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Low-temperature plasma-induced degradation of aqueous 2,4-dinitrophenol

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Abstract

The degradation behavior of 2,4-dinitrophenol (DNP) by low-temperature plasma was investigated and the effect of some factors that might affect the degradation process was further examined. The results indicated that DNP could be effectively removed from aqueous solution. The degradation value was 83.6% when the input power was 150 W and 60 s was selected as the discharge time. Increasing the input power increased the degradation efficiency. The degradation process fitted first-order dynamics and the reduction was mainly caused by the reaction of DNP with •OH. The degradation efficiency decreased with the increase of initial concentration at the same discharge time. H_2O_2 at the concentration of 0.25% enhanced the degradation process, however, hindered the degradation at 1.00 and 2.00%. The presence of Fe^{2+} could benefit DNP degradation. However, the increment in degradation efficiency might be suppressed to some extent at a high concentration level. Cu^{2+} inhibited the degradation process within 30 s and enhanced the reduction after 30 s. Furthermore, the increment of Cu^{2+} concentration could enhance the effect. A little acid environment was conducive to DNP degradation and the pH value became lower with increasing discharge time by low-temperature plasma.

Keywords: Degradation; 2,4-Dinitrophenol; Low-temperature plasma

1. Introduction

2,4-Dinitrophenol (DNP) is widely used as raw materials and intermediates in chemical industries for the manufacture of pesticides [1]. Discharge of DNP into the environment poses significant health risks due to its high carcinogenicity [2]. Because of its high stability and solubility in water, the pollution of drinking-water reservoirs and the environment by it is a dramatic problem recently. The U.S. Environmental Protection Agency has listed DNP as "priority Pollutant" [2]. It is noteworthy that the pollution resulting from DNP discharge into the aqueous environment is considered as one of the general problems in the dye industry in China.

Due to DNP's high stability and solubility in water, the conventional technologies used for the purification of wastewaters that contained DNP were not effective [3]. The degradation processes using microorganisms like bacteria were relatively very slow and inefficient [2]. Hence more studies were being concentrated for the development of new methods for DNP degradation. The advanced oxidation process (AOP) was possibly to be an effective technology for treating DNP in wastewater, however, there was some trouble with economics, equipment, or efficiency [4,5]. Contact glowdischarge electrolysis has been employed to destroy DNP in the solution and the results showed that this technology was effective for DNP degradation [6]. Nowadays, low-temperature plasma is widely used in environmental protection field. When the discharge of low-temperature plasma begins, both physical and chemical processes happen [7]. The former could lead to large quantities of UV light and intense shock waves and the later could cause the formations of chemically active species. This technology that integrates light, electronic and chemical oxidation into one process has a collective effect on degrading organic species. The detailed mechanisms are as follows:

(1) The role of high-energy electron. When the discharge begins, high-energy electrons are formed [8]. High-energy

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electrons could react with water in 10^{-7} s and then a lot of radicals are produced [9,10].

$$H_2O \xrightarrow{e} {}^{\bullet}OH + e_{aq}^{-} + {}^{\bullet}H + H_2O_2 + H_3O + H_2 \quad (1)$$

At the same time, the following reactions happen and $O^{\bullet}$ and O_3 are also formed [8].

$$O_2 \xrightarrow{e} 2^{\bullet}O \xrightarrow{H_2O} 2^{\bullet}OH \quad (2)$$

$$O_2 + O^{\bullet} \rightarrow O_3 \quad (3)$$

(2) The role of ozone. When the discharge begins, ozone is also formed. Ozone is of highly solubility in water and reported to be an effective oxidant. Furthermore, it could remove pollutants by $^{\bullet}OH$ formed as follows [11,12]:

$$O_3 \rightarrow O_2 + O^{\bullet} \quad (4)$$

$$O^{\bullet} + H^{+} + e \rightarrow {}^{\bullet}OH(\text{intheacidmedia}) \quad (5)$$

$$O_3 + H_2O_2 \rightarrow {}^{\bullet}OH + O_2 + HO_2^{\bullet} \quad (6)$$

$$O_3 + HO_2^{\bullet} \rightarrow {}^{\bullet}OH + O_2 + O_2^{-} \quad (7)$$

(3) The role of UV light. The efficiency of producing $^{\bullet}OH$ in water only by UV light is very low. But the efficiency is relatively high in the presence of ozone [12]:

$$O_3 + h\upsilon + H_2O \rightarrow H_2O_2 + O_2 \quad (8)$$

$$H_2O_2 + h\upsilon \rightarrow 2^{\bullet}OH \quad (9)$$

e_{aq}^{-} and $^{\bullet}H$ are subject to be scavenged by dissolved oxygen in water [10] and $^{\bullet}OH$ is the most oxidative radical among these radicals mentioned above. So, $^{\bullet}OH$ is the main radical that is responsible for the degradation of pollutants.

The degradation behavior of DNP by low-temperature plasma has not yet been studied and it was possibly different from that by contact glowdischarge electrolysis. The purpose of the present study was to investigate the possibility of DNP degradation from aqueous solution by low-temperature plasma. Furthermore, the degradation processes of DNP in the presence of H_2O_2, Fe^{2+} and Cu^{2+} were also examined.

2. Experimental

2.1. Experimental apparatus

The experimental apparatus was bought from Nanjing Suman Electronics Co., Ltd., PR China and shown in Fig. 1. It consisted of a reaction cell (DBD-50) and a power supplier (CTP-2000 K) that could provide a steady voltage of 100 V. The reaction cell, which was between the high voltage electrode and ground electrode, consisted of two parts. The upper part of the reaction tank was a little bigger than the lower part. The lower part was used to contain the solution, which was 84 mm in inner diameter, 88 mm in outer diameter and 6 mm in height. The reaction tank was put in the center of the two electrodes. The power was supplied by an AC source, which could be operated at an adjustable amplitude voltage. The intensity of discharge in the reaction tank could be denoted by the input power, which was calculated by the average voltage and current of the AC power. The dielectric barrier was made of quartz.

2.2. Chemicals and reagents

DNP was obtained from Shanghai Chemicals Factory and used without further purification. Methanol used in the analysis was HPLC grade. All chemicals were of reagent grade with purity higher than 99%.

2.3. Sample preparation

DNP solution at initial concentration of 0.025 mmol L^{-1} was used to test the effect of input power, 2-propanol, *tert*-butanol, H_2O_2, Fe^{2+}, Cu^{2+} and initial pH value on the degradation and to examine the change of pH value by low-temperature plasma. The input power of 150 W was employed to investigate the effect of 2-propanol, *tert*-butanol, DNP initial concentration, H_2O_2, Fe^{2+}, Cu^{2+} and initial pH value on the degradation and to determine the change of pH value by low-temperature plasma. The pH value of the solutions was adjusted using HCl (0.01 mol L^{-1}) or NaOH (0.01 mol L^{-1}) solution. All the samples were treated at the voltage of 100 V.

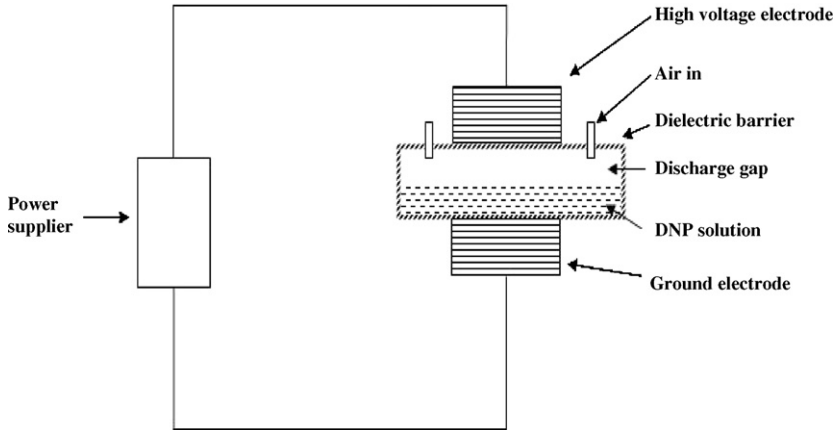

Fig. 1. Scheme of the experimental apparatus.