



A mechanism of photocatalytic and adsorptive treatment of 2,4-dinitrophenol on a porous thin film of TiO₂ covering granular activated carbon particles

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ABSTRACT

The present work investigates the mechanism of the photocatalytic and adsorptive treatment of an aqueous DNP (2,4-dinitrophenol) solution in an annular-flow reactor installed with a TiO₂/AC-PET film (a polyethylene terephthalate film adhesively fixing activated carbon particles covered with a thin and porous film of titanium dioxide). Unfortunately, the experimental result indicates that it is impossible to correctly measure the time courses of product ion concentrations because they are adsorbed onto or desorbed from AC particles. Therefore, a computer simulation methodology using mathematical models is introduced in order to elucidate the treatment mechanism. Treatments of aqueous DNP solutions using the TiO₂-PET film reveal that the diffusion of DNP from a bulk solution to a TiO₂ film is based on the gradient of DNP concentration, generated by a rapid adsorption of DNP onto AC and photocatalytic reaction, in the very neighborhood of TiO₂ film, and this diffusion increases the DNP concentration at the surface of TiO₂ film, thereby enhancing the rate of photocatalytic decomposition. Moreover, it is found that the TiO₂/AC-PET film can lower the burden of the adsorption of DNP onto AC compared with the AC-PET film because a part of DNP molecules are photocatalytically decomposed and the percentage of this decomposition is increased at a lower linear velocity. In conclusion, the mathematical model taking into consideration a film-diffusional effect can successfully explain the complicated mechanism of the treatment of an aqueous DNP solution using the TiO₂/AC-PET film.

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1. Introduction

A number of wastewaters containing various kinds of organic compounds are treated by microbial decomposition processes. When the wastewaters contain organic compounds highly toxic to microbial cells, however, introduction of some other method must be considered [1–4]. For example, wastewaters containing 2,4-dinitrophenol (DNP), which is mainly used as a raw material of black dyes, polymerization inhibitor, and wood preservative, significantly restrict cell growth even when the DNP concentration level is of the order of 1 ppm (parts per million). According to the PRTR (Pollutant Release and Transfer Register) data in 2007, it is estimated that DNP of about 0.38 tons per year was released into the environment in Japan [5].

Titanium dioxide (TiO₂) irradiated with UV light can decompose a wide variety of organic compounds to carbon dioxide, water, and mineral acids or their salts [3,6,7]. Hence, the decomposition method using TiO₂ has a potential for the treatment of wastewa-

ters containing toxic organic compounds such as DNP [1,2,4,8–10]. Unfortunately, it is not easy to enhance the rate of photocatalytic decomposition to a level of practical application because TiO₂ does not sufficiently adsorb organic compounds, especially when they are hydrophobic.

To solve this problem, many researchers have attempted to combine TiO₂ with adsorptive materials such as activated carbon (AC) and zeolite particles [4,11–14]. A high photocatalytic activity may be achieved if the surface area of TiO₂ per unit volume is successfully increased. One of the best ways is to completely cover the surface of adsorptive materials with a TiO₂ film in order to get as much field for the photocatalytic reaction as possible. In this case, however, the adsorption ability of AC particles cannot be utilized efficiently.

In a previous work [15], we prepared a TiO₂/AC-PET film, where the surface of AC particles adhesively fixed onto a PET film was completely covered with a porous and thin film of TiO₂ crystal particles in large sizes, and investigated its performance for the treatment of an aqueous DNP solution. As a result, we found that the TiO₂/AC-PET film can rapidly treat it compared to a TiO₂-PET film where the TiO₂ particles were directly loaded onto a PET film. Interestingly, in this reaction system, the rate of a decrease in the DNP concentration by the TiO₂/AC-PET film without UV irradiation was almost

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the same as that by the AC-PET film. This finding implies that the adsorption ability of AC is not weakened in the presence of the TiO₂ film because it is very thin and porous. In addition, the TiO₂/AC-PET film was able to treat a 1.8 times larger amount of DNP than did the AC-PET film until AC on each PET film was saturated with DNP. This experimental fact suggests that DNP may be decomposed at a higher reaction rate by the TiO₂/AC-PET film than by the TiO₂-PET film, because the DNP concentration on the TiO₂/AC-PET film would be more increased by a high attraction force of AC; consequently, the burden of AC adsorption of DNP is lowered and a larger amount of DNP can be treated by the TiO₂/AC-PET film than by the AC-PET film.

The purpose of the present work is to elucidate the mechanism of the photocatalytic and adsorptive treatment of DNP using the TiO₂/AC-PET film. To achieve this purpose, the scheme of the photocatalytic decomposition of DNP is firstly investigated on the basis of the decomposition experiment using the TiO₂-PET film. Secondly, the treatment of DNP using the TiO₂/AC-PET film is experimentally analyzed, which indicates that there is a limitation to experimental elucidation of its mechanism. Therefore, mathematical models are constructed to theoretically elucidate the mechanism of the photocatalytic and adsorptive treatment.

2. Experimental method

2.1. Materials

DNP used as a reactant was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). A nonionic surfactant (polyoxyethylene lauryl ether with a degree of polymerization of 23) used to increase the affinity of an aqueous TiO₂ coating solution to a PET film was also the product of Wako Pure Chemical Industries, Ltd. The coating solution (aqueous H₂O₂ solution) containing anatase TiO₂ fine particle in sizes of 10–25 μm was a product of Sundecor Co. Ltd. (Fukuoka, Japan). The details of this coating solution are described elsewhere [16]. A 6-W blacklight blue fluorescent lamp (Matsushita Electric Industrial Co., Ltd., Osaka, Japan; FL6BL-B) was used as a light source of UV light (wavelengths; 300–400 nm). Granular AC particles in sizes of roughly 1–2 mm were purchased from Japan EnviroChemicals Ltd. (WH2CSS; Osaka, Japan).

2.2. Preparations of TiO₂-, AC- and TiO₂/AC-PET films

Polyethylene terephthalate (PET) films, 0.085 m × 0.195 m in size and 0.01 mm thick, were used as supports of TiO₂, AC and AC coated with TiO₂. The preparation methods are detailed elsewhere [15]. In the following, the PET film covered with a thin film of TiO₂ is referred to as TiO₂-PET film, the PET film where AC particles are adhesively fixed onto its surface is referred to as AC-PET film, and the PET film where the surface of the AC particles adhesively fixed is completely covered with a thin film of TiO₂ is referred to as TiO₂/AC-PET film. The weights of TiO₂ loaded on TiO₂- and TiO₂/AC-PET films were determined to be about 0.09 and 0.12 g, respectively. However, since the measured weight for the TiO₂/AC-PET film includes the weight of water absorbed into AC particles, we consider that there is not remarkable difference between the amounts of TiO₂ loaded on the TiO₂- and TiO₂/AC-PET films.

2.3. Experimental procedures

The removal experiments of DNP from aqueous solutions were conducted in a batch-recirculation system with an annular-flow photocatalytic reactor [17–21] as shown in Fig. 1. The plastic photocatalytic reactor consists of a cylindrical vessel (0.20 m long and 0.0285 m in inlet diameter), a 6-W blacklight blue fluorescent lamp,

a quartz glass tube (0.024 m in outer diameter) used for protection of the UV lamp, and a PET film with TiO₂ and/or AC particles. The photocatalytic reactor was connected with a mixed-flow container via a peristaltic pump (RP-2; EYELA, Tokyo, Japan) as shown in Fig. 1. A reaction mixture flows through an annulus between the inside wall of the cylindrical vessel and the outside wall of the quartz glass tube. The PET film was inserted into the annulus so that it contacts closely to the inside wall of the cylindrical vessel. The volume of the annulus in the photocatalytic reaction zone was $3.7 \times 10^{-5} \text{ m}^3$.

A $5.0 \times 10^{-4} \text{ m}^3$ aqueous solution of DNP at different initial concentrations was poured into the mixed-flow container and then circulated at different flow rates. The UV lamp was switched on to start the photocatalytic reaction. At appropriate time intervals, an aliquot of the reaction mixture in the mixed-flow container was withdrawn to determine the DNP concentration by measurement of an absorbance at 357 nm with a spectrophotometer (Ultrospec 1100Pro; Amersham Biosciences, Sweden). The concentrations of ions (NO₂⁻, NO₃⁻, NH₄⁺, and CO₃²⁻) produced during the DNP decomposition were determined by ion chromatography (ICS 90; Japan Dionex, Osaka, Japan).

3. Mathematical models

3.1. Constitution of reaction systems and characteristics of experimental data

The present work treats DNP solutions in a batch-recirculation mode. That is, a reaction mixture of the volume V_L in a mixed-flow container is circulated by passing through an annular-flow photocatalytic reactor. The rate of recirculation is very large compared to the rate of decomposition (the rate of treatment). Therefore, the present treatment can be approximately regarded as a batch mode, which means that the reactant concentration profile along the reactor can be neglected [22,23]. On the other hand, the experimental data given in a previous paper [15] possess the following characteristics.

- (1) There is no significant difference between the time courses of DNP concentrations in bulk solutions in the treatments of aqueous DNP solutions using the TiO₂/AC-PET film without UV irradiation and the AC-PET film. This means that the thin film of TiO₂ covering the surface of AC particles on the TiO₂/AC-PET film hardly lowers the ability of AC to attract DNP.
- (2) In repeated treatments of aqueous DNP solutions, the amount of DNP required to saturate the AC on the TiO₂/AC-PET is 1.8 times larger than that on the AC-PET film. This means that the burden of the adsorption of DNP on AC is lowered as a result of photocatalytic decomposition of DNP.

The mathematical models to be constructed must be satisfied with these facts.

3.2. Mathematical model for decomposition of DNP using a TiO₂-PET film

In the batch-recirculation annular-flow reactor installed with a TiO₂-PET film, reactant molecules diffuse through a liquid film from a bulk solution to a photocatalyst surface excited with UV light and are then decomposed photocatalytically. The present system is kept at a steady state and the flux of reactant molecules diffusing through the liquid film is equal to the rate of decomposition on the TiO₂ film. Thus, a differential mass balance gives

$$-V_L \frac{dC_b}{dt} = k_{Lp} A_s (C_b - C_p) \quad (1)$$

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