PHOTOCATALYTIC DEGRADATION OF PARAQUAT BY USING TITANIUM DIOXIDE ON RICE HUSK SILICA AND ZEOLITE Y IN SODIUM FORM

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Abstract

Photocatalysts were prepared by using TiO_2 at 10 and 30 wt% grafted on rice husk silica (RHS) and zeolite NaY. The photocatalysts were characterized by X-ray diffraction and N2 adsorption-desorption analysis. The TiO_2 in the anatase phase was well dispersed on the external surface area of the supports. Paraquat adsorption on the catalysts (determined before the photocatalytic testing) mainly occurred on the supports. The adsorption on the TiO_2/NaY was much higher than that on the TiO_2/RHS. In photocatalytic testing, both the 10 and 30% TiO_2/NaY catalysts were not active probably due to high adsorption of the paraquat on the supports. In contrast, both of the TiO_2/RHS catalysts were active and the best photocatalyst was the 30% TiO_2/RHS. The supported catalyst showed a higher activity than the bare TiO_2 indicating the enhancement from the dispersion of the RHS. Moreover, the photocatalytic degradation of paraquat on the 30% TiO_2/RHS was similar to commercial TiO_2 (P25) with the same TiO_2 content.

Keywords: Paraquat, photocatalyst, photocatalytic degradation, rice husk silica, zeolite Y, precipitation

Introduction

Paraquat (1,1´-dimethyl-4,4´-dipyridinium dichloride) is a herbicide widely used in Thailand, including Nakhon Ratchasima, to control weeds in a variety of crops. It has high solubility in water and does not photodegrade in aqueous solution (United States Environmental Protection Agency, 1994) resulting in its accumulation in water. It is highly toxic but can be removed by adsorption on porous materials (Rongchapo *et al*., 2013). Although adsorption is an easy process for removing paraquat, the toxicity of the paraquat is not reduced. Thus, degradation of paraquat is necessary. Paraquat can be degraded by photocatalysis of titanium dioxide (TiO_2)

(Florêncio *et al*., 2004; Moctezuma *et al*., 1999). Paraquat can be reduced by excited electrons (e-) and further degraded to other products (Florêncio *et al*., 2004). TiO_2 is a semiconductor with a band gap energy of 3.2 eV. Since it can be activated by light such as ultraviolet and sunlight, TiO_2 is widely used as a photocatalyst (Sobczyński and Dobosz, 2001). However, TiO_2 has a small particle size, a low surface area, a high tendency to agglomerate in a suspension, and a low adsorption ability for pollutants (Kaneko and Okura, 2002).

Incorporation of an adsorbent with a high surface material such as SiO_2 into TiO_2 could enhance the photocatalytic activity (Vohra and Tanaka, 2003). Previously, paraquat removal by adsorption on rice husk silica (RHS) and porous materials synthesized from RHS including zeolite NaY, NaBEA, and MCM-41 was reported (Rongchapo *et al*., 2013). RHS and NaY which had the lowest and highest paraquat adsorption capacity, respectively, were used as supports in this work. Artkla *et al*. (2009) reported that TiO_2 at 10 wt% grafted on RH-MCM-41 from tetrabutyl orthotitanate (TBOT) had an anatase phase which was more active for photocatalytic degradation of methyl orange than Ti-RH-MCM-41 prepared by adding TBOT in a synthetic gel of RH-MCM-41. TiO_2 was obtained only from the grafting method and the framework Ti was produced from the hydrothermal method. In this work, TiO_2 was prepared with the same precursor, TBOT, with the grafting method to produce only the active anatase. The TiO_2 precursor which was prepared with 10 wt% (Artkla *et al*., 2009) and 30 wt% was incorporated with RHS and NaY to increase the paraquat interaction on the surface and improve dispersion of the TiO_2 and, in both cases, to promote photocatalysis of the paraquat.

Experimental Procedure

Chemicals and Materials

The chemicals for the preparation of the RHS and zeolite NaY synthesis were hydrochloric acid (37% HCl, Carlo Erba Reagents, Sabadell, Spain), sodium aluminate (~55-56% of $NaAlO_2$, Riedel-de Haën AG, Buchs, Switzerland), sodium hydroxide (97% NaOH, Carlo Erba

Reagents), and rice husk. The RHS and NaY were used as a support of the photocatalyst which had been prepared following the procedure described in Rongchapo *et al*., 2013. TBOT (99% $C_{16}H_{36}O_4Ti$, Acros Organics, Fisher Scientific International, Inc., Pittsburgh, PA, USA), nitric acid (65% HNO_3, Carlo Erba Reagents), and NaOH were used in the TiO_2 synthesis and TiO_2 on the support preparations. A commercial TiO_2 powder (P25, Evonik-Degussa GmbH, Essen, Germany), known as the best photocatalyst, was used as a benchmark for comparison. Paraquat, commercial grade (27.6 % w/v, Masda Chemical Sdn. Bhd., Kuala Lumpur, Malaysia), was used in the photocatalytic activity.

Preparation of Photocatalyst

The preparation of the TiO_2 sol was by an acid catalyzed sol-gel formation method modified from the literature (Artkla *et al*., 2009). First, an appropriate amount of TBOT to produce 10 and 30 wt% titania was added gradually to an aqueous solution of 1 M HNO_3 acid (40 mL) under continuous stirring for 1.5-2 h to produce a transparent sol. Subsequently, the mixture was diluted with deionized water and the pH was adjusted to 3 with 1 M NaOH to give a turbid colloid. The required amount of RHS and NaY to produce TiO_2/RHS and TiO_2/NaY, respectively, was added to the turbid colloid suspension. The resulting mixed suspension was agitated with a magnetic stirrer for another 2 h at room temperature, separated by centrifugation, and washed several times with deionized water until the pH of the filtrate was about 6. The resulting TiO_2/RHS and TiO_2/NaY were dried overnight in an oven and calcined in a muffle furnace at 300°C for 1 h.

Characterization of Photocatalysts

The phase and structure were confirmed by powder X-ray diffraction (XRD) using a Bruker-AXS diffractometer D5005 (Bruker Corp., Billerica, MA, USA) with Cu K_α radiation. The N_2 adsorption-desorption analysis was done on a Micromeritics ASAP 2010 analyzer (Micromeritics Instrument Corp., Norcross, GA, USA). The samples were degassed at 300°C under a vacuum for 8 h before the measurement. The surface area was obtained from the Brunauer-

Emmett-Teller (BET) method. The amount of TiO_2 on the RHS and NaY was determined using an energy dispersive X-ray fluorescence (EDXRF) spectrometer (ED 2000, Oxford Instruments plc, Abingdon, UK).

Paraquat Adsorption of All Catalysts

　　Paraquat adsorption was done in a 1 L beaker. The system comprised 0.1 g/L of the catalyst concentration and 250 mL of 15 ppm paraquat solution. The mixture was stirred at room temperature and monitored at 5, 10, 15, 30, 45, 60, 90, and 120 min. The adsorbent was separated by a 0.45 μm nylon syringe filter. The paraquat concentration was determined with an ultraviolet-visible spectrophotometer (Varian Cary 1E, Agilent Technologies, Inc., Santa Clara, CA, USA) at λ_{max} of 257 nm (Nur *et al*., 2005; Iglesias et al., 2010).

Photocatalytic Testing

　　The photocatalytic testing was divided into 3 parts including photolysis of the paraquat, the optimum catalyst concentration, and photocatalytic degradation of the paraquat. All experiments were carried out in a 1 L beaker containing 250 mL of 15 ppm paraquat solution and radiated with 4 18W fluorescent black light lamps (Toshiba Corp., Tokyo, Japan) with the wavelength range of 300-400 nm). In photolysis, the paraquat concentration was monitored after illumination without a catalyst at 5, 10, 15, 30, 45, 60, 90, and 120 min. From the optimum catalyst concentration, the dispersed solutions were varied at 3 concentrations: 0.3, 0.1, and 0.05 g/L by using the P25 as a standard photocatalyst. The photocatalysis was carried out by stirring 250 mL of 15 ppm paraquat solution with the optimum concentration of the catalyst at room temperature. Samples were taken at various times and the catalyst was separated with a syringe filter. The paraquat concentration in the filtrate was determined with the ultraviolet-visible spectrophotometer at λ_{max} of 257 nm.

Results and Discussion

Characterization of Catalysts

　　The XRD patterns of all the prepared catalysts are shown in Figure 1. The patterns of both the P25 and prepared TiO_2 show characteristic peaks of the TiO_2 (Figure 1(a)). The anatase phase (A) was observed at 25.32,
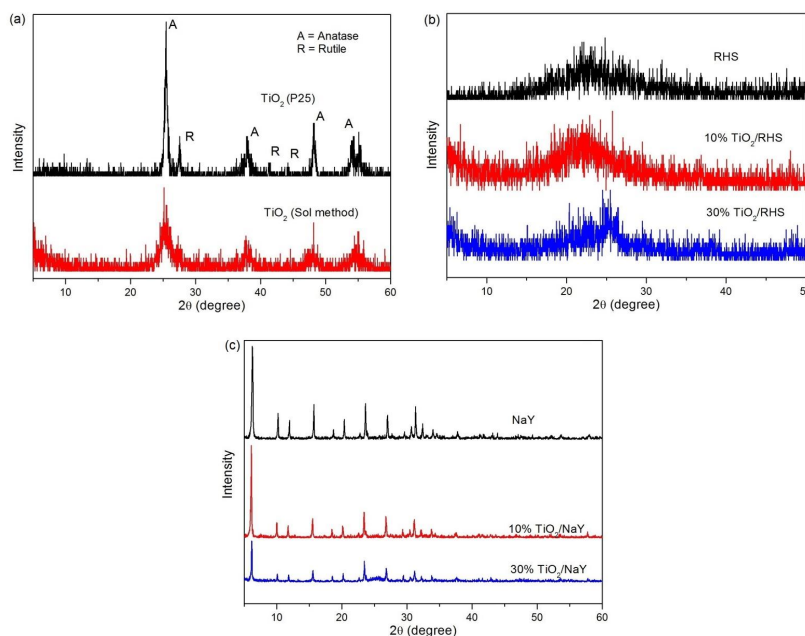

Figure 1. XRD patterns of TiO_2 (a), RHS and TiO_2/RHS (b), and NaY and TiO_2/NaY (c)

37.85, 48.09, and 53.93 degrees and a strong peak of the rutile phase (R) was observed at 27.48 degrees (Brigante and Schulz, 2011). P25 has a mixed phase of anatase and rutile (Raj and Viswanathan, 2009). The prepared TiO_2 from the sol-gel method showed only the anatase phase. Figure 1(b) shows the XRD patterns of the RHS and TiO_2/RHS. The RHS shows a broad peak around 22 degrees which is a characteristic of amorphous silica (Rongchapo et al., 2013). The pattern of the RHS after grafting with the TiO_2 was different. The intensity of the broad peak around 22 degrees decreased in the pattern of the 10% TiO_2/RHS and a peak around 25 degrees (anatase phase) was observed from the 30% TiO_2/RHS. The XRD patterns of the NaY and TiO_2/NaY (Figure 1(c)) also confirmed the structure of the NaY after TiO_2 grafting. The peaks of the TiO_2 were not observed from the 10% and 30% TiO_2/NaY indicating a good dispersion.

The N_2 adsorption-desorption isotherms of all the prepared catalysts are shown in Figure 2. Figure 2(a) shows the isotherm of the P25

which was type II which is a characteristic of non-porous materials (Raj and Viswanathan, 2009). The isotherm of the prepared TiO_2 was type IV (Zhang et al., 2015) which is a characteristic of mesoporous materials with a type H_2 hysteresis loop which is a characteristic of interconnected pores (Rouquerol et al., 1999). The isotherm of the RHS and TiO_2/RHS (Figure 2b) indicated that there was a broad pore range with both micropores and mesopores. (Figure 2(b)) shows the isotherm of the NaY and TiO_2/NaY. Both isotherms were type I which is a characteristic of microporous materials (Rongchapo et al., 2013). A type H_2 hysteresis loop was observed in the isotherm of the 30% TiO_2/NaY, indicating the pores' interconnectivity.

The properties of all the prepared catalysts including the amount of TiO_2, surface area, external surface area, and pore volume are shown in Table 1. The mass percentage of the TiO_2 confirmed the different content, as expected from the preparation. On the NaY support, the surface area, external surface area, and
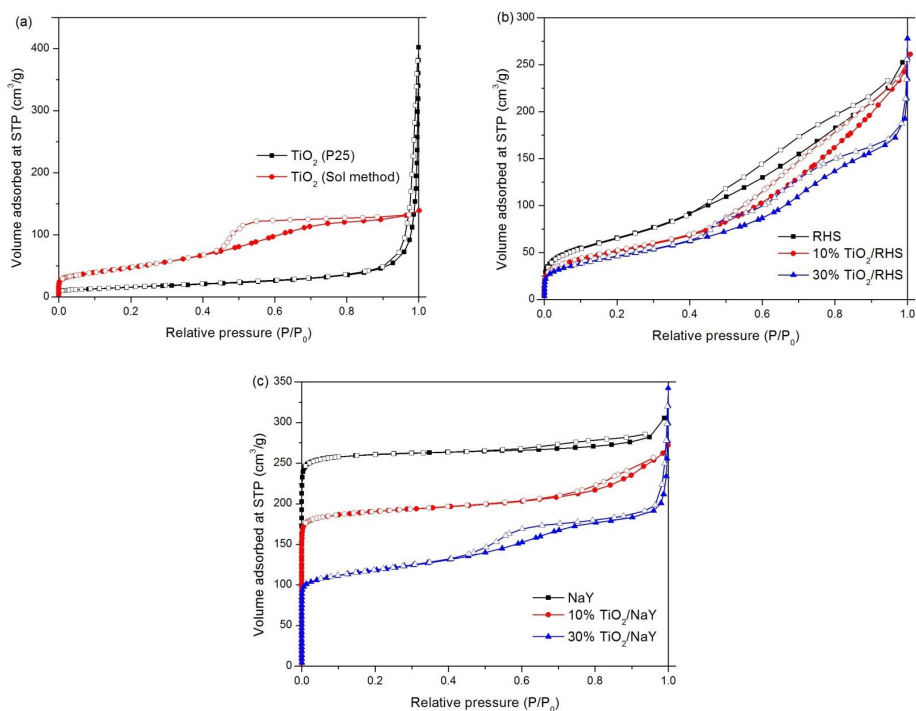

Figure 2. Nitrogen adsorption (filled)–desorption (empty) isotherm of TiO_2 (a), RHS and TiO_2/RHS (b), and NaY and TiO_2/NaY (c)

pore volume decreased with the TiO_2 amount indicating that the TiO_2 was located on both the external surface and pore area. On the RHS support, the surface area decreased with the TiO_2 amount but the external surface area increased and the pore volumes were not significantly different. The results indicated that the TiO_2 was located on the external surface of the RHS.

Adsorption and Photodegradation of the Paraquat

Figure 3 shows the paraquat concentration after irradiation with UV light at various times.

The concentration was essentially unchanged, confirming that the paraquat could not be degraded by UV light without the catalyst.

Figure 4 shows the photocatalytic degradation of the paraquat with the P25 with various catalyst amounts. The degradation with the catalyst concentration of 0.05 g per liter of paraquat (0.05g/L) was slow. The degradations from the concentrations of 0.1 g/L and 0.3 g/L were similar with a complete degradation in 150 min. Because the lesser amount of catalyst would cause less light obstruction, the concentration of 0.1 g/L was considered to be more suitable and was used in further
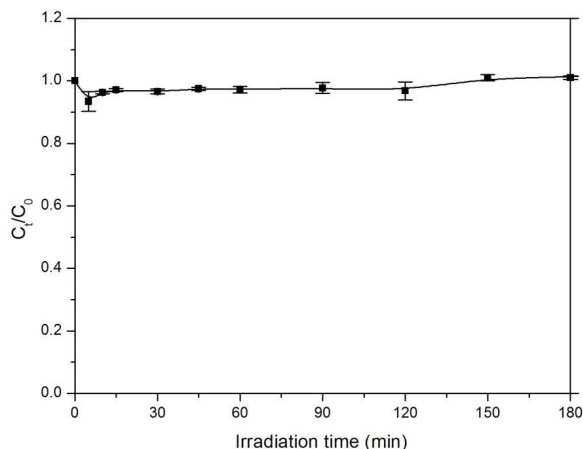

Figure 3. Photolysis (degradation with only light) of paraquat under UV light

Table 1.   Properties of supporting material and photocatalysts

Sample	TiO_2 (%mass) from EDXRF	Surface area[a] (m²/g)	External surface area[b] (m²/g)	Pore volume[b] (cm³/g)
TiO_2 (P25)	100.0	55	57	0
TiO_2				
(Sol-gel method)	100.0	176	21	0.17
RHS	-	220[c]	58	0.19
10% TiO_2/RHS	9.9	184	101	0.17
30% TiO_2/RHS	25.9	165	61	0.16
NaY	-	870[c]	66	0.37
10% TiO_2/NaY	10.0	674	83	0.26
30% TiO_2/NaY	33.0	529	40	0.25

[a] BET method
[b] t-plot method
[c] Rongchapo *et al*., 2013

experiments.

Figure 5 shows the paraquat adsorption on all the photocatalysts at various times using a 15 ppm paraquat concentration. The P25 had the lowest adsorption because it had the lowest surface area. The prepared TiO_2 had a higher adsorption than the P25 because it had a higher surface area. The low adsorption on the TiO_2 indicated that it was not the main adsorption site for the paraquat. The adsorption on all the catalysts became nearly constant with time, indicating a monolayer adsorption. The NaY-supported catalysts had higher adsorption than the RHS-supported catalysts. Moreover, a lesser TiO_2 content gave a higher adsorption ability.

The results indicated that adsorption depended on the supporting materials. The adsorption of each sample reached equilibrium in approximately 60 min. Thus, this time was applied for the dark condition before the irradiation. Moreover, the concentration after adsorption of each catalyst was used as an initial concentration for photocatalytic degradation.

Prior to the photocatalytic testing of the TiO_2/NaY and TiO_2/RHS, the activity was determined on the NaY and RHS for comparison. Degradation was not observed, indicating that the bare supports had no contribution to the photocatalysis. Bhattacharyya et al. (2004) reported a similar behavior that zeolite and
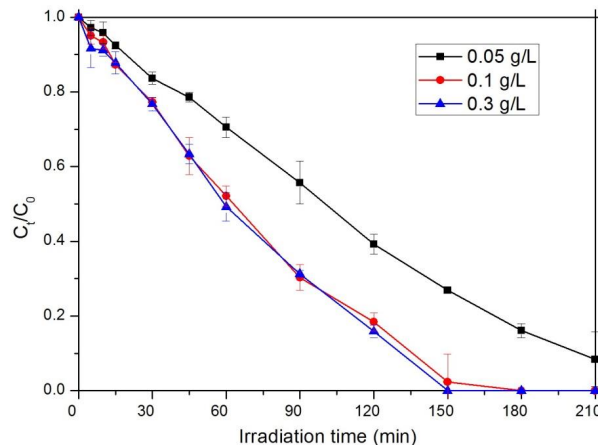

Figure 4. Photacatalytic degradation of paraquat with P25 at various catalyst concentrations
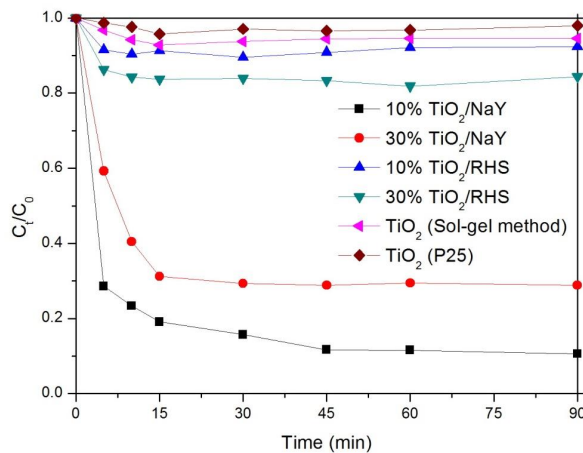

Figure 5. Adsorption of paraquat in darkness with all catalysts

siliceous materials were not significantly active in removing methyl orange by photodegradation.

Figure 6 shows the photocatalytic activity of all the prepared catalysts. Degradation was not observed from the TiO_2/NaY, probably due to the high adsorption ability. Paraquat might just act as a transporter for the excited electrons without degradation. The results indicated that NaY, which had the high adsorption ability, was not a suitable support for the photocatalysts. A slight increase of the paraquat with time indicated that some paraquat was released back to the solution.

On the RHS, the 10% TiO_2/RHS did not show photocatalytic activity, probably due to a low TiO_2 loading. A decrease of the paraquat concentration was observed from the test over the 30% TiO_2/RHS. Thus, it was the best photocatalyst in this study. In addition, the 30% TiO_2/RHS showed a higher activity than the prepared TiO_2. This result indicated that the photodegradation activity of the TiO_2 could be enhanced by support on a material with low adsorption ability.

Finally, comparisons between the 30% TiO_2/RHS and TiO_2 from the sol-gel synthesis with the standard P25 at the same TiO_2 content
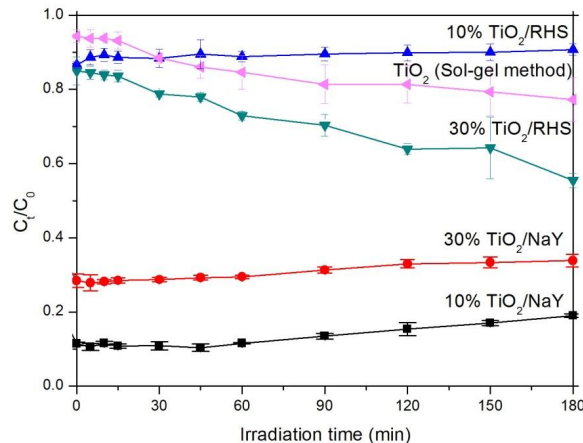

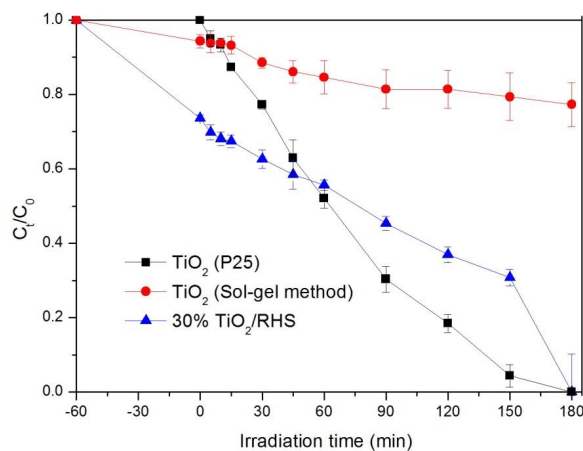**Figure 6. Photocatalytic activities of prepared catalysts after adsorption in the dark**

Figure 7. Comparison of photocatalytic activity between 30% TiO_2/RHS and TiO_2 from sol-gel with the commercial P25 at the same TiO_2 content

are shown in Figure 7. The ability of the 30% TiO_2/RHS to degrade paraquat was comparable to the P25. Both of them showed a complete paraquat removal within 180 min.

Conclusions

Photocatalysts were prepared by grafting $TiO2_2$ on RHS and NaY. The amounts of the TiO_2 were 10 and 30 wt%; the phase of the TiO_2 was anatase. The $TiO2_2$/RHS and TiO_2/NaY catalysts had lower surface areas and pore volumes than the parent supports; more of a decrease was obtained from the higher TiO_2 loading. Before the photocatalytic testing, paraquat adsorption on the samples was determined. The adsorption on the TiO_2/NaY was higher than on the TiO_2/RHS. The adsorption on the TiO_2/NaY decreased with the higher TiO_2 loading. In contrast, the adsorption on the TiO_2/RHS increased with the TiO_2 loading. In the photocatalytic testing, the TiO_2/NaY catalysts were not active, probably due to the high paraquat adsorption. For the TiO_2/RHS catalysts, degradation ability was observed on the 30% TiO_2/RHS with a better performance than on the unsupported TiO_2. Based on the same TiO_2 content, the photocatalytic degradation of paraquat on the 30% TiO_2/RHS was comparable to the commercial P25 and was completed in 180 min.

Acknowledgements

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