Chemical Engineering Journal 233 (2013) 369–376

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Reaction mechanism of photocatalytic decomposition of 2,4-dinitrophenol in aqueous suspension of TiO_2 fine particles

Rumi Chand, Fumihide Shiraishi *

Section of Bio-Process Design, Department of Bioscience and Biotechnology, Graduate School of Bioresource and Bioenvironmental Sciences, Kyushu University, 6-10-1, Hakozaki, Higashi-Ku, Fukuoka 820-8581, Japan

HIGHLIGHTS

- A mathematical model was proposed for photocatalytic decomposition of DNP in TiO_2 suspension.
- Initial DNP decomposition rate decreased with increasing initial DNP concentration.
- DNP decomposition followed zero-order kinetics in spite of very low initial DNP concentration.
- Nitrate ion was found to strongly inhibit DNP decomposition.
- Calculated results using the mathematical model successfully explained experimental ones.

ARTICLE INFO

Article history:
Received 27 May 2013
Received in revised form 12 August 2013
Accepted 15 August 2013
Available online 30 August 2013

Keywords:
Photocatalytic decomposition
Mathematical model
2,4-Dinitrophenol
Reactant inhibition
Product inhibition

ABSTRACT

The aims of the present study are to propose a mathematical model for photocatalytic decomposition of 2,4-dinitrophenol (DNP) in an aqueous suspension of TiO_2 fine particles and to elucidate the reaction mechanism using this model. The following three facts were found experimentally: (i) although a reactant usually decomposes more quickly at higher concentrations, DNP decomposed more slowly; (ii) photocatalytic reaction usually obeys firstorder kinetics when the initial reactant concentration is approximately 10 g m^{-3}, although the DNP concentration decreased almost linearly according to zeroorder kinetics; and (iii) the resulting NO_3 ion significantly decreased the DNP decomposition rate. A mathematical model constructed by taking into consideration these findings can successfully explain the experimental data, implying that DNP molecules are highly aggregated in the neighborhood of TiO_2 particle. The DNP aggregate layer suppresses the generation of active radicals, which leads to reactant inhibition. The photocatalytic decomposition of DNP supplied from the aggregate layer of highly concentrated DNP around TiO_2 is observed by zero-order kinetics.

1. Introduction

Adding titanium dioxide (TiO_2) particles to organic compounds containing aqueous solution and irradiating it with ultraviolet (UV) light, can easily decompose a wide variety of organic compounds [1–5]. Because this reaction can utilize both artificial light and sunlight as UV light sources, its practical application to wastewater-treatment process is being investigated globally [6–10].

For the practical application of this method, it is necessary to completely understand the mechanism of photocatalytic reactions. However, the mechanisms of different photocatalytic reactions must be studied individually, because the observed reaction patterns in aqueous TiO_2 suspension are different for different organic compounds. The reaction rate is strongly affected by the reactant types, pH of the reaction mixture, coexisting ion species, and so on [11,12]. The surface charge of TiO_2 is another important factor that makes the reaction mechanism difficult to understand. TiO_2 surface can be protonated or deprotonated based on the solution pH, resulting in a change in the surface charge of TiO_2. The isoelectric point for TiO_2 is at pH 6.2 [13]. Hence, TiO_2 surface is positively charged at pH lower than 6.2 and negatively charged above this pH, leading to a change in affinity between the TiO_2 particle and coexisting ion species with change in pH, which in turn remarkably changes the reaction rate [14–16].

Organic compounds with nitro groups are widely used in industry. They are frequently employed as raw materials or intermediates for manufacturing explosives, pharmaceuticals, pesticides, pigments, dyes, wood preservatives, and rubber chemicals. However, some of the phenols with nitro groups have been listed as "Priority Pollutants" by the US Environmental Protection Agency (EPA) because of their hazardous effects on ecosystems and human health [17,18]. For example, 2,4-dinitrophenol (DNP) is hardly destroyed in conventional wastewater treatment; therefore, there is a

* Corresponding author. Tel./fax: +81 92 642 7603.
E-mail address: fumishira@brs.kyushu-u.ac.jp (F. Shiraishi).

1385-8947/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2013.08.069

pressing need for developing an efficient and economical method for treating wastewaters containing DNP [15,16]. Fortunately, TiO_2 based heterogeneous photocatalysis can effectively decompose nitrophenols [19,20].

We have previously investigated both experimentally and theoretically the photocatalytic decomposition of DNP over a TiO_2 film immobilized on a glass surface and found that the decomposition rate is greatly lowered by diffusional resistance in the neighborhood of TiO_2 film [21–24]. On the other hand, there are no reports on the detailed mechanism of photocatalytic decomposition of DNP in aqueous TiO_2 suspension.

In the present study, there, we will observe the decomposition of DNP in aqueous TiO_2 suspension at different initial concentrations and propose a mathematical model for this reaction to elucidate its mechanism.

2. Theory

TiO_2 is positively charged below and negatively charged above its isoelectric point 6.2 [13]. The aqueous DNP solution used in the present study is acidic (nearly pH 4.5), which allows us intuitive prediction that negatively charged DNP molecules are strongly attracted to the surface of positively charged TiO_2 particle and localized around it at significantly high concentration (Fig. 1). The photocatalytic decomposition of DNP in aqueous TiO_2 suspension has the following features.

(1) Although a reactant is usually decomposed more quickly at higher concentrations, DNP is decomposed more slowly.
(2) Although the photocatalytic reaction usually obeys firstorder kinetics at a low level of reactant concentration such as 10 g m^{-3}, the photocatalytic decomposition of DNP exhibits almost linear reduction in the DNP concentration. In other words, it obeys zeroorder kinetics.
(3) The produced NO_3^- ion decreases the rate of photocatalytic reaction.

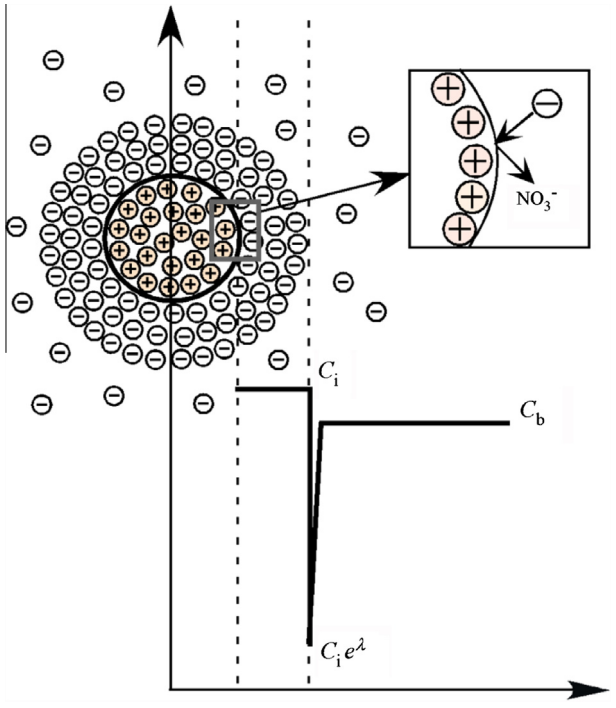

Fig. 1. Schematic of the localization of DNP molecules in the neighborhood of TiO_2 particles.

Thus, the following factors must be taken into account in constructing a mathematical model for the reaction:

(1) DNP decomposition is inhibited by itself.
(2) DNP decomposition apparently obeys zeroorder kinetics.
(3) DNP decomposition is inhibited by NO_3^-.
(4) DNP molecules are highly localized in the neighborhood of a TiO_2 particle and are present at very high concentration.

In order to formulate the partition of DNP molecules between the surface of a TiO_2 particle and liquid solution in its very neighborhood, we will utilize a mathematical modeling approach used to describe an electrostatic effect in an immobilized enzyme reaction [25,26]. When the liquid solution is not mixed well, the DNP molecules must diffuse from a bulk liquid to the TiO_2 surface, so that they are adsorbed on it. In this case, the diffusion occurs by a difference between DNP concentrations in the bulk liquid and in the very neighborhood of TiO_2. When the liquid solution is completely mixed, the DNP molecules can reach the TiO_2 surface quickly by forced convection. If the TiO_2 surface and DNP have charges of opposite sign, the concentration of DNP strongly partitioned onto the TiO_2 surface is significantly higher than that in the very neighborhood of TiO_2.

In mathematical modeling, we will divide the reaction field into two regions, *i.e.*, DNP aggregation and reaction regions. In the DNP aggregation region, DNP molecules aggregate around the TiO_2 particle (designated by the symbol "D") and interfere with the UV excitation of TiO_2 (designated by the symbol "T"), which, in turn, decreases the formation of OH radicals. We will express the process of this reactant inhibition by the following scheme:

$$\begin{aligned} &T + D \rightleftharpoons TD \\ &TD + D \rightleftharpoons TD_2 \end{aligned} \qquad \text{(Scheme I)}$$

In the reaction region, on the other hand, the reactant is constantly supplied from the DNP aggregation region and intermediates (designated by the symbol "I") produced are also consumed as reactants. We will express the reactions taking place in this region by the following scheme.

$$\begin{aligned} &T + D \rightleftharpoons TC \rightarrow T + I_1 \\ &T + I_1 \rightleftharpoons TI_1 \rightarrow T + I_2 \\ &\quad\vdots \quad\vdots \quad\quad\vdots \quad\vdots \\ &T + I_i \rightleftharpoons TI_i \rightarrow T + I_{i+1} + CO_2 \\ &T + I_j \rightleftharpoons TI_j \rightarrow T + I_{j+1} + NO_3^- \\ &T + I_n \rightleftharpoons TI_n \rightarrow T + CO_2 \end{aligned} \qquad \text{(Scheme II)}$$

As a result, this reaction field apparently obeys zeroorder kinetic reaction in spite of very low DNP concentration. Moreover, a part of the nitrate ions NO_3^- produced during the DNP decomposition stays in the neighborhood of TiO_2 and inhibit the reaction as follows:

$$T + NO_3^- \rightleftharpoons TNO_3^- \qquad \text{(Scheme III)}$$

We will thus set up a mathematical model by separating the DNP aggregation region from the DNP decomposition region. When DNP is photocatalytically decomposed in aqueous TiO_2 suspension under UV irradiation, the rate of decomposition of DNP can be described as

$$r = -\frac{dC_b}{dt} = \frac{(w/V_L)k_w K_H C_b}{(e^{\lambda} + K_H C_b)\left(1 + \dfrac{C_{bo}^2}{K_{ir}} + \dfrac{C_{bo}}{K_{ip}}\dfrac{C_{bo-C_b}}{\phi + C_{bo} - C_b}\right)} = (w/V_L)r_w \qquad (1)$$