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Optimizing degradation of Reactive Yellow 176 by dielectric barrier discharge plasma combined with TiO_2 nano-particles prepared using response surface methodology

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ABSTRACT

The central composite design (CCD) was applied to optimize the preparation conditions of nano-particle TiO_2 photocatalysts in plasma catalysis system. The prepared TiO_2 photocatalysts were used to degrade C.I. Reactive Yellow 176 (RY176) in combination with dielectric barrier discharge (DBD) plasma. Their photocatalytic activity was studied by degradation efficiency of RY176 in aqueous solutions. The individual and interactive effects of the four main independent parameters (molar ratio of acetic acid to titanium butoxide, molar ratio of water to titanium butoxide, calcination temperature and calcination time) on the photocatalytic activity of nano-TiO_2 photocatalysts could be investigated by the CCD and the optimum value was found to be 2, 3.42, 577.60 °C and 3.25 h, respectively. The degradation efficiency of RY176 treated by DBD plasma combining nano-TiO_2 (0.1 g/L) prepared under these preparation conditions was 83.54%, which was 17.33% higher than that of the value (66.21%) only treated by DBD plasma under same operation condition. The decrease of peak intensity in the UV–vis spectrum indicated that degradation of dye took place in plasma catalysis system. The XRD results showed that the TiO_2 nano-particles prepared under the optimal conditions had a mixed crystal structure containing anatase phase (77.4%) and rutile phase (22.6%) and the particle size was 18.2 nm. SEM and TEM images defined the nanocrystalline nature of the prepared TiO_2.

1. Introduction

Azo dyes are the largest class of synthetic dyes widely used for textile dyeing because of its cost effectiveness, the variety of colors available [1] and large amounts of dyeing wastewater that are generated by the textile industry. Reactive azo dyes are characterized by the presence of one or more azo bonds (–N=N–) in association with one or more aromatic systems [2,3]. These dyes are specifically designed to withstand long-term exposure to various environmental conditions due to its complex chemical structure. Some conventional water treatment processes such as conventional biological (*e.g.*, activated sludge) or physico-chemical (*e.g.*, adsorption) treatment process had been put into use [4], which was restricted to transfer dye pollutants from solid phase to the liquid or gas phase. Not only did it not completely eliminate the dye pollutants and chemicals, but also it would cause the dyeing wastewater accumulation and secondary pollution. Consequently, in order to remove dyes from the dyeing wastewater before discharging it to the environment, a better and more appropriate method of treating dyeing wastewater is needed.

For the past few years, novel methods, especially advanced oxidation processes (AOPs) have attracted considerable attention to the treatment of dyeing wastewater that are non-biodegradable and toxic to microorganisms [5,6]. More recently, among the AOPs, low temperature plasma technology has gradually become a remarkable new technique in the field of environmental protection. The low temperature plasma discharging in water is effective in the formation of chemically active species such as radicals (•OH, •O) and molecules (H_2O_2, O_2, O_3) [7], which play an important role in damaging harmful organic pollutants in dyeing wastewater [8].

The methods of generating low-temperature plasma applied to the wastewater treatment are mainly high voltage pulse discharge [9], glow discharge [10], gliding arc discharge [11] and DBD [12]. Among them, DBD has the characteristics of stability, uniformity and high safety, which was especially suitable for the treatment of dyeing wastewater [13].

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Reddy [14] reported that the DBD was an efficient technology for the removal of dye and showing good performance. The study about examining degradation of 13 different textile dyes in a pilot DBD plasma batch reactor was conducted by Tichonovas [15]. The high voltage pulsed DBD was utilized by Huang [16] to decolorize dyeing wastewater and the results showed that appropriate conductivity played a role in chroma removal. Mok [17] conducted a research that a wastewater treatment system was designed to utilize both ozone and ultraviolet light generated in the DBD reactor for the degradation of organic contaminant. The DBD reactor was immersed in the wastewater that was grounded and the wastewater could act not only as an electrode but also the cooling medium for the DBD reactor.

Although the DBD technology had high degradation efficiency, there still existed many problems. For example, energy utilization efficiency was less efficient and some strong oxidizing particles, ultraviolet light and electromagnetic wave generated in discharge process could not be fully utilized. So the combination of catalytic technology and DBD technology was considered to degrade dyeing wastewater.

TiO_2 as an effective photocatalyst with photochemical and photoelectrochemical properties had been applied in plasma catalysis system [18]. The TiO_2 with UV light irradiation leads to the formation of excited-state conduction band electron (e^-) and valence band hole (h^+) pairs, which are capable of initiating a large variety of oxidation and reduction reactions. The main reactions in the cooperative system include [19,20]:

$$TiO_2 + h\upsilon \rightarrow e^- + h^+ \quad (1)$$

$$h^+ + H_2O \rightarrow H^+ + OH\cdot \quad (2)$$

$$e^- + O_2 \rightarrow O_2^- \quad (3)$$

$$O_2^- + H^+ \rightarrow HO_2 \quad (4)$$

The generated hydrogen peroxide in the solutions enhances according to the following reactions:

$$e^- + H_2O_2 \rightarrow OH\cdot + OH^- \quad (5)$$

$$h^+ + H_2O_2 \rightarrow H^+ + HO_2 \quad (6)$$

Besides, hydrogen peroxide can be damaged into two hydroxyl radicals by absorbing photons:

$$H_2O_2 + h\upsilon \rightarrow OH\cdot + OH\cdot \quad (7)$$

In order to get the optimum synergetic effects of catalytic oxidation between DBD plasma and TiO_2, the preparation conditions of TiO_2 in the plasma catalysis system must be optimized with the degradation efficiency of dyeing wastewater taken as index. A statistical-based technique commonly called the response surface method (RSM) as a powerful experimental design tool has been used to the Fenton [21], solar photo-Fenton [22,23], photo-Fenton [24], peroxi-coagulation [25], solar photoelectro-Fenton [26] treatments of some organic compounds. However, so far as we know the research that RSM with central composite design (CCD) which used in plasma catalysis system have been less reported domestically and abroad.

In this paper, CCD was adopted to optimize the preparation conditions of TiO_2 *via* sol–gel method, which was combined with DBD plasma to degrade RY176 and investigate the factors that influenced its photocatalytic activity. Degradation efficiency of RY176 was chosen as the dependent factor (response) and molar ratio of acetic acid to titanium butoxide, molar ratio of water to titanium butoxide, calcination temperature and calcination time were selected as variables. The optimal preparation conditions of TiO_2 were also determined from the model obtained *via* experimental data. The prepared TiO_2 nano-particles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

2. Materials and methods

2.1. Materials

RY176 of 55% purity were kindly supplied by Shandong Qing Shun Chemical Co., Ltd. China. The detailed chemical structure was provided in Fig. 1. Titanium butoxide was reagent grade and acitic acid, ethyl alcohol, hydrochloric acid were of analytical grade purchased from Sigma-Aldrich and Merck products. Aqueous solutions were prepared by using double distilled water.

2.2. Experimental procedure

The TiO_2 nano-particles were prepared by sol–gel method. At room temperature, 17.6 mL of titanium butoxide was added to a mixture of 38.9 mL ethyl alcohol and 8.6 mL acitic acid drop-wise at a rate of 1 mL/min under vigorous stirring for 90 min. Then a mixture of 19.4 mL ethyl alcohol and 3.6 mL deionized water was added dropwise with its pH 3 adjusted by hydrochloric acid under vigorous stirring for 60 min. The prepared solution was kept under dark condition for nucleation process for 12 h. It was then gelated in an oven at 60 °C for 12 h. The gel was dried at 60 °C and subsequently the resulting material was powdered and then calcined in a muffle furnace at 500 °C for 3 h. The obtained photocatalysts were ground in agate mortar before further analysis or use.

DBD combined with the prepared TiO_2 was used to degrade RY176 in water. The schematics of the experimental setup were given in Fig. 2. The main device used to treat the RY176 solution was DBD reactor containing a quartz reaction kettle and electrodes. The top of the reaction kettle was dielectric material and its diameter and thickness were 90 mm and 0.5 mm respectively. The reaction tank containing the solution was 6 mm in height. The reaction kettle was placed in the center of two aluminum electrodes. The frequency of alternating current high-voltage power supply of this experiment was 50 Hz. The adjusting output frequency and voltage was 5–20 kHz and 0–20 kV, respectively. Output of current sampling resistance and capacitor were 50 Ω and 0.47 μF, respectively. The intensity of discharge in the reactor depended on the input power, which was fixed at 70 W. The RY176 solution (200 mg/L) was prepared in double distilled water. For each run, 10 mL of solution was added to the reactor and 0.1 g prepared TiO_2 as a photocatalyst was placed in RY176 solutions. The gas above the water surface in the reaction tank was ambient air.

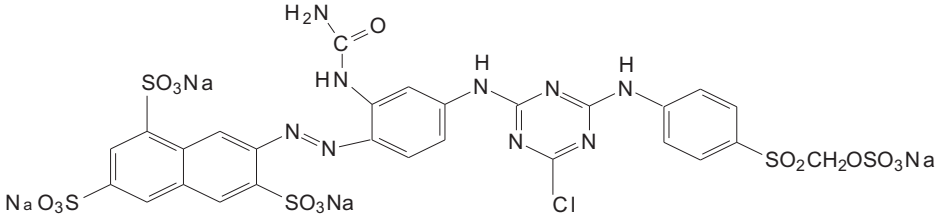

Fig. 1. Chemical structure of RY176.