

Degradation of indole in aqueous solution using contact glow discharge plasma

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Received: 28 April 2009 / Accepted: 23 November 2009 / Published online: 2 December 2009
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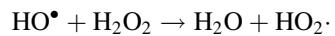
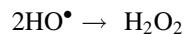
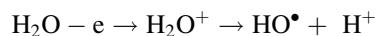
Abstract Exhaustive indole oxidation in aqueous solution was studied using contact glow discharge plasma. The results indicated that the rate of indole degradation increases with the decrease in the solution conductivity. The degradation rate can be enhanced under the following situations. First, the increase in temperature. Second, introduce active carbon and hydrogen peroxide to the solution. Third, the degradation process is performed in alkaline or acidic media rather than the neutral media. Fourth, add Fe^{2+} to solution to undergo Fenton's reaction. However, n-butanol was found decelerate the degradation of indole. Some major intermediates produced during the degradation were detected by using both HPLC and GC-MS.

Keywords Contact glow discharge plasma · Degradation · Plasma · Indole

1 Introduction

Several oxidation techniques such as electrochemical oxidation, ozonation and biological treatment etc. [1–3] have recently attracted a great deal of attention of the environmental chemists. However, not all toxic organic compounds can be degraded in a simple and effective way. The electrochemical oxidation is relatively the most convenient method for oxidation because the most powerful oxidizing

species such as hydroxyl radicals can be easily produced at laboratory. Hydroxyl radicals (HO^\bullet) can directly attack organic compounds leading to the production of CO_2 and H_2O . HO^\bullet can be produced with an anodic reaction using water as the reactant. The mechanism is hypothesized as [4–10] follows:



Currently, most of the researches focus on the degradation of low toxic organic substances, while others are attempted to develop more complicated apparatus including costly boron-doped diamond anodes [10–14]. In the present paper, contact glow discharge electrolysis (CGDE) was employed for the degradation of indole. CGDE is a powerful electrochemical technique which produces plasma directly through the electrical discharge against water. In CGDE, various active species such as hydroxyl radicals, hydrogen peroxide were produced either in the plasma zone or on the plasma/solution interface. These highly activated species can diffuse into the solution to oxidize the pollutants in water. The mechanism in the production of plasma has been studied by Malik et al. [15–19]. Recently, some research studied the degradation of certain target organic compounds in water by using CGDE [17, 18, 20–23]. The results convinced that CGDE was promising in term of the degradation of toxic substances. Heterocyclic nitrogen containing substances are mainly from coking wastewater, petrochemicals, dyes, rubber and other industrial wastes. Some water soluble heterocyclic nitrogen containing substances are highly toxic. In the present paper, indole was chosen as a representative pollutant. A series of experiments were performed along with the

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systematic analysis. The factors that affect the rate of degradation were discussed in detail.

2 Experimental

The experimental apparatus consists of a reactor and a high voltage power supply as is shown in Fig. 1. The reactor vessel contains mainly a dual glass tubes and an electrode system. The reticulating water was introduced to keep the reaction temperature at 20–25 °C. A platinum wire anode (I.D. 0.5 mm) and a stainless steel rod (I.D. 0.5 cm) cathode were set with a distance of 3 cm. The anode was placed in the center of a glass cylindrical reactor, while its needle tip protruded 1 mm from the glass tube. The cathode was inserted through the top of the reactor. A high positive voltage was applied to the anode by a WYJ-1000 V 2 A dc power unit (Shanghai Changjiang Electron Instrument Company) which can provide a voltage of 0–1000 V and current of 0–2 A.

The indole was dissolved in a 1.0 g L⁻¹ potassium sulfate solution [24]. The pH of the solution was adjusted by the diluted sodium hydroxide and diluted sulfuric acid aqueous solution. The concentration of potassium sulfate was adjusted to vary the electric conductivity in solution. During the reaction, a small portion of the solution (roughly 0.1 mL) was periodically taken out from the sampling port. The UV spectra of the sample was performed with a UV–Vis spectrophotometer (Analytic Jena). The intermediates were detected by using GC-MS and HPLC (Shimadzu Company).

The total volume of the reactants were set at 200 mL; the initial concentration of indole was 100 ppm; the applied voltage was 700 V; the pH value of the solution was adjusted at 7.48.

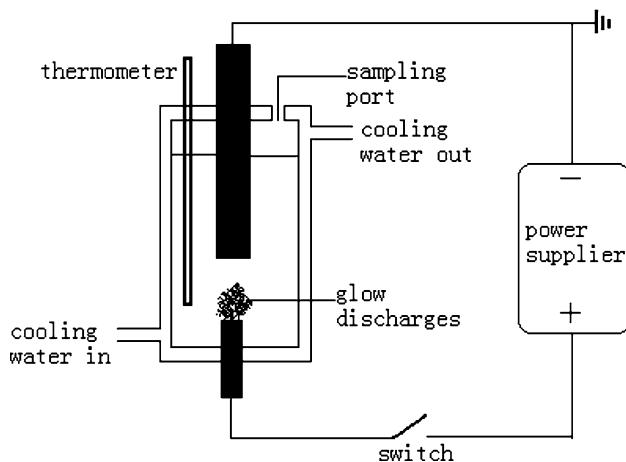


Fig. 1 The schematic diagram of the experimental apparatus

3 Results and discussion

3.1 Effect of the solution electric conductivity

Electric conductivity in the solution can affect the efficiency in the removal of the pollutant. Figure 2 displays the effect of electric conductivity on the removal of indole. The results show that the removal efficiency is increased with the decreasing in the conductivity. This implies that streamers are formed at high electric conductivity which hinders the hydroxyl radicals from being produced. Because glow discharge was discontinuous as the solution electric conductivity was lower than 800 $\mu\text{S cm}^{-1}$, in the present work, the conductivity of the solution was controlled under 1200 $\mu\text{S cm}^{-1}$.

3.2 Effect of the temperature

The removal of indole at different temperatures (293, 306 and 313 K) was observed and the temperature dependence is shown in Fig. 3. The colorless solution first became red

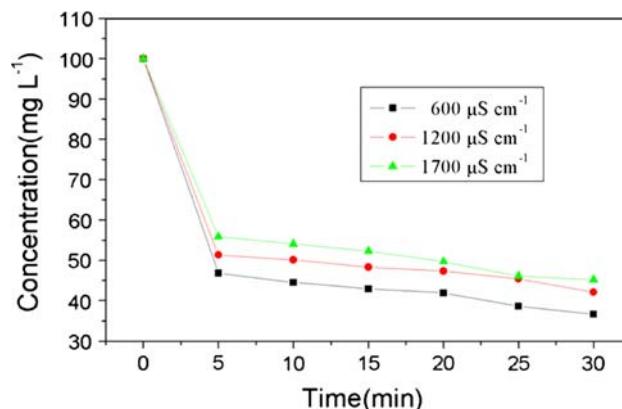


Fig. 2 Effects of solution electric conductivity, ($U = 700$ V, $T = 293$ K, $C_0 = 100$ mg L⁻¹, $V = 200$ mL, pH = 7.48)

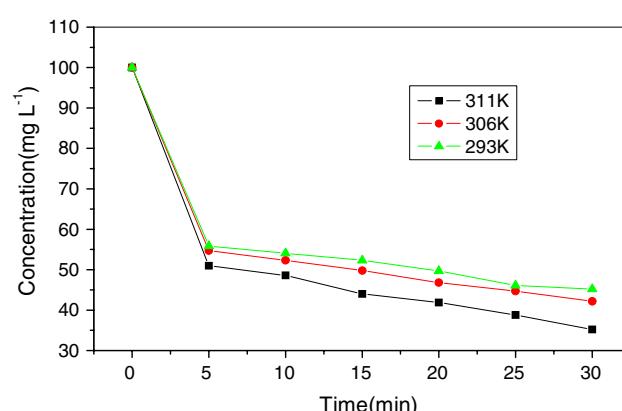


Fig. 3 Effect of the temperature on the degradation, ($U = 700$ V, $C_0 = 100$ mg L⁻¹, $V = 200$ mL, pH = 7.48)

and eventually turned back to colorless within 60 min at 293 K. The same color changing process endured 30 min as the temperature rose to 313 K. This indicates that the increase in the solution temperature favors the degradation of indole. In the present work, the temperature of the solution was controlled at 293 K.

3.3 pH Effects

Given that the pH value often plays an important role in the wastewater treatment, effects of solution pH on the degradation of indole was studied carefully in the present work. The result showed that degradation proceeded much faster in a relatively higher alkalinity or acidity media than in the neutral conditions. Considering that the concentration of $\cdot\text{OH}$ is critical in the degradation process, the observation on the pH dependence indicates that more $\cdot\text{OH}$ might be produced in either acidic or basic conditions. Granted that most industrial wastewater is either acidic or alkaline, the plasma process exhibits its advantage in the treatment of the industrial wastewater without further adjustment of pH value in the solution.

3.4 Effects of active carbon and hydrogen peroxide

In order to find out the effect of catalyst, 100 mg L^{-1} H_2O_2 and 0.5 g active carbon were added into the solution. The results in Fig. 4 indicates the degradation rate of indole is enhanced most in the presence of both hydrogen peroxide and active carbon. The dependence of the degradation rate on the H_2O_2 once again implies that $\cdot\text{OH}$ plays an important role in the indole degradation, because H_2O_2 is a good source for $\cdot\text{OH}$. As for the effect of active carbon, it most likely provides a reaction surface for the degradation.

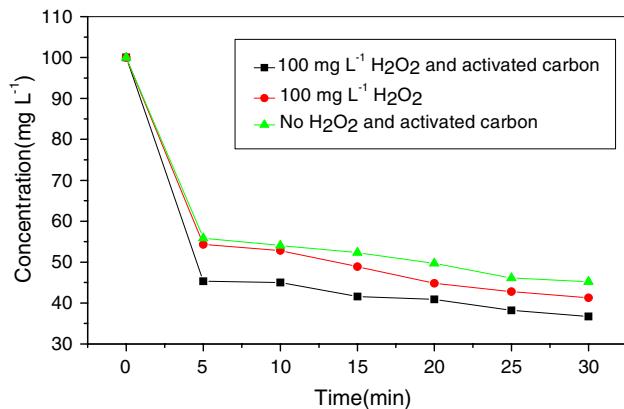


Fig. 4 Effects of activated carbon and hydrogen peroxide, ($U = 700$ V, $T = 293$ K, $C_0 = 100$ mg L^{-1} , $V = 200$ mL, pH = 7.48)

3.5 Effects of n-butanol and ferrous sulfate

Figure 5 indicates that the degradation of indole in the presence of n-butanol and ferrous sulfate. The results show that Fe^{2+} has an obvious catalytic effect for indole degradation. Rapid increase in the reaction rate with the addition of FeSO_4 is likely due to the Fenton's reaction. According to the Fenron's reaction, H_2O_2 can be produced in the presence of Fe^{2+} through discharge. Once again, more $\cdot\text{OH}$ can be produced under this situation, as a result, the degradation process is accelerated [25, 26]. On the other hand, the addition of n-butanol to the system showed a strong inhibition effect on indole degradation as shown in Fig. 5. It is well known that n-butanol reacts with hydroxyl radical with a high rate constant (10^8 L mol $^{-1}$ s $^{-1}$ [4]). Therefore, n-butanol consumed most free $\cdot\text{OH}$ in the solution leading to the deceleration of the degradation of indole.

3.6 Intermediate products and degradation mechanism

In order to better understanding the degradation mechanism, HPLC and GC-MS were used to detect the intermediate products formed in the degradation process. The major intermediates identified by GC-MS are benzoic acid, aniline, paradioxybenzene, benzoquinone, and benzene.

In the early stage of the degradation, some carboxylic acids such as formic, oxalic and malonic acids etc. were formed. Eventually, all of the carboxylic acids formed were decomposed into the carbon in its inorganic forms, such as bicarbonate ions or carbon dioxide molecules. Scheme 1 lists the variation of intermediate products in the CGDE process.

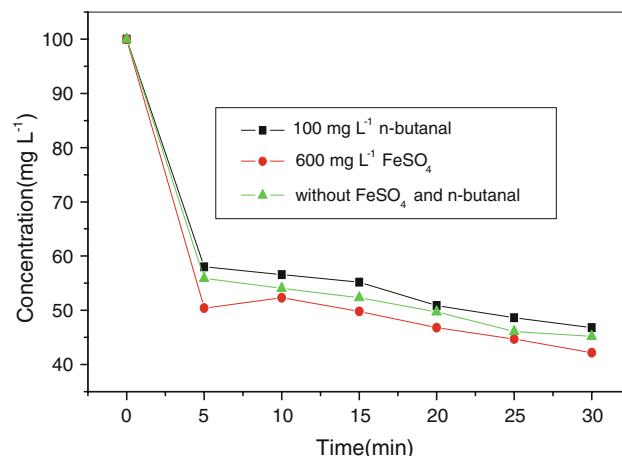
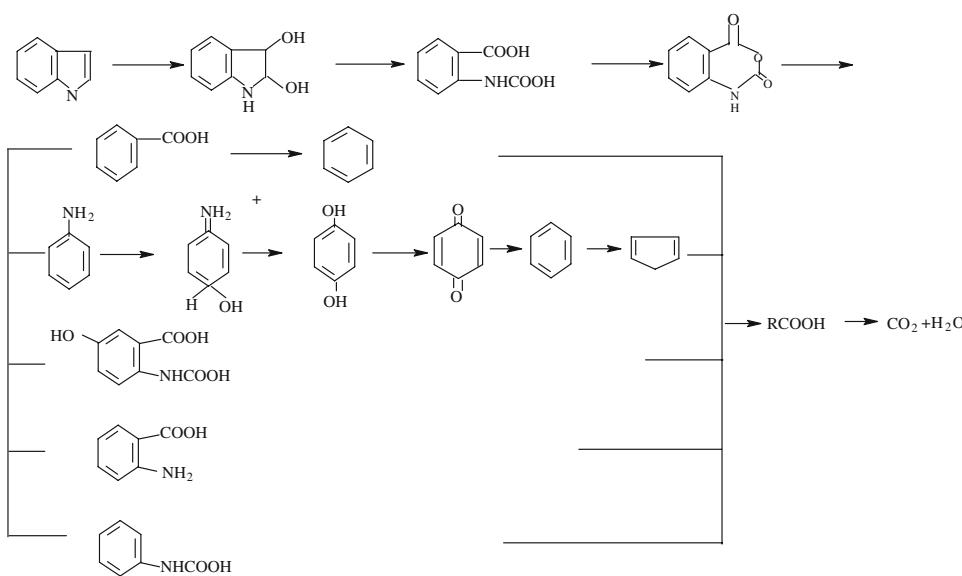


Fig. 5 Effects of n-butanol and ferrous sulfate, ($U = 700$ V, $T = 293$ K, $C_0 = 100$ mg L^{-1} , $V = 200$ mL, pH = 7.48)

Scheme 1 Indole degradation pathway in CGDE



4 Conclusion

Indole can be rapidly and exhaustively degraded by glow discharge electrolysis under water. The final products were inorganic carbon and inorganic nitrogen. The degradation rate was found sensitively depend on the free $\cdot\text{OH}$ concentration in the system. This is consistent with the mechanism quoted earlier in the present paper where the $\cdot\text{OH}$ radicals are most responsible in the degradation of organic compounds. Glow discharge electrolysis under water technique not only provides many accesses to increase the amount of free $\cdot\text{OH}$ radicals in the system, but also showed some advantages in treating some acidic or basic industrial wastewater without further pH adjustment.

Acknowledgments We acknowledge the School of GANSU Province Graduate Student Teacher Research Item Project Stake (No. 0910-04).

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