

Formation of Active Species and Degradation of Bromamine Acid by Gas-liquid Electrical Discharge in Different Atmospheres

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This study investigated the formation of different active species ($\cdot\text{OH}$, H_2O_2 , O_3) in aqueous solutions using needle-plate gas-liquid discharge non-thermal plasma (NTP) with different atmospheres (air, argon, and oxygen). The changes in the pH and conductivity of a blank solution with different discharge atmospheres were also investigated. The degradation of the model compound, bromamine acid (BAA), in an aqueous solution was investigated. The effects of different factors on the BAA degradation were studied, including the types of discharge atmospheres, initial BAA concentration, and initial pH. The experimental results showed that, after a 60-min treatment, approximately 90.86%, 68.99%, and 49.96% of BAA was removed by plasma with oxygen, air, and argon discharge atmospheres, respectively, and input discharge powers of 49.23 W, 41.49 W, and 16.17 W, respectively. The BAA removal rate was lowest with an argon discharge atmosphere; however, the energy yield with argon was 1.73 and 1.6 times those with air and oxygen, respectively. The plasma degradation of BAA fitted the pseudo-first-order kinetic model. Compared to oxygen and argon, the initial concentration had little effect on the degradation of BAA when air was introduced into the reaction system. UV-vis absorption spectra of the BAA solutions were measured to illustrate the discharge degradation mechanism. No new peaks appeared in the UV-vis analysis of the BAA solution after the 60-min treatments. Therefore, the results essentially demonstrate that NTP is a suitable alternative method for the degradation of organic pollutants.

Keywords: Gas-liquid phase discharge, Non-thermal plasma, Active species, Bromamine acid, Degradation, plasma chemistry

1. INTRODUCTION

In recent years, gas-liquid discharge non-thermal plasma (NTP) as a typical advanced oxidation process has gained increasing interest because of its ability to remove organic pollutants from water and

wastewater. Compared to other advanced oxidation processes, gas-liquid electrical discharge plasmas can provide a rich variety of reactive species (e.g., $\cdot\text{OH}$, $\cdot\text{O}$, HO_2 , H_2O_2 , O_3 , etc.), which could effectively decompose most contaminants [1-3].

In addition, this oxidation process is a combination of several oxidation technologies (e.g., high-energy electron irradiation, ultraviolet light, and shock wave, etc.) and its unique advantages, such as simple operation, high efficiency, and less secondary pollution, have drawn the attention of water treatment researchers[4]. Therefore, this technology has great potential for application to contaminated water treatments and is regarded as a promising future advanced oxidation process. In reported studies, gas-liquid discharge NTPs have been successfully applied to the treatment of different wastewater contaminants, such as dyes[5], pesticides[6, 7] and antibiotics [8, 9]. In the oxidation process, activated species play a vital role in the discharge plasma degradation of organic compounds. For example, the hydroxyl radical ($\cdot\text{OH}$) is one of the strongest oxidants, which has a higher reduction potential (2.80 eV) and can react with most organic pollutants without selectivity [10, 11].

Bromamine acid (BAA), the structure of which is shown in Fig. 1, is a typical anthraquinone dye intermediate that widely exists in dyeing wastewater (Fei, et al, 2012). Because of its high water-solubility, biotoxicity, stable structure and non-biodegradability, conventional treatments are not sufficiently capable of removing BAA in wastewater [12, 13]. Therefore, BAA was selected as the model organic pollutant for this research, in which the influence of different discharge atmospheres and other performance parameters on organic degradation was explored.

The type and the amount of active species are closely related to the type of discharge atmosphere [2, 14]. In previous studies, the active species produced by the gas-liquid discharge process were always determined using a spectrometric method [2, 15]. In this study, a needle-plate plasma discharge was used to study the formation of the activated species in the liquid with different discharge atmospheres. Three types of discharge atmospheres (air, argon, and oxygen) were selected, and the different activated species ($\cdot\text{OH}$, H_2O_2 , and O_3) generated in aqueous solutions were studied. The influence of pH on the generation of these active species and the change in the conductivity of the solution was also investigated.

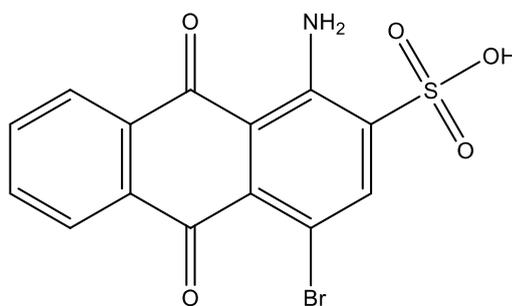


Figure 1. Molecular structure of BAA

2. EXPERIMENTAL SECTION

2.1 Chemicals and materials

Potassium indigo trisulfonate was purchased from Sigma-Aldrich. Other chemicals such as BAA, NaOH, H₂SO₄, and H₂O₂ were purchased from Sinopharm Chemical Reagent Co. Ltd., China. The pure oxygen and argon were supplied by high-pressure cylinders. The air was supplied by an air supply pump. The chemical reagents used in this study were analytical grade and were used without further purification. All of the solutions used in this study were prepared using distilled-deionized water from a Millipore system. The synthetic wastewater consisted of 40 mg/L BAA in deionized water.

2.2 Experimental setup

A schematic of the plasma reactor is shown in Fig. 2, which was described in our previous work[16]. The reactor was made of glass with an inner diameter of 80 mm and a height of 100 mm. The plasma generator was composed of a hollow gold needle (inner diameter = 0.6 mm), a concentric dielectric cone-shaped glass tube (upper I.D = 50 mm, lower I.D = 0.8 mm) that enclosed the needle, and a stainless-steel (diameter = 80 mm) beneath them. The hollow gold needle served both as the powered electrode and the working gas inlet channel. Its tip was located 10 mm from the end of the tube nozzle in the axial direction. The discharge generator was powered by a sinusoidal excitation voltage of 0–40 kV with a frequency of 0–30 kHz. The applied voltage and discharge current were measured using a high-voltage probe (Tektronix P6015A) and a current probe (Tektronix TCP202) via a digital oscilloscope (Tektronix DPO4034). The solution was circulated continuously at a speed of 30 mL/min using a peristaltic pump (BT100-2J) connected to the inlet.

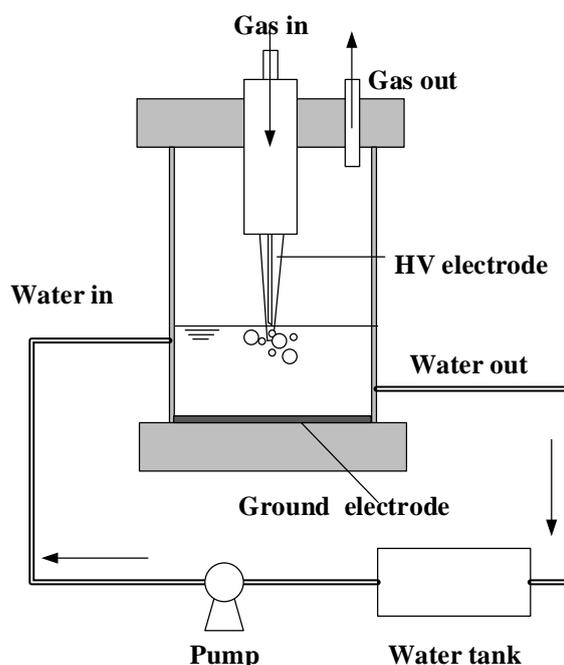


Figure 2. Experimental set-up

2.3 Analytical methods

The solution pH and conductivity were determined using a Multi-parameter portable meter (MultiLine® Multi 3620 IDS, German). The BAA concentration in the solution was quantitatively analyzed by using a UV-vis absorption spectrophotometer (DR500, HACH, USA) in accordance with the Beer-Lambert law at $\lambda_{\max} = 484\text{nm}$. The UV-vis absorption spectrum was monitored as a function of time and was quantified using a UV-vis spectrophotometer between the wavelengths of 200 nm and 800 nm.

The nitrate ions and nitrite ions were analyzed using an ion chromatograph (ICS-3000, Dionex, USA) with a conductivity detector. Separation was achieved via an anionic column (IonPac AS19, Dionex, USA). Tert-butanol was used as scavenger of the hydroxyl radical. The tert-butanol reacts with hydroxyl radicals to form formaldehyde, and the amount of formaldehyde formed was determined via spectrophotometry. The yield of hydroxyl radicals is twice the yield of formaldehyde[17-19]. The concentration of hydrogen peroxide which generated in the solution was measured using the potassium titanium (IV) oxalate method[20]. The concentration of gas-phase ozone was monitored by ozone analyzer (202,2B Technologies, USA). The dissolved concentrate of ozone in the solution was detected with the indigo method[21].

The BAA degradation rate was measured using the following equation:

$$\text{Degradation rate}(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where C_0 is the initial concentration of BAA, mg/L; C_t is the BAA concentration at discharge treatment time t , mg/L. C_0 and C_t were calculated based on the absorbance of the BAA solution at $\lambda_{\max} = 484\text{nm}$.

The degradation of BAA by gas-liquid discharge plasma was in accordance with the pseudo-first-order kinetic model, which was calculated using the following equation

$$\ln\left(\frac{C_0}{C_t}\right) = kt \quad (2)$$

where C_0 and C_t are the same definition as in Eq (1); k is the reaction rate constant; t is the reaction time, min.

The ionization energies of oxygen and argon are different, and different discharge powers cannot be normalized to allow comparisons. Therefore, energy yield (EY) was introduced as a new measuring standard, EY is defined as the amount of pollution degraded by per energy consumed in the process as following equation (3):

$$\text{EY}(\text{g/kWh}) = \frac{V(C_0 - C_t)}{P \times t} \quad (3)$$

Where C_0 and C_t are the same definition as in Eq (1), V is the volume of the solution, L, P is the average power in the discharge, kW, t is the treatment time, h.

3. RESULTS AND DISCUSSION

To compare the characteristics of the discharge in the different atmospheres, ultrapure water was introduced to the treatment system. The activated species and the changes in the conductivity and pH of the aqueous solutions were then investigated.

3.1 Generation of activated species in the discharge

3.1.1 Changes in the pH and conductivity with different discharge atmospheres

The discharge atmosphere is an important control parameter that not only affects the type of active species but also affects the changes in the solution characteristics. The changes in the conductivity and pH of the solutions are shown in Figs. 3(a) and 3(b), respectively, with different discharge atmospheres.

The results show that, even though the discharge powers were different (that for oxygen was similar that for air but larger than that for argon), after 60 min of discharge with an air atmosphere, the conductivity of the solution rose rapidly to 1813 $\mu\text{s}/\text{cm}$, which is 24 and 64 times the conductivity measured with oxygen and argon atmospheres, respectively. According to previous reports, nitrate and nitrite can form in aqueous solutions during plasma discharge with a nitrogen-containing atmosphere; then, nitric acid can be formed, such that the solution pH drops sharply and the solution exhibits strong acidity [22]. In this study, the changes in the concentrations of nitrate and nitrite ions in the aqueous solution with an air discharge atmosphere were also studied, as shown in Fig. 3(c).

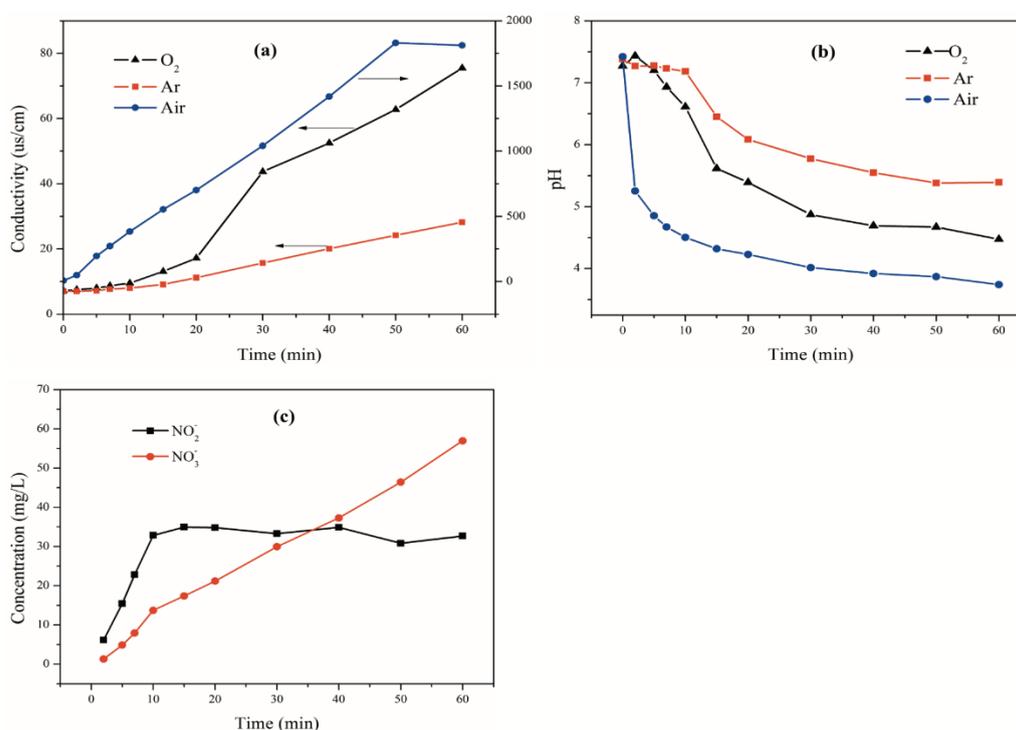
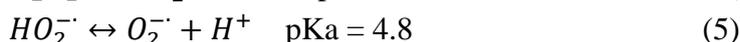
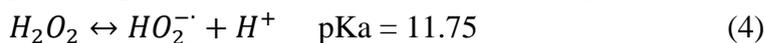


Figure 3. Change in the (a) conductivity and (b) pH of ultrapure water under a discharger with different discharge atmospheres. The discharge powers with oxygen, air, and argon were 49.23 W, 41.49 W, and 16.17 W, respectively. (c) Change in the nitrite and nitrate ions in ultrapure water with an air discharge atmosphere.

In the first 10 min of the reaction, the concentration of nitrite ions in the solution increased to approximately 32 mg/L and then stabilized. The concentration of nitrate ions increased nearly linearly with the reaction time and reached 56.98 mg/L at 60 min. The accumulation of nitrate ion indicated that

the nitrate ion was the final product in the aqueous solution with an air discharge atmosphere. The formation and accumulation of nitrate and nitrite ions were the most important reasons for the increase in the conductivity and the decrease in pH with an air discharge atmosphere; these results agreed with those of previous studies [15, 23].

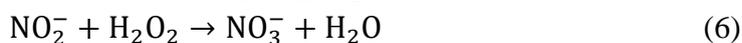
Another interesting result indicated that, when oxygen and argon were selected as the discharge atmospheres, the pH decreased and the conductivity increased. This may be partly linked to the accumulation of hydrogen peroxide in the solution during the discharge process. Hydrogen peroxide is a weak acid, and depending on the concentration, its pH can be as low as 4.5, as shown in Eqs. (4) and (5). The reaction with the oxygen discharge atmosphere produced more hydrogen peroxide than that with the argon discharge atmosphere; therefore, the pH of the aqueous solution with the oxygen discharge atmosphere was lower and the conductivity of the solution changed accordingly.



3.1.2 Generation of hydrogen peroxide different discharge atmospheres

Hydrogen peroxide is a vital activated species in the discharge process, the generation mechanism of which was reported by Reddy [24]. Hydrogen peroxide has a longer half-life than other active species in solution. The generation of hydrogen peroxide resulting from discharge with different atmospheres was evaluated, and the results are shown in the Fig. 4.

When oxygen, air, and argon were used as the discharge atmospheres, after 60 min, the concentrations of hydrogen peroxide in the liquid phase were 86.9, 26.59, 3.69 mg/L, respectively. When oxygen was used as the discharge atmosphere, a large amount of reactive oxygen radicals was generated, which contributed to the formation of hydrogen peroxide. Therefore, the highest yield of hydrogen peroxide in solution was obtained with the oxygen discharge atmosphere. With the lower ionization energy of argon, the discharge power of argon was much smaller than the discharge powers of oxygen and air. With an argon discharge atmosphere, there are two ways to generate hydrogen peroxide: high-energy electron reactions with water and excited argon atom reactions with water. With an air discharge atmosphere, not only reactive oxygen species but also a large amount of reactive nitrogen species were produced. Because nitrogen accounted for a larger proportion in air, the reactive nitrogen species were more numerous than the reactive oxygen species. Hydrogen peroxide can behave as an oxidant (1.77 eV) and a reductant (-0.7 eV) in a redox environment. For example, in the presence of nitrite ions in the solution, nitrate ions can also form via the reaction of nitrite anions with hydrogen peroxide, which decreases the amount of hydrogen peroxide, as indicated in Eq. (6). Similar results were also obtained by Wandell [22], who studied the production of nitrogen oxides during gas-liquid two-phase discharge and found that the production rate of all produced NO_x species increased significantly with the nitrogen concentration while the hydrogen peroxide formation decreased slightly.



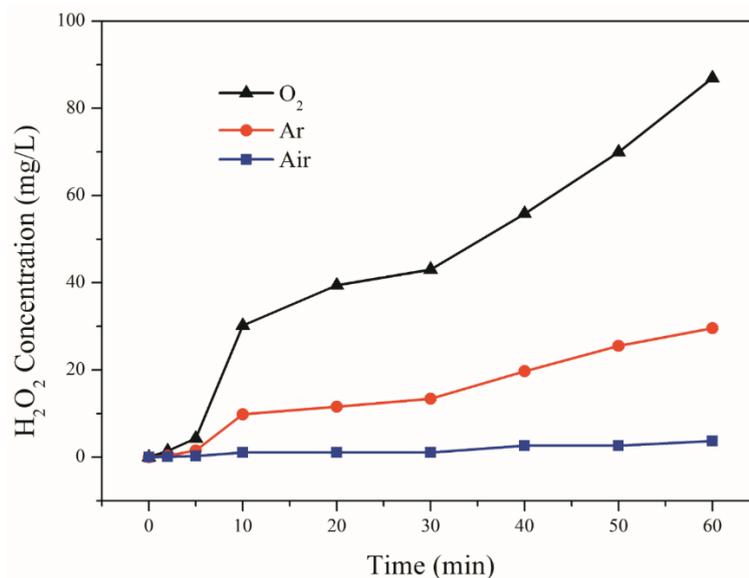


Figure 4. Concentration of H₂O₂ as a function of the discharge time with different atmospheres (the discharge powers with oxygen, air, and argon were 49.23 W, 41.49 W, and 16.17 W, respectively).

3.1.2 Generation of ozone with different discharge atmospheres

Ozone is an important oxidant used in water and wastewater treatment. Ozone is generated by gas–liquid discharge and can transfer from the gas phase into the liquid phase and then oxidize organic contaminants in a solution. Ozone can oxidize contaminants in liquid either directly via molecular oxidation or indirectly via oxidation by radicals produced by its decomposition. The generation of ozone in the discharge plasma process with different discharge atmospheres is shown in Fig. 5. It can be seen that, with a pure oxygen discharge atmosphere, the concentration of ozone in aqueous solution slowly increased, reached 7.5 mg/L at 50 min, and then remained stable. In the gas phase, the concentration of ozone rapidly increased to 25.1 mg/L within 10 min and then slowly increased, reaching 39.7 mg/L at 60 min. This result indicates that a large amount of ozone was generated and that most of this ozone was not effectively used, possibly as a result of mass transfer; the ozone was then emitted with the exhaust. With an argon discharge atmosphere, almost no ozone was generated in the liquid phase or the gas phase because no oxygen was involved in the discharge. The highest concentration of ozone produced with the air discharge atmosphere was only 3.5 mg/L in the aqueous solution, which was much lower than the concentration of ozone produced with an oxygen discharge atmosphere. Because of the proportion of oxygen in the air, the maximum concentration of the gas-phase ozone was less than 10 mg/L with the air discharge atmosphere. Conversely, nitrites were rapidly oxidized to nitrates and oxygen by the ozone, therefore eliminating the ozone content in the water, as shown in Eq.(7).[25].



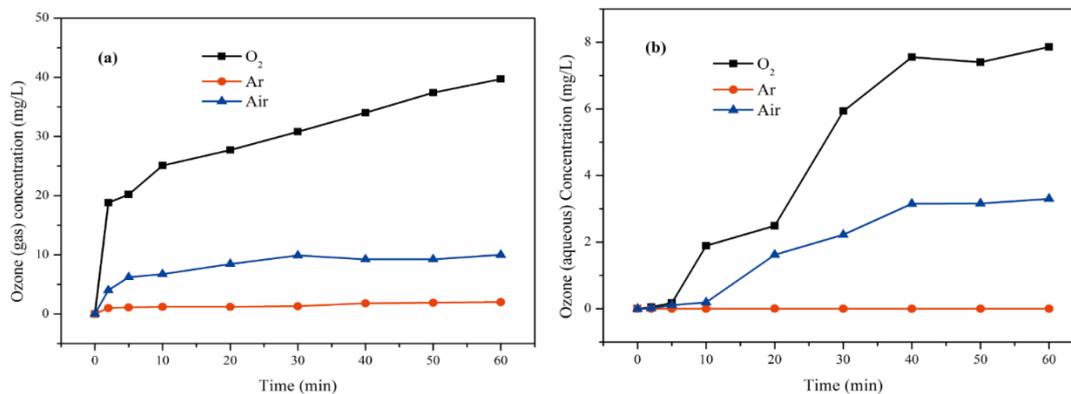


Figure 5. Concentration of O₃ as a function of discharge time with different gases (a, gas phase, b, liquid phase)

3.1.2 Generation of ·OH in different discharge atmospheres

Hydroxyl radical is the most important free radical in gas–liquid two-phase discharge plasma. Because of its high activity, low concentration, and short lifetime, it is difficult to monitor using direct methods; therefore, tert-butanol is usually used to trap hydroxyl radicals. Prior to the discharge process, 200 mM of tert-butanol was added to the deionized water and the generation of hydroxyl radicals was evaluated. Tert-butanol reacts with hydroxyl radicals to form formaldehyde, and the amount of formaldehyde formed was determined via spectrophotometry. The yield of hydroxyl radicals is twice the yield of formaldehyde.

$$k_{\cdot OH} = \frac{d[\cdot OH]}{dt} = 2 \frac{d[HCHO]}{dt}$$

The change of the formaldehyde concentration with different discharge atmospheres is shown in Fig. 6 and suggests that the highest reaction rate constant of formaldehyde occurred with the oxygen discharge atmosphere and lowest with the air discharge atmosphere. Tert-butanol was added to the deionized water, and the reaction rate constants of formaldehyde with the oxygen, argon, and air discharge atmospheres were 0.0775 mol/L/min, 0.0322 mol/L/min, and 0.0135 mol/L/min, respectively. This result indicated that, under the same reaction conditions, the hydroxyl radical generation rates with these atmospheres are 0.155 mol/L/min, 0.0644 mol/L/min, and 0.027 mol/L/min, respectively. The discharge powers with oxygen and air were similar. However, the reaction rate constant of hydroxyl radicals with an oxygen discharge atmosphere was 5.74 times that with an air discharge atmosphere. This result indicated that the formation of hydroxyl radicals was related to the oxygen content.

In previous studies, the production of hydrogen peroxide was selected as an index to measure the production of hydroxyl radicals and was positively correlated with the generation of hydroxyl radicals [26, 27]. One of the pathways of hydrogen peroxide formation is through the recombination of hydroxyl radicals, as shown in Eq. (8). During the discharge process with an oxygen discharge atmosphere, a large amount of hydroxyl radicals was detected, which corresponds to the generation of hydrogen peroxide.



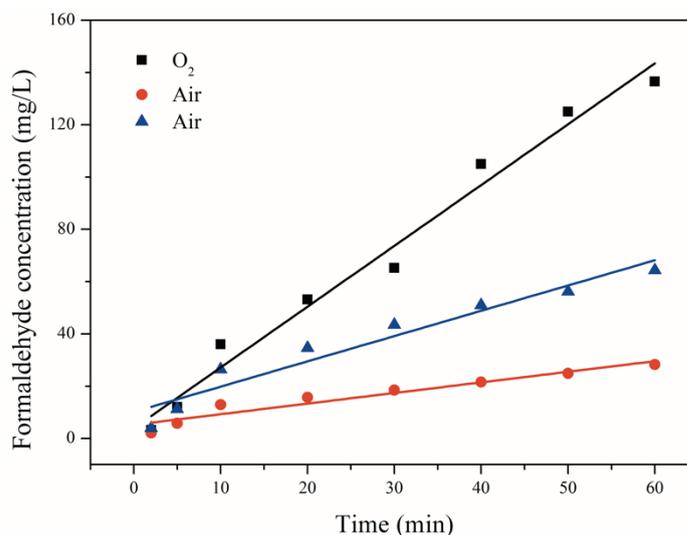


Figure 6. Concentration of formaldehyde as a function of discharge time with different atmospheres

3.2 Degradation of BAA by electrical discharge with different atmospheres

3.2.1 Effects of the kinds of gases on the degradation of BAA

Different discharge atmospheres result in the different production of active species. To study the effects of different discharge atmospheres on the degradation of organic pollutants, experimental assays for the degradation of solutions containing BAA by discharge plasma with different discharge atmospheres and degradation yields were performed; the results are plotted in Fig. 8. The operational conditions were as follows: the gas flow rate was 1.0 L/min, the solution flow rate was 10 mL/min, the discharge treatment time was 60 min, and the 300-mL BAA solution had an initial concentration of 40 mg/L.

As seen in Fig. 7, the BAA concentration of the solution decreased gradually as the oxidation reaction progressed. This indicated that the BAA molecules were destroyed and the chromophore groups were attacked. A lower decolorization efficiency was observed with the argon discharge atmosphere than with the oxygen and air discharge atmospheres. Even though the discharge powers with the different atmospheres were different (the discharge powers with oxygen, air, and argon were 49.23 W, 41.49 W, and 16.17 W, respectively), after 60 min, the BAA degradation rates with the oxygen, argon, and air discharge atmospheres were 90.86%, 49.96%, and 68.99%, respectively. With the oxygen and air discharge atmospheres, there were higher concentrations of ozone in the solution, which may have promoted the decolorization of BAA. Interestingly, when argon was used as the discharge atmosphere, no ozone was generated in the process but the BAA removal rate was as high as 49.96%. This result indicates that non-ozone active species, such as hydroxyl radicals, play a vital role in the decolorization of BAA. Note that, when argon was used as the discharge atmosphere, after a 60-min treatment, the highest energy yield obtained was 0.35 g/kWh, which was 1.6 and 1.73 times those with the oxygen and air discharge atmospheres, respectively.

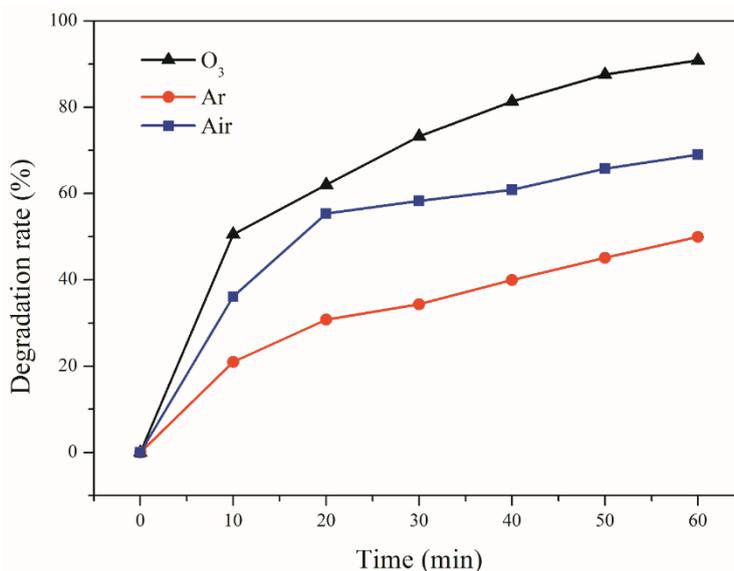


Figure 7. Degradation of BAA as a function of the discharge time with different atmospheres. The discharge powers with the oxygen, air, and argon atmospheres were 49.23 W, 41.49 W, and 16.17 W, respectively.

3.2.1 Effects of the initial concentration on the degradation of BAA with different gases

In the plasma discharge process with different atmospheres, the effect of the initial BAA concentration on its degradation efficiency was investigated with concentrations in the range of 20–60 mg/L. Fig. 8 shows the evolution of the degradation rate and pseudo-first-order of BAA degradation as a function of the discharge time for different initial concentrations. It can be seen that the BAA degradation efficiencies decreased with the initial BAA concentration from 20 mg/L to 60 mg/L with the oxygen and argon discharge atmospheres. The kinetic fitting results of BAA are shown in Table 1.

For example, with the oxygen discharge atmosphere, the BAA removal efficiencies were 95.4%, 90.9%, and 82.2% for a 60-min treatment when the initial BAA concentrations were 20, 40, and 60 mg/L, respectively. The same trend was obtained with the argon discharge atmosphere. This phenomenon can be explained by the higher initial BAA concentration in the solution, which caused more intermediate products. The intermediate products strongly competed for reactions with the active radicals with BAA molecules. The results are consistent with those of Zeng et al.[28] in ibuprofen degradation via corona discharge, as well as those of Magureanu et al.[29]. At the same time, the rate constant was closely related to the initial BAA concentration in the solution, with higher initial concentrations resulting in lower rate constants. We found that the half-life increased with the initial concentration, which means that a higher degradation efficiency was obtained for higher concentrations.

However, with the air discharge atmosphere, the initial concentration did not have a large effect on the BAA degradation rate. This may be because anthraquinones are unstable under acidic conditions and are prone to redox reactions. To verify this result, a BAA decolorization test under acidic conditions was performed. The test conditions were as follows: the initial BAA concentration was 40 mg/L, the pH

was 3, and the nitrate and nitrite ion concentrations were 30 mg/L. The solution was mixed well and left to rest for 2 h, during which time the BAA concentration decreased by approximately 25%.

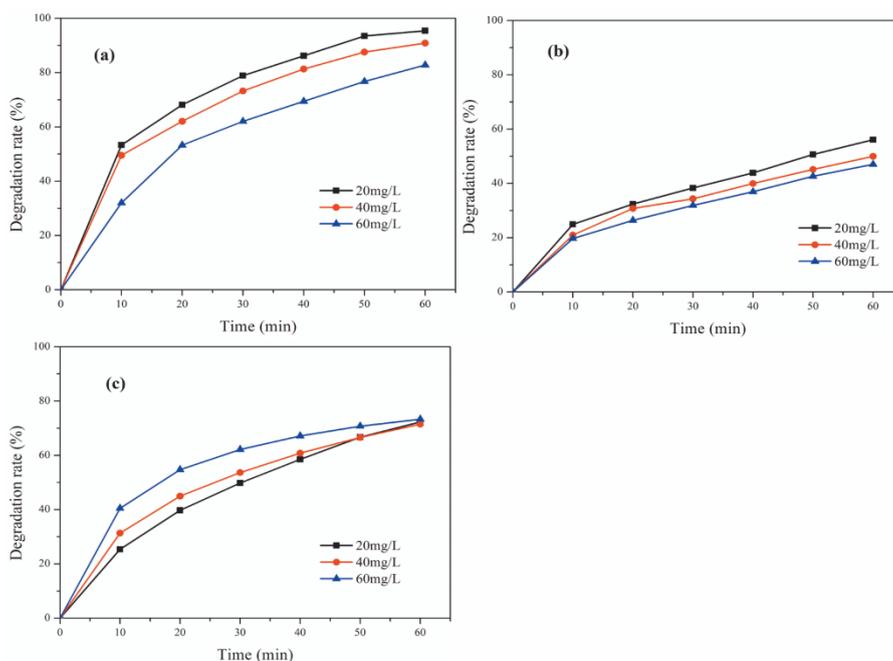


Figure 8. Variation in the degradation rates for different initial BAA concentrations by plasma treatment with different atmospheres: (a) oxygen, (b) argon, and (c) air.

3.2.2 Effects of the initial pH on the degradation of BAA with different atmospheres

The initial pH of the aqueous solution is the key parameter governing the degeneration of organic pollutants in the discharge process. The pH can not only control the existing forms of the organic pollutants but also affects the radical species in the discharge process. To examine this effect, the initial pH of the BAA solution varied between 3 and 10 in the discharge processes with oxygen and argon atmospheres. The other operational parameters in the reaction were consistent with the parameters used in Section 3.2.1. Regardless of the initial pH of the solution, when air was used as the discharge atmosphere, the pH of the solution rapidly dropped to approximately 3.5 because of the large amounts of nitric and nitrous acids produced in the solution. Therefore, in this study, the effect of different initial pH values on the BAA degradation rate was not explored further with the air discharge atmosphere.

The BAA removal efficiency at different initial pH values with various atmospheres is shown in Fig. 9. It can be observed that, regardless of the initial pH, the BAA removal rate with the oxygen discharge atmosphere was higher than that with the argon discharge atmosphere. A higher degradation efficiency was achieved in the acidic environment, and a lower removal rate was obtained in the alkaline environment. For example, within 60 min with an oxygen discharge atmosphere, only 78% of BAA was removed at an initial solution pH of 10; this was enhanced to 89.6% and 96.8% with initial solution pH values of 3, and 5.67, respectively. The reasons for this phenomenon can be explained. In the discharge process, the BAA concentration was calculated via spectrophotometry at the maximum absorption

wavelength. Unlike hydroxyl radicals, ozone can degrade chromophore groups selectively. In acidic solutions, ozone is relatively stable and the concentration of ozone in the acidic solution was 4.5 times that in the alkaline solution. However, with the mineralization of BAA, carbonate and bicarbonate form in the alkaline solution and these compounds are scavengers of hydroxyl radicals [30]. Furthermore, anthraquinones are unstable under acidic conditions and the degradation of BAA is promoted. The same results were obtained when argon was selected as the discharge atmosphere. Therefore, acidic conditions contribute to the degradation of BAA.

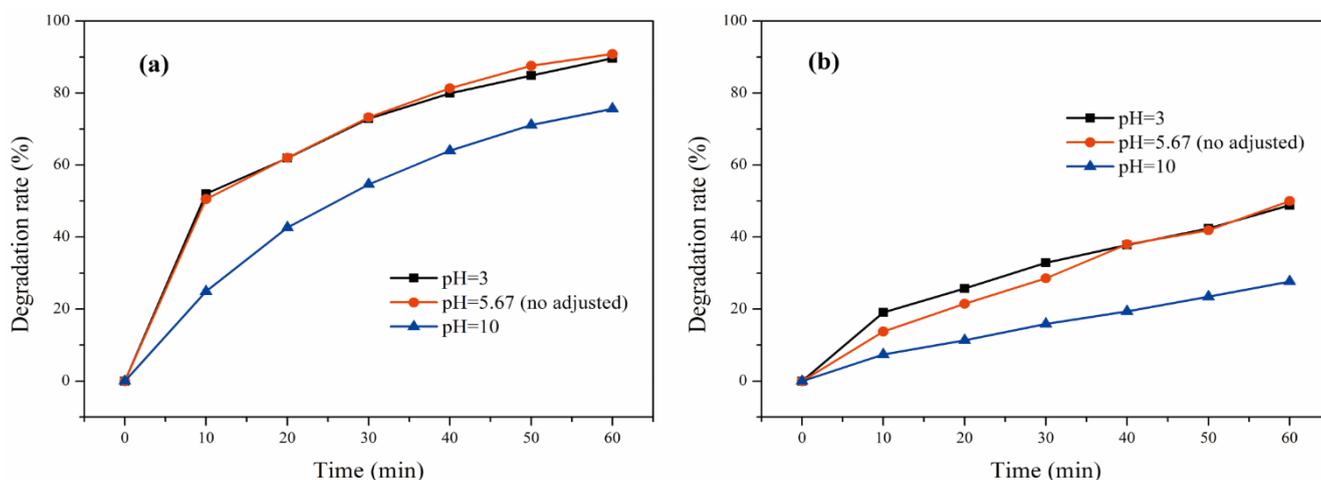


Figure 9. Variation of degradation rates with different initial pH of BAA by plasma treatment in different atmospheres. (a: O₂; b: Ar)

3.2.3 Spectrophotometry analysis of the degradation of BAA in the discharge plasma system

Several specific organic compounds can be analyzed via spectrophotometry using their characteristic peaks. Accordingly, the BAA solutions degraded by discharge plasma with different atmospheres were analyzed according to their UV–vis adsorption spectra at wavelengths of 200–600 nm to illustrate the BAA degradation process. The experimental parameters were set to a frequency of 20 kHz, a gas flow rate of 1 L/min, an initial BAA concentration of 40 mg/L with an initial pH of 5.67, and average discharge powers of 49.23 W, 41.49 W, and 16.17 W with the oxygen, air, and argon atmospheres, respectively. The UV–vis absorption spectra of the treated BAA solutions with respect to time are shown in Fig. 10.

Prior to plasma treatment, the spectrum of the untreated BAA solution exhibited two absorption bands in the ultraviolet spectral region at 232 nm and 250 nm. The absorbance at 482 nm in the visible region of the spectrum is linearly dependent on the BAA concentration of the solution. The degradation rate was calculated from the absorbance at this wavelength. It can be seen from Fig. 11 that the peak at 482 nm with the three atmospheres decreased with the treatment time; however, the fastest decolorization effect was obtained with the oxygen discharge atmosphere. During the degradation of the BAA solution by plasma treatment with oxygen and argon, the peaks across the entire UV–vis range significantly

weakened or even disappeared, indicating that the relevant structures were destroyed. The position of the peak did not change substantially, and no new absorption peaks appeared. BAA was effectively degraded, and no new substances formed or accumulated during the degradation process.

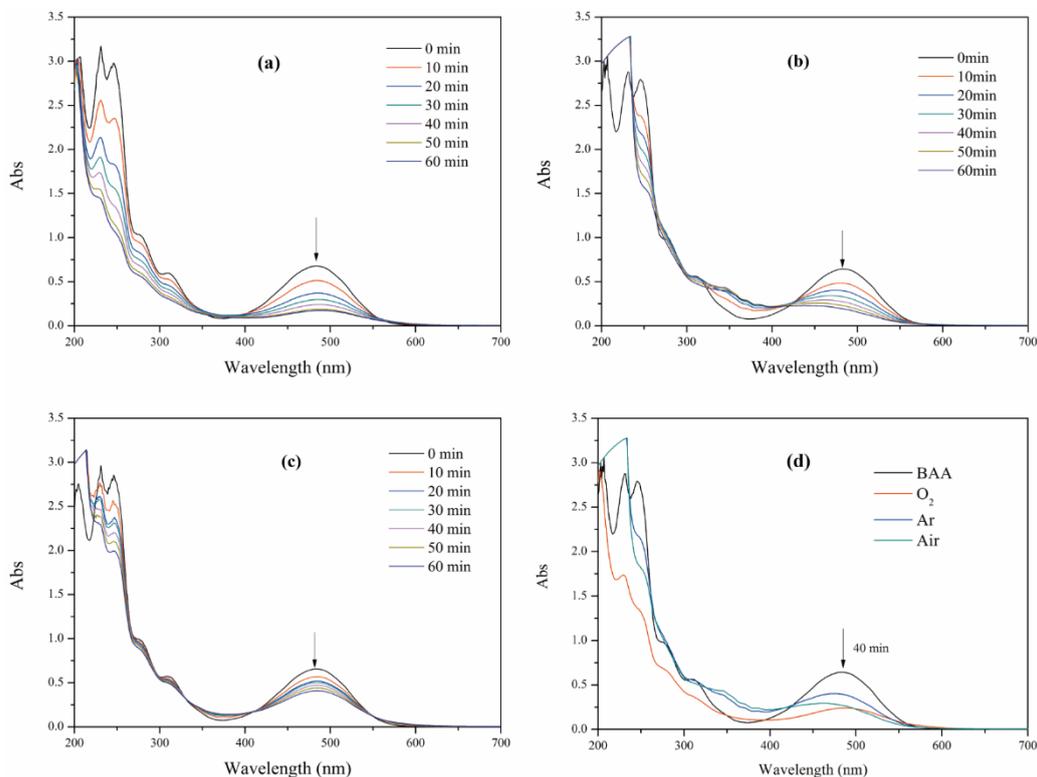


Figure 10. Absorbance variation of UV–vis for BAA during the discharge plasma treatment with different atmospheres: (a) oxygen; (b) air; (c) argon; and (d) treatment BAA with different discharge atmospheres in 40min.

Table 1. Rate constants and half-life degradation times for BAA decomposition by plasma discharge at different initial concentrations and initial pH values with various discharge atmospheres.

Atmosphere	BAA concentration (mg L ⁻¹)	Rate constant (min ⁻¹)	R ²
O ₂	20	0.0504	0.9916
	40	0.0380	0.9859
	60	0.0280	0.9893
	40 (pH = 3)	0.0348	0.9753
	40 (pH = 10)	0.0236	0.9946
Ar	20	0.0131	0.9870
	40	0.0105	0.9524
	60	0.0098	0.9636
	40 (pH=3)	0.0102	0.9724
	40 (pH=10)	0.0052	0.9947
Air	20	0.0208	0.9954
	40	0.0198	0.09726
	60	0.0204	0.9043

With an air discharge atmosphere, the maximum absorption wavelength of BAA in the visible region was blue-shifted. The reason might be that with the air discharge atmosphere, nitrogen-containing groups could be added to organic structures to form aromatic ring-type nitrate. This result corresponds to the light-yellow color of the solution after BAA was treated by plasma discharge with air. After 10 min of degradation, the peak at 254 nm exceeded the maximum detection limit. This is primarily because the large amount of nitrate and nitrite generated in the aqueous solution affected the absorption peak at 254 nm with an air discharge atmosphere.

4. CONCLUSIONS

This study investigated the formation of active species and the degradation of BAA in the needle-plate gas–liquid discharge NTP system by varying the experimental parameters of the discharge atmospheres, the initial pH, and the initial BAA concentration. It was found that the applied atmosphere had a major effect on the BAA degradation. With an air discharge atmosphere, nitrate and nitrite ions, which influence the active species, were produced in the solution. The discharge powers with the different atmospheres were different; the discharge powers with oxygen, air, and argon were 49.23 W, 41.49 W, and 16.17 W, respectively. After 60 min, the BAA degradation rates with the oxygen, argon, and air discharge atmospheres were 90.86%, 49.96%, and 68.99%, respectively. However, the highest energy yields with the argon discharge atmosphere were 1.6 and 1.73 times of those with the oxygen and air discharge atmospheres, respectively. Regardless of the selected discharge atmosphere, compared to alkaline conditions, acidic conditions contributed to the removal of BAA; this result is related to the chemical properties of BAA.

ACKNOWLEDGEMENT

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