Degradation of imidacloprid in wastewater by dielectric barrier discharge system

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Abstract: The degradation behavior of imidacloprid in wastewater was investigated with dielectric barrier discharge (DBD) system and the effect of several factors that could influence degradation process was explored in this study. The study showed that imidacloprid could be effectively removed by DBD system under certain conditions. The optimal removal efficiency was 75.6% when applied voltage was 75 V and 160 min was selected as the discharge time. Moreover, lower conductivity and alkaline environment were favorable for the imidacloprid degradation. The presence of Cu\(^2+\) and Fe\(^2+\) could benefit for the imidacloprid degradation, however the catalytic effect of Cu\(^2+\) was lower than that of Fe\(^2+\). Furthermore, methanol as scavenger decreased the removal efficiency of imidacloprid owing to the scavenger inhibited the generation of hydroxyl radicals during the DBD process.

1. Introduction
Neonicotinoids is a new growing class of effective pesticides and active against many sucking biting insects as agonist for insect nicotinic acetylcholine receptors, which partly replaced the organophosphate insecticides and play an important role in agriculture[1, 2]. However the environmental toxicity of neonicotinoids can give rise to serious risks for the health and safety of the consumers of the agricultural products. Moreover, neonicotinoids in the environment showed that it is mobile, persistent and it could be dissipated to water. So neonicotinoids treatment has become a research subject with considerable concern [3, 4]. Imidacloprid (C\(_9\)H\(_{10}\)ClN\(_5\)O\(_2\)) is a representative of a third generation of neonicotinoid insecticides, and its properties such as high toxicity, relatively high solubility (0.58 g/L) and stable in water made it urgent to be solved [5].

The traditional processing for pesticides is mostly biological and physical method. Biarefractory hazardous substances have inhibitory effect on biological growth, such as imidacloprid, thus the widespread application of biodegradation technology has been limited in wastewater treatment [6]. Physical unit processes and chemical oxidation are effective on the treatment of pesticides, but these might cause secondary pollution, high cost and high energy consumption [7, 8]. Thus, there is a growing need for the development of fast and simple methods for the characterization and determination of neonicotinoids.

Advanced oxidation process (AOP) is a promising technology (such as photocatalysis, ozonation, Fenton, electrochemical oxidation) [9, 10]. In AOPs, the organic compounds could be completely mineralized into carbon dioxide and water, mostly by hydroxyl radicals. Dielectric barrier discharge (DBD) is one of efficient AOPs, which has great potential for application in wastewater treatment field due to its effective degradation capacity. DBD combines the advantages of multiple oxidation processes, high-energy electrons, active radicals (HO\(^*\), O\(^*\), HO\(_2\)^*) ozone, neutral and UV light can be
generated during operation process. These contribute to the process of pollutants decomposition. The detailed processes are as follows (Eqs. (1–10)) [11-15]:

\[
\begin{align*}
O_2 & \rightarrow O^* + O^* \\
O^* + O_2 & \rightarrow O_3 \\
O^* + H_2O & \rightarrow HO^* + HO^* \\
O^- + H_2O & \rightarrow HO^- + OH^- \\
O_2^- + H_2O & \rightarrow HO_2^- + OH^- \\
2H_2O & \rightarrow H_2O_2 + H_2 \\
O_3 + H_2O_2 & \rightarrow HO^* + O_2 + HO_2 \\
O_3 + HO_2^* & \rightarrow HO^* + O_2 + O_2 \\
O_3 + H_2O & \rightarrow H_2O_2 + O_2 \\
H_2O_2 & \rightarrow HO^* + HO^* \\
\end{align*}
\]

The objective of this study is to explore the degradation effects of imidacloprid in DBD system under different conditions, such as discharge voltage, initial conductivity, initial pH, catalytic ions and alcohol scavenger. Accordingly, various optimum conditions were confirmed for degradation of imidacloprid in the study.

2. Materials and methods

2.1 Materials
The regents used in this study were analytical grade: imidacloprid (Jinan Pesticide Testing Center), methanol (Tianjin Fuyu Chemical Industry Co., Ltd.), FeSO_4 and CuSO_4 (Tianjin Guangcheng Chemical Industry Co., Ltd.), NaOH and HCl (adjust the pH value of solution), Na_2HPO_4 (adjust the conductivity of solution).

2.2 Experimental set up
The experimental device was the dielectric barrier discharge (DBD), which is shown as schematic diagram (Figure 1). The main parts include high-voltage power supply (CTP-2000 K), reactor (height 700 mm, inner diameter 100 mm and outer diameter 140 mm) and a peristaltic pump. In addition, a quartz glass (diameter 90 mm) as isolation medium is located below the high-voltage electrode.

![Figure 1 Schematic diagram of the experimental apparatus](image)

2.3 Analysis methods
The concentration of imidacloprid was analyzed by high efficiency liquid chromatography (HPLC, Thermo Ultimate 3000) equipped with C-18 column (Atlantis). The mobile phase used in HPLC was a
mixed solvent of methanol and water (80/20, v/v) with a flow rate of 0.2 mL/min. According to Beer–Lambert law, the removal rate of imidacloprid can be calculated from following equation:

$$\eta = \frac{c_0 - c_t}{c_0} \times 100\%$$ (11)

where $\eta$ is the removal rate (%), $c_0$ is the initial concentration of imidacloprid and $c_t$ is the concentration of imidacloprid after ‘t’ minutes.

3. Results and Discussions

3.1 Effect of applied voltage for imidacloprid degradation
Discharge intensity is an important parameter influencing the removal efficiency of contaminants in the DBD system, so three different voltage values were chosen as the applied voltage to observe the efficiencies of imidacloprid degradation. As Figure 2a shown, various applied voltages could effectively impact the removal efficiency of imidacloprid. Obviously, appropriate increase of applied voltage (65 V – 75 V) could effectively enhance the degradation efficiency, the degradation efficiency reached to 75.6%. In DBD system, high intensity ultraviolet light appears with high applied voltage [11], and ultraviolet light can inspire some active particles (HO•, O•, H•) in reaction interface, thus the effect of oxidizing organic compounds can be improved. Moreover the electric field became stable when increase discharge voltage properly, it was benefit for the generation of ozone in this system [13, 16].

However, when applied voltage reached 85 V, the efficiency was reduced to 60.2%. The discharge effect diagrams were shown in Figure 2b, clearly, the discharge with 75 V was brighter than that with 65 V. But unstable discharge appeared in 85 V, it caused arcing and a large amount of ozone was decomposed with sharply increased temperature [17]. These factors resulted in the declined removal efficiency at 85 V.

![Figure 2(a)](image-url) Effect of different discharge voltage on imidacloprid degradation; (b) Photographs of plasma discharges with different voltage

3.2 Effect of initial conductivity for imidacloprid degradation
To study the influence of initial conductivity on degradation of imidacloprid, Na₂HPO₄ was chosen as modifier to change the initial conductivity of solution, the different degradation efficiencies were shown in Figure 3a. It revealed that higher initial conductivity was against to the decomposition of imidacloprid. It could be explicated by that excessive salt changed the discharge way and hinder high-energy electrons into the reaction interface [18]. Besides, salt particles might compete with pollutant molecules for active particles in the system, it also results in the decreased efficiency in higher initial conductivity [19]. Moreover, the change of conductivity values during the degradation was shown in Figure 3d, which showed that the conductivity increased with the degradation process. The small molecules produced in the degradation process may be caused the increasing of conductivity.

Figure 3b showed the change of degradation efficiency with 100 μS/cm conductivity by different
regulator (Na₂HPO₄, K₂HPO₄, KCl). It revealed that effect of Na₂HPO₄ and K₂HPO₄ have no obvious difference, but the efficiency with KCl is slight lower than the two former. It may be due to that Cl⁻ is the scavenger of HO*, and the addition of Cl⁻ decreased the concentration of HO* thus the efficiency was reduced. It also indicated that HO* play an important role in imidacloprid degradation.

3.3 Effect of initial pH for imidacloprid degradation

As reported in previous studies, the initial pH is a significant influencing factor for degradation efficiency of organic pollutants, and actual wastewater is also divided into acidic or alkaline. Therefore, it is necessary to study the removal efficiency of imidacloprid with various pH. The removal efficiencies with three different pH were shown in Figure 3c. The removal efficiencies were approximately similar under acidic and neutral conditions, and the highest efficiency was in alkaline solution (pH= 9.0). As we known, in DBD processing system, ozone plays a significant role for the decomposition of organics. In acid environment, ozone could react with organic pollutants directly. Under alkaline condition, ozone rapidly decompose into HO* in solution [20]. Furthermore, in alkaline environment, DBD plasma could produce more HO* and HO₂*, which is benefit for the degradation [21], so imidacloprid had optimal degradation in neutral environment the that in acid or alkaline environment.

The changes of pH values in the degradation process were shown in Figure 3d. As shown, the pH value of the solution decreased with the degradation process. It illustrated that the degradation process was an acidification process that acidoid were produced. Another reason for the solution acidification might be that N₂ was converted to NO₃⁻ by discharge process.

3.4 Effect of catalytic ions for imidacloprid degradation

As reported that some metal ions had a remarkable catalytic effect for degradation of organic pollutants [22]. So Cu²⁺ acted as the additive to investigate the effect of catalytic ion on imidacloprid degradation by DBD. In Figure 4a, with the increasing of Cu²⁺, the final removal efficiencies enhanced in first and then decreased. It was revealed that appropriate Cu²⁺ could promote the degradation of
imidacloprid, and excess Cu$^{2+}$ would inhibit the removal.

![Figure 4](image)

**Figure 4** Effect of catalytic ions on imidacloprid degradation: (a) Cu$^{2+}$; (b) different additive

Undoubtedly, Fe$^{2+}$ had been proved to be an efficient catalytic ion. Figure 4b showed the comparison of catalytic effect between Cu$^{2+}$ and Fe$^{2+}$. As seen from Figure 4b, similarly, appropriate Fe$^{2+}$ promoted the degradation efficiency and excess Fe$^{2+}$ inhibited the removal of imidacloprid. Moreover, the addition of Fe$^{2+}$ had a higher catalytic effect than Cu$^{2+}$. The reasons could be explained as follows [23-25]:

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{HO}^{-} + \text{HO}^{-} & (12) \\
\text{Fe}^{2+} + \text{HO}^{-} & \rightarrow \text{Fe(OH)}^{2+} & (13) \\
\text{Fe(OH)}^{2+} + h\nu & \rightarrow \text{Fe}^{2+} + \text{HO}^{-} & (14) \\
\text{Cu}^{2+} + \text{H}_2\text{O}_2 & \rightarrow (\text{Cu}^{2+}\text{OOH}^{-})^+ + \text{H}^+ & (15) \\
(\text{Cu}^{2+}\text{OOH}^{-})^+ & \rightarrow \text{Cu}^{2+} + \text{HO}^{-} + 1/2\text{O}_2 & (16)
\end{align*}
\]

As the above equations described, Cu$^{2+}$ and Fe$^{2+}$ could both improve the degradation efficiency of imidacloprid by increasing the content of HO$^{-}$ in solution. The reaction product of Fe$^{2+}$ and HO$^{-}$ could be decomposed to HO$^{-}$ under UV irradiation. A portion of Cu$^{2+}$ was converted to (Cu$^{2+}\text{OOH}^{-})^+$, and slow decomposition of (Cu$^{2+}\text{OOH}^{-})^+$ resulted in lower utilization of Cu$^{2+}$.

3.5 Effect of methanol for imidacloprid degradation

Actually, it is possible that wastewater is mixture and contains more than one pollutant. So methanol was chosen as a radical scavenger to investigate the influence of methanol on the removal behavior of imidacloprid. Figure 5a showed that the concentration of imidacloprid reduced with the progress degradation in absence and presence of methanol. However, the removal efficiency of imidacloprid with methanol was lower than that without it. When the concentration of methanol was enhanced from 75 mg/L to 150 mg/L, the removal was evidently decreased. These results indicated that methanol had a strongly inhibitory effect on degradation of imidacloprid. It could be interpreted that methanol could quickly scavenge HO$^{-}$ in solution (Eq. (17)) [26]:

\[
\text{HO}^{-} + \text{CH}_3\text{OH} \rightarrow \text{H}_2\text{C'O} + \text{H}_2\text{O} & (17)
\]

The product (H$_2$C’OH) was inert radical [27]. The consumption of HO$^{-}$ was hinder the oxidation of imidacloprid in the system. Thus, it also confirmed that HO$^{-}$ was an important oxidizing substance for the degradation of imidacloprid in DBD processing system.

3.6 Changes of removal efficiency for 24 h after the completion of discharge

Numbered samples, which taken in the imidacloprid degradation process after a certain period of time, were stand for 24 h to study the effect of standing to the degradation. The comparison of the degradation efficiencies was shown in Figure 5b. The degradation of samples after 24 h was slightly higher than the sample in real-time detection, and all group samples have the same change. It may be due to the residual active materials in the degradation solution. It indicated that after degradation, standing is good for better degradation efficiency.
Figure 5 (a) Effect of methanol on imidacloprid degradation; (b) The comparison of degradation after 24 h

4. Conclusions
The results in this study indicated that imidacloprid could be effectively degraded by DBD and applied voltage, pH, conductivity, catalytic ions and alcohol scavenger have apparent effects on degradation of imidacloprid in DBD process. The optimal applied voltage was 75 V and unsuitable voltage could lead to low degradation efficiency even collapsed plasma zone. Alkaline environment and low initial conductivity were conducive to degradation of imidacloprid. Both Cu2+ and Fe2+ could catalyze the decomposition of imidacloprid, moreover the catalytic effect of Fe2+ was better than that of Cu2+. Methanol scavenger could capture HO⦁ effectively and inhibit the degradation reaction, and it also proved the important role of HO⦁ in DBD treatment system.

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