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Application of TiO_2 nanotubes with pulsed plasma for phenol degradation

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HIGHLIGHTS

- ▶ TiO_2 nanotubes film was applied with streamer discharge along water surface.
- ▶ TiO_2 nanotubes film has high photocatalytic activity and long usage life.
- ▶ The formation of activity species such as H_2O_2 was enhanced by plasma/TiO_2 system.
- ▶ The byproducts of phenol were analyzed to analyze the synergistic effect of plasma/TiO_2 system.
- ▶ High energy utilization efficiency was obtained during the plasma/TiO_2 system.

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ABSTRACT

This report describes a method for phenol degradation by photocatalysis using a streamer discharge above the liquid surface combined with a film of TiO_2 nanotubes. The removal efficiency was about 98% after a 60 min reaction when a 20 kV discharge was combined with the film of TiO_2 nanotubes. The removal efficiency was only 60% with discharge alone. The phenol degradation was fitted to a pseudo-first-order kinetic model. The energy utilization efficiency of the phenol oxidation was higher for the plasma/TiO_2 photocatalysis system due to the synergy effect between the plasma discharge and the photocatalysis. The film of TiO_2 nanotubes was calcined at 673 K. The degradation rate was significantly enhanced by the presence of TiO_2. The crystal structure and surface morphology of the TiO_2 showed no change after use and the photocatalytic activity of TiO_2 was not affected. Higher concentrations of hydrogen peroxide and some intermediates from phenol oxidation were obtained using the combined plasma/TiO_2 photocatalysis system.

1. Introduction

The use of pulsed high voltage discharge plasma is one of several Advanced Oxidation Processes (AOPs) that has been widely used in the treatment of persistent liquid phase organic pollutants [1]. During the pulsed high voltage discharge in the liquid, chemical and physical effects are induced [2,3]. Active chemical radicals, such as $^{\cdot}OH$, $O^{\cdot}$, $H^{\cdot}$, $O_2^{\cdot}$, $^{\cdot}HO_2$, and molecular species such as H_2O_2 and O_3, formed during the chemical effect have been considered to directly degrade the pollutants. In addition, pyrolysis, ultraviolet degradation and ultrasonic degradation have also been used to destroy pollutants using a pulsed discharge system. However, the physical properties of the discharge, especially for the ultraviolet, are not fully utilized for the degradation of pollutants.

Titanium dioxide (TiO_2) is extensively used for photocatalytic degradation in water or wastewater [4]. It is a semiconductor that absorbs UV light with wavelengths shorter than 385 nm to promote an electron (e^-) from the valence band to the conduction band. Fujishima et al. [5] indicated that even a few photons (i.e. as low as 1 $\mu W\ cm^{-2}$) can be sufficient to induce reaction on the surface of the TiO_2 photocatalyst. During the excitation process, a positively charged vacancy or hole (h^+) can generate several active species, such as $HO^{\cdot}$ and $O_2^{\cdot}$, to mineralize the pollutants in water. In addition, the reaction rate has been shown to increase linearly with light intensity at low intensities (<25 mW cm^{-2}) [6]. Clearly, even though the UV intensity produced in the microdischarge is small [7], it can activate the TiO_2 catalyst. In order to improve the utilization efficiency of ultraviolet light in a plasma system, the photocatalysis technology is combined with plasma discharge and their combined effects on the degradation of pollutants has been investigated.

TiO_2 powder (P-25) has already been used in high voltage discharge systems [8–11]. Subsequently, instead of using powdered TiO_2, the effects of films loaded onto glass beads [12–15] or active carbon fibers [16,17], and TiO_2 particles [18], have been studied in

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