Photocatalytic degradation of azo dye using TiO$_2$ supported on spherical activated carbon

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Abstract—TiO$_2$ supported on spherical activated carbon (TiO$_2$/SAC) was prepared through an ion-exchange method followed by a heat-treatment process. The adsorption characteristic of TiO$_2$/SAC was evaluated using azo dye methyl orange (MO) as a target substance, and the photocatalytic degradation of MO under UV irradiation was also discussed. A synergistic effect of both the adsorption capacity of activated carbon and the photocatalytic activity of TiO$_2$ on the removal of MO from aqueous solution was observed. Experimental results revealed that the photocatalytic degradation of MO improved with increasing photocatalyst dosage and followed a pseudo-first order kinetic. After five-cycle runs, TiO$_2$/SAC still exhibited relatively high photocatalytic characteristic for the degradation of MO. Besides, the prepared TiO$_2$/SAC can be helpful in the easy separation of photocatalyst from solution after photocatalysis of MO. Furthermore, the use of liquid chromatography/mass spectrometry (LC/MS) technique, identified three intermediates as degradation products during the photocatalytic reaction of MO with TiO$_2$/SAC.

Key words: Titanium Dioxide, Photocatalytic Degradation, Spherical Activated Carbon, Azo Dye, Methyl Orange

INTRODUCTION

About 15% of dyes are lost during the dyeing process which is released into the environment as industrial wastewater [1,2]. The textile effluents are deeply colored, unattractive, and affect aquatic life by blocking sunlight penetration, which in turn significantly decreases the amount of dissolved oxygen [3]. Approximately 70% of azo dyes, which contain one or more azo bond (-N=N-), are widely used in the textile, paint, plastic, foodstuff, and cosmetic industries [3-6]. Some azo dyes are toxic, even mutagenic to organisms, and known to have potential carcinogens and thus may cause direct destruction of aquatic communities [7-9]. Therefore, it is highly imperative that textile effluents containing dyes be treated prior to their discharge into water bodies.

Photocatalysis has been extensively studied for the purification of contaminated water and air [10,11]. The process is one of the advanced oxidation processes that can decompose pollutants in the presence of semiconductor catalyst and UV illumination without adding oxidation agent. Among various semiconductor materials, TiO$_2$ has been widely used in photocatalysis due to its non-toxicity, affordability, high activity and relatively high chemical stability [10-12]. TiO$_2$ powder used in conventional photocatalytic reaction results in high photocatalytic performance due to its large surface area and high degree of dispersion in reaction media, but there are difficulties in recycling and reuse of TiO$_2$ powder [9,12-17]. To overcome this problem, recent studies have focused on the immobilization of the catalysts on certain supporting materials, especially, activated carbon [16-19]. Generally, the traditional methods for preparing the supported catalysts are impregnation, precipitation, and sol-gel, etc [20,21]. In our previous study [22], TiO$_2$ supported on spherical activated carbon was prepared by methods such as powder coating, sol-gel, and impregnation method. We found that photocatalyst was exfoliated and also eluted in water after 24 h. On the other hand, TiO$_2$/SAC prepared through the ion-exchange method and activation process could immobilize titanium ion without a binder and had spherical shape with smooth surface. The smooth surface can prevent problems of surface abrasion by inter-particle collision in floating photocatalytic application. Moreover, TiO$_2$/SAC, which has spherical shape, can be removed from the solution without a special separation process after photocatalytic reaction, and leaching of titanium during long-term water treatment did not occur. The development of semiconductor photocatalyst supported on spherical activated carbon, and the photocatalytic for degradation of humic acid and phenol as organic pollutants in a fluidized bed photoreactor have been reported [22-28].

In this study, TiO$_2$ supported on spherical activated carbon was prepared using the ion-exchange method and heat-treatment process by following our previous studies. The adsorbability and photocatalytic activity of TiO$_2$/SAC was evaluated by the adsorption and photocatalytic degradation of methyl orange (MO), which is one of the azo dyes mostly constituting textile effluents. The effects of photocatalyst dosage and light source on the photocatalytic activity of TiO$_2$/SAC were studied and kinetics of the degradation of MO was also analyzed. The stability of the photocatalyst was investigated through repeated use of TiO$_2$/SAC. Furthermore, the degradation products of MO were identified by LC/MS analysis.

EXPERIMENTAL SECTION

1. Preparation and Characterization of TiO$_2$/SAC

TiO$_2$/SAC was prepared via the ion-exchange method and heat-treatment process as described in previous studies [27,28], Titanium trichloride (TiCl$_3$, 20%, Kanto Chemical) and double-dis-
tilled water with a weight ratio of TiCl₃ : H₂O=1 : 30 were mixed while being stirred for 10 min. Strong acid ion-exchange resin (Dionex SK1BH, Samyang Co., Ltd.) was added to TiCl₃ solution, and was continuously stirred at 150 rpm for 1 h at room temperature. The product was rinsed many times and then dried at 100 °C for 1 h. The dried product was heated using a tube furnace to convert it to a carbonaceous porous material. The product was stabilized under atmospheric condition at a heating rate of 1 °C/min up to 300 °C and was held for 5 h. The stabilized sample was carbonized at 700 °C for 10 min under a nitrogen flow of 2 L/min and then activated under a nitrogen/steam at 900 °C for 30 min. The heating rate was 3 °C/min up to 700 °C and then 1 °C/min up to the final temperature. TiO₂ content was calculated to be 10 wt% [28].

The surface morphology and size of TiO₂/SAC was examined by scanning electron microscopy (SEM, JSM-6700F, JEOL), and also chemical composition of TiO₂/SAC was analyzed by energy-dispersive X-ray spectroscopy (EDS, Bruker Quantax 200). To identify the crystalline phase of titanium in TiO₂/SAC, X-ray diffraction analysis was carried out using a X-ray diffractometer (XRD, D/MAX-III B, Rigaku) over the range 2θ from 20° to 80°, with a scanning speed of 5°/min. The specific surface area of TiO₂/SAC was determined by Brunauer-Emmet-Teller method using Micromeritics ASAP 2010.

2. Adsorption and Photocatalytic Activity

Azo dye methyl orange (MO, C₁₇H₁₈N₂O₃Sn, MW=327.33 g/mol) selected as a target substance was purchased from Aldrich and used without any pre-treatment. The stock solution of 1,000 mg/L was prepared in double distilled water, stored in a refrigerator at 4 °C in the dark to prevent degradation of MO by natural light, and used within one month after preparation.

Batch experiments for degradation of MO were performed in a fluidized bed photoreactor, which was made of stainless steel (10 cm diameter, 40 cm height, and 2 L capacity). Low pressure mercury lamp (UV-C, λₑₓₘ=254 nm) and black light blue lamp (UV-A, λₑₓₘ=365 nm) used as light sources were placed in the middle of the photoreactor. Air was bubbled to reaction solution through the bottom of the reactor with an air flow of 1 L/min. Adsorption experiments were conducted by adding different photocatalyst dosage (5-40 g/L) with initial MO concentration of 50 mg/L. Photocatalytic activity was evaluated under UV irradiation after stirring in the dark for 3 h to reach an adsorption-desorption equilibrium. At this time, the concentration of MO was noted C₀. Every sample was taken out at regular time intervals. The absorbance of the solution was measured by UV-vis spectrophotometer (Qvis 4000, Cmac) at a wavelength of 468 nm, corresponding to the maximum absorption wavelength of MO. The concentration of MO was calculated by a calibration curve. The correlation coefficient for calibration curve assessed by using MO standard solution of 5, 10, 25, 50, 100 mg/L concentration was 0.996. Mineralization (TOC removal) of MO was monitored by determining total organic carbon (TOC) concentration with TOC analyzer (Torch, Teledyne Tekmar). The calibration plot for standard solution of known TOC concentration had a correlation coefficient of 0.999. All measurements of the absorbance and TOC of the sample for each experiment were done in triplicate. The relative standard deviation (RSD) of the measured values was around 0.3-4.5%. For comparison with commercially available TiO₂, Degussa P25 was chosen for the photocatalytic reaction. After photocatalytic reaction using Degussa P25 TiO₂, collected samples were centrifuged at 13,000 rpm for 30 min to separate P25 TiO₂ particles from MO solution before analysis. The reactions were carried out at natural pH and temperature conditions. The degradation ratio (%) of MO was calculated by Eq. (1), where D is degradation ratio, C₀ and C are the equilibrium concentration after adsorption and the remaining concentration of MO at certain time, respectively.

\[ D(\%) = \left( \frac{C_o - C}{C_o} \right) \times 100 \] (1)

3. LC/MS Analysis

To identify degradation products, the samples before and after photocatalytic reaction were analyzed by liquid chromatography (LC, Hewlett Packard 1100 Series) with mass selective detector. Extend C18 column (4.6 mm×150 mm×3.5 μm) was used for separation of sample. The detection system was 1100 UV-vis diode array detector (Agilent, USA). The mobile phase was acetonitrile : 10 mM ammonium acetate (30 : 70, v/v) at a flow rate of 0.4 mL/min, and samples of 20 μL was injected. Mass analysis in the negative ions mode was performed on a mass spectrometer equipped with electrospray ionization (ESI). The minimum detection limit was in the range of a few tens to a few hundreds of ppb level.

RESULTS AND DISCUSSION

1. Characterization of TiO₂/SAC

The specific surface area of TiO₂/SAC was found to be 458 m²/g by using the nitrogen adsorption-desorption method. Fig. 1 shows SEM image and the result of EDS analysis for TiO₂/SAC. TiO₂/SAC showed spherical shape with smooth surface, and the diameter observed under SEM was in the range of 0.37-0.59 mm. From the EDS analysis, Ti element in TiO₂/SAC was confirmed.

XRD was analyzed to determine crystalline structure of titanium immobilized on spherical activated carbon. The strong peak at 2θ=25.4° and small peaks at 2θ=37.8°, 48.0°, 54.1°, 62.8°, 70.0°, and 75.0° corresponding to (101), (004), (200), (105), (211), (204), (116), (220), and (215), respectively, indicate TiO₂ anatase phase [5]. The peaks at 2θ of 27.5°, 36.1°, 41.3°, and 56.1° which correspond to (110), (101), (111), and (220), respectively, indicate the presence of the rutile phase in TiO₂/SAC [5]. The XRD result showed that the titanium immobilized on spherical activated carbon existed as titanium dioxide of mixture of anatase and rutile. The relative content of anatase and rutile was determined by Spurr-Myers equation [5,29].

\[ A(\%) = \frac{I_x}{I_x + 1.265I_o} \times 100 \] (2)

Where, A(%) is the relative content of anatase, Iₓ and Iₒ are the intensities of the anatase (101) peak at 2θ=25.4° and the rutile (110) peak at 2θ=27.5°, respectively. The phase composition obtained by above equation was 81.8% anatase and 18.2% rutile, which is very close to commercial P25 TiO₂ (anatase : rutile=8 : 2) and possesses very high photocatalytic activity [5]. Thus, it can be said that TiO₂/SAC may show high photocatalytic activity.

2. Adsorption of MO on TiO₂/SAC

Adsorption of MO on TiO₂/SAC is important in determining the photocatalytic degradation of MO [30]. To evaluate the adsorption...