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Photocatalytic Reduction of Nitrate over Fe-Modified TiO_2

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Abstract

This research work investigated the photocatalytic nitrate reduction under the system using Fe-TiO_2 thin film catalyst with formic acid as the hole scavenger and irradiation with black-light fluorescence lamps. The Fe-TiO_2 thin films with 0.1% weight by volume (w/v) of Fe as dopant were coated onto the 304 stainless steel surface by the sol-gel method. The system showed the overall nitrate removal efficiency of 70.44% with the net photocatalytic nitrate reduction efficiency of 65.97%. The stoichiometric ratio of net formate to nitrate was 2.86 to 1.0, which is close to the theoretical ratio of 2.5 to 1.0 for nitrate reduction to nitrogen gas. The presence of nitrite in the system together with the aforementioned formate to nitrate ratio indicated that the main mechanism of nitrate removal was nitrate reduction to nitrogen gas.

Keywords: Denitrification, Formic Acid, Hole Scavenger, Thin film

1. Introduction

The doping of photocatalyst, especially TiO_2, with metals is a practice widely adopted to improve the photocatalyst activity. Noble metals, such as Pt, Au, Ag, Pd, Rh and Ru, were typically utilized to modify or dope TiO_2-based photocatalysts [1]. The catalysts in suspended form were applied during the aqueous phase photoreactions [2-3]. As noble metals are costly, the low cost metals with similar applicability and comparable performance, such as Fe, were chosen as alternatives [5]. In previous studies, Fe-doped TiO_2 in suspended form was used as photocatalyst for nitrate reduction in the aqueous phase [4-6]. Nonetheless, the

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drawback of the use of suspended photocatalysts is the difficulty of separating the photocatalysts from the solution.

In this research work, Fe-TiO_2 was applied on stainless steel sheets to form thin films. The stainless steel sheets function as the surface for photocatalyst reaction and mixing paddles in the batch reactor. The photocatalyst thin film was prepared by the sol-gel method modified from that of Rojviroon et al. [7]. Typically, the nitrate reduction process requires the addition of organic compound that functions as a hole scavenger to fill electron holes in the valence band. Moreover, it was reported that the most efficient hole scavenger for nitrate reduction over TiO_2 is formic acid [2]. As such, this research paper investigates the efficiency of photocatalytic nitrate reduction over Fe-TiO_2 catalyst with formic acid as hole scavenger; and the stoichiometric requirement of this reaction.

2. Experimental Procedure

2.1. Materials

In this study, titanium tetraisopropoxide (TTIP, > 99.999%, Sigma-Aldrich) and isopropanol (C_2H_7O, > 99.5%, Sigma-Aldrich) were used for the preparation of titanium dioxide nanoparticle. Iron (III) nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$, 99.99%, Sigma-Aldrich) was used as the Fe source. Hydrochloric acid (HCl, 37%, Merck) was used to adjust pH for the preparation of the Fe-TiO_2 solution, while potassium nitrate (KNO_3, > 99%, Merck) was used as the nitrate source for the synthetic water. In addition, formic acid (HCOOH, >95%, Sigma-Aldrich) was used as hole scavenger for the reaction.

2.2. Preparation of Fe-TiO_2

Fe-TiO_2 thin films were prepared by dip coating of Fe-modified-TTIP acid catalyzed sol-gel onto the surface of 304 stainless steel sheets (40.0 x 85.0 x 0.3 mm). Five (5) layers of Fe-TiO_2 thin films were coated on the stainless steel sheets according to the process in Rojviroon et al. [7] to achieve 0.1% by Fe atom on the surfaces of TiO_2 thin films.

2.3. Photocatalytic activity test

Photocatalytic reactions occurred in the 5-liter cylindrical glass of 3-mm thick photoreactor (Fig. 1) with the working volume of 4.5 liters. The photoreactor was irradiated with three 15W black light bulbs. The average light intensity in the photoreactor was 125 $\mu W/m^2$ after filling the reactor with the synthetic solution mixture containing nitrate and formic acid of 1:8 (M/M) ratio [3]. In the reactor, a total of twelve coated stainless steel sheets were mounted at three different locations, i.e. four sheets in each location, along the shaft rotated by a 12V DC motor (Fig. 1). Throughout the experiment, the velocity of motor was maintained at 60 rpm. The top cover contained two gas valves and two sampling ports. The first gas valve was used to feed nitrogen gas to displace oxygen while the second valve to release oxygen out of the reactor. The reactor was always flushed with nitrogen gas during the experiments. The water samples were collected from both sampling ports that withdraw water from two different levels of depth. The water samples were collected every 30 minutes for 360 minutes. The total of 5 mL (2.5 mL from each sampling port) was collected per each sampling round. The analytical results of the water samples from both levels were averaged and used as the representative results for the whole reactor. The control experiment using uncoated stainless steel sheets together with synthetic water containing nitrate and formic acid was carried out to determine the net removal efficiency of the proposed system. In addition, another control experiment of coated stainless steel sheets with