Vietnam Journal of Science and Technology ***55*** *(4C) (2017) 277-283*

PHOTOCATALYTIC DEGRADATION OF PARAQUAT USING N-TiO_2/SiO_2 UNDER VISIBLE LIGHT

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Received: 1 August 2017; Accepted for publication: 17 October 2017

ABSTRACT

In the present paper, photocatalytic degradation of paraquat using N-TiO_2/SiO_2 with different molar ratio of titanium: nitrogen (Ti:N) under visible light was investigated. The catalyst was prepared via immersed SiO_2 in N-TiO_2. N-TiO_2 was synthesized by sol-gel method. The N-TiO_2/SiO_2 catalyst was characterized using X-ray diffraction, UV diffuse reflectance spectroscopy, scanning electron microscopy, energy dispersive X-ray spectroscopy. The results from characterizations indicated that N-doped anatase TiO_2 had a 20-25 nm size. Degradation of paraquat, at an initial concentration of 10 mg/L was determined by UV-Vis. Chemical oxygen demand (COD) was used for process performance. Based on the COD tests, the COD values in residual paraquat was lower than that in initial paraquat concentration after 8 hours illumination of visible light. Moreover, the experiment's results indicated that 80% of paraquat was degraded within 8 h of illumination time. These results showed that N-TiO_2/SiO_2 with molar Ti:N=2:1 gives the highest degradation efficiency of paraquat under visible light. This catalyst was stable and reusable suggesting it can be applied to treat organic pollutant in water.

Keywords: TiO_2, photocatalyst, N dopping , paraquat.

1. INTRODUCTION

Paraquat (1,1'-dimethyl-4,4'-bipyridinium dichloride) is one of the most popular herbicide which has been used widely in the productions agriculture for control broad leaf weeds in the world. Although paraquat is considered to be potentially dangerous to human and environment [1, 2], this herbicide is still used in developing countries such as Philippines, Thailand, Senegal and Vietnam [3 – 5]. Some studies reported that paraquat is contaminated in surface water and groundwater [4, 6, 7]. According to WHO, the maximum acceptable concentration for paraquat as dichloride in drinking water is 10 μgL^{-1}.

Paraquat herbicide is known as high toxicity, so the removal of paraquat residue in wastewater is a necessary to protect water resource. Several methods of removal of herbicides in water including oxidation [8] processes, biopolymer membrane [9], absorption on porous materials [1, 2], photocatalytic [3, 5, 10, 11]. Among types of photocatalyst, TiO_2 is widely applied to remove organic pollutants as they are nontoxic, low cost and high-activity. Photocatalytic degradation of paraquat using TiO_2 under UV light has been studied [8, 10–12]. However, these studies have not investigated in degradation of paraquat under visible light. In order to degrade paraquat using visible light, nitrogen is used as the non-metal dopant to improve photocatalysis activity by reducing the band gap of TiO_2.

This research is aimed to synthesize the N-TiO_2/SiO_2 with a high photocatalysis activity; to examine the impact of the molar ratio Ti:N on the photocatalytic efficiency and to degrade paraquat under visible light using N-TiO_2/SiO_2 photocatalyst.

2. MATERIALS AND METHODS

2.1. Material methods

Paraquat (1,1'-dimethyl-4-4-bipyridinium dichloride) with purity 100, titanium-tetra-isopropoxide (TTIP), diethanolamine (DEA) and ethanol (EtOH) and other chemicals are analytical graded and provided by Sigma-Aldrich, USA. SiO_2 beads with 1.7 – 4.00 mm size were provided by Fuji Silysia Chemical., Ltd, Japan.

N-TiO_2 with different molar ratio of titanium: nitrogen in the range of 1:0.5; 1:1; 2:1 was prepared by sol – gel method. The procedure contained following steps: a specific amount of TTIP (1 mol, as a Ti precursor) was dissolved in 100 mL ethanol (as a solvent) and mixed in 30 minutes under vigorous stirring then a specific amount of DEA (as a nitrogen precursor) was added dropwise stirring with a specific the molar ratio of titanium: nitrogen (1:0.5; 1:1 and 2:1). Finally, the solution was mixed and stirred in 5 hours at room temperature.

The N-TiO_2 coated on SiO_2 beads (N-TiO_2/SiO_2) was prepared by dip-coat method. Firstly, SiO_2 beads were immersed into N-TiO_2 sol in 1 minute. Subsequently, SiO_2 beads were pulled out from N-TiO_2 sol solution and dried at room temperature to evaporate ethanol. In the last stage, N-TiO_2/SiO_2 calcined at 500 ^{o}C for 5 hours in an electric furnace. Dip-coat-calcination procedure was repeated 10 times.

2.2. Characterization of N-TiO_2/SiO_2

The nano crystalline structure of N-TiO_2/SiO_2 photocatalysis was determined by X-ray diffraction (XRD) method (D8 Advance – Bruker, Germany) operating at 40 kV and 30 mA using Cu Ka radiation source of λ=1.5056Å. The structural morphology of TiO_2/SiO_2 was characterized with a scanning electron microscopy (FE-SEM S4800, Hitachi, Japan). Chemical characterization of photocalalysis was performed by energy-dispersive X-ray spectroscopy (EMAX, Horiba, Japan). The UV-vis diffuse reflectance spectra was obtained using Carry 5000 UV-VIS- NIR spectrophotometer, Agilent.

2.3. Photocatalytic experiments

Photocatalytic experiments were performed in a photoreactor with continuous flow rate, as shown in Fig. 1. In experimental design, the reactor consists of quartz tubles (10 mm internal diameter; 300 mm length) that contained 2 g N-TiO_2/SiO_2. These tubes were placed in the box in which visible light is illuminated. Two fluorescent lamps (20 W) was used as the light source. The quartz tubes were connected with pump (Isamatec ISM 940, Switzerland) by peristaltic pump tubing. Photocatalytic degradation of 50 mL paraquat at initial concentration of 10 mg/L at natural pH of paraquat solution (ca.6.5) under visible light irradiation with 2 g photocatalyst was continuously circulated through the tubes. Removal of paraquat by SiO_2 beads was examined with the same condition as above. Samples were taken from 15 to 60 min interval irradiation. Change in the residual concentration of paraquat was analyzed by UV-Visible spectroscopy (Shimadzu 2450, Japan) at the wavelength of maximum absorption (λmax = 257 nm). Photocatalytic efficiency is evaluated by the following the equation:

$$D(\%) = \frac{A_o - A_t}{A_o}$$

where D (%) is degradation percentage, Ao is initial absorption of paraquat solution and At is the absorption of paraquat solution at time t.

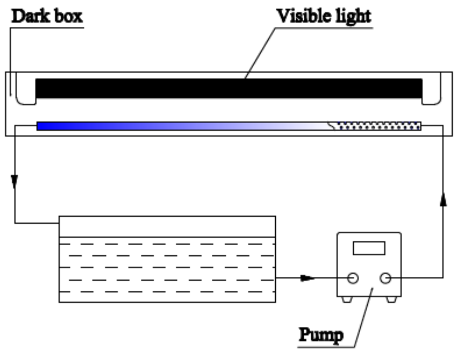

Figure 1. Photocatalytic reactor with continuous flow rate.

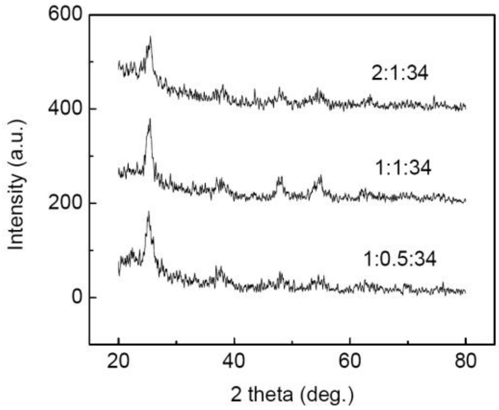

Figure 2. Evaluation of XRD pattern of the N-TiO_2/SiO_2.

3. RESULTS AND DISCUSSION

3.1. Structural characterization of N-TiO_2/SiO_2

3.1.1. XDR analysis

Figure 1 shows the X-ray diffraction (XRD) pattern of nano photocatalyst. The XRD of sample indicated that nano N-TiO_2/SiO_2 has crystalline anatase phase with 2θ = 25.3 (relativity intensity 100 %), 37,9^o; 48,1^o, 55,0^o, 62,7^o and 68,8^o, which are in good agreement with the standard values reported by International Centre of Diffraction Data number 211272 (ICDD-211272).

3.1.2. SEM-EDX analysis

Figures 3 and 4 illustrate the SEM photograph and EDX spectrum of N-TiO_2/SiO_2 prepared with varying molar ratios of titanium to nitrogen. The SEM images showed that N-TiO_2 particles coated on the surface of SiO_2 beads. The high magnification images shown the presence of nano TiO_2 with size ranging from 20 to 40 nm. EDX analysis, simultaneously accomplished during the SEM observation. EDX spectrum of N-TiO_2/SiO_2 confirmed that Ti, N, O, and Si ions present in all catalysts. It is clearly demonstrated that N-TiO_2 coated on SiO_2 beads was synthesized by dip-coat-calcination method.

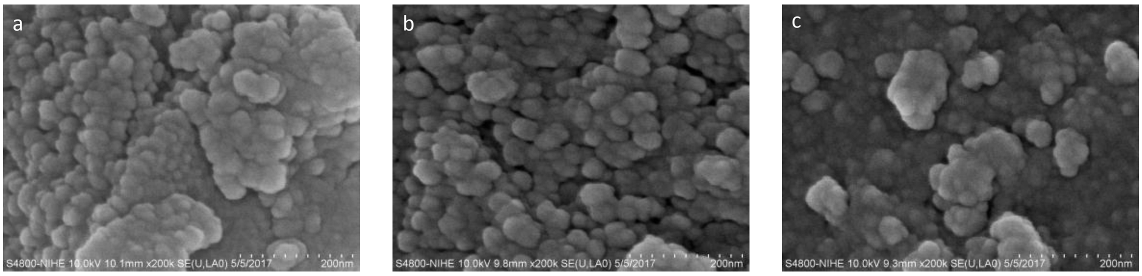

Figure 3. SEM images of N-TiO_2/SiO_2 with different Ti:N mole ratios (a) 1:0.5:34; (b) 1:1:34; (c) 2:1:34.

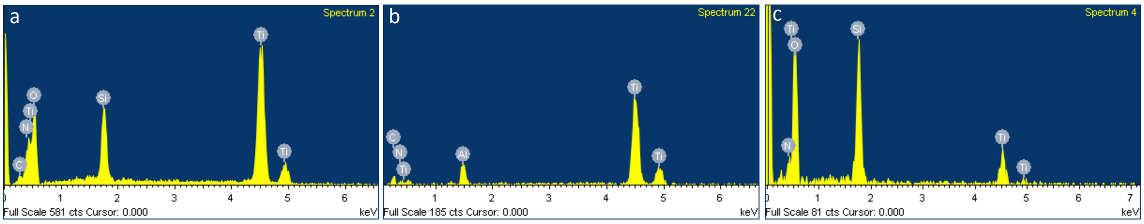

Figure 4. EDX spectrum of N-TiO_2/SiO_2 with different Ti:N mole ratios (a) 1:0.5:34; (b) 1:1:34; (c) 2:1:34.

Figure 5 shows the diffuse reflectance UV-Vis spectra of pure TiO_2 and N-doped TiO_2 with different Ti:N mole ratios. The N-doped samples had an apparent adsorption the visible region between 400 and 500 nm. Compared to N-TiO_2, there was no absorption of visible light by pure TiO_2 (P25) it is demonstrated that the present of nitrogen in sample can increase the optical absorption of N-TiO_2.

3.2 Photocatalytic activity

3.2.1. Photocatalytic degradation of paraquat under visible light

Figure 6 presents the degradation of paraquat with various types of catalyst. Removal of paraquat was observed with SiO_2 and all catalysts. The result indicated that SiO_2 accelerated paraquat adsorption within 15 minutes due to the hydroxyl (OH) groups on the surface of silica and the adsorption equilibrium was reached after 30 minutes, after 8 hours illumination of visible light, the initial concentration of paraquat reduced by 80 %. For all catalysts, under the same light condition, the paraquat concentration decreased by 70 % compared to the initial state. This results is consisted with the results obtained by Sorrolla et al. [3] who carried out photocatalytic experiments by 2 wt. % Cu- TiO2/SBA-15, but was a little lower than 84.39% estimated by Zahedi et al. [10]. Higher removal of SiO_2 compared to N-TiO_2/SiO_2 catalysts is due to higher adsorption capacity and surface area. After the 4th cycle, degradation efficiency of paraquat by SiO_2 was negligible (Fig. 7). This may be due to decreased in adsorption of SiO_2 and increased in phototacatalytic activity of N-TiO_2/SiO_2. It is suggested that N-TiO_2/SiO_2 synthesis has the photocatalytic activity for paraquat decomposition. Thus, N-TiO_2/SiO_2 is a good catalyst for degradation of paraquat in water. The result stated that paraquat degradation by

N-TiO$_2$/SiO$_2$ with molar ratio Ti:N = 2:1 was higher than that with other ratios (1:0.5 and 1:1). The result of N-TiO$_2$/SiO$_2$ recycling show that N-TiO$_2$/SiO$_2$ with ratio Ti:N = 2:1 was higher than other ratio after 6 recycling times (Fig. 7). It is suggested that selecting N-TiO$_2$/SiO$_2$ with molar ratio Ti:N = 2:1 to improve photocatalytic performance. The high catalytic performance of Ti:N = 2:1 is due to high specific surface area (204. 4 m^2/g), large pore size volume (0.83 cm^3/g), small crystallite size and higher crystallinity of the sample.

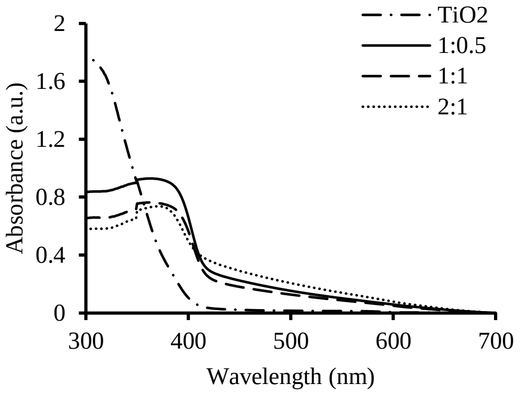

Figure 5. UV-vis diffuse reflectance spectra of pure TiO$_2$ and N-TiO$_2$ with different Ti:N mole ratios

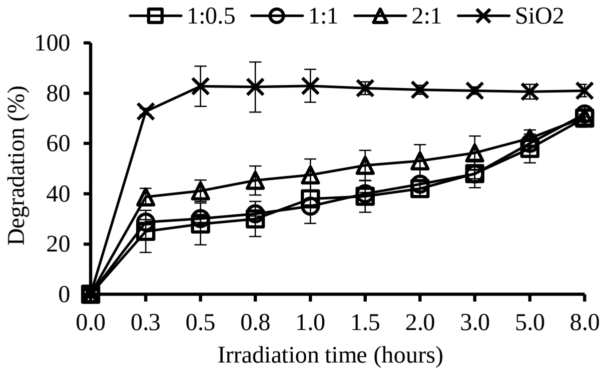

Figure 6. Photocatalysis degradation of paraquat with various type of catalysis under visible light irradiation

3.2.2. Effect of catalyst recycling

We carried out experiment with six repetitions to find out the stability, durability and photoactivity of immobilized photocatalyst in paraquat solution. Each experiment was repeated six times with 2 grams of material. Immobilized catalyst was washed with clean water in order to completely remove any adsorbed intermediate organic products after each run. Degradation of paraquat after six cycles under visible light illumination was observed in Fig. 7. The result shown that degradation efficiency decreases after 6th and 4th cycle for N-TiO$_2$/SiO$_2$ and SiO$_2$ beads, respectively. The decrease in the degradation efficency may be due to the reduction of the paraquat adsorption ability. These results confirmed that N-doped TiO$_2$ coated on SiO$_2$ beads was stable and reusable as it was able to degrade paraquat herbicide until 6th cycle.

3.2.3. COD investigation

Chemical Oxygen Demand (COD) or Total Organic Carbon (TOC) analysis is commonly used as a convenient method to determine amount of organic matter in wastewater. In the COD test, most organic compounds can be fully oxidized to CO_2 and H_2O, thus, in this study, analysis of COD in solutions were carried out before and after the photocatalytic activity. COD analyzed by standard method for the examination of water and wastewater, section 5220-B. COD measurements were carried out with various N-TiO$_2$/SiO$_2$ materials. In this study, paraquat aqueous solution (10 mg/L) was used to determine COD concentration. The result of COD measurements in samples for 8 h of visible light irradiation showed that COD decrease from 304 ppm to 42, 35 and 35 ppm for catalysts with molar ratios of titanium to nitrogen of 1:0,5; 1:1 and 2:1, respectively. It indicated that N-TiO$_2$/SiO$_2$ is a good catalyst for decontamination of organic compounds in water.

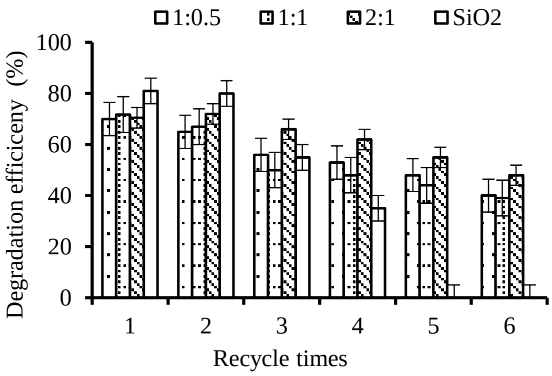

Figure 1. Photodegradation efficiency of paraquat with varying Ti:N mol ratio under visible light with 6 cycles.

4. CONCLUSIONS

The results of the present study indicated that N-TiO_2 coated on SiO_2 beads, which was prepared by dip-coat-calcination method, can degrade paraquat under the illumination of visible light. These results shown that N-TiO_2/SiO_2 with molar Ti:N = 2:1 gives the highest degradation efficiency of paraquat. Moreover, this catalyst was stable and reusable; therefore, it can be applied to treat organic pollutant in water.

***Acknowledgements**:* This study was financially supported by grant No. VAST 07.02/16-17 from Vietnam Academy of Science and Technology.

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