# DBDP collaboration Cu@PAF-45-COOH experimental study on catalytic degradation of chloramphenicol in water

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*Abstract:* Antibiotics, as a new type of pollution, have received much attention in recent years. However, there is currently an incomplete analysis of its environmental hazard mechanism, mechanism of action, and governance measures. This study takes chloramphenicol as the research object and uses dielectric barrier discharge plasma technology to investigate the degradation effect under different discharge voltage, air carrier gas flow rate, and initial concentration of chloramphenicol. The quantitative relationship between them is explored, and the degradation path and degradation products are studied. The main results of this study are as follows: when other parameters are controlled to be consistent, the discharge voltage and carrier gas (air) flow rate of the system are positively correlated with the degradation rate of CAP, while the initial concentration of CAP is negatively correlated with the degradation rate. The degradation rate of chloramphenicol in water after 100 minutes of removal alone is 92.26%; Through characterization analysis, it can be concluded that PAF-45 has a significant high surface area and complex pore structure, which is load coupled Cu@PAF-45-COOH On the basis of developed PAF-45 pores, it overcomes the defects of aromatic main chains and increases the adsorption ability of active particles such as CAP particles and superoxide radicals; Exploring through synergistic catalysis, it was found that the removal rate of CAP is related to PAF-45 Cu@PAF-45-COOH There is a positive correlation between the dosage. By comparison, it was found that the removal rate of DBDP in collaboration with PAF-45 system increased by 24.39%; DBDP Collaboration Cu@PAF-45-COOH The removal rate of the system is about 30% and 10% higher than that of the first two; Based on the analysis of LC-MS detection results, it is believed that the main sites for the structural damage of chloramphenicol are the amide group and the benzene ring. Roughly, the oxidation of the carboxyl group on the benzene ring of chloramphenicol causes the C-Cl bond to break, leading to the dechlorination of the chloramphenicol structure and the removal of biological toxicity; The obtained product undergoes a series of nitro reduction processes such as denitrification and deoxidation, further breaking and finally oxidizing and ring opening degradation to obtain particles such as $H_2O$, $CO_3^{2-}$, $NO_3^-$, Cl -.

# 1. Introduction

Antibiotics are an important type of medication and personal care products used for long-term diagnosis, treatment, disease prevention, and relief of physical discomfort. It is mainly synthesized through two pathways: one is the secondary metabolites formed by natural microorganisms (mainly actinomycetes and fungi) and higher animals and plants in their own metabolism[1], such as erythromycin, keyomycin, tetracycline; The other is through artificially synthesized analogues, such as quinolones β- Lactams[2].

At present, the main antibiotics entering the environment are medical antibiotics that cannot be fully absorbed by the human body[3], antibiotics in untreated wastewater from pharmaceutical factories[4], antibiotics that are not utilized during agricultural planting[5], and antibiotics used for disease prevention and control in animal husbandry and feed[6]. These antibiotics, which have not been fully absorbed and utilized, enter the environment and are fixed or transformed through environmental behavior, thus remaining in the environment. Du et al. used HPLC-MS analysis to study the distribution of 25 antibiotics in the Yancheng area of the Yellow Sea and found that their total concentration in seawater reached 1349.2 ng/L, with fluoroquinolone accounting for 46.5% and sulfonamide accounting for 21.4%.

Chloramphenicol is a broad-spectrum antibiotic that has good inhibitory effects on Gram positive negative bacteria, Rickettsia, Chlamydia, etc., especially on Bacteroides, Salmonella, and Influenza bacteria[7], making it widely praised in the field of disease treatment. However, excessive use of chloramphenicol can cause fatal toxicity, bone marrow suppression, genetic toxicity, aplastic anemia, and potential carcinogenicity to the human body[8]. At present, CAP entering the environment mainly comes from four channels: medical treatment, aquaculture, pharmaceuticals, and domestic sewage. Compared with traditional pollutants, CAP has poor biodegradability and is difficult to degrade during sewage treatment or in natural water environments. It cannot be completely removed and has a toxic effect on the environment, affecting the physiological functions of animals and plants. Commonly used processing techniques include photocatalysis, electrochemical technology, and advanced oxidation method. M.N. Abellan et al.[9] explored the possibility of photocatalytic degradation of SMX and TMP, and the results showed that both SMX and TMP are prone to photocatalytic degradation under 310nm light irradiation. Jorge Vidal[10]compared the elimination of mineralization and antibacterial activity of ampicillin in solution using different electrochemical oxidation processes. The results showed that under the condition of adding $Fe^{2+}$, the concentration of AMP remained unchanged during 120 minutes of non application of ultraviolet light irradiation system, indicating that there was no degradation effect on the system itself. Under other unchanged conditions, using hydrogen peroxide oxidation (EO-$H_2O_2$) or electric Fenton (EF) processes, the removal rates of AMP in the solution reached 68% and 73% respectively during 120 minutes, and the mineralization rates reached 32% and 43%, respectively.

Plasma is mainly composed of free radicals, ions, neutral ions, and electrons, and is the fourth state of matter outside the solid, liquid, and gas states. Containing extremely high electrical potential energy, it can remove pollutants in an extremely short time.

# 2. Experimental

## 2.1 Chemicals

Anhydrous ethanol, chloramphenicol, hydrochloric acid, sulfuric acid, pure water, copper chloride, chloroform, anhydrous aluminum chloride, ethanol, biphenyl, biphenyl dicarboxylic acid

## 2.2 Preparation of catalysts

Mix a certain amount of anhydrous aluminum chloride and trichloromethane thoroughly and stir vigorously for 24 hours to form liquid A; Simultaneously mix a certain amount of biphenyl, biphenyl dicarboxylic acid, and trichloromethane and sonicate to fully dissolve them to obtain liquid B; Then, a water bath heating method is used to prepare, and the stirred liquid A after 24 hours is transferred to a round bottom beaker and placed in a constant temperature water bath heater with electromagnetic stirring function; When the reaction temperature remains constant again, add liquid B and an appropriate amount of CuCl2 to liquid A, while setting a certain temperature, and continue heating the reaction in a water bath for 1 hour; After cooling the reaction mother liquor to room temperature, we need to use a filtering device to filter out the crude product. Then, it is stirred in a dilute ethanol solution for 4 hours, filtered, and washed several times with ethanol to obtain a finer product; The experimenter acidified the washed product in a 1mol/L dilute hydrochloric acid solution and stirred for 24 hours; Rinse and dry with water, filter again, and rinse with deionized water until the pH value is neutral. The experimenter placed it in a vacuum drying oven and dried it at 80 °C to obtain a dry powder like product; The experimenter used a muffle furnace for high-temperature calcination for 200 minutes to obtain Cu@PAF-45-COOH.

In this experiment, based on the different mass ratios between biphenyl, biphenyl diacid, and CuCl2 (2:1, 1:1, 1:2), the experimental prepared Cu@PAF-45-COOH Recorded as X-Cu@PAF-45-COOH (where X is 1, 2, and 3), the composite materials are abbreviated as P1, P2, and P3.

## 2.3 Synergistic degradation experiments

The experimenter weighed a certain amount of composite material and added it to 100mL of reaction solution. Ultrasound for 5 minutes to evenly disperse it in the reaction solution. After adjusting the pH with plasma water, the experimenter added the mixed reaction solution to the plasma reactor and started the peristaltic pump circulation. At the same time, the carrier gas device was opened to introduce a certain flow rate of air, control the single factor effect, and start the discharge treatment. During the plasma discharge treatment process, 1 milliliter of reaction solution was taken at an interval of 5 minutes, and the concentration of CAP was measured using UV visible spectrophotometry.

## 3. Results and discussion

## 3.1 Research on individual degradation systems

### 3.1.1 Impact of different parameters
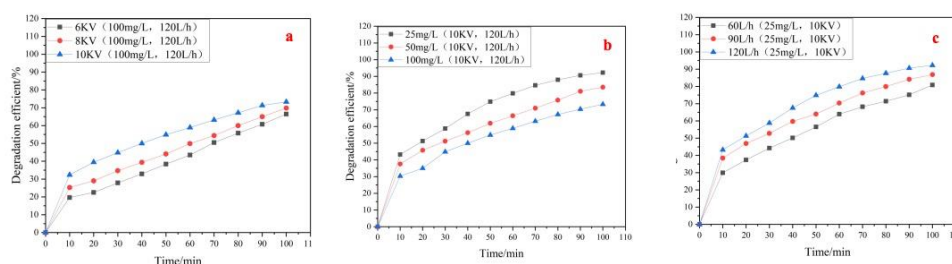


(a: discharge voltage; b: initial concentration; c: carrier gas flow rate)

Figure 1: Effect of Individual Discharge System

From Figure 1 (a), it can be seen that when other experimental parameters remain relatively consistent, the degradation rate of chloramphenicol shows a gradually increasing trend within the discharge voltage range of 6-10 KV, basically maintaining in the range of 10% -25%. This is mainly due to the increase in discharge voltage, which increases the electric field intensity and energy in the reaction system, resulting in the production of more active particles in water electrolysis, The increase in discharge voltage further increases the possibility of collision between active particles and chloramphenicol, allowing chloramphenicol to decompose in water. At the same time, when the discharge voltage increases, the carrier gas (air) introduced into the reaction system is more likely to be fully breakdown, producing a large number of high-energy particles such as high-energy electrons and ions[]11,12. The high-energy particles will also collide fiercely with chloramphenicol in water to achieve the effect of decomposing chloramphenicol. Furthermore, internal energy will increase with the increase of discharge voltage during the reaction process. In addition to the heat energy required for the reaction, the remaining internal energy will be emitted in the form of heat. Therefore, as time increases, the temperature in the system gradually increases, making the collision between active substances and high-energy particles in the system more severe[13] , accelerating the degradation of chloramphenicol.

It can be clearly observed from Figure 1(b) that an increase in initial concentration will inhibit the degradation of chloramphenicol itself. On the one hand, under certain discharge conditions such as discharge voltage and carrier gas flow rate, the number of high-energy particles and active radicals generated by DBDP is roughly the same. However, as the initial concentration of chloramphenicol increases, it will cause the system to require more high-energy electrons and active radicals. Therefore, although the concentration of chloramphenicol increases, there is no sufficient number of high-energy particles and active radicals in the system to meet its decomposition, and the degradation rate actually decreases. On the other hand, the number of active particles that collide with chloramphenicol per unit time during the reaction process is limited. As the reaction time increases, chloramphenicol gradually decreases, and the continuously increasing intermediate products will also collide with high-energy particles and active radicals, which will compete with chloramphenicol in water[14]. Therefore, as the concentration of chloramphenicol in the water environment increases, although the actual degradation amount increases, due to stronger competition in the discharge area, the degradation rate of chloramphenicol solutions with low concentrations in the same discharge area is ultimately higher.

It can be intuitively observed from Figure 1(c) that as the flow rate increases, the degradation rate of chloramphenicol shows a gradually increasing trend, but at the same time, the increase rate slows down significantly. When the flow rate increases from 60L/h to 90L/h, the increase in degradation rate is between 10% -13%, but when the flow rate increases from 90L/h to 120L/h, the increase in degradation rate is only about 5%. The main reason for this phenomenon is that a large amount of air entering the system increases the number of high-energy electrons and other active particles generated by ionization, greatly enhancing the probability of collision between the active substance and chloramphenicol in water, resulting in an increase in degradation rate. However, when a large flow of air enters the system, it also causes the active particles in the system to accelerate and detach from the device, and some active ions may not completely collide with chloramphenicol before being blown away from the device. Therefore, although the degradation rate has increased, the increase is not high.

## 3.2 Study on DBDP Synergistic Catalytic Degradation of Chloramphenicol

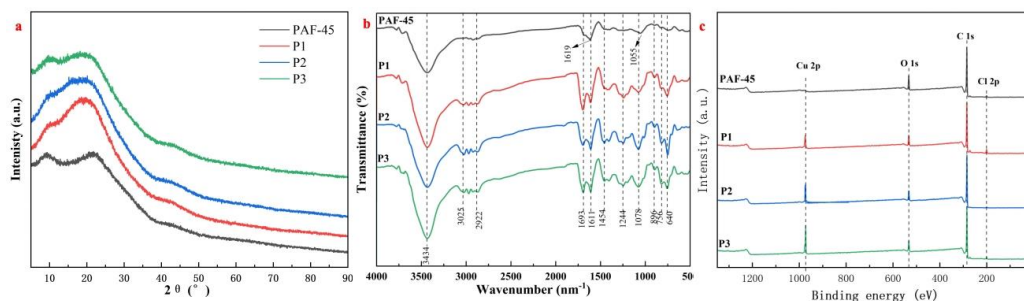### 3.2.1 XRD, FT-IR, XPS characterization analysis



Figure 2: Characterization of PAFs

This study utilized XRD, FT-IR, XPS and other methods to analyze PAFs.

From Figure 2 (a), it can be seen that the synthesized PAFs material is amorphous and amorphous. It may be caused by the interpenetration and structural distortion between benzene rings；From figure 2 (b), it can be seen that the main absorption peaks are concentrated at several locations: 600-900cm-1, 1200-1500cm$^{-1}$, 1693cm$^{-1}$, 2922-3050cm$^{-1}$, and 3434cm-1, with different mass ratios Cu@PAF-45-COOH Having the same FT-IR absorption peak indicates having the same chemical bonds and functional groups. Comparison can reveal that Cu@PAF-45-COOH In the infrared spectrum of the composite, the absorption peak of PAF-45 at 1055cm$^{-1}$ was shifted to the wavelength of 1078cm$^{-1}$; The PAF-45 absorption peak at a wave number of 1611cm$^{-1}$ also experienced a similar shift. The former represents the substitution of C-H on the benzene ring, while the latter represents 1, 2 disubstituted on the benzene ring. This proves that the addition of Cu changes the polymerization method of PAF-45, and also indicates that PAF-45 successfully loaded Cu.

From figure 2 (c), it can be observed that the prepared PAFs materials contain elements such as C, O, and Cl; among Cu@PAF-45-COOH The presence of Cu element can be clearly observed in. After calcination in an air atmosphere, Cu@PAF-45-COOH A display peak belonging to $Cu^{2+}$appeared in the composite material near the binding energy of 945.75eV. The width and intensity of $Cu^{2+}$ display peaks are significantly different under different ratios. As the Cu content in the ratio increases, the display peaks show a positive correlation, indicating an increase in $Cu^{2+}$content in the prepared samples.

## 3.3 Research on Collaborative Degradation System

### 3.3.1 PAF-45 Collaborative System

According to Figure 3, it can be seen that under the same DBDP discharge conditions, PAF-45 has a promoting effect on the decomposition of chloramphenicol, and the dosage is positively correlated with the chloramphenicol degradation rate. The results showed that when the initial concentration was controlled at 25 mg/L and the carrier gas flow rate was 120 L/h, the degradation rate of chloramphenicol remained basically unchanged when different amounts of PAF-45 skeleton materials were added when the system was not discharged. After 50 minutes of reaction, the degradation rates were 14.36%, 18.62%, and 20.40%, respectively; When the system is discharged (with a discharge voltage of 10KV), with the increase of n dosage, the degradation rate of chloramphenicol is significantly improved compared to individual discharge, with degradation rates increased by 10.47%, 15.35%, and 24.39%, respectively.
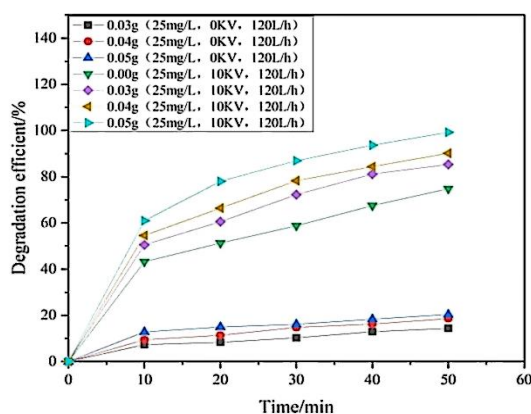
Figure 3: PAF-45 Collaborative Catalytic System

The main reason why the removal effect of chloramphenicol can be improved before and after the addition of PAF-45 in the system is that during the dielectric barrier plasma discharge process, a large number of active particles such as carboxyl radicals and superoxide anion radicals are generated in the system, which collide with chloramphenicol to achieve the removal effect. However, the physicochemical interaction between active particles and chloramphenicol is limited by various conditions, resulting in unsatisfactory removal efficiency. After the addition of PAF-45 material, on the one hand, due to its $\pi$ - conjugated structure ,it can utilize the ultraviolet light generated during the discharge process to form hole oxidation, absorb photoelectrons through $O_2$, generate $\cdot O^{2-}$, and promote the degradation of chloramphenicol. On the other hand, the presence of multiple benzene ring structures in PAF-45 molecules increases its affinity for benzene based compounds, effectively improving the adsorption selectivity of CAP and allowing some CAP to be adsorbed on the surface of PAF-45; In addition, the high specific surface area and complex pore structure of PAF-45 also result in active particles being adsorbed on the surface. Some CAP and active particles adsorbing on the surface of PAF-45 at the same time will greatly increase the probability of collision between chloramphenicol and active ions, leading to further degradation of chloramphenicol.

### 3.3.2 Cu@PAF-45-COOH Collaborative system

During the reaction process, the discharge remains constant at 10KV, the initial concentration of the reaction solution is 25mg/L, and the carrier gas (air) flow rate is 120L/h. The experimenter added 2:1, 1:1, and 1:2 mass ratios to the reaction apparatus, respectively Cu@PAF-45-COOH (P1:2:1, P2:1:1, P3:1:2) Three gradients of 0.03g, 0.04g, and 0.05g were used to study their effects on the degradation rate of chloramphenicol.

**(1) Cu@PAF-45-COOH The effect of dosage on degradation rate**

Figures 4 (a), (b) and (c) respectively show the effects of different dosages of P1, P2, and P3 on the removal rate of CAP in water. From Figure figure 4 (a), it can be seen that adding different amounts of P1 material increases the removal rate by 22.9%, 29.62%, and 36.82% compared to individual discharge after 30 minutes of reaction; Compared to PAF-45, the removal rate increases by 9.4%, 10.04%, and 8.64% at the same dosage, respectively; Compared to the 0.03g dosage of P1 material, with the increase of dosage, the removal rate increased by 6.72% and 13.92% after 30 minutes of reaction, respectively. From figure 4 (b), it can be seen that adding different amounts of P2 material increases the removal rate by 25.85%, 33.74%, and 40.69% compared to individual discharge after 30 minutes of reaction; Compared to PAF-45, the removal rate increases by 12.35%, 14.16%, and 12.51% at the same dosage, respectively; Compared to the 0.03g dosage of P2 material,

with the increase of dosage, the removal rate increased by 7.88% and 14.84% after 30 minutes of reaction, respectively. From figure 4(c), it can be seen that adding 0.03g, 0.04g, and 0.05g of P3 material increases the removal rate by 23.38%, 31.22%, and 38.24% respectively compared to individual discharge after 30 minutes of reaction; Compared to PAF-45, the removal rate increases by 9.88%, 11.64%, and 10.06% at the same dosage, respectively; Compared to the 0.03g dosage of P3 material, with the increase of dosage, the removal rate increased by 7.84% and 14.86% after 30 minutes of reaction, respectively.
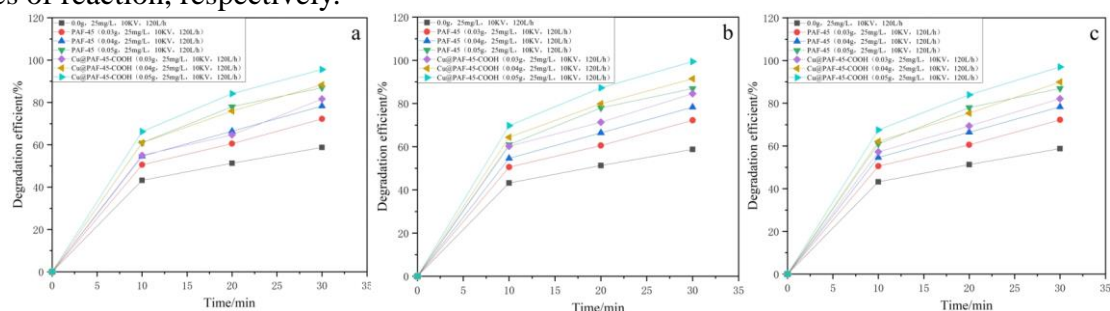


Figure 4: Effect of Different Dosages (0.03g, 0.04g, 0.05g) on Chloramphenicol Degradation Rate (a: $P_1$; b: $P_2$, c: $P_3$)

The above results indicate that whether compared to individual discharge or synergistic discharge with the addition of FAF-45, the system Cu@PAF-45-COOH The addition of $CO_2$ can more effectively promote the removal of CAP, with a removal rate increase of about 30% compared to a single discharge system; Compared to the PAF-45 synergistic system, the removal rate increases by about 10%; Compared to its own synergistic system, an increase in the dosage of P1, P2 or P3 can also promote the reaction, with a removal rate increase of about 8%. This is mainly due to the carboxylation of PAF-45 and its combination with Cu, which generates polar motifs on the surface, significantly increasing its surface wettability and greatly enhancing its Cu@PAF-45-COOH The diffusion rate in the water environment enables it to be fully dispersed in the system in a short period of time, promoting physical and chemical reactions such as collisions between active particles and CAP. In addition, as the dosage increases, on the one hand, it can promote the generation of more active particles in the system, enabling it to degrade more target pollutants per unit time. On the other hand, the system can simultaneously adsorb more particles and CAP on its surface per unit time, increasing its collision probability and promoting degradation. Finally, Cu@PAF-45-COOH The - COOH carried by the reaction in the pore will also be ionized by plasma into active particles such as carboxyl radicals, increasing the number of particles in the system, increasing the probability of collision between particles and target pollutants, and promoting the progress of the reaction.

### 3.4 Analysis of pollutant degradation pathways

Qualitative and semi quantitative analysis of the reaction solution before and after chloramphenicol degradation was performed using liquid chromatography-mass spectrometry (LC-MS) in a positive and negative ion mode. As shown in Figures 7 (a), the absorption peak of the reaction solution significantly decreased after degradation, indicating that chloramphenicol was effectively degraded in the aqueous environment. Qualitative analysis of intermediate products generated during the degradation process reveals that CAP molecules are attacked by highly oxidizing active particles, leading to the cleavage of CAP chemical bonds and the formation of intermediates.
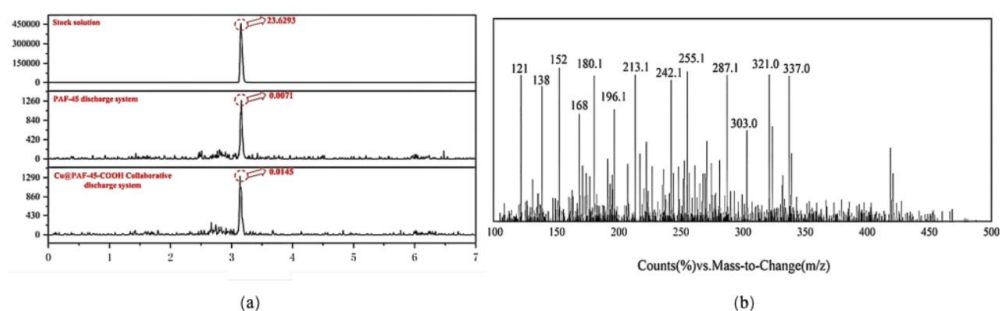
Figure 5: Liquid chromatography-mass spectrometry before and after reaction

Based on the mass spectrum of chloramphenicol degradation products, it can be inferred that the degradation pathway and degradation products of chloramphenicol are shown in Figure 5 (b). The main degradation site of CAP ([M-H] - m/z=321) occurs on the acyl amino group in the molecular structure and on the aromatic ring. The first degradation reaction channel exhibits the oxidation hydroxylation product m/z=337 on the ring, and further breaking the C-Cl bond yields the product m/z=303. The dechlorination of CAP is an important step in removing biological toxicity. The second degradation reaction channel is the cleavage of the C-Cl bond to obtain the product m/z=287, and further degradation and denitrification to obtain the product m/z=242；The product m/z=285 is obtained by dechlorination of product m/z=287, followed by deoxidation and further oxidation and deamination to obtain product m/z=180, followed by oxidation to obtain nitroso benzoic acid m/z=152; The third path also involves dechlorination of product m/z=287 to obtain product m/z=255. However, subsequent product m/z=255 undergoes C-N bond cleavage to remove ketene to obtain m/z=213, oxidative deamination to obtain m/z=196, and further oxidation to obtain nitrobenzoic acid m/z=168. The denitrification results in benzoic acid m/z=121 or decarboxylated hydroxylated nitrophenol m/z=138. The above products can further oxidize and open the ring, ultimately degrading to inorganic molecules such as $H_2O, CO_3^{2-}, NO_3^{-}, Cl^{-}, NH_4^{+}$.

## 4. Conclusions

This study takes CAP as the research object, explores the removal effect of individual discharge system and collaborative discharge system, and makes a preliminary analysis of the degradation path and mechanism. The results are as follows: in the individual discharge system, the maximum degradation rate can reach 92.26% after 100 minutes of discharge; In a collaborative system, the removal rate is related to Cu@PAF-45-COOH There is a positive correlation between the dosage. Based on the analysis of LC-MS detection results, it is believed that the main sites for the structural damage of chloramphenicol are the amide group and the benzene ring. The approximate process is that the carboxyl group on the benzene ring of chloramphenicol undergoes oxidation, causing the C-Cl bond to break, causing the chloramphenicol structure to undergo dechlorination and removing biological toxicity; The obtained product undergoes a series of nitro reduction processes such as denitrification and deoxidation, further breaking and finally oxidizing and ring opening degradation to obtain particles such as $H_2O, CO_3^{2-}, NO_3^{-}, Cl^{-}$.

This study mainly focuses on DBDP technology, exploring the DBDP system, DBDP collaborative PAF-45 system, and DBDP collaboration respectively Cu@PAF-45-COOH The removal effect of CAP in water. Although certain achievements have been made, there is still room for progress in related research due to time and conditions.

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