OH produced by plasma at the vicinity of water surface.

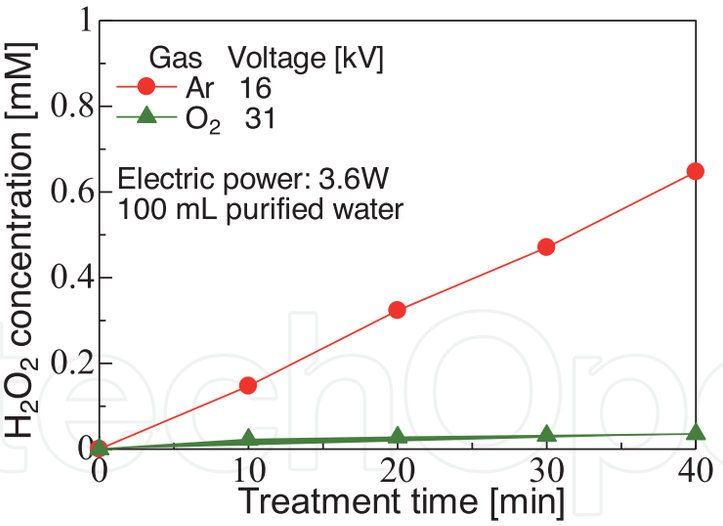


Figure 9.
Time change of the H_2O_2 concentration produced by plasma treatment.

described later, as a function of treatment time by plasma generated inside Ar or O_2 bubbles. In this case, 100 mL of dye solution was treated by plasma discharges generated inside bubbles produced by multiple pores, as shown in **Figure 3(c)**. The gas flow rate is 4.5 L/min. Pulse voltages with an amplitude of 20 kV, a pulse width of 160 ns, and a pulse repetition rate of 250 Hz are applied to the wire electrode placed in the gas phase to generate plasma [73]. The electric power into the plasma is the same in both gas species at 3.4 W. H_2O_2 concentration, *i.e.*, OH production, with Ar gas is higher than that with O_2 gas, which is in good agreement with the emission spectra, as shown in **Figure 6**. Thus, Ar injection is preferred for highly efficient OH production.

Many researchers have analyzed the amount of dissolved OH in water using chemical probes such as terephthalic acid [55, 56]. The energy yield for the surface pulsed streamer discharge on the liquid with argon gas is estimated to be $13 \sim 27 \times 10^{-9}$ mol/J with disodium terephthalate solution [57]. The typical energy yield of dissolved OH in water supplied by plasma, which can react with solutes in water, is estimated to be $4 \sim 5 \times 10^{-9}$ mol/J using the indigo carmine solution as a chemical probe [29]. Because plasma directly generated under water has a high OH density, the reaction rate of OH loss reactions is very high, which decreases the energy efficiency for OH supply.

When the feeding gas contains O_2, highly concentrated O_3 is generated in the plasma through reactions (1) ~ (3). Henry's law constants for O_3 and OH are 0.011 and 30 M/atm at 298 K, [58] respectively, which shows that the solubility of O_3 is lower than that of OH. Additionally, the oxidation potential of O_3 is lower than that of OH. However, the lifetime of O_3 in water is on the order of several min [59–61] and much longer than that of OH. Thus, when wastewater contains only organic compounds that can be easily oxidized by O_3, the treatment efficiency utilizing O_3 is higher than that utilizing OH. In this case, O_2 is preferred for use as a feeding gas for high-efficient O_3 production. O_3 dissolved in water can contribute to OH production via the following reaction with hydroperoxide anion (HO_2^-) species, the conjugate base of H_2O_2, under alkaline conditions with a high reaction rate [62].

$$O_3 + H_2O_2 \rightarrow O_2 + OH + HO_2 \quad (20)$$

$$H_2O_2 \leftrightarrow HO_2^- + H^+ \; pKa = 11.6 \quad (21)$$

$$O_3 + HO_2^- \rightarrow O_2 + OH + O_2^- \quad (22)$$

The pKa value of the equilibrium reaction (R14) is 11.6. Because the reaction rate of O_3 and H_2O_2 is very low ($10^{-2}\ M^{-1}\ s^{-1}$), O_3 mainly reacts with HO_2^- with a reaction rate constant of $5.5 \times 10^6\ M^{-1}\ s^{-1}$ and hardly reacts with H_2O_2 directly. Thus, pH adjustment is required to induce this OH production reaction.

When the feeding gas contains nitrogen, nitrous (HNO_2) and nitrite (HNO_3) acids, are generated by plasma as byproducts through the following reactions; [46, 63–65].

$$O(^3P) + NO + N_2 \rightarrow NO_2 + N_2 \quad (23)$$

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (24)$$

$$NH + OH \rightarrow NO + H_2 \quad (25)$$

$$OH + NO + M \rightarrow HNO_2 \quad (26)$$

$$OH + NO_2 \rightarrow HNO_3 \quad (27)$$

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O \quad (28)$$

$$HO_2 + NO_2 \rightarrow O_2NOOH \quad (29)$$

$$H_2O_2 + HNO_2 \rightarrow HOONO + H_2O \quad (30)$$

$$HOONO + H_2O_2 \rightarrow O_2NOOH + H_2O \quad (31)$$

Peroxynitric acid ($HOONO_2$) contributes to HOO production via equilibrium decomposition reaction, [66].

$$HOONO2 \rightarrow HOO + NO_2 \quad (32)$$

When HNO_2 and HNO_3 are dissolved in water, nitric and nitrate ions are easily produced in water through acid dissociations of HNO_2 and HNO_3 because of their low pKa values, of 3.35 and − 1.8, respectively, and the pH of the solution significantly decreases [65, 67].

$$HNO_2 \rightarrow H^+ + NO_2^- \quad (33)$$

$$HNO_3 \rightarrow H^+ + NO_3^- \quad (34)$$

NO_2^- is oxidized to NO_3^- by O_3 in solution [68]. When the pH is lower than 3.5, NO_2^- is oxidized by H+. These reactions are follows:

$$NO_2^- + O_3 \rightarrow NO_3^- + O_2 \quad (35)$$

$$NO_2^- + 3H^+ \rightarrow NO + NO_3^- + H_3O\ (\text{or } H_2O + H^+) \quad (36)$$

These nitrogen species can contribute to the inactivation of bacteria in wastewater as described later. In the case of plasma discharges inside multiple air bubbles using a reactor similar to that in **Figure 3(b)** with eight glass tubes in which total air gas with a flow rate of 5 L/min is injected, approximately 9 mM NO_3^- is generated in 20 L of solution with 24 hours of plasma treatment, [69] which is a sufficient concentration for using fertilizers in plant cultivation. This effect is described in Section 5.

When metals that are easily oxidized by electrolysis, such as iron and copper, are used as an electrode immersed in water, metal ions such as Fe^{2+}, Fe^{3+}, $Cu^{+,}$ and Cu^{2+} are generated by electrooxidation by a large discharge current, and the metal ion concentration increases. These metal ions contribute to the oxidation of organic compounds in wastewater not only directly but also through OH production by

redox reactions well known as Fenton reactions with H_2O_2 produced by plasma as follows: [70–73].

$$Fe^{2+} + H_2O_2 \rightarrow OH + OH^- + Fe^{3+} \quad (37)$$

$$Fe^{2+} + OH \rightarrow Fe^{3+} + OH^- \quad (38)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 + H^+ \quad (39)$$

$$Fe^{3+} + HO_2 \rightarrow Fe^{2+} + O_2 + H^+ \quad (40)$$

$$Fe^{2+} + HO_2 \rightarrow Fe^{3+} + HO_2^- \quad (41)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (42)$$

$$H + Fe^{3+} \rightarrow Fe^{2+} + H^+ \quad (43)$$

$$Cu^+ + OH \rightarrow Cu^{2+} + OH^- \quad (44)$$

$$O_2^- + O_2^- + 2H^+ \rightarrow H_2O_2 \quad (45)$$

Reactions related to iron ions are well known as Fenton reactions and occur under acidic conditions. Generally, electrodes immersed in water are used as grounded electrodes to keep the voltage potential of water zero for safety reasons. Therefore, when a positive (or negative) high voltage is applied to a high voltage electrode, iron (or copper) ions are dissolved from the grounded electrode immersed in water and used as the anode (or cathode). For example, in the case of 1,4-decomposition as described in Section 4, the decomposition efficiency can be improved by approximately three times, by using iron wire as an electrode immersed in water, compared with that achieved using stainless steel wire [73].

The chemical species dissolved in the water react with not only organic compounds but also inorganic compounds. **Table 1** shows reaction the rate constants for

Solute	Reaction rate constant for O_3 [M^{-1} s^{-1}]	Reaction rate constant for OH [M^{-1} s^{-1}]
Cl^-	0.003	4.3×10^9
Br^-	160	1.1×10^9
I^-	1.2×10^5	1.1×10^{10}
NO_2^-	3.7×10^5	1.0×10^{10}
NO_3^-	—	1.0×10^5
HSO_3^-	3.7×10^5	4.5×10^9
SO_3^{2-}	1.5×10^9	5.1×10^9
HSO_4^-	$<10^{-4}$	6.9×10^5
H_2SO_4	—	1.4×10^7
H_2O_2	0.01	2.7×10^7
HO_2^-	5.5×10^6	7.5×10^9
HCO_3^-	0.01	8.5×10^6
HCO_2^-	100	5.1×10^9
CO_3^{2-}	0.01	3.9×10^8
CO_2	—	1×10^6
OH^-	210	1.2×10^{10}

Table 1.
Reaction rate constant for O_3 and OH reacting with inorganic compounds.

O_3 and OH reacting with inorganic ions [74–78]. Halogen ions such as chloride ions (Cl^-), bromide ions (Br^-) and iodide ions (I^-) have high reactivity toward O_3 and OH and act as O_3 and OH scavengers, which inhibits the decomposition reactions of organic compounds. Furthermore, toxic compounds such as hypochlorite ions (ClO^-) and bromate ions (BrO_3^-) are produced via oxidation reactions, as shown in **Figures 10** and **11**. Carbon dioxide radicals (CO_2^-), carbonate radicals (CO_3^-), and

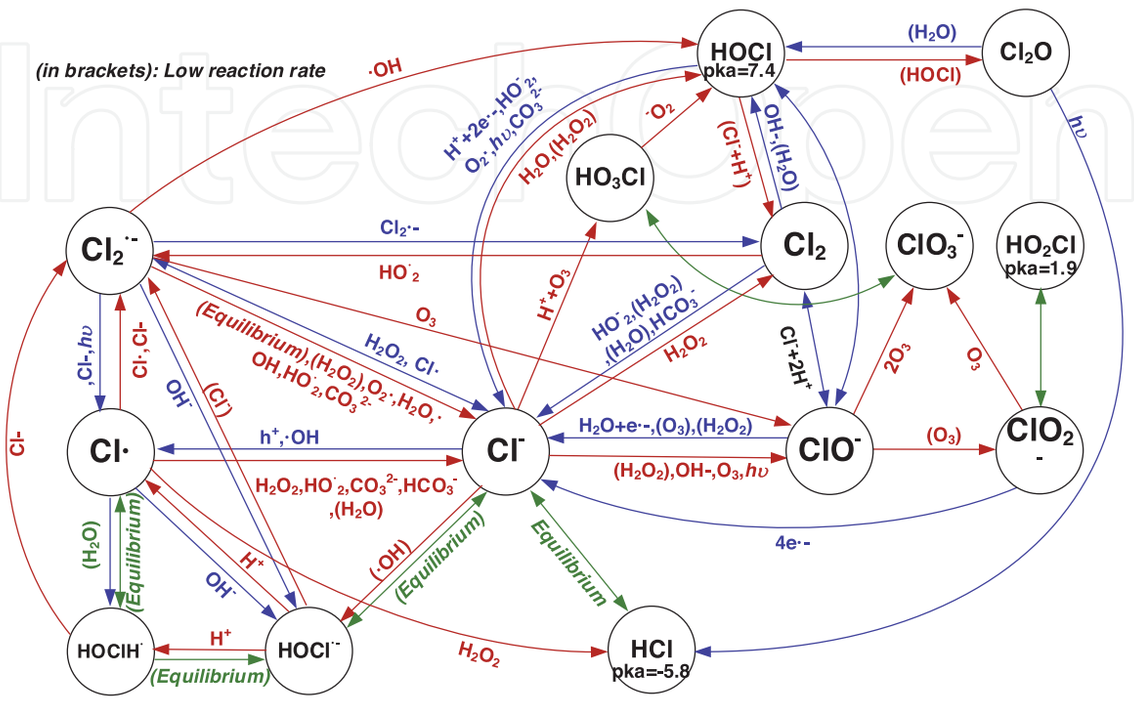


Figure 10.
Schematic illustrations of reactions involving Cl.

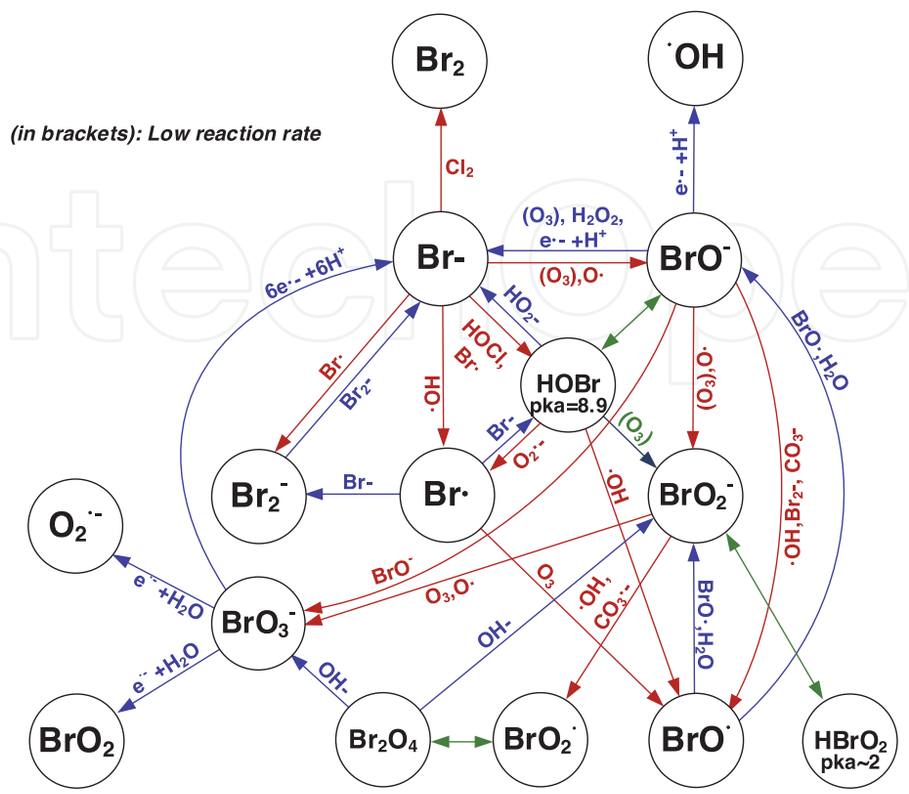


Figure 11.
Schematic illustrations of reactions involving Br.

sulfate radicals (SO_4^-) are produced through reactions of OH with formate ions (HCO_2^-), carbonate ions (CO_3^{2-}), and hydrogen sulfate ions (HSO_4^-) with hydroxyl radicals in liquid [79]. These radicals also contribute to the decomposition of organic compounds dissolved in wastewater as synergistic effects. Although hydroxide ions (OH^-) and per hydroxyl ions (HO_2^-) act as scavengers of OH, OH can be produced via reaction with O_3 under high-pH conditions. Thus, the influence of these ions on treatment efficiency and water quality after wastewater treatment using plasma should be considered.

4. Decomposition of persistent organic pollutants

Organic pollutants entering the water environment cause industrial, agricultural, domestic, livestock, and medical wastewater drainage into and leakage from polluted soil. Because most organic pollutants have strong toxicity, carcinogenicity, and genotoxicity, even at low concentrations, it is urgent to develop effective technologies for the highly efficient removal of these contaminants from water. 1,4-Dioxane has been widely used as a solvent. Because it has high solubility and is hard to absorb to the bottom material, it can be widely spread in water environments [80, 81]. Dichloromethane (DCM) is a chlorinated volatile organic compound (Cl-VOC) and has high volatility. It is also used as a solvent, cleaner, degreasing agent, and liquid fuel and released into the environment through water discharge from chemical industries [82, 83]. These compounds are very difficult to decompose using conventional oxidation treatment methods such as chlorine, ozone oxidation, and bioremediation owing to their chemical and biological stability.

In wastewater treatment systems using plasma discharges, high-density powerful oxidants such as OH and O_3 produced by plasma contribute to the decomposition of persistent organic pollutants and the inactivation of bacteria. This method provides high-speed treatment and decomposition of organic compounds that are difficult to remove with conventional methods and has attracted much attention as an advanced oxidation technology. Many researchers have proposed that plasma treatment is effective for the decomposition of various kinds of toxic aromatic hydrocarbons, such as chlorophenol, [84] naphthalene, toluene [85], and bisphenol A [86], and volatile organic compounds such as trichloroacetic acid [87]. Oxidants also contribute to the quick decolorization of wastewater containing dye solutions [88, 89]. In this section, the decomposition of various kinds of organic compounds in water is systematically described. The decomposition characteristics of indigo carmine, a common blue dye, 1,4-dioxane [73] which has a high solubility in water, and formic acid, [90] which is an intermediate product of various organic compounds, such as dichloromethane (DCM), [91] which is a volatile organic compound, are introduced as an example.

Chemically active species dissolve in water in the vicinity of the water surface and induce oxidation reactions such as hydrogen atom abstraction, electron transfer, electrophilic addition, and chain oxidation reactions triggered by these reactions. The following reactions are typical oxidation reactions of organic compounds induced by OH.

$$RH + OH \rightarrow R^{\bullet} + H_2O \tag{46}$$

$$R + OH \rightarrow R^{\bullet +} + OH^- \tag{47}$$

$$R - + OH \rightarrow R^{\bullet} + OH^- \tag{48}$$

$$R + OH \rightarrow {}^{\bullet}ROH \tag{49}$$

$$OH + R_2C = CR_2 \rightarrow R_2(OH)C - CR_2^{\bullet} \quad (50)$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \quad (51)$$

$$R^{\bullet} + R^{\bullet} \rightarrow RR \quad (52)$$

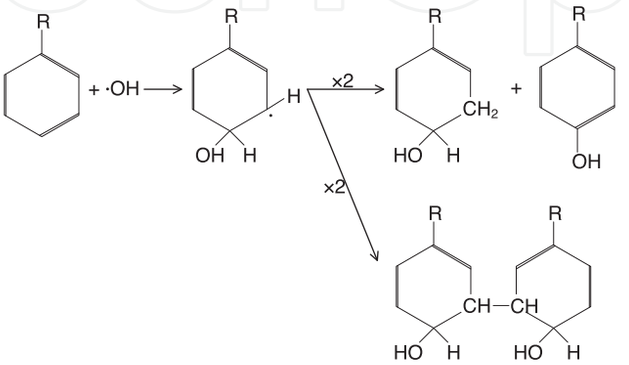
$$R^{\bullet} + RO_2^{\bullet} \rightarrow RO_2R \quad (53)$$

$$RO_2^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \quad (54)$$

$$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet} \quad (55)$$

$$RO_2^{\bullet} + HO_2^{\bullet} \rightarrow RO^{\bullet} + O_2 + OH^{\bullet} \quad (56)$$

$$RO_2^{\bullet} + RO_2^{\bullet} \rightarrow RO2R \quad (57)$$



(58)

Indigo carmine and azo phloxine are common dyes and have blue and red colors, respectively. **Figure 12** shows the time change of appearance and UV–vis spectra of two dye solutions, (a) indigo carmine and (b) azo phloxine, by treatment using plasma generated inside O_2 gas bubbles. In this case, 100 mL of dye solution was treated by plasma discharges generated inside bubbles produced by multiple pores as shown in **Figure 3(c)**. The gas flow rate is 4.5 L/min. Pulse voltages with an amplitude of 20 kV, a pulse width of 160 ns, and a pulse repetition rate of 250 Hz are applied to the wire electrode placed in the gas phase to generate plasma [73]. The energy input into a pulse is fixed at 13.5 mJ for each gas species by adjusting the voltage amplitude. From the input energy and pulse repetition rate, the input power can be estimated as 3.4 W. Indigo carmine and azo phloxine have absorbance peaks at wavelengths of 610 nm and 531 nm, which are responsible for the blue and red colors of their solutions, respectively. These peaks decrease, the colors disappear after 20 s and 180 s of plasma treatment, and then the solutions are fully decolorized after treatment. This result shows that plasma treatment is effective for the decolorization treatment of wastewater. **Figure 13** shows the decolorization rate of these solutions using Ar and O_2 as feeding gases to generate bubbles. Decolorization of both solutions in the case of O_2 injection is much faster than that of Ar injection. The energy efficiency for 50% decolorization of indigo carmine is 1.3×10^3 mmol/kWh for O_2 injection and 6.1 mmol/kWh for Ar injection, and those of azo phloxine are 77 mmol/kWh for O_2 injection and 4.8 mmol/kWh for Ar injection. The absorbance peaks of these dyes are due to the carbon–carbon double bond in the H-chromophore of indigo carmine and the nitrogen-nitrogen double bond of the azo chromophore of azo phloxine as shown in **Figure 14**, which are responsible for the blue and red colors of the solution. These double bonds have high electron density and high reactivity to electrophilic OH. It is well known that O_3 reacts with C-C and N-N double bonds rapidly; however, the reaction of OH with dyes is at least four orders of magnitude faster than that of O_3. As already mentioned, the lifetime of OH in water is much shorter than that of O_3 because of its high reactivity and high rate constant of recombination loss reactions, and only OH generated in the vicinity

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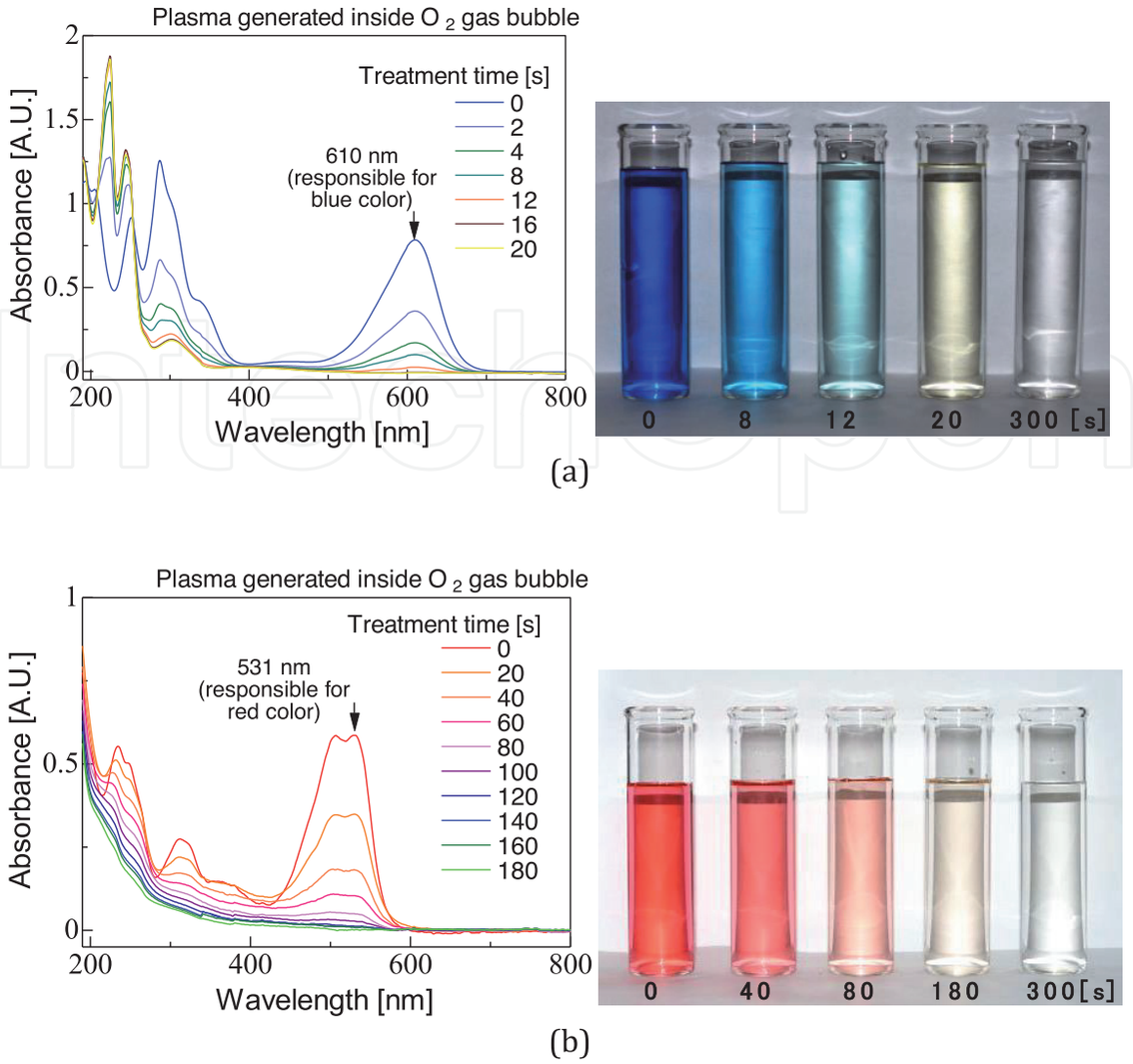


Figure 12.
Time change of appearance and UV–vis spectra of two dye solutions, (a) indigo carmine and (b) azo phloxine, by treatment using plasma generated inside O_2 gas bubble.

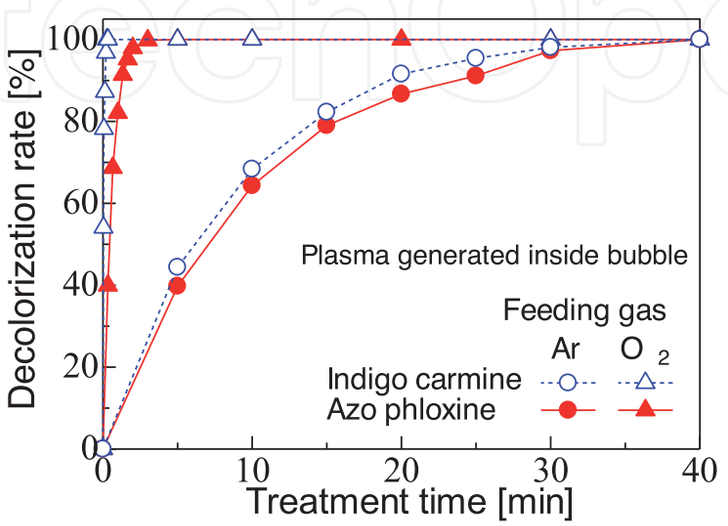


Figure 13.
Time change of decolorization rate of indigo carmine and azo phloxine solutions by plasma treatment using Ar and O_2 gases.

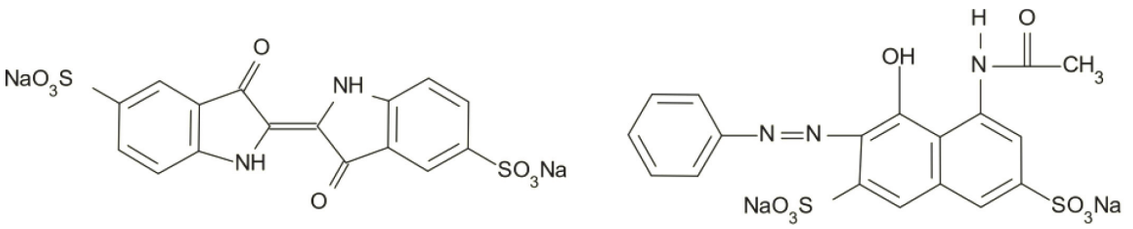


Figure 14.
Chemical structure of (a) indigo carmine and (b) azo phloxine.

of the bubble surface can be dissolved in the solution. In this case, these two dyes can be easily oxidized by O_3. Therefore, O_2 injection to generate O_3 at high efficiency is preferred for the decomposition of compounds that have high reactivity to O_3. The reactivity of an azo group with ozone is very low compared to that of olefins, [92] which is one of the reasons that indigo carmine is more readily decolorized than azo phroxine.

Since 1,4-dioxane has low reactivity to O_3 due to its high chemical stability, plasma treatment is a promising method for 1,4-dioxane removal. **Figure 15** shows one of the proposed decomposition processes of 1,4-dioxane by hydroxyl radicals [93–95]. The reaction is initiated by hydrogen atom abstraction, and various reactions, such as chain reactions, are involved. Carboxylic acids such as formic acids (HCOOH) and oxalic acid ($(COOH)_2$) are produced as intermediate products.

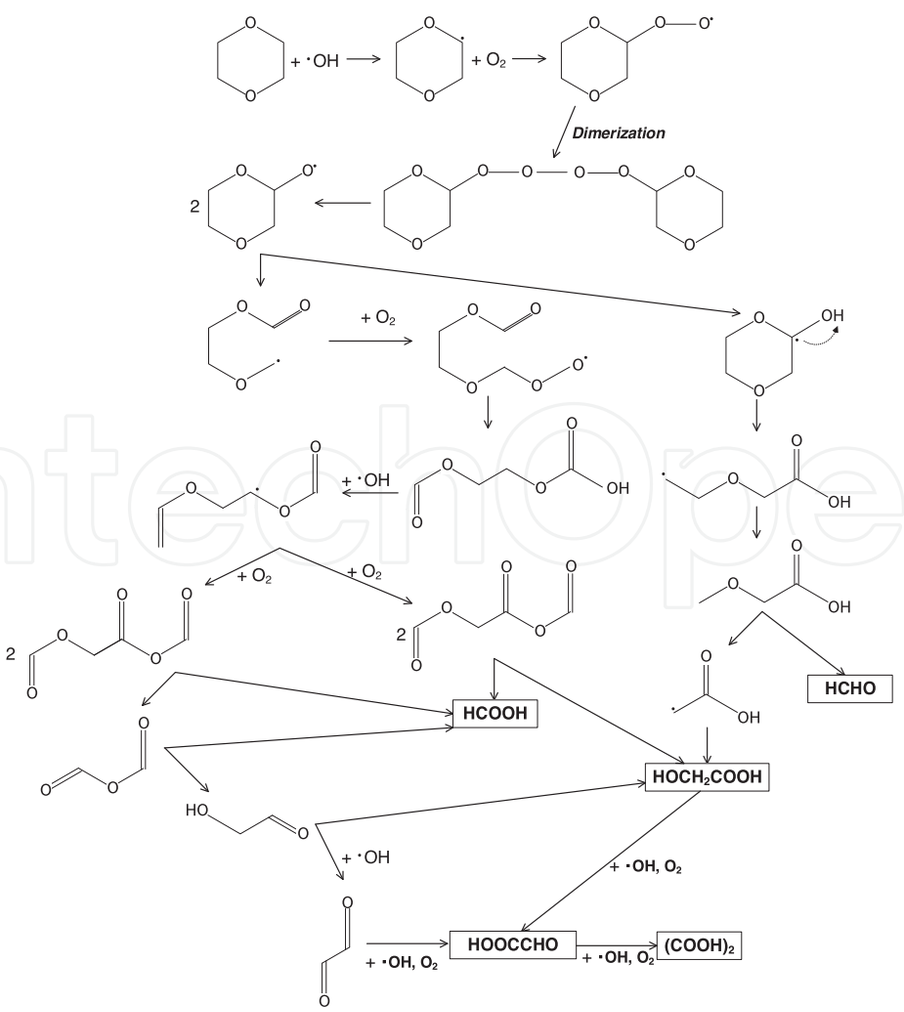


Figure 15.
Oxidation process of 1,4-dioxane by OH.

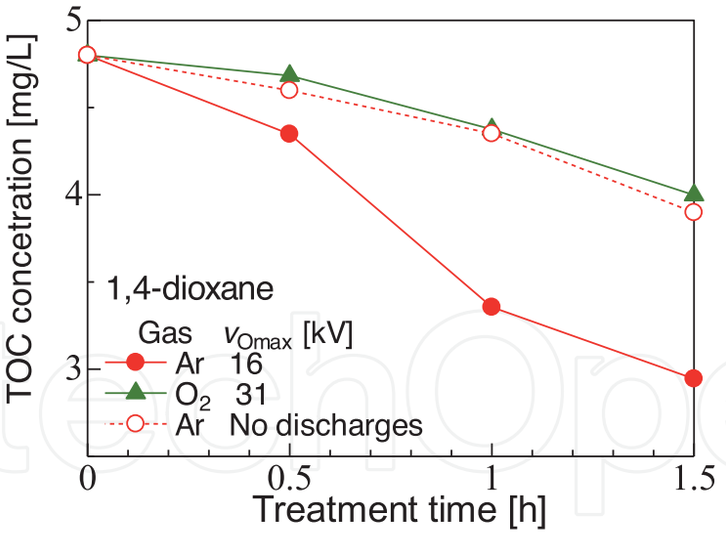


Figure 16.
Time change of the TOC concentration of a 1,4-dioxane solution by plasma treatment.

Figure 16 shows the time change of the TOC concentration of the 1,4-dioxane solution with an initial concentration of 0.23 mM with two different injected gases and with and without discharges. The experimental conditions were the same as those mentioned above. The electric power in the plasma is the same in both gas species. The TOC decreases without discharges because of the volatilization by bubbling gas, and the TOC concentration in the O_2 injection is almost the same without discharges. The rate of TOC decrease rate in the case of Ar injection is much higher than that in the case of O_2 injection. 1,4-dioxane hardly reacts with O_3 because of its low reaction rate ($0.32\ M^{-1}\ s^{-1}$) [78]. The rate constant of reaction between OH and 1,4-dioxane is $2.4*10^9\ M^{-1}\ s^{-1}$ [96]. The production rate of OH in the case of Ar injection is much higher than that in the case of O_2 injection. Thus, Ar injection is preferred for the decomposition of organic compounds that have

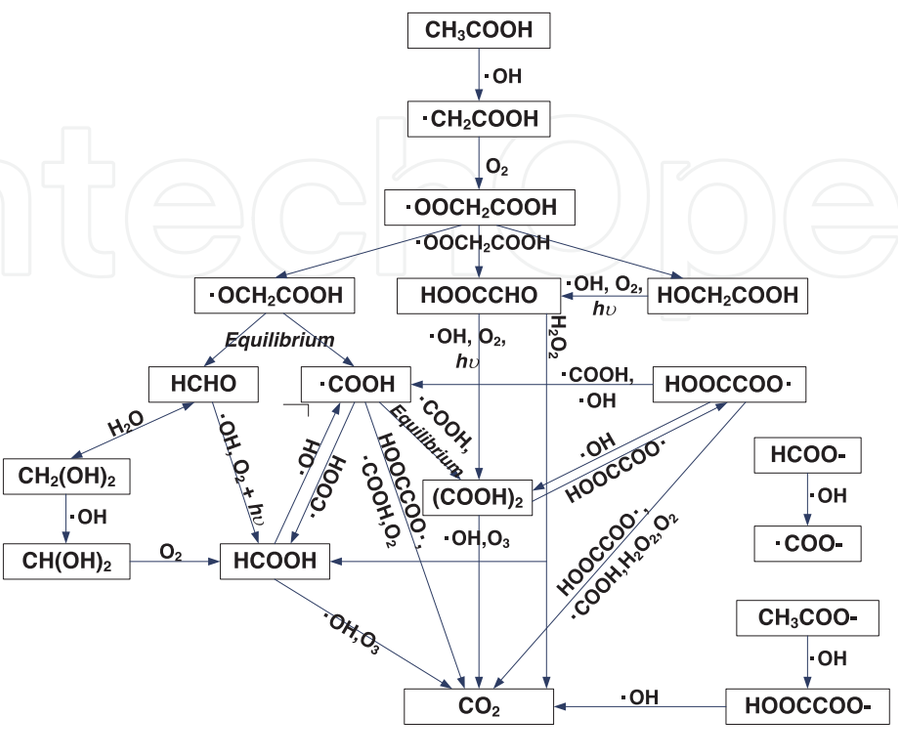


Figure 17.
Oxidation process of CH_3COOH by OH.

low reactivity to O_3. The energy efficiency for 1,4-dioxane decomposition is 2 mmol/kWh.

Figure 17 shows the oxidation of acetic acid (CH_3COOH) by OH radicals. CH_3COOH has also low reactivity to O_3. It can be decomposed into formic acid, oxalic acid, and finally, CO_2 and H_2O by oxidation reactions with OH. These acids have an acidity constant and are in equilibrium with their conjugated bases. For example, formic acid is in equilibrium with its conjugate base, formate, as follows:

$$HCOOH \rightleftarrows HCOO - + H+ \quad (59)$$

The pKa value of this equilibrium reaction is 3.75. The reaction processes of formic acid and formate with OH and O_3 are represented by the following: [76, 78].

$$HCOOH + O_3 \rightarrow CO_2 + OH + HO_2 \quad (60)$$

$$HCOOH + \cdot OH \rightarrow H_2O + COOH \quad (61)$$

$$HCOO^- + O_3 \rightarrow CO_2 + OH + O_2^- \quad (62)$$

$$HCOO^- + OH \rightarrow H_2O + COO^- \quad (63)$$

The rate constant of reaction (62) is 100 M^{-1} s^{-1} and is 20 times higher than that of reaction (60) (5 M^{-1} s^{-1}). Similarly, the rate constant of reaction (63) is 3.2×10^9 M^{-1} s^{-1} and is 25 times higher than that of reaction (61) (1.3×10^8 M^{-1} s^{-1}). Therefore, decomposition of these acids at higher pH is preferred. It has been reported that the decomposition rate of formic acid can be improved twice by increasing the pH from 3.5 to 4.2 with the addition of sodium carbonate, in the case of plasma generated inside oxygen bubbles using the reactor shown in **Figure 3(a)** [90]. Thus, pH adjustment is an important factor for wastewater treatment, while active species can be directly supplied from plasma.

The decomposition process of DCM is different from that of other soluble compounds because of its high volatility. The rate constant of DCM reacting with OH in a liquid is 2.2×10^7 $M^{-1}S^{-1}$ [97] and is much lower than that of reactions of other soluble organic compounds, such as 1,4-dioxane, phenol, and formic acids, with OH (on the order of 10^9 M^{-1} s^{-1}). **Figure 18** shows the TOC and the amount of decomposed DCM as a function of treatment time using plasma generated inside Ar

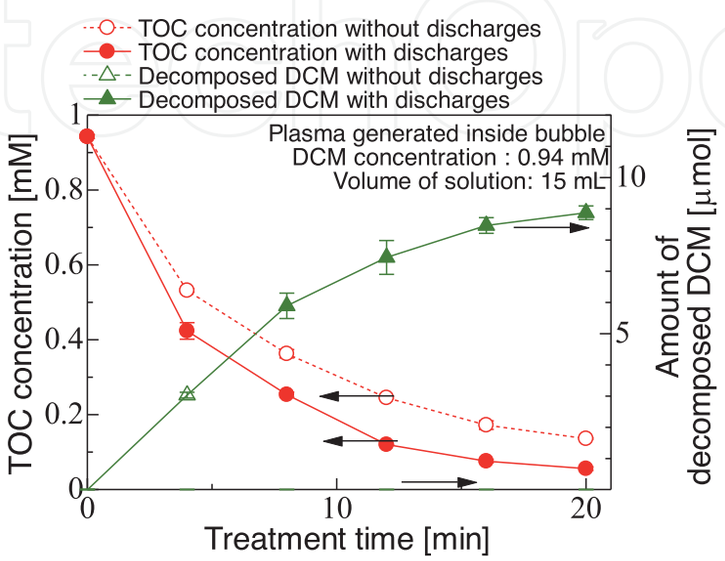


Figure 18.
Time change of the TOC concentration of DCM solution and amount of decomposed DCM by plasma treatment.

bubbles using the reaction shown in **Figure 3(a)**. The gas flow rate is 30 mL/min. Pulse voltages with an amplitude of 16 kV, a pulse width of 160 ns, and a pulse repetition rate of 250 Hz are applied to the wire electrode placed in the gas phase to generate plasma [91]. The amount of decomposed DCM is calculated from the Cl^- concentration detached from DCM during the decomposition process. The TOC decreases without discharges because of volatilization by bubbling gas. DCM can be successfully decomposed by discharges generated inside Ar bubbles [91]. The energy efficiency for DCM decomposition is approximately 60 mmol/kWh and is much higher than that for decolorization of dye solutions and 1,4-dioxane decomposition, as mentioned above, although the rate constant for DCM reacting with OH is low. This result suggests that almost all DCM is decomposed in the gas phase in the bubble, not in the liquid phase. DCM is quickly volatilized due to its high volatility and is transferred into the gas phase in the bubble when Ar gas is fed into the DCM solution, and DCM is exposed by plasma discharges generated inside the bubble. DCM can be decomposed by OH with the following reactions: [98].

$$CH_2Cl_{2(g)} + OH_{(g)} \rightarrow CHCl_{2(g)} + H_2O_{(g)} \quad (64)$$

$$CHCl_{2(g)} + OH_{(g)} \rightarrow CHOCl_{(g)} + HCl_{(g)} \quad (65)$$

$$CHOCl_{(g)} + OH_{(g)} \rightarrow COCl_{(g)} + H_2O_{(g)} \quad (66)$$

$$COCl_{(g)} + OH_{(g)} \rightarrow CO_{2(g)} + HCl_{(g)} \quad (67)$$

The Cl-H bonding energy of CH_2Cl_2 is 4.28 eV and is lower than the energy of metastable Ar (11.55 eV) produced by electron impact, as shown in reaction (9) [99]. Therefore, CH_2Cl_2 is also possibly decomposed by Penning ionization by the energy transfer collision of metastable Ar (Ar*) as shown in the following reactions: [99, 100].

$$CH_2Cl_{2(g)} + Ar*_{(g)} \rightarrow {CH_2Cl_2}^+{}_{(g)} + Ar_{(g)} \quad (68)$$

$${CH_2Cl_2}^+{}_{(g)} \rightarrow {CH_2Cl}^+{}_{(g)} + Cl_{(g)} \quad (69)$$

$${CH_2Cl}^+{}_{(g)} + e^-{}_{(g)} \rightarrow CH_2Cl_{(g)} + Cl_{(g)} \quad (70)$$

Because the concentration of DCM inside the gas bubble is on the order of several hundred ppm as mentioned previously, and is much lower than the Ar and H_2O concentrations, the DCM dissociation by electron impact is negligible [98, 101].

5. Novel applications for agriculture

Agricultural applications of plasma have been widely investigated in recent years and have become one of the most attractive research topics in plasma science [102–105]. As already mentioned in this article, plasma in contact with water can produce various types of chemically active species, which have various effects on the environment of plant growth.

As a production process of fruits and vegetables, hydroponics, which is the method of growing plants without soil using the nutrient solution, has been widely used. In hydroponics, the nutrient solution is recirculated in a closed system to reduce the cost and the environmental load. In the system, plant diseases caused by microbial contamination of artificial nutrient solution rapidly spread in the circulation system and cause serious damage to the entire plant. During the entire period

of plant growth, contamination with pathogens can never be excluded since pathogens are introduced in the nutrient solution via the irrigation water supply. Therefore, the nutrient solution should be remedied by continuous water treatment system operation during the cultivation period. Active species such as OH and O_3 produced by discharges can contribute to the inactivation of pathogenic bacteria-contaminated in liquid fertilizer. A plasma treatment system for the inactivation of *Ralstonia solanacearum* bacteria in liquid fertilizer for a tomato hydroponic culture system has been developed [106]. The number of colony-forming units (CFU) of *R. solanacearum* in the liquid fertilizer decreased from 10^7 to 10^2 CFU/mL when treated with discharge plasma. Tomato seedlings treated with discharge plasma were relatively healthy, while the infected positive controls all wilted and died, as shown in **Figure 19**. Plasma was also used for the removal of allelochemicals, organic compounds exuded from the root of plants, which have autotoxic effects on plant growth. 2,4-Dichlorobenzoic acid (DCBA), an allelochemical of cucumber, was almost completely decomposed by plasma treatment. The discharge-treated solution is used as a nutrient solution for cultivating cucumber plants in a rockwool hydroponic system. Plant growth was significantly inhibited by adding DCBA to the nutrient solution, on the other hand, the plants grew healthy using discharge treatment, as shown in **Figure 20** [69]. Furthermore, when the feeding gas contains nitrogen, NO_2^- and NO_3^- are generated as mentioned already. These ions can act as

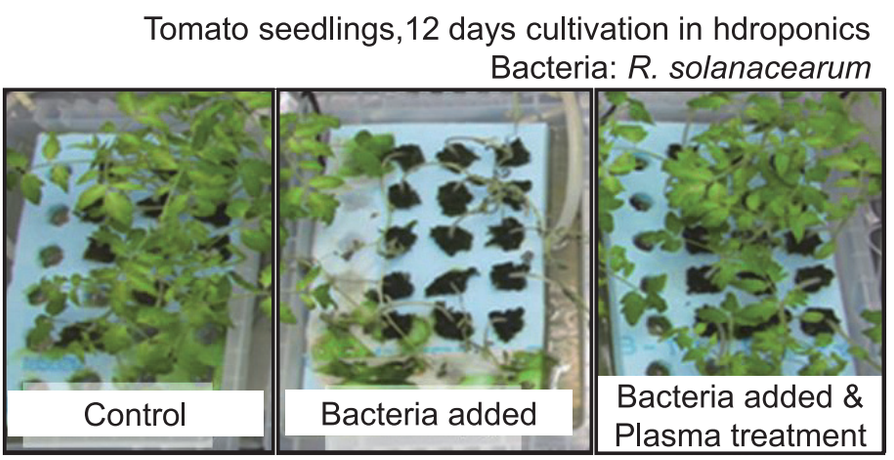


Figure 19.
Photograph of tomato seedlings after 12 days of cultivation in bacteria-contaminated nutrient medium in a hydroponic system.

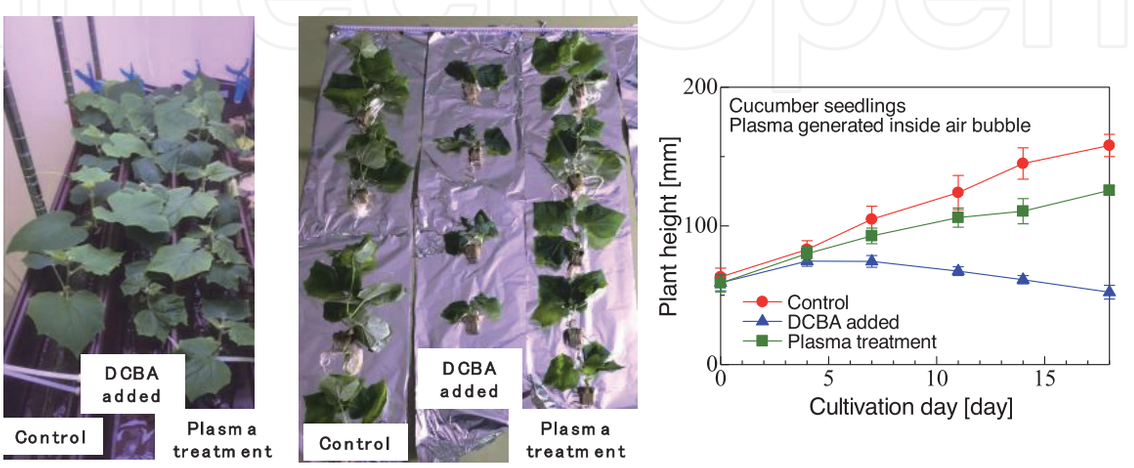


Figure 20.
Photographs of cucumber seedlings after 18 days and diurnal changes in plant height for seedling cultivated in DCBA-contaminated nutrient medium in a hydroponics system.

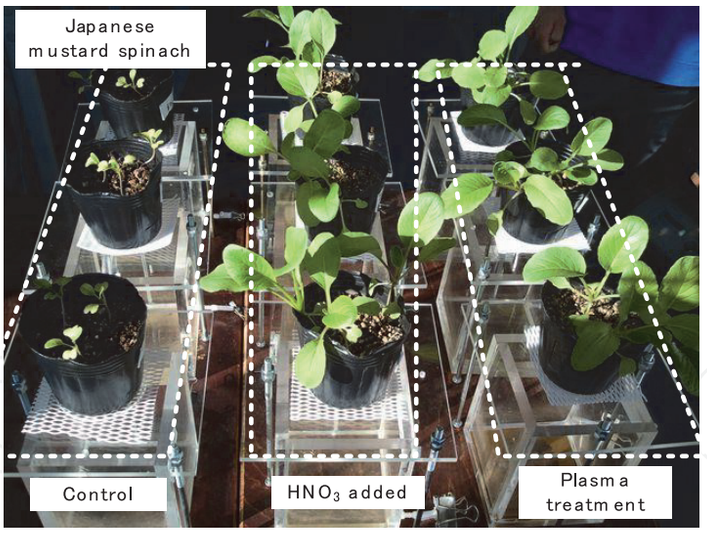


Figure 21.
Photograph of Japanese mustard spinach seedlings after 28 days of cultivation using plasma-treated nutrient medium-supplied soil.

fertilizers for plants, which improves the growth rate of plants in hydroponic systems, as shown in **Figure 21** [107]. Therefore, plasma treatment of nutrient solution for plant cultivation can control the environment of plant growth through the decomposition of toxic organic compounds, the inactivation of pathogenic bacteria, and the nutrient supply, which are promising new applications of plasma. A plasma treatment system for tomato cultivation in a greenhouse was developed, and a pilot test was performed over several months [108]. The CFU of *R. solanacearum* was kept at a low value, and the infection risk of the plant was significantly reduced during continuous treatment. All plant bodies grow healthily and bear fruits, and the onset of bacterial wilt disease is not observed.

Not only radicals such as O_3 and OH, but also nitrogen species such as $ONOO^-$ and O_2NOOH can be key inactivation agents that cause cell damage and inactivation under acidic conditions. Because these nitrogen species have a long lifetime in the liquid phase, nitrogen species generated by plasma treatment remain for a long time after nonthermal plasma irradiation. It has been reported that nonthermal plasma-activated water (PAW), water irradiated by nonthermal plasma, can inactivate bacteria on the surface of fruits and vegetables [109] such as strawberries, [110] mushrooms [111] and endives, [112] which contributes to maintaining the freshness of fruits and vegetables.

6. Conclusion

The fundamental physical and chemical properties of plasma discharge generated over a water surface and its applications for the decomposition of persistent compounds are described. Plasma can directly generate powerful oxidizing agents such as hydroxyl radicals, which can realize high-speed decomposition of persistent compounds in wastewater, such as 1,4-dioxane and dichloromethane, without pretreatment of samples. Because of these advantages over other advanced oxidation processes, a pulsed discharge plasma in water and in contact with water has attracted much attention as a promising technology in not only wastewater treatment but also various new application fields such as agriculture.

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Conflict of interest

The authors declare no conflict of interest.

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