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Aqueous tetracycline degradation by non-thermal plasma combined with nano-TiO_2

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HIGHLIGHTS

- Non-thermal plasma technology was firstly applied to treat TC wastewater.
- The nano-TiO_2 showed efficient synergistic activity with pulsed discharge plasma.
- Identification of intermediates and pathway of TC degradation were evaluated.

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ABSTRACT

The combined application of nanoscale TiO_2 and corona discharge plasma for the degradation of tetracycline (TC) in aqueous solution was tentatively investigated. The anatase TiO_2 was synthesized by sol–gel method. The basic characteristics of TiO_2 were analyzed by XRD, SEM, TEM, BET and XRF. The catalytic property, the decomposition intermediates and the degradation pathway of aqueous TC were also evaluated. The results showed that the nano-TiO_2 exhibited excellent catalytic effects on TC degradation. 250 mL TC with initial concentration of 50 mg L^{-1} could be remarkably improved from 61.9% to 85.1% in 24 min at input discharge power of 36.0 W relative to the TiO_2 cooperated as 1.5 g L^{-1}. Meanwhile, the total organic carbon was eliminated from 25.3% to 53.4%. The synthesized catalyst could embody a considerable synergism with the corona discharge plasma in removing TC, and a possible degradation pathway of TC was derived on the basis of the detected intermediates. This research implied a promising application of degrading TC in wastewater treatment.

1. Introduction

Antibiotics, as a kind of antibacterial compounds, have aroused particular concern because of their excessive application to human beings, agriculture and planting [1,2]. As their ineffective metabolism and low absorption of the treated species, a large number of antibiotics are let off through the excretory system [3–5]. In recent years, the overspend of antibiotics has caused many serious problems, including interfering the photosynthesis of aquatic plants and disturbing the metabolism of microbial community [6,7]. The use of some antibiotics may induce resistance genes among microbe along with the hyperstimulation and the footprint of them rest in the ecological system, the results caused severe effects on human health and environmental balance [8,9].

Tetracycline (TC) is a kind of antibiotic, which has been extensively used in planting and breeding [10]. Specifically, high proportion of TC with different forms would get rich in groundwater, surface water and soil due to their ineffective biodegradability [11] and the conventional technologies to treat antibiotic were limited [12]. As a result, an effective technology attempted for TC degradation has been on the agenda.

Plasma driven by nanosized TiO_2 catalyst is recognized as a potential technology, which has been applied to treat multifarious water contaminant, characterized by high energy utilization, excessive demineralization and less byproduct state [13–15], TiO_2 has also been extensively investigated to dispose biodegradable pollution [16]. Non-thermal plasma technology (NTP) have been widely studied for decades and regarded as one of the potential technologies to purify the pollution of contaminants, the generation of reactive species such as electrons, highly excited atoms, ions, radicals, molecules, shock waves and UV light could embody a promise for controlling pollutant [17,18]. Corona discharge plasma technology, as one of NPT, has played an important

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role in wastewater treatment by motivating active species, such as $\cdot OH$, O_3, $\cdot H$, H_2O_2 and UV light [19,20]. Consequently, the combination of corona discharge plasma and nanosized TiO_2 photocatalyst could be an alternative way to improve the degradation efficiency of organic pollutants in environment system.

The main reaction mechanisms of the plasma catalyst system are showed as follows [21,22]:

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

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

$$H_2O + e^- \rightarrow H^\cdot + \cdot OH + e^- \quad (3)$$

$$e^- + O_2 \rightarrow 2O^\cdot + e^- \quad (4)$$

$$O^\cdot + O_2 \rightarrow O_3 \quad (5)$$

$$H^\cdot + O_2 \rightarrow HO_2^\cdot \quad (6)$$

$$2HO_2^\cdot \rightarrow O_2 + H_2O_2 \quad (7)$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \quad (8)$$

$$O_3 + e^- \rightarrow O^\cdot + O_2 + e^- \quad (9)$$

In this study, TiO_2 nanoparticles were synthesized by sol–gel method and the basic characteristics of the catalyst were studied, TC was selected as the target pollutant for investigating the synergistic effect between corona discharge plasma combined and TiO_2 nanoparticles for the first time. Meanwhile, the intermediates and degradation pathway of TC in this system were also evaluated.

2. Experimental

2.1. Experimental setup

Fig. 1 showed the schematic of plasma-catalyst system experimental setup which included a high frequency high voltage power source, a plasma reactor and a gas delivery system. In this experiment, 250 mL TC solution with the initial concentration of 50 mg L^{-1} was dumped into the plasma reactor and kept reaction time of 24 min. The air, which was supplied by an electromagnetic air pump (ACO-006, Zhejiang dense industrial Co., Ltd., China), was bubbled into the plasma reactor with a velocity of 0.06 $m^3\ h^{-1}$. The air velocity was controlled by an aerometer (LZB-4, Shanghai splendor instrument and meter plant, China), and the discharge region was generated at the interface between air and liquid. Each sample was taken for every 4 min with a small relatable standard deviation.

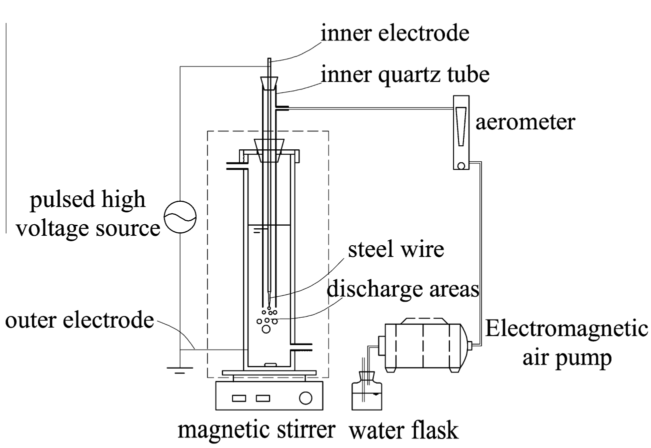

Fig. 1. Schematic diagram of the experimental apparatus.

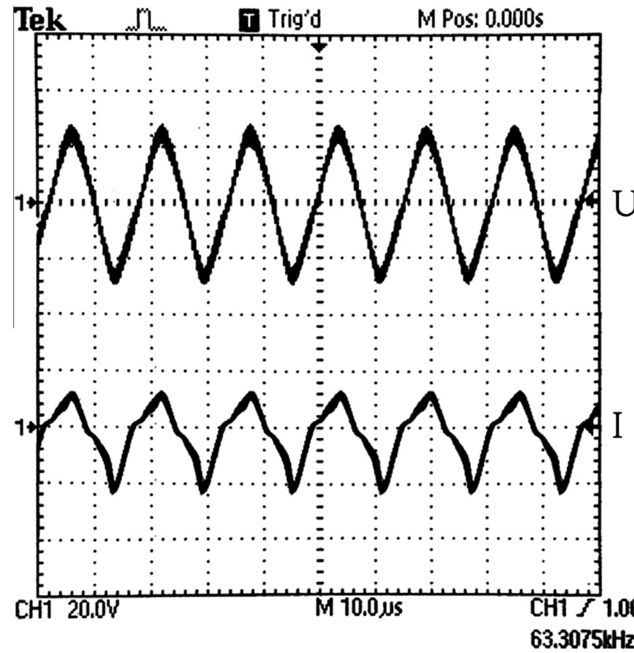

Fig. 2. The current and voltage waveforms in the discharge system.

The plasma reactor consisted of a co-axial organic glass cylinder (60 mm at effective diameter and 250 mm in effective length), with an inner discharge electrode and a quartz tube (diameter: 15 mm), the negative electrode was directly connected with the solution. A copper rod was nested with a steel needle (No. 9), and used as the inner electrode, the discharge was drived by a high voltage AC power source (CTP-2000K, Nanjing Suman Electronics Co., Ltd., China). The air from the aerometer was bubbled through a quartz tube and the catalyst was suspended with a stirring mixer.

Fig. 2 showed a typical waveform of the discharge voltage and current in the reaction system which was tested by an oscilloscope. It could be indicated that the energy transmission property per period displayed a tendency of sine function, the equivalent voltage and current per delivered could be integrated by the region area of corresponding state variables, and the input discharge power could be calculated by the latent relationship.

2.2. Synthesis of nanosize TiO_2

All the chemical reagents in this study were of reagents grade and used without further purification. The nanoscale TiO_2 used in this experiment was prepared by a sol–gel method [23]. 30 mL butyl titanate and 20 mL ethyl alcohol were firstly mixed by magnetic agitating, and then dropwised by 100 mL water solution with ethyl alcohol (25 mL) and acetic acid (25 mL) under stirring. Subsequently, the mixture was stewed for 1 h followed by ultrasonic purifying of 15 min, and then the solution was dried at 80 °C for 12 h. Finally, the film was calcined at 500 °C for 1 h to transfer amorphous TiO_2 to nanostructure.

2.3. Catalyst characteristics

The phase structure and crystallinity of TiO_2 particles were identified by X-ray diffraction (XRD) (Swiss ARL X' TRA) which was recorded over the 2θ from 10° to 80° by step scanning at 5° min^{-1} with Cu Ka radiation (λ = 1.540562 Å) under 40 kV and 40 mA. The morphologies and microstructures of the catalyst