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ORGANIC POLLUTANTS DEGRADATION USING PULSELESS CORONA DISCHARGE : APPLICATION IN ULTRAPURE WATER PRODUCTION

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Abstract : The use of ozone gained acceptance in the production of ultrapure water because of its powerful oxidizing ability. Ozone is currently used to deactivate microorganisms and remove organic contaminants. However, interest also exists in using radical species, which are stronger oxidants than ozone, in such processes. One means of producing radical species is by corona discharge. This work investigates the use of a novel pulseless corona-discharge system for the removal of organic substances in ultrapure water production. The method combines corona discharge with electrohydrodynamic spraying of oxygen, forming microbubbles. Experimental results show that pulseless corona discharge effectively removes organics, such as phenol and methylene blue, in deionized water. The corona-discharge method is demonstrated to be comparable to the direct use of ozone at a high-applied voltage. The results also show that a minimum applied voltage exists for operation of the corona-discharge method. In this work, the minimum applied voltage is approximately 4.5 kV. The kinetic rate of phenol degradation in the reactor is modeled. Modeling results show that the dominant species of the pulseless corona-discharge reactor are hydroxyl radical and aqueous electron. Several radical species produced in the pulseless corona-discharge process are identified experimentally. The major species are hydroxyl radical, atomic hydrogen species, and ozone.

Key Words : Ultrapure water, Corona discharge, Ozonation, Radical species

INTRODUCTION

Because of recent innovations in high-technology applications such as pharmaceuticals, biotechnology, and semiconductors,[1] a large demand currently exists for ultrapure water. Ultrapure water is considered to be a solvent of extremely high purity, with many physical and chemical advantages.[2] Governal[3] noted that every time the semiconductor industry improves its manufacturing technologies, it raises the definition of ultrapure water by an order of magnitude. Governal also observed that while the semiconductor device capacities have increased by a factor of 25, requirements for maximum acceptable particle and bacterial concentration have decreased by 50 and 250 times, respectively. Thus, the performance of each unit in the ultrapure water production process must be improved. Ultrapure water is characterized by its impurity content. The parameters include ionic concentration (resistivity), total oxidizable carbon (TOC), bacteria and other microorganisms, particles, silica, and dissolved gases.[3] These parameters should meet the level of purity standards listed by Governal[3] before the water can be used in semiconductor industries.

The production of ultrapure water is a com-

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plex multi unit process. A typical production flowsheet,[1] includes filtration by carbon and polymeric filters for particle removal, filtration by reverse osmosis (RO) and ion exchange for ion removal, and disinfection by ultraviolet (UV) radiation and ozone for microorganism removal. Each of these unit processes should maintain a required level of performance. Complicating the process is the fact that some contaminant-removal technologies interfere with one other and sometimes add contaminants.[3] Thus, innovations in all removal technologies involved are essential to the production of ultrapure water. To cope with this demand, several researchers have tried to improve the performance of each process.[4-8] The work presented here describes an innovative approach for the removal of organic compounds in ultrapure water production using a pulseless corona-discharge method. This approach could also be used to deactivate microorganisms.

Use of Ozonized Ultrapure Water for Surface Cleaning

An ultraclean silicon surface is essential for volume production of deep submicron ultralarge-scale integrated devices in the semiconductor industries. Since the wafer surface is subject to contamination by impurities in the dry process currently used, an advanced wet process is required to achieve a high degree of cleanliness on the wafer surface.[8,9] Ultrapure water plays an important role in the wet process because it is used in the final rinsing step. Deposition of particles over 0.2 μm in certain locations can ruin the printing of high-density circuits with 1-μm line widths. Trace organics can be deposited on a thin film, resulting in defective thin oxides. Bacteria are often considered to cause the worst contamination. They multiply exponentially, causing the same problems as particles, and decompose to form ionic impurities.[1] Biotechnology/pharmaceutical applications also find bacteria intolerable. Bacteria compete for nutrients and contaminate cultures. Furthermore, trace amounts of organics can stress or kill cell systems.

Ozone is a clean and powerful oxidizer that is currently employed in water treatment systems for sterilization, disinfection, decoloration, and degradation of refractory organic materials. Ozone has the capacity to oxidize bacteria and protozoa in water, as demonstrated in the literature,[10,11] as well as a strong ability to oxidize organic substances. Isagawa et al.[9] demonstrated the use of ozonated ultrapure water for the removal of organic molecules adsorbed on the silicon wafer. Since organic molecules remain on the wafer surface after the cleaning process and become adsorbed onto the surface, ultrapure water must have strong oxidation and cleaning power. The conventional method of cleaning the organic molecules uses H_2SO_4/H_2O_2. This process requires high temperature, which may cause damage on the wafer surface. Unlike H_2SO_4/H_2O_2, ozonized ultrapure water offers lower process temperature and less chemical handling in the cleaning process.

Use of Corona Discharge in Microorganism Sterilization

Molecular ozone is a strong oxidant that selectively attacks organic contaminants.[12] At a high pH range, molecular ozone decomposes rapidly to form radicals. These radicals are nonselective oxidants and have higher oxidation power than molecular ozone. This finding initiated the concept of advanced oxidation processes (AOPs). Common AOPs involve a combination of O_3/UV or O_3/H_2O_2 (PEROXONE). Both UV and H_2O_2 stimulate the decomposition of molecular ozone into radicals, the hydroxyl radical being the most important one. Kawada et al.[13] demonstrated the use of O_3/UV for semiconductor ultrapure water systems. They showed that the O_3/UV system changes nonionic silica to ionic silica, which is easy to remove with ion exchange and RO.

In addition to AOPs, a novel approach to forming radicals and ozone in water has been studied by many researchers[14,15] and involves corona discharge. Corona-discharge processes are

well explained in the literature.[16] Sun et al.[14] showed that discharge of a spark in water could produce UV radiation and active radical species, while, Joshi et al.[15] showed radical formation using a pulsed streamer corona discharge in aqueous solutions. The conclusion of these studies is that corona discharge provides active radical species.

The pulseless corona system can be achieved under high-electric-field conditions. The advantage of using high electric fields in gas-liquid systems was demonstrated by Shin et al.[17] and Tsouris et al.,[18-20] who studied the effect of electrostatic spraying on bubble formation. They showed that electric fields could be used to generate microbubbles for mass transfer enhancement.

In this work, the use of a novel, pulseless corona-discharge system in ultrapure water production is investigated. The pulseless corona-discharge method is suitable for ultrapure water production because of the low electrical conductivity of the water that allows energy-efficient radical formation. The objectives are the following: (1) demonstrate the effectiveness of such a system in combination with oxygen or ozone in removing organics from water, using phenol and methylene blue dye as surrogate contaminants; (2) examine the effects of the input gases (oxygen and ozone) on organic removal under corona-discharge conditions; and (3) identify the active species of the corona-discharge process.

MATERIAL AND METHODS

Removal of organic compounds from deionized water was performed in a cylindrical electrostatic ozonation reactor (EOR) shown in Figure 1, which had 7.5-cm diameter and 30-cm height. All experiments were performed with 0.01-in.-i.d. conical capillary tubes for the gas inlet to the reactor. The capillary design is similar to that used in our previous studies.[17,21] Either pure oxygen or a mixture of oxygen and ozone was fed to the reactor using a three-way valve. The oxygen fed to the reactor and ozone generator was extra-dry, high-purity compressed oxygen (Air Products and Chemicals, Inc., Allentown, PA). A corona-discharge ozone generator (O_3 Associates, Model O_3-22, Kensington, CA) was used to produce ozone. A UV/visible spectrophotometer (Hewlett-Packard Diode Array Spectrophotometer Model HP8452, Palo Alto, CA) was connected on-line for the monitoring of ozone concentration. For some experiments, the ozone gas was drawn into three 50-mL gastight syringes (Popper and Sons, New Hyde Park, NY) and delivered to the line by a syringe pump (Sage Instruments, Model 361, Boston, MA) for accurate gas delivery into the reactor. The corona discharge was generated by the high-voltage power supply (Model SL1200, Spellman High Voltage Electronics Corporation, Plainview, NY).

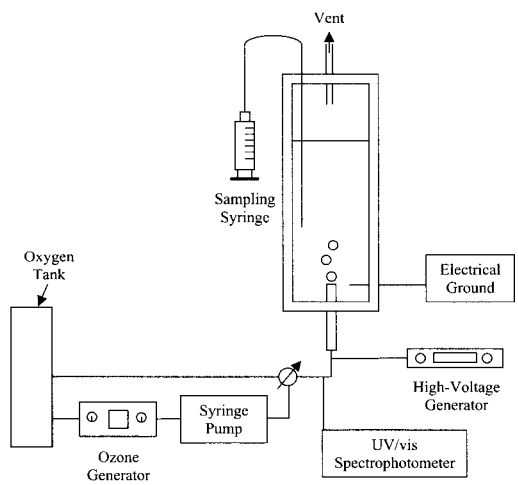

Figure 1. Experimental setup for pulseless corona discharge.

Aqueous samples for determination of concentration were taken from a sampling port, which was connected to a piece of Teflon tubing placed into the reactor, approximately 15 cm from the top. Phenol analyses were performed using solid-phase microextraction.[22] The following materials (all from Supelco, Inc., Bellefonte, PA) were required to perform the analyses: a PTE-5 fused-silica capillary column,

a 85-μm polyacrylate-coated fiber for polar semivolatiles, a sampling stand and holder, 4-mL vials with septa, an inlet liner for the gas chromatograph (GC), and stir bars and plates. The GC system was a Varian 3600*CX* GC with a flame ionization detector (Varian Chromatography Systems, Walnut Creek, CA). Methylene blue analyses were performed using the UV/vis spectrophotometer. Methylene blue concentrations of up to 0.02 mol/m^3 obey the Beer-Lambert law. The difference in color intensity during the experiments was measured at the wavelength of 660 nm.

Ultraviolet absorption was used to analyze the concentration of ozone in the gas phase entering the reactor. The UV/vis spectrophotometer was placed in line and run continuously in single-cell kinetics mode, using a quartz flow-through cell with a 1-cm pathlength to give constant readings of the ozone concentration in the gas phase. The measurements were made at 254 nm, and the absorbance readings were converted to concentrations, using molar absorptivity data available in the literature.[23]

Identification of chemical species produced by corona discharge was achieved by collecting the emission spectra, using a SPEX 500M monochromator with a 1200-groove/mm grating blazed at 500 nm. The dispersed radiation was detected using a charge-coupled device (CCD) detector with a 1-in. CCD chip.

RESULTS AND DISCUSSION

At least two approaches are possible for the application of electric fields in ultrapure water production. In the first approach, electric fields can be used to form microbubbles of a gas mixture containing ozone in water and thereby increase the surface area for mass transfer (e.g., Shin et al., 1997, 1999).[17,21] Tsouris et al.[18-20] discussed the advantages of a high applied voltage in gas-liquid systems, which include a higher rate of mass transfer by smaller bubbles and enhanced liquid mixing by electrohydrodynamic (EHD) flows. In the second approach, stronger electric fields can be used to induce corona discharge. This approach is investigated in the present work. In deionized water systems, using the geometry shown in Figure 1, corona discharge is observed above 3-kV applied voltage. Figure 2 illustrates EHD spraying of oxygen into water by electric fields. This photograph was taken at 7 kV of applied voltage, a level at which intense pulseless corona discharge occurs at the tip of the capillary.

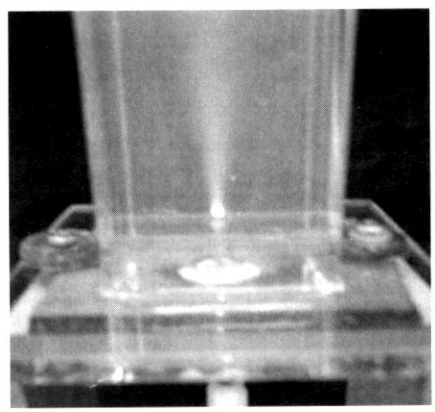

Figure 2. EHD spraying of oxygen under corona discharge at the applied voltage of 7 kV.

Effect of Corona Discharge on Methylene Blue Oxidation with Oxygen

Methylene blue dye was selected as one of the two representative organic compounds in this study. The effects of applied voltage and polarity of the corona on oxidation by methylene blue dye are shown in Figure 3. In these experiments, oxygen was supplied to the reactor

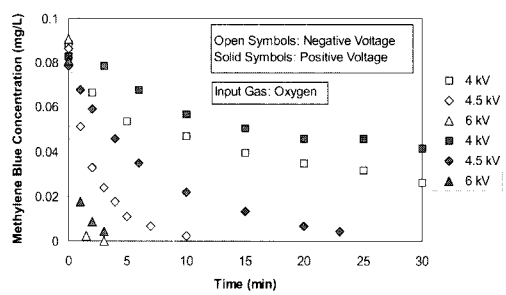

Figure 3. Methylene blue oxidation by oxygen under corona discharge conditions; oxygen flow rate: 2 mL/min.

at the rate of 2 mL/min, using a syringe pump. Both positive and negative electric polarities were tested at the applied voltages of 4, 4.5, and 6 kV.

As seen in this figure, applied voltage exerts a strong effect on methylene blue oxidation. For both polarities, the rate of oxidation increases as the level of applied voltage is raised. An applied voltage of 6 kV had the highest oxidation rate among the three voltages tested, because of increased electron flux. The higher electron flux produces more radical species to react with the solute in the solution.

The effect of electric polarity is also shown in Figure 3. For all three applied voltages, the negative polarity is more effective than the positive polarity. The applied voltage of 4.5 kV shows the greatest difference for the two polarities. The current histories for the experiments of Figure 3 are shown in Figure 4. In this figure, it is shown that, with positive polarity, the current increases more rapidly than with negative polarity. Although the positive polarity is associated with higher electric current, based on the oxidation results of Figure 3, it is clear that more radical species are produced by the negative-polarity voltage. These observations suggest that the negative polarity has several advantages over the positive-polarity voltage in pulseless corona discharge in water.

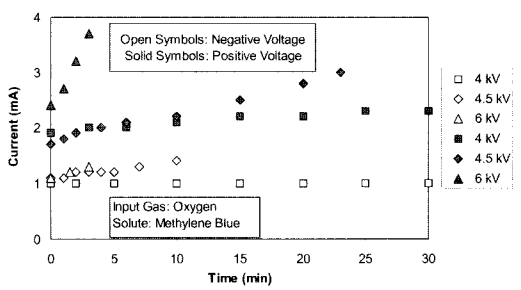

Figure 4. Current profile during methylene blue oxidation experiment (Figure 3); oxygen flow rate: 2 mL/min.

Effect of Corona Discharge on Methylene Blue Oxidation with Ozone

In these experiments, ozone, instead of oxygen, was introduced into the reactor. Only negative electric polarity was examined because of its better performance. The input ozone concentration was 3.5 mg/L, and the flow rate was maintained at 2.17 mL/min. The effect of ozone input at the applied voltages of 2 and 4 kV is shown in Figure 5. As previously mentioned, corona discharge is observed above 3 kV. Thus, at the applied voltage of 2 kV, we can assume that the effect on the oxidation of methylene blue derives solely from the presence of ozone. Oxidation results for ozone input at 2 kV are much better than those for oxygen input at 4 kV with corona discharge, which indicates that at 4 kV, insufficient quantities of radical species are produced in the corona-discharge process to compete with 3.5 mg/L of ozone.

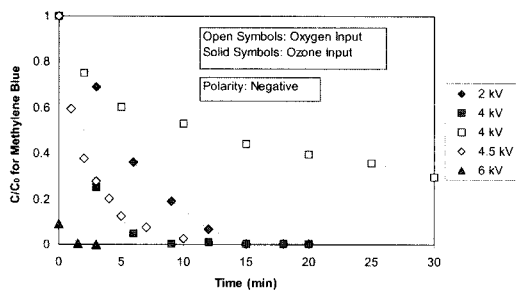

Figure 5. Comparison of methylene blue oxidation by oxygen under corona discharge conditions and ozone; ozone flow rate: 2.17 mL/min; ozone concentration: 3.5 mg/L; oxygen flow rate: 2 mL/min.

However, corona discharge becomes competitive at the applied voltage of 4.5 kV. The rate of methylene blue oxidation at 4.5 kV in the corona process with oxygen input is almost identical to that for ozone input at 4 kV. When the results for 4 and 4.5 kV are compared, it is clear that a sudden enhancement in oxidation occurs at 4.5 kV. Based on this observation, we can conclude that the formation of radical species in the corona-discharge process is not linearly related to the applied voltage or that a threshold exists in the applied voltage beyond which the formation of radicals increases significantly. This threshold is between 4 and 4.5 kV in this work.

Effect of Corona Discharge on Phenol Oxidation with Oxygen and Ozone

In this experiment, phenol was used as a representative organic molecule for oxidation. The flow rate of oxygen and ozone was maintained at 15 mL/min, and the ozone input concentration was 34 mg/L. The results of phenol oxidation with oxygen and ozone are shown in Figure 6. Enhanced oxidation is observed with oxygen between 4- and 5-kV applied voltage. This result supports the previous assumption of the threshold voltage of corona discharge, which was found between 4 and 4.5 kV.

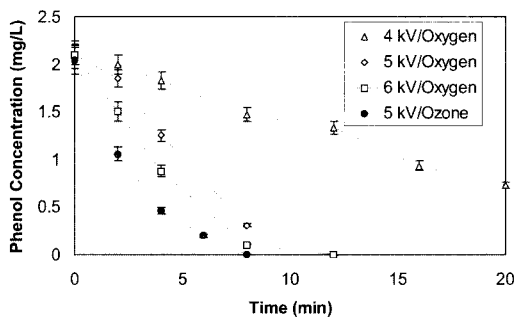

Figure 6. Phenol oxidation by ozone and oxygen under corona discharge conditions; flow rate of ozone or oxygen: 15 mL/min; ozone input concentration: 34 mg/L.

To compare the effectiveness of corona discharge, we used ozone as the input gas instead of oxygen. The ozone experiment was conducted with 5-kV applied voltage, 15-mL/min ozone flow rate, and 34-mg/L ozone concentration. As shown in Figure 6, the phenol oxidation was completed within 8 min with ozone, while 12 min was required when oxygen was used at the same applied voltage. Thus, at 5-kV applied voltage, better oxidation occurs with ozone than with oxygen. However, oxidation with oxygen becomes comparable when 6-kV voltage is applied. From this experiment, it can be concluded that the corona-discharge process at high-applied voltages is comparable to the ozonation process.

Modeling of Phenol Oxidation in the Pulseless Corona-Discharge Process

In this section, phenol oxidation using the pulseless corona-discharge process is modeled based on the phenol-oxidation model for a pulsed streamer corona-discharge reactor.[24] Grymonpré et al.[24] developed the model based on the fact that hydroxyl radicals formed from a pulsed streamer corona react with phenol to produce oxidation products. The assumptions in developing the model presented here include the following: (1) the reactor is isothermal and well mixed, (2) the volume of the reactor is approximately constant, and (3) the initiation rates are constant over the period of the process and are functions of voltage input. On the basis of these assumptions, a material balance was written for each molecular species, as well as the radicals and ions, involved in the chemical reactions shown in Table 1. Because 14 chemical species were involved in the reaction process, a total of 14 ordinary differential equations were obtained. The rate constants for reactions involved in the process were taken from the literature (see Grymonpré et al., 1999)[24] except for the initiation rate constants k_1, k_2, and k_3, which were obtained through model fitting of experimental data. The initiation reactions [Eqs. (1), (2), and (3) in Table 1] were assumed to be directly associated with the corona-discharge process, and the reaction constants were assumed to be functions of applied voltage. The rest of the reactions were assumed to be independent of the corona-discharge process. This model was employed in our work to permit comparison of the pulsed and pulseless corona-discharge methods.

The ordinary differential equations obtained from chemical reaction systems are known as *stiff* equations.[25] Thus, the 14 equations obtained here were simultaneously solved using the computer program *STIFF*,[26] which is suitable for stiff initial-value problems. The initiation rate constants (k_1, k_2, and k_3) were optimized to fit the experimental data of this work since no experimental data are available in the literature for the same experimental conditions.

Modeling and experimental results of phenol

Table 1. Chemical Reactions in the Aqueous Solution of the Pulseless Corona Reactor

Chemical reaction	Rate constant	Eq. no.
initiation reactions		
$H_2O \xrightarrow{k_1} H\cdot + \cdot OH$	*see* Table 2	(1)
$2H_2O \xrightarrow{k_2} H_2O_2 + H_2$	*see* Table 2	(2)
$2H_2O \xrightarrow{k_3} H_3O^+ + e_{aq}^- + \cdot OH$	*see* Table 2	(3)
propagation reactions		
$H\cdot + O_2 \xrightarrow{k_4} HO_2\cdot$	$k_4 = 1.0 \times 10^{10}\ M^{-1}s^{-1}$	(4)
$H\cdot + H_2O_2 \xrightarrow{k_5} H_2O + \cdot OH$	$k_5 = 1.0 \times 10^{10}\ M^{-1}s^{-1}$	(5)
$\cdot OH + H_2O_2 \xrightarrow{k_6} H_2O + HO_2\cdot$	$k_6 = 5.0 \times 10^{7}\ M^{-1}s^{-1}$	(6)
$e_{aq}^- + \cdot OH \xrightarrow{k_7} OH^-$	$k_7 = 3.0 \times 10^{10}\ M^{-1}s^{-1}$	(7)
$e_{aq}^- + H\cdot + H_2O \xrightarrow{k_8} OH^- + H_2$	$k_8 = 2.5 \times 10^{10}\ M^{-1}s^{-1}$	(8)
$e_{aq}^- + H_2O_2 \xrightarrow{k_9} \cdot OH^- + OH^-$	$k_9 = 1.2 \times 10^{10}\ M^{-1}s^{-1}$	(9)
termination reactions		
$H\cdot + \cdot OH \xrightarrow{k_{10}} H_2O$	$k_{10} = 2.4 \times 10^{10}\ M^{-1}s^{-1}$	(10)
$2\cdot OH \xrightarrow{k_{11}} H_2O_2$	$k_{11} = 4.0 \times 10^{9}\ M^{-1}s^{-1}$	(11)
$2HO_2\cdot \xrightarrow{k_{12}} H_2O_2 + O_2$	$k_{12} = 2.0 \times 10^{6}\ M^{-1}s^{-1}$	(12)
$H\cdot + HO_2\cdot \xrightarrow{k_{13}} H_2O_2$	$k_{13} = 1.0 \times 10^{10}\ M^{-1}s^{-1}$	(13)
$2\cdot H \xrightarrow{k_{14}} H_2$	$k_{14} = 1.0 \times 10^{10}\ M^{-1}s^{-1}$	(14)
$HO_2\cdot + \cdot OH \xrightarrow{k_{15}} H_2O + O_2$	$k_{15} = 1.0 \times 10^{10}\ M^{-1}s^{-1}$	(15)
$H_3O^+ + OH^- \xrightarrow{k_{16}} 2H_2O$	$k_{16} = 3.0 \times 10^{10}\ M^{-1}s^{-1}$	(16)
oxidation reactions		
phenol + $\cdot OH \xrightarrow{k_{17}}$ hydroquinone + $H\cdot$	$k_{17} = 6.5 \times 10^{9}\ M^{-1}s^{-1}$	(17)
phenol + $\cdot OH \xrightarrow{k_{18}}$ catechol + $H\cdot$	$k_{18} = 8.0 \times 10^{9}\ M^{-1}s^{-1}$	(18)
phenol + $\cdot OH \xrightarrow{k_{19}}$ resorcinol + $H\cdot$	$k_{19} = 1.0 \times 10^{9}\ M^{-1}s^{-1}$	(19)
hydroquinone + $\cdot OH \xrightarrow{k_{20}}$ products	$k_{20} = 1.0 \times 10^{11}\ M^{-1}s^{-1}$	(20)
catechol + $\cdot OH \xrightarrow{k_{21}}$ products	$k_{21} = 1.0 \times 10^{10}\ M^{-1}s^{-1}$	(21)
resorcinol + $\cdot OH \xrightarrow{k_{22}}$ products	$k_{22} = 1.0 \times 10^{10}\ M^{-1}s^{-1}$	(22)

concentration with time are shown in Figure 7. As shown in this figure, the model provides good fit to the experimental data for all cases. The resulting initiation reaction constants (k_1, k_2, and k_3) are shown in Table 2 for each applied voltage. In this table, we can see that k_3 is about one order magnitude greater than k_1 and k_2 for all applied voltages. This result implies that the reaction described by Eq. (3) is the dominant mechanism of the pulseless corona-discharge process, producing hydroxyl radical and aqueous electron as the major species. Although several species are produced, these two dominant species are assumed to be responsible for the complete degradation of phenol in this work, either with oxygen at 5- and 6-kV applied voltage or with ozone at 5 kV.

If we compare 5 kV with oxygen input and 5 kV with ozone input, we see that the value of k_3 is higher with ozone than with oxygen, as shown in Table 2. This result is expected since the experimental results showed faster degradation of phenol in the case of ozone input. Since the model employed here does not include ozone in the reactions, the k_3 value is treated as a lumped constant having both the effect of corona discharge and the effect of ozone. Upon entering the reactor, the ozone in input gas is

Table 2 Initiation Rate Constants Obtained from the Model (Units are Ms^{-1})

Initial rate constant	Applied voltage				PSC*
	4 kV	5 kV	6 kV	5 kV/ozone	at 57 kV
k_1	3.0×10^{-9}	7.0×10^{-9}	7.7×10^{-9}	8.0×10^{-9}	9.25×10^{-10}
k_2	3.0×10^{-9}	7.0×10^{-9}	7.7×10^{-9}	8.0×10^{-9}	1.2×10^{-6}
k_3	1.3×10^{-8}	5.5×10^{-8}	7.0×10^{-8}	1.0×10^{-7}	2.35×10^{-9}

* Values obtained from Grymonpré et al.[24] for pulsed streamer corona discharge reactor.

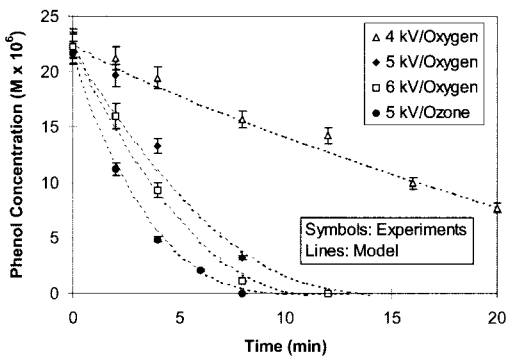

Figure 7. Comparison of phenol degradation modeling results with experimental data; lines represent modeling results.

transferred to water via reactions listed in Shin et al.[21] producing hydroxyl radical, which disintegrates phenol. Thus, ozone in input gas independently disintegrates phenol in the solution along with the pulseless corona-discharge process. Therefore, the value of k_3 in the 5-kV experiment with ozone includes the effect of ozone in input gas as well as the effect of pulseless coronal discharge on phenol degradation.

For comparison, the initiation constants for pulseless corona discharge and pulsed streamer corona are shown in Table 2 for each applied voltage. As shown in this table, these constants are different. Grymonpré et al.[24] reported a higher value of k_2 than k_3, while here we report a higher value for k_3. The reason for this discrepancy may be the different conditions of the two reactors. Based on the initiation reaction constants, it can be inferred that hydrogen peroxide produced by reaction (2) is the dominant species in the pulsed streamer corona system, while the aqueous electron and hydroxyl radical produced by reaction (3) are dominant for the pulseless corona-discharge system. Although the model presented in this work needs to be extended with additional reactions, the values of rate constants presented in Table 2 show a good comparison of the two different corona-discharge systems.

Identification of Chemical Species Formed Under Corona Discharge

The chemical species produced in the corona-discharge process were qualitatively identified using emission spectra (see also Sato et al., 1996; Clements et al., 1987).[27,28] These chemical species are responsible for the destruction of bacteria and organic compounds, such as methylene blue and phenol. Figure 8 shows the emission spectra of corona discharge at 7 kV of applied voltage with oxygen input. The emission spectra were obtained between 200 and 600 nm using a monochromator. Several species were identified in this experiment. The major species responsible for the oxidation of methylene blue and phenol are hydroxyl radical (.OH), ozone (O_3), hydroxyl ion (OH^-), and atomic hydrogen

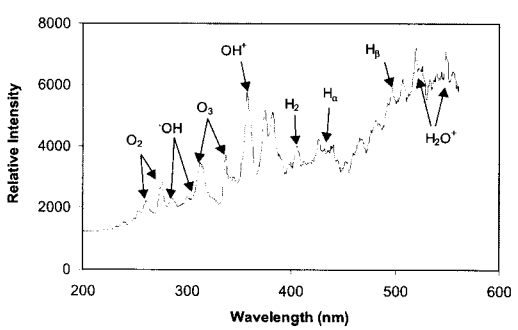

Figure 8. Emission spectra for the identification of the chemical species formed under discharge; applied voltage: 7 kV; input gas: oxygen.

(H_α and H_β). The emission spectra for all species identified appear in the following wavelength ranges: hydroxyl radical: 280-340 nm; ozone: 310-340 nm; hydroxyl ion: 350-360 nm; α atomic hydrogen (H_α): 434 nm; and β atomic hydrogen (H_β): 486.1 nm.[27,29] These emission spectra verify that H and OH radicals are produced by pulseless corona discharge in the presence of oxygen and water. They also suggest that more chemical/electrochemical reactions need to be considered in the modeling.

CONCLUSIONS

This article describes the application of electric fields to simultaneously generate radical species and microbubbles of oxygen or ozone in water for the oxidation of methylene blue dye and phenol as representative organic molecules in the production of ultrapure water. The objectives of using dc electric fields in this process are to (1) form radical species from oxygen and water and (2) generate microbubbles of oxygen, thus enhancing the interfacial area for mass transfer. Also, dc electric fields are suitable for ultrapure-water production because of the low electrical conductivity of the water that allows higher efficiency of radical formation.

The oxidation of methylene blue dye was successfully performed at 5- and 6-kV applied voltage. The effect of the polarity of input power was investigated. Negative-polarity voltage showed approximately 20% better performance than positive polarity in methylene blue destruction. Two corona-discharge processes with either oxygen input or ozone input were compared. At 4 kV, ozone performed better than oxygen. However, at the applied voltages of 4.5 kV and 6 kV, oxidation by oxygen and corona discharge became comparable to that with ozone.

The results of phenol oxidation showed a similar behavior with methylene blue oxidation. Phenol was completely oxidized within approximately 10 min with oxygen input at the applied voltages of 5 and 6 kV. These results prove the effectiveness of the pulseless corona-discharge process in the removal of organic compounds and suggest more studies to investigate bacterial sterilization for ultrapure water production. From the results of this work, we can conclude that a minimum applied voltage exists, above which the oxidation rate in the corona-discharge process increases significantly. The threshold voltage was found to be approximately 4.5 kV. Thus, it is recommended that the corona-discharge process be operated above 4.5 kV.

The phenol-degradation model developed for a pulsed streamer corona by Grymonpré et al.[24] was employed in this work to predict the initiation rate constants. Modeling results showed that the dominant species are aqueous electron and hydroxyl radical for pulseless corona discharge as opposed to hydrogen peroxide for the pulsed streamer corona system. These two species, aqueous electron and hydroxyl radical, are responsible for the complete degradation of phenol in the pulseless corona-discharge system.

The radical species produced from the corona-discharge process were identified using emission spectra. The results showed that the major radical species produced from the process were hydroxyl radicals, ozone, and atomic hydrogen. Emission spectra results also suggest that more chemical/electrochemical reactions need to be included in the modeling.

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