Degradation of carbamazepine by high-voltage direct current gas–liquid plasma with the addition of H$_2$O$_2$ and Fe$^{2+}$

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Abstract
Carbamazepine (CBZ) is a typical psychotropic pharmaceutical which is one of the most commonly detected persistent pharmaceuticals in the environment. The degradation of CBZ in the aqueous solution was studied by a direct current (DC) gas–liquid phase discharge plasma combined with different catalysts (H$_2$O$_2$ or Fe$^{2+}$) in this study. The concentrations of reactive species (H$_2$O$_2$, O$_3$, and NO$_3^-$) and •OH radical yield in the liquid were measured during the discharge process. The various parameters that affect the degradation of CBZ, such as discharge powers, initial concentrations, initial pH values, and addition of catalysts, were investigated. The energy efficiency was 25.2 mg·kW$^{-1}·$h$^{-1}$ at 35.7 W, and the discharge power at 35.7 W was selected to achieve the optimal balance on the degradation effect and energy efficiency. Both acidic and alkaline solution conditions were conducive to promoting the degradation of CBZ. Both H$_2$O$_2$ and Fe$^{2+}$ at low concentration (10–100 mg/L of Fe$^{2+}$, 0.05–2.0 mmol/L of H$_2$O$_2$) were observed contributing to the improvement of the CBZ degradation rate, while the promotional effect of CBZ degradation was weakened even inhibition would occur at high concentrations (100–200 mg/L of Fe$^{2+}$, 2.0–5.0 mmol/L of H$_2$O$_2$). The degradation rate of CBZ was up to 99.1%, and the total organic carbon (TOC) removal efficiency of CBZ was up to 67.1% in the plasma/Fe$^{2+}$ (100 mg/L) system at 48 min, which suggested that high degradation rate and mineralization efficiency on CBZ could be achieved by employing Fe$^{2+}$ as a catalyst. Based on the intermediate products identified by Ultra Performance Liquid Chromatography Tandem Mass Spectrometry (UPLC–MS), the possible degradation pathways were proposed. Finally, the growth inhibition assay with Escherichia coli (E. coli) showed that the toxicity of plasma/Fe$^{2+}$-treated CBZ solution decreased and a relatively low solution toxicity could be achieved. Thus, the plasma/catalyst could be an effective technology for the degradation of pharmaceuticals in aqueous solutions.

Keywords Carbamazepine (CBZ) · Gas–liquid discharge · Plasma · Catalyst · Degradation mechanism

Introduction
Organic pollutants are among the most common sources of pollution and have attracted significant attention in recent years due to their wide range of potential influences (Li et al. 2020). Pharmaceuticals and personal care products (PPCPs) such as triclosan, carbamazepine, diclofenac (Leong et al. 2021; Yu et al. 2013) and emerging contaminants (ECs) such as X-ray contrast media and flame retardant (Koch et al. 2019; Wang et al. 2019b) are not easily detected in the environment, yet it can stay in the environmental media for a long time and has a potential impact on the ecological environment as well as human health (Amarasiri et al. 2019; Gonsioroski et al. 2020). With the increase of drug consumption, hazardous drug residues have been detected in water, soil, aquatic organisms, and other environmental...
media at different levels. What is more, PPCPs have been monitored in the inlet and outlet water of sewage plants, surface water, and groundwater in some countries and regions, and the concentration is up to ug/L (Watkinson et al. 2007). However, it has been proven that even low concentrations of hormone drugs have a significant impact on human health (Santos et al. 2010). Therefore, the potential hazards of PPCPs should not be ignored.

As a typical representative of PPCPs, carbamazepine (CBZ, Table 1) is consumed about 1014 tons per year worldwide due to its good therapeutic effects (Mohapatra et al. 2014). Edward Archer et al. (Archer et al. 2017) found that the removal rate of CBZ in traditional sewage treatment plants was less than 15%. Residual CBZ had been found in surface water, groundwater, and even drinking water, and its long-term accumulation may cause certain harm to aquatic systems, such as damaging the livers of aquatic organisms (Jarvis et al. 2014) and changing the physiological function of vertebrates (Suwalsky et al. 2006). There is evidence that the concentration of CBZ in the wastewater discharged from sewage treatment plants can cause harmful effects (Magurenau et al. 2015). Therefore, to ensure the safety of effluents discharged from sewage treatment plants, it is urgent to explore new technologies to deal with such pollutants.

The application of advanced oxidation processes (AOPs) to reduce harmful effects of emerging contaminants had been proved to be an effective way (Kim et al. 2020). 2021. The main characteristic of AOPs is that they are effective means to generate highly reactive species (RS) for chemical oxidation of macromolecular organic contaminants into harmless mineralized products. The most commonly used AOPs include photocatalysis (Bualoudj et al. 2021; Rabahi et al. 2019), ozonation (Ostman et al. 2019), fenton oxidation (Giri and Golder 2014), ultraviolet (UV) (Kamagate et al. 2018; Zeghioud et al. 2018), etc. However, oxidative process such as ozone is laborious to keep in reserve and UV treatment is powerless to achieve a high level of mineralization (Santos et al. 2015). Therefore, there is still room for the development of more reliable technologies for removing contaminants.

Recently, plasma processes for the treatment of pollutants such as volatile organic compounds (VOCs) (Dobslaw et al. 2018) and wastewater (Liu et al. 2021) have aroused extensive attention of scholars due to their efficient and clean technologies (Qu et al. 2021; Xu et al. 2022a, b). Plasma was generated by high-voltage discharge at the liquid or gas–liquid interface. High-energy electrons generated by high-voltage discharge collided with surrounding gas molecules and reactive species such as short-lived free radicals (•OH, •H, •O, etc.) and long-lived molecules (H2O2, O3, etc.) formed through direct and indirect electron collision process and chemical reaction (Malik et al. 2016). Xin et al. (Xin et al. 2020) applied gas–liquid plasma to remove bromoamine acid in dye wastewater and efficient removal was achieved by the system within 15-min treatment. Feng et al. (Feng et al. 2016) used a wire cylinder DBD reactor to remove atrazine in aqueous solution, and 93.7% of degradation rate and 12.7% of TOC removal rate were achieved after 18 min of treatment. Since the sole plasma exhibited restricted penetration depth into the liquid, short-lived reactive species generated by plasma, such as •OH (considered to be one of the most important reactive species to degrade liquid-phase harmful organic compounds), unable to diffuse to the deep parts of the solution, resulting in low mineralization level and limited efficiency to a certain extent. The H2O2 generated by the plasma has a long lifetime and can reach a relatively far position in solution by diffusion, the addition of Fe2+ can fully utilize H2O2 to trigger the catalytic degradation of fenton reaction to generate •OH, thus achieving improved organic pollutants degradation rates. Specifically, homogeneous catalysts possess remarkable properties as the lower investment cost, no phase-transfer problems, high activity, and selectivity. Sang et al. (Sang et al. 2019a) studied the degradation of aniline by dielectric barrier discharge (DBD) combined with Fe2+ and found that the removal efficiency increased obviously when Fe2+ was added. Fahmy et al. (Fahmy et al. 2018) employed Fe2+ as a catalyst in discharge plasma treatment and 95.05% of decolorization efficiency was obtained after 20 min time of treatment. Feng et al. (Feng et al. 2015) discovered that the removal rate of TOC and the degradation efficiency of 3,4-DCA increased dramatically with adding Fe2+. In previous study, we have explored the effect of H2O2 and Fe2+ on the degradation of antibiotics by DBD in an alternating current (AC) power supply condition. Different discharge forms will affect the composition and concentration of reactive species in the liquid induced by plasma, and these reactive species are an important factor in the degradation of pollutants in water. Compared with the dielectric barrier discharge excited

| Name       | MW  | pKa | CAS     | Structure         |
|------------|-----|-----|---------|------------------|
| Carbamazepine | 236.27 | 13.90 | 298-46-4 | ![Structure](image) |

Table 1 The molecular structure and information of CBZ.
by the AC high-voltage power supply, the structure of the DC high-voltage discharge plasma is simpler, and the price of power supply device is relatively low. However, compared with the dielectric barrier discharge plasma, there are fewer studies on DC high-voltage discharge plasma for the degradation of pollutants in water, especially the effect of the liquid phase reactive species and the addition of catalysts on the degradation of organics in the water caused by this plasma. Therefore, this research is a continuation of our previous research and hopes to provide an option for actual wastewater treatment in the future.

In this study, CBZ was selected as the target organic contaminant to examine the degradation effected by DC gas–liquid phase plasma with a catalyst (Fe²⁺ or H₂O₂) system. Both of these catalysts should promote the removal rate of organic substances. The hydroxyl radical yield (•OH) and three representative long-lived reactive species (H₂O₂, O₃, and NO₃⁻) that may promote the oxidization of CBZ have been quantified. Moreover, the influence of various parameters like initial solution concentration, initial solution pH value, and the catalyst concentration on the performance of the reactor was investigated to obtain the optimal condition on CBZ degradation for a higher degradation rate. Furthermore, the primary degradation intermediates of CBZ and potential degradation pathways were identified by analyzing UPLC-MS results. The possible toxicity of intermediate products was also evaluated through growth inhibition assays using the E. coli bacterium as the testing organism.

Materials and methods

Materials and reagents

Carbamazepine (CBZ), ferrous sulfate (FeSO₄·7H₂O), hydrogen peroxide (H₂O₂, ≥30%), sodium hydroxide solution (NaOH), and hydrochloric acid (HCl) were purchased from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). Terephthalic acid (TA) and 2-hydroxyterephthalic acid (HTA) were purchased from TCI (Shanghai) Development Co., Ltd. (Shanghai, China). Both acetonitrile and methanol were from Aladdin Industry Co., Ltd. (Shanghai, China). Acetonitrile and methanol used in the HPLC and UPLC-MS analyses were chromatographic grade, and the other chemicals applied to the experiments were all analytical grade. Ultra-pure water was employed in all experiments.

Experimental apparatus

The schematic diagram of our experimental device to generate the gas–liquid phase discharge is illustrated in Fig. 1. Briefly, the experimental setup primarily consists of a direct current (DC) high-voltage power supply, plasma device, flowmeter, and air pump. The plasma device consists of a hollow stainless steel needle surrounded by a quartz glass tube with an inner diameter of 2.6 mm placed inside a quartz container. The needle (8 cm length and 2 mm inner diameter) is the anode electrode which is connected to the gas inlet and driven by a positive high-voltage DC power supply. The ground electrode is the CBZ aqueous solution. Air was used as working gas in this experiment at a flow rate of 1.5 L/min. Discharge occurs in the gas channel of the quartz tube under the CBZ liquid interface, and 40 mL of CBZ solution (unless otherwise specified, 20 mg/L was used) was treated for each test.

The applied voltage and discharge current of the plasma were measured by a high-voltage probe (Tektronix P6015A) and a current probe (Tektronix P6021) via a digital oscilloscope (Tektronix MSO 5104). The average discharge power (P) in the system was calculated by the following Eq. (1) (Xiao et al. 2014):

\[
P(W) = \frac{1}{T} \int_{0}^{T} U(t)I(t)dt
\]

(1)

where P represents the average discharge power, U(t) and I(t) are the discharge voltage and current at time t, respectively.

![Fig. 1 Schematic diagram of experimental setup](image)
and T is the discharge period. The optical emission spectra from the gas–liquid plasma was recorded by a spectrometer (Maya2000 Pro, Ocean Optics, USA) with an fiber probe. The fiber probe was mounted on the exit of the glass tube nozzle and about 20 mm apart from the plasma source.

**Analysis methods**

A high-performance liquid chromatography (Agilent 1260 Infinity II, USA), consisted of a C18 column (250 × 4.6 mm i.d., 5 µm; Agilent, USA) maintained at 30.0 °C, was used to measure CBZ concentration at 286.0 nm by a UV detector. Mobile phase A was acetonitrile, while mobile phase B was Milli-Q water, and they were at the ratio of 60/40 (v/v) with a flow rate of 1.0 ml/min. The sample volume of the degradation solution was 20 µl. The data were analyzed by using the software Agilent ChemStation (Agilent, USA).

The degradation rate of CBZ for each sample was calculated according to Eq. (2) (Markovic et al. 2015):

\[
\eta(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \tag{2}
\]

where \(\eta(\%)\) indicates the degradation rate of CBZ, \(C_0\) (mg/L) is the initial concentration of CBZ, and \(C_t\) (mg/L) represents the residual concentration of CBZ after different plasma discharge treatment time (mg/L).

The energy efficiency \(Y(\text{mg} \cdot \text{kW}^{-1} \cdot \text{h}^{-1})\), defined by the amount of CBZ degraded per unit energy delivery in the reactor, is calculated by Eq. (3) (Wang et al. 2016):

\[
Y(\text{mg} \cdot \text{kW}^{-1} \cdot \text{h}^{-1}) = \frac{C_0 V \eta}{P t} \tag{3}
\]

where \(Y(\text{mg} \cdot \text{kW}^{-1} \cdot \text{h}^{-1})\) represents the energy efficiency, \(C_0\) (mg/L) refers to the initial concentration of CBZ, \(V\) (L) was the reactor volume, \(\eta(\%)\) indicates the degradation rate of CBZ, \(P\) (kW) is the average discharge power, and \(t\) (h) is the plasma discharge time.

To better understand the degradation mechanism of CBZ, the major degradation intermediates of CBZ were investigated. The analytical parameters of MS were as follows: fragmentation at 125.0 V, capillary
voltage of 4.0 kV, desolation gas (nitrogen, 99.99% purity) flow rate of 10.0 L/min, nebulizer pressure of 40.0 psi, temperature of 300°C, scan range of m/z = 100–1000, and argon (99.99% purity) as the collision gas.

Results and discussion

Electrical parameters of the gas–liquid phase plasma

The electrical properties of plasma were closely related to the degradation effect of pollutants; therefore, the variations of current and voltage during plasma discharge and average discharge power were detected and calculated, respectively. The typical voltage and current waveform of the gas–liquid air plasma are presented in Fig. 2. As shown, the peak value of discharge voltage and current were approximately 6.0 kV and 0.3A, respectively. In this work, the variation range of the discharge powers was from 20.9 to 56.4 W.

Optical emission spectroscopy (OES)

The types of reactive species formed in the gas-phase or at the gas–liquid interface can be identified according to their characteristic peaks on the optical emission spectroscopy (OES) of the discharge. The typical optical spectrum of the gas–liquid phase discharge with air over the range of 200 to 900 nm is presented in Fig. 3. The discharge generates a significant UV radiation which belongs to transitions of the OH band from 305.0 to 320.0 nm (Rashid et al. 2020). In particular, the distinct peaks in the range of 315.0–400.0 nm correspond to diverse nitrogen species (Aggelopoulos et al. 2020). In addition to those lines above, the transitions of Hα and Hβ are found at 656.3 nm and 486.1 nm, respectively. Furthermore, the distinct peaks were also detected at 777.3 and 844.6 nm could be attributed to the formation of excited atomic oxygen (Rezaei et al. 2014). Notably, the atomic oxygen come from oxygen molecules and water molecules excited by high energy particles, while the atomic hydrogen was generated by high energy particles exciting...
water molecules. Identifying excited particles formed in the air phase can explain the source of liquid products more clearly since the liquid phase product will be triggered by the gas phase product. In the air gas–liquid discharge, the reaction between charged particles and water molecules is to generate more reactive species (H$_2$O$_2$, NO$_3^-$, O$_3$ and •OH).

**Measurement of RS in deionized water induced by plasma and plasma/catalyst**

The plasma-induced aqueous RS has attracted much attention due to its significant role in transforming and degrading organic compounds. As a significant indicator of the performance of gas–liquid plasma, the generation of RS in aqueous solution is frequently monitored (Vanraes et al. 2015). The plasma discharge could produce various ions and free radicals and further lead to the generation of RS in liquid phase by physical and chemical reactions, which would interact with the organic pollutants synergistically (Ognier et al. 2015; Rozas et al. 2017). The aqueous RS could be divided into long-lived (H$_2$O$_2$, NO$_3^-$, O$_3$, etc.) and short-lived (•OH, O$_2^-$, HO$_2^-$, etc.) ones. The simplified formation mechanisms of these species during the discharge are as follows (6)–(20) (Dojcinovic et al. 2011; Reddy and Subrahmanyam 2012):

\[ O_2 + e^- \rightarrow 2O + e^- \] (6)

\[ O_2 + e^- \rightarrow O_2^- \] (7)

\[ O_2 + O^* \rightarrow O_3 \] (8)

\[ H_2O + e^- \rightarrow \bullet H + \bullet OH + e^- \] (9)

\[ \bullet OH + \bullet OH \rightarrow H_2O_2 \] (10)

\[ O^* + H_2O \rightarrow H_2O_2 \] (11)

\[ \bullet OH + H_2O_2 \rightarrow H_2O + HO_2^* \] (12)

\[ 3O_3 + H_2O \rightarrow 2\bullet OH + 4O_2 \] (13)

\[ O_3 + H_2O_2 \rightarrow \bullet OH + O_2 + HO_2^* \] (14)

\[ O_3 + HO_2^* \rightarrow \bullet OH + O_2 + O_2^- \] (15)

\[ O_3 + \bullet OH \rightarrow HO_2^* + O_2 \] (16)

\[ H_2O_2 + O_2^- \rightarrow \bullet OH + OH^- + O_2 \] (17)

\[ H_2O_2 + hv \rightarrow 2\bullet OH \] (18)

\[ 4NO + 3O_2 + 2H_2O \rightarrow 4HNO_3 \] (19)

\[ 2NO_2 + H_2O \rightarrow HNO_3 + HNO_2 \] (20)

\[ 2H_2O_2 \rightarrow H_2O + O_2 \] (21)

\[ H_2O_2 \rightarrow H_2O + O^* \] (22)

\[ Fe^{2+} + O_3 \rightarrow Fe^{3+} + \bullet O_3^- \] (23)

\[ 3H_2O_2 + NO \rightarrow 3H_2O + NO_3^- + H^+ \] (24)

\[ H_2O_2 + NO_2 \rightarrow 2NO_3^- + 2H^+ \] (25)

\[ N_2 + e^- \rightarrow 2N^* + e^- \] (26)

\[ N^* + O^* \rightarrow NO^* \] (27)

\[ NO^* + O^* \rightarrow NO_2^* + e^- \] (28)

\[ NO_2^* + e^- + OH^- \rightarrow HNO_3 \] (29)

The •OH yield and the aqueous concentrations of H$_2$O$_2$, O$_3$, and NO$_3^-$ generated by plasma treatment and catalyst at discharge power of 35.7 W are presented in Fig. 4, respectively. As shown in Fig. 4a, the concentrations of the •OH radicals reached 4.40 mM, 5.69 mM and 0.66 mM under the condition of sole discharge, H$_2$O$_2$ (0.1 mM), Fe$^{2+}$ (100 mg/L) after 4 min of treatment, respectively. •OH was formed in the discharge process mainly due to high-energy electrons’ bombardment on H$_2$O (Eq. (9)) and the conversion from H$_2$O$_2$ and O$_3$ (Eq. (13) and Eq. (17)), thus leading to a gradually enhancing •OH concentration for the sole plasma and plasma/H$_2$O$_2$ (0.1 mM) system from 0 to 4 min. There were no accumulation effects of •OH radicals in the liquid due to its short lifetime (about 10$^{-9}$ s); therefore, the •OH production rate was calculated indirectly by using the amounts of HTA formation per unit time. Consequently, the production rates of •OH in the liquid were estimated to be of the order of 1.83×10$^{-8}$ M s$^{-1}$ and 2.37×10$^{-8}$ M s$^{-1}$ for the sole plasma and plasma/H$_2$O$_2$ (0.1 mM) system under the present experimental condition. The values were higher than the production rates of the order of 10$^{-9}$ M s$^{-1}$ under the condition of pulsed discharges on the surface of liquid (Kanazawa et al. 2011) and 1.67×10$^{-8}$ M s$^{-1}$ for the direct discharge in water at an applied voltage of 45 kV and input power.
Shen et al. (Shen et al. 2019) have estimated •OH production which were on the order of $1.2 \times 10^{-8}$ M s$^{-1}$ and $2.2 \times 10^{-8}$ M s$^{-1}$ for the air and oxygen gas–liquid plasma treatment, respectively. As a matter of fact, power supply, applied voltage, plasma device, liquid conductivity, and plasma instability would have a significant impact on the •OH generation (Yue et al. 2022). After comprehensive comparison, the production rate of •OH in this work was similar to that in these researches. The measured •OH concentrations decreased slightly after 4 min of plasma discharge treatment. When the discharge time reaches 4 min, there may not be sufficient TA to react with the •OH radical to transform into HTA at a TA initial concentration of 0.2 mM. In addition, the decomposition of HTA due to the reaction with • OH radicals and other species must be considered, thereby leading to a decreasing •OH yield after 4 min (data not shown). It is noteworthy that the measured •OH production rate in the plasma/Fe$^{2+}$ (100 mg/L) system was always kept in a low level of the order of $2.75 \times 10^{-9}$ M s$^{-1}$, and the reason may be that the reaction probability between Fe$^{2+}$ and •OH was higher than that of TA and •OH due to the significant difference in concentration between Fe$^{2+}$ and TA. Due to the reaction between •OH and Fe$^{2+}$, •OH might be scavenged by Fe$^{2+}$ (Eq. (31)) (Abou Dalle et al. 2017; Lodha and Chaudhari 2007), thus leading to a low •OH measured value in plasma/Fe$^{2+}$ (100 mg/L) system.

Figure 4b depicts the variations of H$_2$O$_2$ under different treatment conditions. The aqueous H$_2$O$_2$ concentration increased markedly from 0 to 2.37 mM, 0.1 to 2.85 mM, 0 to 1.45 mM for the sole plasma, plasma/H$_2$O$_2$ (0.1 mM), plasma/Fe$^{2+}$ (100 mg/L)-treated dH$_2$O.
of treatment. The H$_2$O$_2$ concentration measured in the sole plasma system was higher than that reported in these researches, nearly 60 ppm (1.76 mM) at 18 kV after 25 min of plasma treatment (Manoj Kumar Reddy et al. 2013), and 15 mg/L (0.44 mM) in underwater parallel-multi-tube air discharge plasma jet system (Rashid et al. 2020). The H$_2$O$_2$ concentration more than 120 mg/L (3.52 mM) reported in Sang et al. (Sang et al. 2019b) was higher than that achieved in the present paper. However, the value was obtained using a relatively small aqueous solution (10 mL), while it is 40 mL in this work. In fact, due to the differences in experimental conditions and environments, plasma devices, and power supplies, the concentration of reactive species would have been quite different. The H$_2$O$_2$ concentration was produced by plasma mainly due to the high-energy electrons impact O$_2$ to produce oxygen atoms and later react with water to form H$_2$O$_2$ (Eq. (6) and Eq. (11)) (Hayashi et al. 2016). In addition, the combination of •OH was also an aspect of enhancement of H$_2$O$_2$ concentration (Eq. (10)). As shown in Fig. 4b, when the treatment time exceeded 12 min, the H$_2$O$_2$ concentration remains substantially unchanged in the sole plasma system. Significantly, the H$_2$O$_2$ concentration of the plasma/H$_2$O$_2$ (0.1 mM) system was much higher than that in the other two systems during the whole discharge period. This phenomenon is probably due to the additional H$_2$O$_2$ that may accelerate and enhance the formation of various reactive species, which was mentioned by Liu et al. (Liu et al. 2016). The production of these reactive species may promote the increase of H$_2$O$_2$ to a certain extent. However, the specific reasons still require further study. Furthermore, for the plasma/Fe$^{2+}$ (100 mg/L) system, as H$_2$O$_2$ had been continuously generated by plasma and the relatively low reaction efficiency for the Fenton reaction (Eq. (30)) due to the nearly neutral solution pH in the early term (Feng et al. 2006), hence the aqueous H$_2$O$_2$ concentration increased steadily. It is worth mentioning that as with declining solution pH, the H$_2$O$_2$ generated by plasma may not be adequate to meet the demand of the rapidly enhancing reaction efficiency of the Fenton reaction (Xu et al. 2020), thus resulted in a higher consumption of the accumulated H$_2$O$_2$. Consequently, the H$_2$O$_2$ concentration declined from 1.91 mM (24 min) to 1.58 mM (48 min).

Figure 4c exhibits the change of aqueous O$_3$ concentration under different treatment conditions. The O$_3$ concentration, respectively, increased from 0 to 0.59 mg/L, 0.052 to 1.30 mg/L, 0 to 0.21 mg/L after 48 min of treatment for the sole plasma, plasma/H$_2$O$_2$ (0.1 mM), plasma/Fe$^{2+}$ (100 mg/L) system. The concentration of O$_3$ by plasma/ H$_2$O$_2$ (0.1 mM) treatment in water was the highest compared with the other two groups. The probable cause was the dissolved O$_3$ reacted with O$^-$ generated from the additional H$_2$O$_2$ decomposition to form more O$_3$ (Eq. (8) and Eq. (22)) (Reddy and Subrahmanyam 2012). For the plasma/Fe$^{2+}$ (100 mg/L) system, although O$_3$ could be continuously generated by plasma, it is worthy to mention that Fe$^{2+}$ would consume a portion of plasma-generated O$_3$ to produce Fe$^{3+}$ (Eq. (23)) (Huang et al. 2019; Malik et al. 2019). The consumption could mainly account for the lower aqueous concentration of O$_3$ compared with that from the sole plasma system.

As illustrated in Fig. 4d, the aqueous NO$_3^-$ concentration increased steadily from 0 to 105 mg/L, 0 to 151.3 mg/L, 0 to 135.6 mg/L for the sole plasma, plasma/H$_2$O$_2$ (0.1 mM), plasma/Fe$^{2+}$ (100 mg/L) system after 48 min of discharge treatment. The aqueous NO$_3^-$ was mainly generated by plasma discharge, and it kept increasing during the whole treatment period for all systems. Specifically, in the plasma/ H$_2$O$_2$ (0.1 mM) system, the added H$_2$O$_2$ would react with NO and NO$_2$ generated by plasma to promote the formation of NO$_3^-$ (Eqs. (24) and (25)) thus leading to the highest aqueous NO$_3^-$ concentration in the late period. Notably, in the plasma/Fe$^{2+}$ (100 mg/L) system, the aqueous NO$_3^-$ concentration was higher compared with the sole plasma system. When air was bubbled, nitrogen molecules around the discharge electrode would be excited and decomposed into active nitrogen species. Due to the Fenton reaction (Eq. (30)) produced more •OH, active nitrogen species could react with •OH to generate NO$_3^-$ according to Eqs.(26–29) (Bian et al. 2009), thus promoted the measured NO$_3^-$ concentration. In present work, the measured NO$_3^-$ concentrations were lower than the detected NH$^+_4$ and NO$_3^-$ of 316.53 mg/L in the residual atrazine solution (Zhu et al. 2014) and higher than that of 1.96 mM (66.6 mg/L) with bubbling air and 2.34 mM (79.5 mg/L) with bubbling pure nitrogen under the condition of pulsed high-voltage discharge for 30 min (Bian et al. 2009). It must be emphasized that relatively high concentration of nitrate was formed during plasma treatment in air atmosphere, thus leading to a relatively low pH value, even though a certain contribution to the pH variation during the plasma treatment may come from the N-containing heterocyclic structure of CBZ. However, the degraded solution with low pH cannot be directly discharged into the environment without secondary treatment. How to reduce the secondary problems produced in the process of CBZ degradation still requires further studies, using oxygen enriched air (Bian et al. 2009), adjusting energy density (Dojcinovic et al. 2011), shortening the processing time, and adopting a lower gas flow may play a role.

**Effect of discharge power on CBZ degradation**

The discharge power is considered a significant parameter because it is directly related to the production, transmission, and diffusion of reactive species, which plays a vital role in pollutant degradation. Figure 5a presents the degradation of CBZ under various discharge power intensities. With regard to a discharge time of 48 min, the maximum degradation
efficiencies were 90.1% and 62.5% in 35.7 W and 20.9 W, respectively, while the CBZ in aqueous solution was almost completely degraded under the condition of 56.4 W. The main reason was that more reactive species was generated with the increase of discharge power, which could lead to the complete degradation of CBZ in liquid phase.

Figure 5b displays the energy efficiency under various discharge power intensities during the degradation process. It can be seen that the energy yield declined over time at different discharge power. As shown in Fig. 5b, the degradation of CBZ decreased from 29.9 mg•kW−1 h−1 (20.9 W) to 17.7 mg•kW−1 h−1 (56.4 W) after 48 min. A possible reason for this phenomenon is that an excessive input power would make part of the energy converted into heat in the system, resulting in a waste of energy (Zhang et al. 2017). Although the energy efficiency at 20.9 W was higher than the other two discharge powers, the degradation rate of CBZ was still at a relatively low level. Furthermore, the energy efficiency at discharge power of 35.7 W is higher than that at 56.4 W during the whole discharge period. In order to achieve a relatively optimized balance of degradation efficiency and energy efficiency in the CBZ degradation process, 35.7 W was selected as the discharge power in subsequent experiments to pursue a higher CBZ removal rate and economic benefits.

**Effect of initial concentration on CBZ degradation**

The variations of the plasma-treated CBZ solution during the discharge period with different initial concentrations from 10.0 to 40.0 mg/L are displayed in Fig. 6. The volume of the plasma-treated solution was 40.0 ml without pH adjustment (Initial pH = 6.40). In this test, the discharge power was set at 35.7 W. It can be seen from the figure that with the increase of the initial concentration of CBZ solution, the removal efficiency of CBZ decreased at the same discharge time, and the result was similar to that of Zhu et al. (Zhu et al. 2014). A possible cause of this phenomenon is that the RS produced by discharge is at a particular level under the condition of stable discharge. At a high concentration of CBZ, CBZ molecules had lower chances to be attacked by RS (Batista et al. 2014). Meanwhile, the intermediates also consumed a part of RS and increased competition of CBZ for RS, thus leading to a drop in the efficiency of CBZ degradation under the high concentration condition (Guo et al. 2015). Significantly, the middle initial concentration of 20.0 mg/L was selected in later experiments.
Effect of initial pH value on the removal rate of CBZ

The initial pH value is a crucial factor for the removal of contaminants. Thus, different initial pH conditions (pH = 3.85, 9.05 adjusted by HCl or NaOH) and original pH (pH = 6.40, no pH adjustment) were selected to estimate the CBZ degradation. The pH variations of the plasma-treated CBZ solution during the discharge period with different initial solution pH was also investigated. Figure 7a shows the pH variations of CBZ solutions with different pH at an initial concentration of 20.0 mg/L when the volume of the plasma-treated solution and discharge power was set at 40.0 ml and 35.7 W, respectively. The solution pH declined rapidly in the first 18 min of treatment and then decreased by degrees, finally stabilizing at about pH = 2.0 for each initial pH value. Consequently, the solution pH presented a continuous downward trend for each initial pH value, this might be due to the effect of inorganic acids such as HNO₃ and HNO₂ produced during the discharge process (Dojcinovic et al. 2011).

The removal rates of CBZ at various initial pH values are shown in Fig. 7b. It can be seen that the removal efficiency of CBZ increased when the initial conditions were acidic (pH = 3.85) and alkaline (pH = 9.05), and both reached up to 98% after discharge for 48 min. The initial pH of the solution will affect the generation of RS in the discharge process (Joshi and Thagard 2013). There is a higher degradation efficiency in alkaline conditions because O₃ and H₂O₂ were unstable in alkaline environments (Feng et al. 2006), hence they could be rapidly decomposed into •OH in aqueous solution (Feng et al. 2016), more •OH was generated. As one of the reactive species, •OH increased the degradation rate of CBZ. In the acidic solution, the concentration of dissolved ozone increased with the decrease of pH value (Sotelo et al. 1989), which played a certain role in its direct reaction with CBZ. Nevertheless, the oxidation ability of O₃ is weaker than •OH (Zhang et al. 2012), which resulted in a lower degradation of CBZ compared with an alkaline condition. By the way, an original pH without adjustment (pH = 6.40) was chosen in subsequent experiments due to the not particularly significant impact of pH.

Effect of H₂O₂ on CBZ degradation

In order to investigate the effect of H₂O₂ on CBZ degradation by plasma, H₂O₂ was added as the additive at variant concentrations of 0.05, 0.1, 2.0, and 5.0 mM in the aqueous solution, and the results are shown in Fig. 8. Obviously, the degradation rate of CBZ could be accelerated or inhibited in the presence of H₂O₂ depending on the applied dosage. The results indicated that the degradation value of CBZ increased with the addition of low concentrations of H₂O₂ (0.05–0.1 mM). However, it hindered the degradation with the higher aqueous H₂O₂ concentration (2.0–5.0 mM). Specifically, the CBZ degradation rate in the sole plasma system was 53.3% and increased to 65.4% in the plasma/H₂O₂ (0.1 mM) system at the discharge period of 18 min. On the contrary, when the added H₂O₂ concentration was enhanced to 5.0 mM, the degradation rate declined from 53.3% to 37.5%. The reason why CBZ degradation could be improved when H₂O₂ was added at the appropriate concentration might be explained by Eqs. (17) and (18) (Dojcinovic et al. 2011), •OH was formed by the decomposition of H₂O₂ in the liquid phase, and then •OH promoted CBZ degradation. However, when H₂O₂ was added at 5.0 mM, the presence of an excess amount of H₂O₂ lead to the massive consumption of •OH in the aqueous solution (Coulibaly...
et al. 2019) as shown in Eq. (12), which is similar to the results of Aggelopoulos et al. (Aggelopoulos et al. 2020).

**Effect of Fe$^{2+}$ on CBZ degradation**

Plasma could trigger the generation of H$_2$O$_2$ in the liquid, so Fe$^{2+}$ was added to the treated solution to study its effect on degradation of CBZ, which involved the following reactions (Domínguez et al. 2012; Xu et al. 2022a, b):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^{-} \quad (30)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + O_2 \quad (31)$$

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^{-} \quad (32)$$

Figure 9 displays the effect of adding different concentrations of Fe$^{2+}$ in the aqueous solution combined with plasma treatment on the degradation efficiency of CBZ. It was indicated that Fe$^{2+}$ benefited the degradation at the concentration of 10–100 mg/L. However, the enhancement effect was reduced at a higher concentration from 100 to 200 mg/L. Specifically, the CBZ degradation rates in the sole plasma system 18 and 48 min were 53.2% and 90.1%, respectively, it sharply increased, respectively, to 73.3% and 99.1% with the addition of Fe$^{2+}$ in a concentration of 100 mg/L. Although the plasma process can generate •OH, it still exhibited restricted penetration depth into the liquid thus limited its performance (due to the short lifetime of •OH radical). The H$_2$O$_2$ generated by the plasma has a long lifetime and can reach a relatively far position in solution by diffusion, the addition of Fe$^{2+}$ can trigger the catalytic degradation of heterogeneous Fenton reaction (Eq. (30)) with plasma-induced H$_2$O$_2$ to generate •OH (Abou Dalle et al. 2017) at the position further away from the plasma discharge reaction area, which can quickly and non-selectively degrade organic pollutants, thus leading to an improved CBZ degradation rate. Furthermore, the produced Fe$^{3+}$ could be reduced to Fe$^{2+}$ by reacting with the aqueous H$_2$O$_2$ provided by plasma discharge exposure (Eq. (31)), thereby maintaining the Fenton reaction and constantly degrading CBZ. However, the degradation efficiency declined after adding Fe$^{2+}$ into the solution to 200 mg/L compared with 100 mg/L. The lower enhancement of degradation rate at higher Fe$^{2+}$ concentration can be explained by the scavenging effect of oxidation reaction of Fe$^{2+}$, which would result from the competition between excessive Fe$^{2+}$ and the organic substance for •OH (Eq. (32)). The •OH consumption increased, hence the enhancement effect of CBZ degradation was accordingly weakened. Through comparing the degradation rate of CBZ for plasma/Fe$^{2+}$ (100 mg/L) and plasma/H$_2$O$_2$ (0.1 mM) system, plasma/Fe$^{2+}$ (100 mg/L) system could achieve a higher degradation rate on CBZ, thus the plasma/Fe$^{2+}$ (100 mg/L) system was utilized in following UPLC-MS analysis.

**Effect of plasma/catalyst system on TOC removal**

In addition to the degradation rate, the total concentration of organic pollutants in aqueous solution can be exhibited through the removal of the TOC value, which could also reflect the mineralization efficiency of the contaminants in the solution. The mineralization rate of CBZ solution was
estimated by detecting the TOC concentrations after 48 min of sole plasma, plasma/H2O2 (0.1 mM), and plasma/Fe2+ (100 mg/L) systems treatment, respectively. As shown in Fig. 10, the TOC removal efficiency of the treated solution increased continuously with treatment time for all systems. Notably, the solution TOC was reduced by 48.0% after 48 min of the sole plasma discharge treatment, meanwhile, plasma/H2O2 (0.1 mM) and plasma/Fe2+ (100 mg/L) system resulted in a 58.7% and 64.1% TOC diminution, respectively. The mineralization rate in the plasma/Fe2+ (100 mg/L) system was obviously higher than that in the plasma/H2O2 (0.1 mM) system, which were in accordance with the tendency on the CBZ degradation rate. These results indicated that plasma/catalyst treatments could directly carbonize a portion of contaminants in the liquid phase and high mineralization rates on CBZ could be achieved. Nevertheless, certain intermediates in the processing of CBZ degradation still could not be further mineralized due to the stable amount of yielded reactive species under the constant experimental condition.

**Proposed degradation pathways of CBZ**

The primary degradation intermediates of CBZ were detected by UPLC-MS to better understand the degradation mechanism. Based on the mass spectra, ten main degradation intermediates of CBZ by gas–liquid plasma are identified and shown in Table 2. The possible degradation pathways were proposed, as shown in Fig. 11. The olefinic double bond with high frontier electron density on the central heterocyclic ring of CBZ molecule was susceptible to the attack of reactive species, leading to the formation of epoxidized product M1 (m/z 253), which was one of the most frequently detected intermediates in related researches (Li et al. 2013; Miao et al. 2005). M1 (m/z 253) could be further confirmed to be 10, 11-epoxy carbamazepine according to the further hydrolysis product of M2 (m/z 271) (De Laurentiis et al. 2012; Yang et al. 2017), whose further transformation product was M4 (m/z 226). Meanwhile, a direct dehydrogenation reaction occurred at the sites of •OH groups in M2, thus leading to the formation of compound M5 (m/z 267), which could further transform to compound M8 (m/z 224) and M7 (m/z 196) due to the cleavage of aldehyde group and amide group in a certain order (Wang et al. 2019a). In addition, a facile ring contraction and amide group loss process of M1 (m/z 253) led to the formation of M3 (m/z 208). The same compound was identified and reported earlier in chlorine dioxide(ClO2) oxidation of the CBZ molecule (Kosjek et al. 2009). After that, M3 (m/z 208) converted to M6 (m/z 180) by loss of the aldehyde group. Apart from the pathways described above, the attacking of hydroxyl radicals resulting in the carbonylation of the aromatic rings of CBZ, thus yielding the intermediate M9 (m/z = 194). Due to the continuous attack by •OH radicals, the ring of M9 opened, leading to the formation of M10 (m/z = 258), which was also found by other studies (Singh et al. 2017). Previous researches reported that part of these intermediates (M1–M10) would finally be transformed into small inorganic molecules (CO2, H2O, NO3−, NO2−, NH4+, etc.) (Wu et al. 2020; Zheng et al. 2014).

Although organic substance TOC removal rate exceeded 67% in present system, complete mineralization of pollutants cannot be achieved. Recently, Leong et al. (Leong et al. 2021) found that adapted mixed cultures in batch and continuous operating systems had pretty well performance in triclosan biodegradation and mineralization aspect at a large range of initial concentrations. Moreover, a combined process of non-thermal plasma and mineral adsorber showed good performance levels for VOC removal and odor abatement (Dobslaw et al. 2018). Those studies indicated that the combination of various technologies may work better to realize the complete mineralization of refractory organics in future research.

**Biological toxicity evolution during CBZ degradation**

The inhibition index (Iind) of E. coli could reflect the microbial viability thus signifying the variations in biological toxicity during the treatment of plasma/Fe2+(100 mg/L) for different periods. Figure 12 demonstrates the Iind of CBZ solutions degraded for different times for E. coli. In the inhibition test, the blank tests of pH = 2 and 135 mg/L NO3− showed very low inhibition for the growth of E. coli, and 100 mg/L Fe2+ had almost no inhibitory effect. It needs to be emphasized that the blank test samples were only 0.5 mL in the test procedure, 0.5 mL blank test sample, and
50 µL E. coli would mix with 3 mL of sterilized LB medium, which diluted the concentration/acidity of test sample in the system and reduced the effect of 100 mg/L Fe²⁺, pH = 2 and 135 mg/L NO₃⁻ to E. coli to a certain extent. As shown in Fig. 12, the inhibition index (I_{ind}) in a short period of time gradually decreased from 21.1% (0 min) to 5.8% (12 min), and then increase to 11.1% (18 min). This slight increase might have been due to the production of some small molecular-weight intermediates but with higher toxicity on E. coli at the early stages of CBZ degradation. Specifically,

| Number | m/z | Proposed formula | Proposed structure |
|--------|-----|-------------------|--------------------|
| CBZ    | 237 | C₁₃H₁₂N₂O       | ![CBZ](image)       |
| M1     | 253 | C₁₃H₁₂N₂O₂      | ![M1](image)       |
| M2     | 271 | C₁₃H₁₄N₂O₃      | ![M2](image)       |
| M3     | 208 | C₃₄H₈NO         | ![M3](image)       |
| M4     | 226 | C₁₄H₁₁NO₂       | ![M4](image)       |
| M5     | 267 | C₁₃H₁₀N₂O₃      | ![M5](image)       |
| M6     | 180 | C₁₃H₆N          | ![M6](image)       |
| M7     | 196 | C₃₃H₈NO         | ![M7](image)       |
| M8     | 224 | C₁₃H₆NO₂        | ![M8](image)       |
| M9     | 194 | C₁₄H₁₁N         | ![M9](image)       |
| M10    | 258 | C₁₄H₁₁NO₄       | ![M10](image)      |

Table 2 Information and proposed structure of the degradation intermediates from CBZ.
the intermediates Acridine (M6) and Acridone (M7), which were the transformation and oxidation products of CBZ, may be more toxic than the parent compound thus strongly promoting the inhibitory effects (Donner et al. 2013). Notably, when the treatment time exceeded 24 min, the inhibition index (I\text{ind}) declined and then stabilized at around 6.5%. According to the previous TOC removal results, more than half of the organic substances had been mineralized and those degradation intermediates with high toxicity had also been further destructed, thus leading to the reduction on the inhibition rate. Although the biological toxicity of the plasma/Fe\textsuperscript{2+} (100 mg/L)-treated CBZ solution fluctuated in the whole treatment process, it exhibited an overall downward trend and a relatively low solution toxicity could be achieved. Therefore, it may be confirmed that plasma provides an important pathway for CBZ toxicity reduction despite some non-negligible intermediates. Nonetheless, the secondary effects such as high levels of NO\textsubscript{3}\textsuperscript{-} and low pH caused by plasma process and residual Fe\textsuperscript{2+} are still worthy of further study and explore.

**Conclusion**

In summary, the degradation effects and related mechanisms on CBZ in aqueous solution by a gas–liquid plasma combined with different catalysts (H\textsubscript{2}O\textsubscript{2} and Fe\textsuperscript{2+}) were investigated. It is proved by experimental results that CBZ in aqueous solution can be effectively degraded by the plasma/catalyst treatment. During the discharge, RS (●OH, H\textsubscript{2}O\textsubscript{2}, O\textsubscript{3}, etc.) were produced to degrade aqueous organic pollutants. The parameters that affect the degradation of CBZ, such as discharge powers, initial concentrations, pH values, and addition of catalysts were all affected the CBZ degradation efficiency. Specifically, plasma combined with suitable aqueous concentrations of H\textsubscript{2}O\textsubscript{2} (0.1 mM) and Fe\textsuperscript{2+} (100 mg/L) could lead to
high removal rates for more than 97.9% and 99.1%, respectively, at 48 min with the highest energy efficiency at discharge power of 35.7 W. The TOC removal efficiency of CBZ was up to 67.1% in the plasma/Fe\(^{2+}\) (100 mg/L) system at 48 min, which suggested a high mineralization efficiency. Moreover, based on various degradation intermediates identified by UPLC–MS, the proposed degradation mechanism on CBZ by plasma/Fe\(^{2+}\) treatment was investigated. Cleavage of azepine ring, hydroxylation, and deamidation were considered the primary degradation pathways. The biological toxicity of the plasma/Fe\(^{2+}\) (100 mg/L)-treated CBZ solution fluctuated and finally declined, and a relatively low solution toxicity could be achieved. Therefore, this work illustrated the promising potential of using plasma/catalyst systems as a highly effective method in removing pharmaceuticals in aqueous solutions.

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Authors contributions Jinming Yu performed research and was a major contributor in writing. Weiwen Yan analyzed data. Bin Zhu and Wen-hao Xi worked on the diagrams and searched part of the researches. Shuheng Hu and Yan Lan drafted the work and worked on the proof reading of the manuscript. Wei Han revised part of the work. Zimu Xu and Cheng Cheng designed research and revised the work. All authors read and approved the final manuscript.

Data availability Not applicable.

Declarations

Ethical approval Not applicable.

Consent to participate All participants voluntarily agreed to participate in this research study.

Consent to publish All participants consent for Publication.

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References

Abou Dalle A, Domergue L, Fourcade F, Assadi AA, Djelal H, Lendorrim T, Souret I, Taha S, Amran A (2017) Efficiency of DMSO as hydroxyl radical probe in an Electrochemical Advanced Oxidation Process – Reactive oxygen species monitoring and impact of the current density. Electrochim Acta 246:1–8

Aggelopoulos CA, Meropoulis S, Hatzisymeon M, Lada ZG, Rassias G (2020) Degradation of antibiotic enrofloxacin in water by gas-liquid nsp-DBD plasma: Parametric analysis, effect of H\(_2\)O\(_2\) and CaO\(_2\) additives and exploration of degradation mechanisms. Chem Eng J 398:125622

Amarasiri M, Sano D, Suzuki S (2019) Understanding human health risks caused by antibiotic resistant bacteria (ARB) and antibiotic resistance genes (ARG) in water environments: Current knowledge and questions to be answered. Crit Rev Environ Sci Technol 50:2016–2059

Archer E, Petrie B, Kasprzyk-Hordern B, Wolfardt GM (2017) The fate of pharmaceuticals and personal care products (PPCPs), endocrine disrupting contaminants (EDCs), metabolites and illicit drugs in a WWTW and environmental waters. Chemosphere 174:437–446

Baaloudj O, Assadi I, Nasrallah N, El Jery A, Khezami L, Assadi AA (2021) Simultaneous removal of antibiotics and inactivation of antibiotic-resistant bacteria by photocatalysis: A review. J Water Process Eng 42:102089

Batista APS, Pires FCC, Teixeira ACSC (2014) Photochemical degradation of sulfadiazine, sulfamethazine and sulfamethoxazole: Relevance of concentration and heterocyclic aromatic groups to degradation kinetics. J Photochem Photobiol A-Chem 286:40–46

Bian W, Shi J, Yin X (2009) Nitrogen Fixation Into Water by Pulsed High-Voltage Discharge. IEEE Trans Plasma Sci 37:211–218

Coulibaly GN, Bae S, Kim J, Assadi AA, Hanna K (2019) Enhanced removal of antibiotics in hospital wastewater by Fe–ZnO activated persulfate oxidation. Environ Sci: Water Res Technol 5:2193–2201

De Laurentis E, Chiron S, Kouras-Hadef S, Richard C, Minella M, Maurino V, Minero C, Vione D (2012) Photochemical fate of carbamazepine in surface freshwaters: laboratory measures and modeling. Environ Sci Technol 46:8164–8173

Dobslaw D, Ortlingshaus O, Dobslaw C (2018) A combined process of non-thermal plasma and a low-cost mineral adsorber for VOC removal and odor abatement in emissions of organic waste treatment plants. J Environ Chem Eng 6:2281–2289

Dojinovic BP, Roglic GM, Obradovic BM, Kuraica MM, Kostic MM, Nesic J, Manojlovic DD (2011) Decolorization of reactive textile dyes using water falling film dielectric barrier discharge. J Hazard Mater 192:763–771

Dominguez JR, Gonzalez T, Palo P, Cuerda-Correa EM (2012) Fenton + Fenton-like Integrated Process for Carbamazepine Degradation: Optimizing the System. Ind Eng Chem Res 51:2531–2538

Donner E, Kosjek T, Qualmann S, Kusk KO, Heath E, Revitt DM, Ledin A, Andersen HR (2013) Ecotoxicity of carbamazepine and its UV photolysis transformation products. Sci Total Environ 443:870–876

Fahmy A, El-Zomrawy A, Saeed AM, Sayed AZ, Ezz El-Alarab MA, Shehata HA (2018) Modeling and optimizing Acid Orange 142 degradation in aqueous solution by non-thermal plasma. Chemosphere 210:102–109

Feng J, Hu X, Yue PL (2006) Effect of initial solution pH on the degradation of Orange II using clay-based Fe nanocomposites as heterogeneous photo-Fenton catalyst. Water Res 40:641–646

Feng J, Liu R, Chen P, Yuan S, Zhao D, Zhang J, Zheng Z (2015) Degradation of aqueous 3,4-dichloroaniline by a novel dielectric barrier discharge plasma reactor. Environ Sci Pollut Res Int 22:4447–4459

Feng J, Jiang L, Zhu D, Su K, Zhao D, Zhang J, Zheng Z (2016) Dielectric barrier discharge plasma induced degradation of aqueous atrazine. Environ Sci Pollut R 23:9204–9214

Giri AS, Golder AK (2014) Chloramphenicol degradation in fenton and photo-fenton: formation of Fe\(^{3+}\)-chloramphenicol chelate and reaction pathways. Ind Eng Chem Res 53:16196–16203

Gonsioroski A, Mourikis VE, Flaws JA (2020) Endocrine Disruptors in Water and Their Effects on the Reproductive System. Int J Mol Sci 21:1929

Guo ZB, Zhu SN, Zhao YF, Cao H, Liu FL (2015) Radiolytic decomposition of ciprofloxacin using gamma irradiation in aqueous solution. Environ Sci Pollut R 22:15772–15780
Hayashi Y, Takada N, Wahyudiono KH, Goto M (2016) Hydrogen Peroxide Formation by Electric Discharge with Fine Bubbles. Plasma Chem Plasma Process 37:125–135

Huang Z, Gu Z, Wang Y, Zhang A (2019) Improved oxidation of refractory organics in concentrated leachate by a Fe3+-enhanced O2/H2O2 process. Environ Sci Pollut Res Int 26:35797–35806

Jarvis AL, Bernot MJ, Bernot RJ (2014) Relationships between the psychiatric drug carbamazepine and freshwater macroinvertebrate community structure. Sci Total Environ 496:499–509

Joshi RP, Thagard SM (2013) Streamer-like electrical discharges in water: Part II. environmental applications. Plasma Chem Plasma Process 33:17–49

Kamagate M, Assadi AA, Kone T, Giraudet S, Coulibaly L, Hanna K (2018) Use of laterite as a sustainable catalyst for removal of fluoroquinolone antibiotics from contaminated water. Chemosphere 195:847–853

Kanazawa S, Kawano H, Watanabe S, Furuki T, Akamine S, Ichiaki R, Ohikubo T, Kocik M, Mizeraölzyk J (2011) Observation of OH radicals produced by pulsed discharges on the surface of a liquid. Plasma Sources Sci Technol 20:034010

Kim J, Coulibaly GN, Yoon S, Assadi AA, Hanna K, Bae S (2020) Red mud-activated peroxymonosulfate process for the removal of fluoroquinolones in hospital wastewater. Water Res 184:116171

Koch C, Nachev M, Klein J, Koster D, Schmitz OJ, Schmidt TC, Sures S (2019) Degradation of the Polymeric Brominated Flame Retardant “Polymeric FR” by Heat and UV Exposure. Environ Sci Technol 53:1453–1462

Kosjek T, Andersen HR, Kompare B, Ledin A, Heath E (2009) Fate of carbamazepine during water treatment. Environ Sci Technol 43:6256–6261

Leong YL, Krivak D, Kiel M, Laski E, González-Sánchez A, Dobslaw D (2021) Triclosan biodegradation performance of adapted mixed cultures in batch and continuous operating systems at high-concentration levels. Clean Eng Technol 5:100266

Li J, Dodgen L, Ye Q, Gan J (2013) Degradation kinetics and metabolites of carbamazepine in soil. Environ Sci Technol 47:3678–3684

Li S, Ao X, Li C, Lu Z, Cao W, Wu F, Liu S, Sun W (2020) Insight into PPCP degradation by UV/NH2Cl and comparison with UV/NaClO: Kinetics, reaction mechanism, and DBP formation. Water Res 182:115967

Liu DX, Liu ZC, Chen C, Yang AJ, Li D, Rong MZ, Chen HL, Kong MG (2016) Aqueous reactive species induced by a surface air discharge: Heterogeneous mass transfer and liquid chemistry pathways. Sci Rep 6:23737

Liu X, Cheng C, Xu Z, Hu S, Shen J, Lan Y, Chu PK (2021) Degradation of tetracycline in water by gas–liquid plasma in conjunction with rGO-TiO2 nanocomposite. Plasma Sci Technol 23:115503

Lodha B, Chaudhari S (2007) Optimization of fenton-biological treatement scheme for the treatment of aqueous dye solution. J Hazard Mater 148:459–466

Magureanu M, Piroi D, Mandache NB, David V, Parvucescu VI (2015) Degradation of pharmaceutical compound pentoxifylline in water by non-thermal plasma treatment. Water Res 81:124–136

Malik MA, Jiang C, Heller R, Lane J, Hughes D, Schoenbach KH (2016) Ozone-free nitric oxide production using an atmospheric pressure surface discharge – A way to minimize nitrogen dioxide co-production. Chem Eng J 283:631–638

Malik SN, Khan SM, Ghosh PC, Vaidya AN, Das S, Mudliar SN (2019) Nano catalytic ozonation of biogasified distillery wastewater for biodegradability enhancement, color and toxicity reduction with biofuel production. Chemosphere 230:449–461

Manoj Kumar Reddy P, Rama Raju B, Karuppija J, Linga Reddy E, Subrahmanyam C (2013) Degradation and mineralization of methylene blue by dielectric barrier discharge non-thermal plasma reactor. Chem Eng J 217:41–47

Markovic M, Jovic M, Stankovic D, Kovacevic V, Roglic G, Gojic-Cvijovic G, Manojlovic D (2015) Application of non-thermal plasma reactor and Fenton reaction for degradation of ibuprofen. Sci Total Environ 505:1148–1155

Mason TJ, Lorimer JP, Bates DM, Zhao Y (1994) Dosimetry in Sonochemistry - the Use of Aqueous Terephthalate Ion as a Fluorescence Monitor. Ultrason Sonochem 1:S91–S95

Miao XS, Yang JJ, Metcalfe CD (2005) Carbamazepine and its metabolites in wastewater and in biosolids in a municipal wastewater treatment plant. Environ Sci Technol 39:7469–7475

Mohapatra DP, Brar SK, Tyagi RD, Picard P, Suramalli RY (2014) Analysis and advanced oxidation treatment of a persistent pharmaceutical compound in wastewater and wastewater sludge-carbamazepine. Sci Total Environ 470–471:58–75

Ognier S, Rojo J, Liu Y, Duten X, Cavadias S, Thannberger L (2015) Mechanisms of Pyrene Degradation during Soil Treatment in a Dielectric Barrier Discharge Reactor. Plasma Processes Polym 11:734–744

Ostman M, Bjorlenius B, Fick J, Tysklind M (2019) Effect of full-scale ozonation and pilot-scale granular activated carbon on the removal of biocides, antimycotics and antibiotics in a sewage treatment plant. Sci Total Environ 649:1117–1123

Qu M, Cheng Z, Sun Z, Chen D, Yu J, Chen J (2021) Non-thermal plasma coupled with catalysis for VOCs abatement: A review. Process Saf Environ Prot 153:139–158

Rabahi A, Assadi AA, Nasrallah B, Bouazza A, Maachi R, Wolbert D (2019) Photocatalytic treatment of petroleum industry wastewater using recirculating annular reactor: comparison of experimental and modeling. Environ Sci Pollut Res Int 26:19035–19046

Rashid MM, Chowdhury M, Talukder MR (2020) Textile wastewater treatment by underwater parallel-multi-tube air discharge plasma jet. J Environ Chem Eng 8:104504

Reddy PMK, Subrahmanyam C (2012) Green approach for waste-treatment—degradation and mineralization of aqueous organic pollutants by discharge plasma. Ind Eng Chem Res 51:11097–11103

Rezaei F, Abbasi-Firouzjah M, Shokri B (2014) Investigation of antibacterial and wettability behaviours of plasma-modified PMMA films for application in ophthalmology. J Phys D: Appl Phys 47:085401

Rozas O, Baeza C, Nunez K, Rossner A, Urrutia R, Mansilla HD (2017) Organic micropollutants (OMPs) oxidation by ozone: Effect of activated carbon on toxicity abatement. Sci Total Environ 590–591:430–439

Sahni M, Locke BR (2006) Quantiﬁcation of hydroxyl radicals produced in aqueous phase pulsed electrical discharge reactors. Ind Eng Chem Res 45:5819–5825

Sanchez J, Fernandez J, Lanza S, Poulet R, Zuniga M, Paredes J, Vazquez A (2019) Degradation of aniline in aqueous solution by dielectric barrier discharge plasma: Mechanism and degradation pathways. Chemosphere 223:430–442

Sanchez J, Fernández J, Lanza S, Poulet R, Zúñiga M, Paredes J, Vázquez A (2019) Degradation of aniline in aqueous solution by dielectric barrier discharge plasma: Mechanism and degradation pathways. Chemosphere 223:430–442

Sanchez J, Fernández J, Lanza S, Poulet R, Zuniga M, Paredes J, Vazquez A (2019) Degradation of aniline in aqueous solution by dielectric barrier discharge plasma: Mechanism and degradation pathways. Chemosphere 223:430–442

Santos LH, Araujo AN, Fachini A, Pena A, Delerue-Matos C, Monte negro MC (2010) Ecotoxicological aspects related to the presence of carbamazepine and its metabolites in wastewater and in biosolids in a municipal wastewater treatment plant. Environ Sci Technol 47:085401

Santos LH, Araujo AN, Fachini A, Pena A, Delerue-Matos C, Montenegro MC (2010) Ecotoxicological aspects related to the presence of pharmaceuticals in the aquatic environment. J Hazard Mater 175:45–95

Santos LV, Meireles AM, Langle LC (2015) Degradation of antibiotics norfloxacin by Fenton, UV and UV/H2O2. J Environ Manage 154:8–12

Shen J, Zhang H, Xu Z, Zhang Z, Cheng C, Ni G, Lan Y, Meng Y, Xia W, Chu PK (2019) Preferential production of reactive species and
bactericidal efficacy of gas-liquid plasma discharge. Chem Eng J 362:402–412
Silambarasan S, Vangnai AS (2016) Biodegradation of 4-nitroaniline by plant-growth promoting Acinetobacter sp. AVLB2 and toxicological analysis of its biodegradation metabolites. J Hazard Mater 302:426–436
Singh RK, Philip L, Ramanujam S (2017) Rapid degradation, mineralization and detoxification of pharmaceutically active compounds in aqueous solution during pulsed corona discharge treatment. Water Res 121:20–36
Sotelo JL, Beltrán F, Benitez FJ, Beltrán-Heredia J (1989) Henry’s law constant for the ozone-water system. Water Res 23:1239–1246
Suwalsky M, Memmickent S, Norris B, Villena F, Sotomayor CP (2006) Effects of the antiepileptic drug carbamazepine on human erythrocytes. Toxicol in Vitro 20:1363–1369
Tampieri F, Ginebra MP, Canal C (2021) Quantification of Plasma-Produced Hydroxyl Radicals in Solution and their Dependence on the pH. Anal Chem 93:3666–3670
Vanaea P, Willems G, Nikiforov A, Surmont P, Lynen F, Vandamme J, Van Durme J, Verheust YP, Van Hulle SW, Dumoulin A, Leys C (2015) Removal of atrazine in water by combination of activated carbon and dielectric barrier discharge. J Hazard Mater 299:647–655
Wang J, Sun Y, Feng J, Xin L, Ma J (2016) Degradation of triclocarban in water by dielectric barrier discharge plasma combined with TiO2/activated carbon fibers: Effect of operating parameters and byproducts identification. Chem Eng J 300:36–46
Wang S, Hu Y, Wang J (2019a) Strategy of combining radiation with ferrate oxidation for enhancing the degradation and mineralization of carbamazepine. Sci Total Environ 687:1028–1033
Wang X, Wang Z, Tang Y, Xiao D, Zhang D, Huang Y, Guo Y, Liu J (2019b) Oxidative degradation of iodinated X-ray contrast media (iomeprol and iohexol) with sulfate radical: An experimental and theoretical study. Chem Eng J 368:999–1012
Watkinson AJ, Murby EJ, Costanzo SD (2007) Removal of antibiotics in conventional and advanced wastewater treatment: implications for environmental discharge and wastewater recycling. Water Res 41:4164–4176
Wen Q, Chen JX, Tang YL, Wang J, Yang Z (2015) Assessing the toxicity and biodegradability of deep eutectic solvents. Chemosphere 132:63–69
Wu ZL, Wang YP, Xiong ZK, Ao ZM, Pu SY, Yao G, Lai B (2020) Core-shell magnetic Fe3O4@Zn/Co-ZIFs to activate peroxymonosulfate for highly efficient degradation of carbamazepine. Appl Catal B-Environ 277:119136
Xiao D, Cheng C, Shen J, Lan Y, Xie H, Shu X, Meng Y, Li J, Chu PK (2014) Characteristics of atmospheric-pressure non-thermal N2 and N2O gas mixture plasma jet. J Appl Phys 115:033303
Xin YY, Zhou L, Ma KK, Lee J, Qazi HIA, Li HP, Bao CY, Zhou YX (2020) Removal of bromoanilinic acid in dye wastewater by gas-liquid plasma: The role of ozone and hydroxyl radical. J Water Process Eng 37:101457
Xu Z, Xue X, Hu S, Li Y, Shen J, Lan Y, Zhou R, Yang F, Cheng C (2020) Degradation effect and mechanism of gas-liquid phase dielectric barrier discharge on norfloxacin combined with H2O2 or Fe2+. Sep Purif Technol 230:115862
Xu Z, Zhu B, Xue X, Hu S, Cheng C (2022a) Study on immediate and long-term growth inhibition of Microcystis aeruginosa by non-thermal plasma. Chem Eng J 429:132397
Xu Z, Zhu B, Ye Z, Zhang N, Shen J, Lan Y, Hu S, Cheng C, Li Y, Yang F, Chu PK (2022b) Degradation of gemfibrozil in aqueous solutions by gas–liquid dielectric barrier discharge plasma combined with CN3x7Fe2O3. Plasma Processes Polyem 19:e2100122
Yang Y, Ok YS, Kim KH, Kwon EE, Txang YF (2017) Occurrences and removal of pharmaceuticals and personal care products (PPCPs) in drinking water and water/sewage treatment plants: A review. Sci Total Environ 596–597:303–320
Yu H, Nie E, Xu J, Yan S, Cooper WJ, Song W (2013) Degradation of diclofenac by advanced oxidation and reduction processes: kinetic studies, degradation pathways and toxicity assessments. Water Res 47:1909–1918
Yue Y, Kondeti VSSK, Sadeghi N, Bruggeman PJ (2022) Plasma dynamics, instabilities and OH generation in a pulsed atmospheric pressure plasma with liquid cathode: a diagnostic study. Plasma Sources Sci Technol 31:025008
Zeghioud H, Assadi AA, Khellaf N, Djelal H, Amrane A, Rtimi S (2018) Reactive species monitoring and their contribution for removal of textile effluent with photocatalysis under UV and visible lights: Dynamics and mechanism. J Photochem Photobioir A-Chem 365:94–102
Zhang G, Sun Y, Zhang C, Yu Z (2017) Decomposition of acetaminophen in water by a gas phase dielectric barrier discharge plasma combined with TiO2-rGO nanocomposite: Mechanism and degradation pathway. J Hazard Mater 323:719–729
Zhang H, Xu Z, Shen J, Li X, Ding L, Ma J, Lan Y, Xia W, Cheng C, Sun Q, Zhang Z, Chu PK (2015) Effects and Mechanism of Atmospheric-Pressure Dielectric Barrier Discharge Cold Plasma on Lactate Dehydrogenase (LDH) Enzyme. Sci Rep 5:10031
Zhang J, Liu D, Bian W, Chen X (2012) Degradation of 2,4-dichlorophenol by pulsed high voltage discharge in water. Desalination 304:49–56
Zhang W, Xu G, Pei J, He X, Xu P, Liu N, Wu M (2014) EB-radiolysis of carbamazepine: in pure-water with different ions and in surface water. J Radioanal Nucl Chem 302:139–147
Zhu D, Jiang L, Liu RL, Chen P, Lang L, Feng JW, Yuan SJ, Zheng M, Xu G, Pei J, He X, Xu P, Liu N, Wu M (2014) EB-radiolysis of carbamazepine: in pure-water with different ions and in surface water. J Radioanal Nucl Chem 302:139–147
Zhu D, Jiang L, Liu RL, Chen P, Lang L, Feng JW, Yuan SJ, Zheng M, Xu G, Pei J, He X, Xu P, Liu N, Wu M (2014) EB-radiolysis of carbamazepine: in pure-water with different ions and in surface water. J Radioanal Nucl Chem 302:139–147
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