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Pulsed plasma processing of organic compounds in aqueous solution

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Abstract

Non-thermal plasma processing using a pulsed electrical discharge has been investigated as an alternative method for the degradation of organic compounds contained in water. The active species produced by the electrical discharge may play an important role in degrading organic compounds in water. Three types of electrical discharge formed by the needle-plate electrode system were used in this investigation. The degradation of phenol by electrical discharge with the effects of the addition of gas bubbling and chemicals on degradation efficiency was investigated. The results showed that the degradation rate of phenol was affected by electrical discharge types and oxygen gas bubbling. The addition of a small amount of hydrogen peroxide greatly increased the degradation rate of phenol, in which the ultraviolet light from discharge plasma was considered to be a cause of effective degradation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Discharge types; Streamer discharge; Spark discharge; Spark with streamer discharge; Photolysis; Phenol degradation

1. Introduction

Recently, the development of advanced oxidation technologies (AOTs) for the treatment of hazardous chemical wastes has grown rapidly. Several techniques of AOTs, such as electron-beam irradiation [1], TiO_2 photocatalysis [2], photolysis of O_3/H_2O_2 with UV [3], and sonochemistry [4,5] involve an energy input to aqueous solution to produce highly active species, especially OH radicals. They play an important role in degrading organic contaminants in wastewater. However, they have a common problem in that producing radicals may consume significant energy. Non-thermal plasma processing in aqueous solution by applying a pulsed high voltage is considered to be an energy efficient method for the production of highly active species.

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The development of non-thermal plasma AOTs processing in water was started by Clements et al. [6] on pulsed streamer corona discharges generated in water. Related to this topic, a numbers of paper have been published. Sharma et al. [7] and Joshi et al. [8] reported the oxidation of phenol in water solution by pulsed streamer corona discharge. Willberg et al. [9] reported the oxidation of 4-chlorophenol, 3-4 dichloroaniline, and 2,4,6-trinitrotoluene by pulsed arc discharge. Sato et al. [10] and Sun et al. [11] investigated active species produced by pulsed streamer corona discharge.

A basic mechanism of non-thermal plasma in electrical discharge processing for the treatment of hazardous wastewater is considered to be the formation of a strong electric field and a strong non-thermal plasma where high-energy collisions of molecules with electrons generate free radicals and low-energy electrons. Pyrolysis, ultraviolet photolysis, electrohydraulic cavitation and supercritical water oxidation occur in these plasma channels [9], and generate various active species such as $^{\bullet}OH$, $^{\bullet}O$, $^{\bullet}H$, O_3, etc [6,7]. They subsequently

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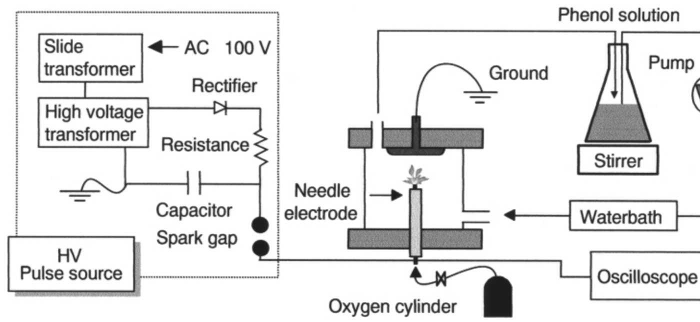

Fig. 1. Schematic diagram of experimental apparatus.

react with the chemical contaminants and degrade them from aqueous solution.

On the other hand, Clements et al. [6] have shown that pulsed corona discharges in aqueous solutions with oxygen bubbling into the reactor produce a large amounts of ozone. It may attack chemical pollutants and may decompose to form hydroxyl radicals [12] which can oxidize chemical compounds.

Since many physical and chemical phenomena occur with electrical discharges, it is important to investigate each phenomenon affecting the oxidation processes in order to achieve an efficient method for the treatment of hazardous wastewater. In the present paper, the effect of electrical discharge types, oxygen gas bubbling and chemical additives on the degrading of an aqueous phenol solution was investigated. In our experiments, three types of electrical discharge forms were used: i.e. streamer discharge, spark discharge, and spark with streamer discharge (combined), and a small amount of hydrogen peroxide was added into the reactor.

2. Experiment

A schematic diagram of the experimental apparatus is shown in Fig. 1. A rotating spark-gap switch was used to generate high voltage pulse. The pulsed power supply consisted of a slide transformer (1 kVA), voltage rectifying circuit, rotating spark-gap, and storage capacitor (6000 pF). The pulse output voltage and current were measured with a high-voltage probe (Tektronix P6015A) and a wide band current transducer (Pearson Electronics M411). The discharge parameters were monitored by a digital oscilloscope (Tektronix TDS360).

The needle-plate electrode was placed in the center of a Plexiglas cylinder (45 mm inner diameter) for generating a pulsed electrical discharge in water. A stainless steel tube needle (0.5 mm inner and 1.5 mm outer diameter) was used that protruded 1 mm from insulator (silicone compounds). The plate electrode was stainless steel of 30 mm diameter and the separation distance between the needle and plate was varied; with 6 mm for spark discharge, 15 mm for spark with streamer discharge (combined), 45 mm for streamer discharge.

The applied voltage was 20 kV with a frequency of 50 Hz. Liquid sample was prepared by dissolving 50 mg phenol into 1 l of distilled water. A little KCl was added into the solution in order to change the liquid conductivity. Since the liquid conductivity has a large effect on the streamer production and propagation. Clements et al. [6] have reported that the streamer length decreased with increasing liquid conductivity. In this investigation, 200 and 250 $\mu S/cm$ initial liquid conductivity was used, respectively. Oxygen gas was continuously injected into the reactor through the tip of the needle electrode. The solution was analyzed using high performance liquid chromatography (Shimadzu, LC-9A).

3. Results and discussion

3.1. Effect of electrical discharge types on phenol degradation

Fig. 2 shows the degradation of phenol with various electrical discharge types. From the figure, it is possible for each type of electrical discharge to degrade phenol from water solution. As a result, the spark discharge showed high degradation rate at the beginning, but the spark with streamer discharge (combined) was found to be effective for the complete degradation of phenol.

This result could be explained as illustrated in Fig. 3; in the case of streamer discharge, there are many plasma channels formed in the liquid, but the energy is rather weak, where only a little reaction could occur by the streamer discharge. Therefore, a small amount of radicals may be produced to attack phenol molecules. Hence, the degradation rate of phenol with streamer discharge was found to be slow.

In the case of spark discharge, a single plasma channel is formed in the liquid, but the energy is very strong, which seems to be ultraviolet light source. During the formation of plasma channels, a strong shockwave is generated in aqueous solution. The highly

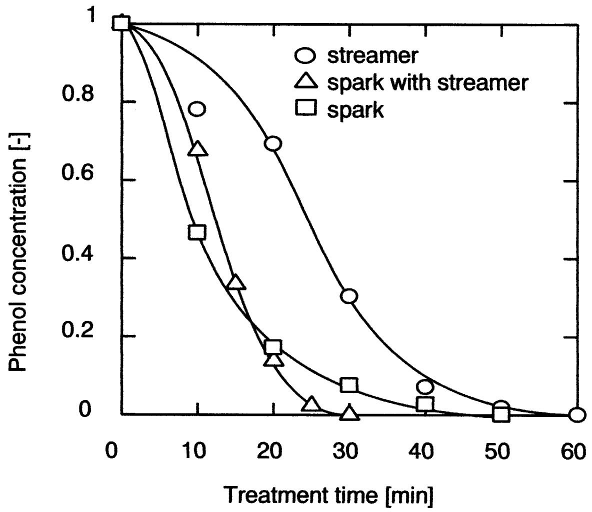

Fig. 2. Degradation rates of phenol with various electrical discharge types (liquid conductivity = 200 μS/cm).

energetic electrons in the plasma channels, strong ultraviolet radiation and shockwaves are very effective in exciting and ionizing the water molecules, and, therefore, more radicals are formed in the spark discharge compared to the streamer discharge. For these reasons, the phenol degradation rate became much higher than the case of streamer discharge.

On the other hand, in the case of spark with streamer discharge (combined), there are many plasma channels produced. Their energy seems to be strong, and the channels are more stretched than in the other cases. Since the distribution of active species occurred mainly around the plasma channels [11], a large number of plasma channels with strong energy would be very effective to generate a large number of active species. As shown in Fig. 2, the degradation rate of phenol was found to be effective by spark with streamer discharge compared to the other cases.

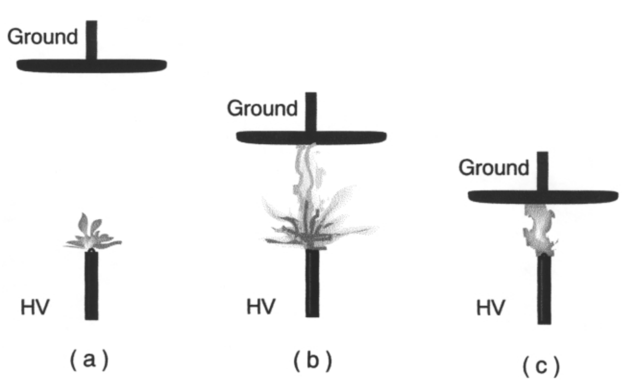

Fig. 3. Illustrated of three electrical discharge types on removal streamer discharge with electrode gap 45-mm spark with streamer discharge with electrode gap 15-mm spark discharge with electrode gap 6 mm.

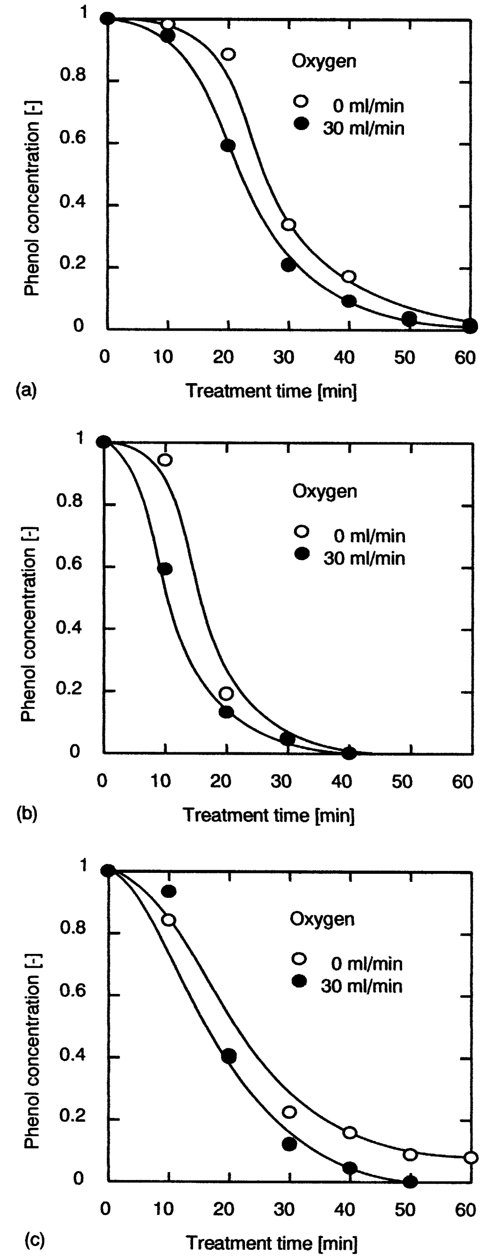

Fig. 4. Degradation rates of phenol with various electrical discharge in the presence of oxygen gas bubbling streamer discharge spark with streamer discharge spark discharge (liquid conductivity = 250 μS/cm).

3.2. *Effect of gas bubbling on phenol degradation*

Fig. 4 shows the degradation of phenol by various discharge plasma types with oxygen gas bubbling into the reactor. Oxygen gas was bubbled into the reactor at 30 ml/min. For all discharge plasma types, the degradation rate of phenol became higher when the oxygen gas was bubbled into the reactor. The ozone was decomposed by UV light or energetic electrons to form O and OH radicals though a series of chain reaction [12], which could attack and degrade organic compounds.

3.3. Effect of chemical additives on phenol degradation

The chemical effects of the electrical discharge plasma are due to direct photolysis (the electrical discharge plasma only), indirect photolysis (combination of chemical additives and the electrical discharge plasma) and pyrolysis destruction in plasma channels [9]. The photolysis could be due to the ultraviolet radiation. A part of vacuum ultraviolet in the region of the spectrum $\lambda = 75-185$ nm is absorbed by the water layer surrounding the plasma channels [13,14], but the ultraviolet (region of the spectrum $\lambda > 185$ nm) expands into the bulk of solution, then it reacts with organic contaminants in aqueous solution.

Fig. 5 shows the degradation of phenol by various discharge plasma types at the presence of hydrogen peroxide. Hydrogen peroxide (100 mg/l and 1000 mg/l) was added into the reactor. As shown in the figure, the degradation rates of phenol became higher when hydrogen peroxide was added, and their concentration was also increased.

Since the reaction of phenol with hydrogen peroxide is very slow at the ambient temperature; the degradation process may be due to the reaction of hydroxyl radicals formed by photolysis of hydrogen peroxide, caused by ultraviolet radiation from electrical discharge plasma. This process has been described by many authors [3,15]:

$$H_2O_2 + hv \rightarrow {}^{\cdot}OH + {}^{\cdot}OH \quad (1)$$

In Eq. (1), 1 mole of H_2O_2 produces 2 moles of hydroxyl radicals by ultraviolet light. Therefore, a large number of hydroxyl radicals are produced in the reactor, the effective degradation of organic contaminants may occur in aqueous solution.

In the presence of hydrogen peroxide, the degradation rate of phenol was found to be very high in the case of spark discharge. This is because the spark discharge produces very strong ultraviolet radiation compared to the other cases. Approximately 30% of the plasma energy is radiated in the UV spectrum according to Robinson [14], and then a large number of hydroxyl radicals can be produced in the reactor.

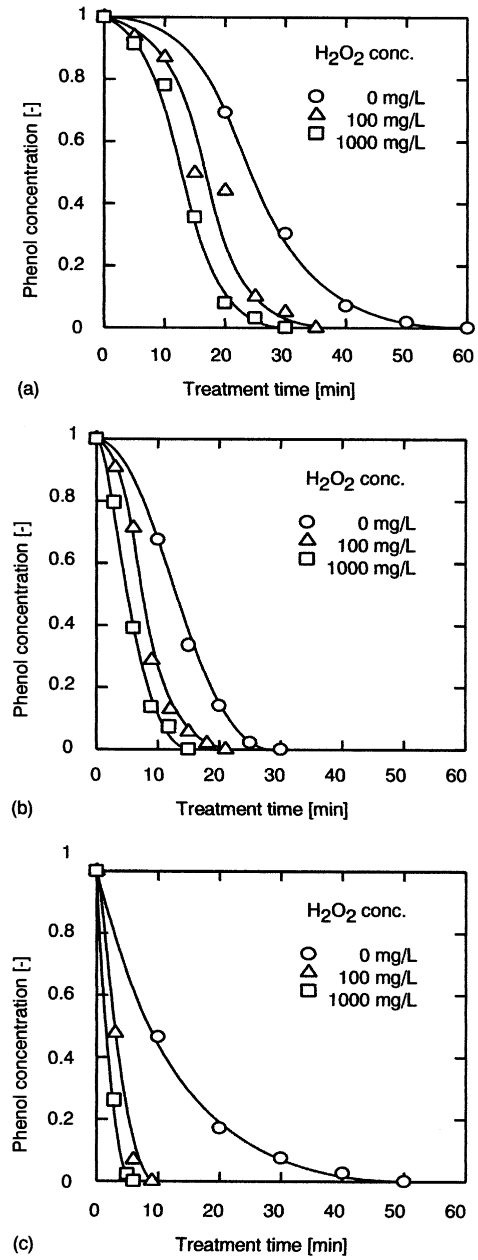

Fig. 5. Degradation rates of phenol with various electrical discharge in the presence of hydrogen peroxide streamer discharge spark with streamer discharge spark discharge (liquid conductivity = 200 μS/cm).

4. Conclusions

The effects of the discharge types, oxygen gas bubbling, and chemical additives on the degradation of phenol in aqueous solution were studied experimentally using a needle–plate electrode system. The results obtained in the present study are:

1. The degradation rates of phenol were affected by electrical discharge type. The spark with streamer discharge was found to be effective for degrade phenol completely.
2. Oxygen gas bubbling into the reactor greatly affected the degradation of phenol. The addition of oxygen enhanced phenol degradation rate.
3. The chemical additives (hydrogen peroxide) into the reactor led to a dramatic increase in the phenol degradation rate. The mechanism behind the increase of the degradation rate was due to the photolysis of additives.

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