Using of TiO_2-Coated Mesoporous Particles for Organic Dye Removal

S. T. T. Le, D. T. T. Trinh, D. Channei, W. Khanitchaidecha, and A. Nakaruk

***Abstract*—In the present work, mesoporous particles was produced by calcining vetiver leaves at 600°C. Then, it was coated by TiO_2 using sol-gel method. The crystal structure of TiO_2 coated particle was investigated using X-Ray Diffraction (XRD) technique. The organic dye removal efficiency were examined using photodegradation of methylene blue (MB) under UV-A irradiation. The pure TiO_2 particle reached only 40% of organic dye removal in 6 hours of irradiation time. On the other hand, the TiO_2-coated mesoporous particles got >90% of organic dye removal in 6 hour of irradiation time. It can be said that the organic dye removal efficiency of TiO_2-coated particles was higher than pure TiO_2 particles. This outcomes suggested that the adding of produced mesoporous particles increased the efficiency of MB adsorption, leading to the improvement of photocatalytic activity.**

***Index Terms*—Mesoporous particle, vetiver grass, titanium dioxide, organic dye.**

I. INTRODUCTION

Among of the present advanced water and wastewater treatment technologies applied, photocatalysis is one of the most promising techniques due to the high degradation activity of organic pollutants [1], [2]. Photocatalysis is referred to the generation of hydroxyl radicals from a semiconductor under the activation of photonic energy [3]. Hydroxyl radicals is a strong and non-selective oxidizing species that is the major reactant responsible for the oxidization of organic compounds [4], [5]. There are metal oxide semiconductors that can be applied in photocatalysis including titanium dioxide (TiO_2), zinc oxide (ZnO), and ferric oxide (Fe_2O_3) [6]. Among above mentioned metal oxide semiconductors, titanium dioxide (TiO_2) is one of the most common used catalyst. TiO_2 has been getting interests because it has high photocatalytic activity and nontoxicity. Furthermore, TiO_2 has the bandgap of 3.0 eV (rutile) and 3.2 eV (anatase) that is possible to apply using natural (solar) UV light (300 nm – 390 nm) [7], [8].

Vetiver grass is a kind of tropical plant that is usually cultivated to control soil erosion. Further, the roots of vetiver grass are commercially used for oil extraction. The fragrant vetiver oil is a valuable precursor of perfumery and cosmetics industry [9], [10]. According to statistics, the oil yield is estimated around 1%wt. of the raw vetiver roots while the annual production of vetiver oil is about 300–350 tonnes [11]. This means approximately 300 thousand tonnes of vetiver roots is globally demanded for oil extraction every year. In the meantime, a huge amount of vetiver leaves are still free at the point of use and are discarded as agriculture wastes or burned in the field [12]. Thus, regarding vetiver leaves as a biomass source, they are a potential precursor to synthesise adsorbents for wastewater treatment application. In addition, the data from the previous work by the authors [13] suggested the vetiver grass had the promising properties as adsorbent materials for water treatment.

In this work, with the aim of enhancing photocatalytic activity by improving adsorption effectiveness of catalyst [14], TiO_2-coated mesoporous particles catalyst was synthesized by the addition of mesoporous particles during TiO_2 sol-gel procedure.

II. METHODOLOGY

A. Synthesis of Catalyst

Mesoporous particles were synthesised from vetiver leaves [13]. After the calcination at 600°C for 3 hours, the calcined vetiver leaves were naturally cooled and then used as substrate to prepare photocatalyst. The catalyst was synthesised by sol-gel method. In particular, mesoporous particles were added to a solution containing 12.5 mL of titanium isopropoxide (TTIP), 80 mL of 2-propanol and 3 mL of deionized (DI) water. The mixture was stirred aggressively for 4 hours and then was filtered to achieve the formed suspension. After that, the suspension was calcined in a muffle furnace at 450°C for 5 hours. The obtained catalyst was naturally cooled and then stored for use. Pure TiO_2 particle was prepared following the same procedure without adding mesoporous particle. The crystal structure of synthesised catalysts was examined using X-ray Diffraction (XRD). Besides, the adsorption and photocatalytic activity of the catalysts were also investigated.

B. Adsorption of Organic Pollutant

The adsorption effectiveness of the synthesised catalysts was tested using methylene blue (MB) dye solution at the concentration of 10 ppm. In a typical experiment, the catalysts were mixed with 50 mL of prepared MB solution by magnetic stirrer. At a specific time, the catalysts were removed from the solution using vacuum filtration. The concentration of MB solution was then measured by UV–visible

Manuscript received August 1, 2015; revised September 15, 2015.

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doi: 10.18178/ijesd.2016.7.7.829

spectrophotometer at λ_{max} = 664 nm. The MB removal efficiency was finally calculated from the MB concentration data.

C. *Degradation of Organic Pollutant*

The photocatalytic activity of the synthesised catalysts was investigated using 10 ppm methylene blue (MB) solution. In a typical experiment, an appropriate amount of catalysts was mixed with 50 mL of prepared MB solution under UV-A irradiation (370 nm). After reaction, the solution was filtered to remove the catalyst from the solution. The MB concentration was measured by UV–visible spectrophotometer at λ_{max} = 664 nm.

III. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the synthesised catalysts consisting of TiO_2-coated mesoporous particle and pure TiO_2. The observed peaks at the plane of [101], [004], [200], [105] and [211] present the anatase crystal form of TiO_2. The XRD patterns reveal the crystalline structure of TiO_2-coated mesoporous particle. The data indicates there are rutile or other contamination phases presented in the pure TiO_2 and TiO_2-coated mesoporous particles. It has to be noted that the degree of crystallinity of TiO_2-coated mesoporous particles was lower than the pure TiO_2 particles.

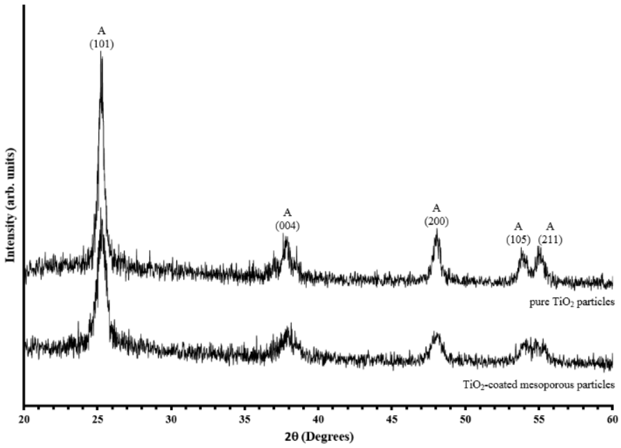

Fig. 1. The XRD patterns of TiO_2 and TiO_2-coated mesoporous particle.

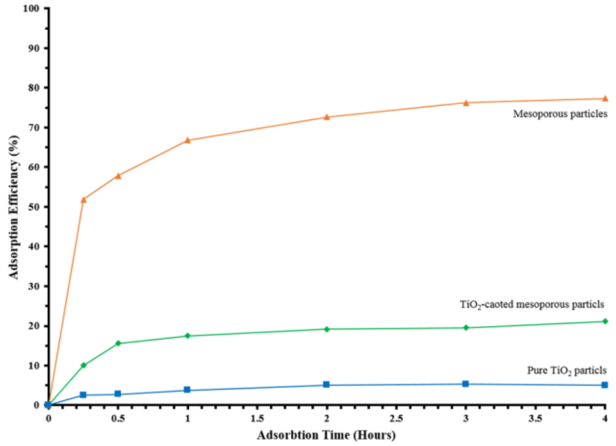

Fig. 2. The MB adsorption efficiency of mesoporous (vetiver) particle, pure TiO_2, and TiO_2-coated mesoporous particle.

Fig. 2 presents the methylene blue (MB) adsorption efficiency of the mesoporous (vetiver) particle, pure TiO_2, and TiO_2-coated mesoporous particle. The adsorption time was varied from 15 minutes to 4 hours. However, the data reveals that the MB adsorption efficiency reached the optimum within the first 30 minutes of reaction. Furthermore, it can be seen that among of the three catalysts, the mesoporous particle showed the highest MB adsorption efficiency of approximately 70%. Additionally, there was about 20% of MB was adsorbed by the TiO_2-coated mesoporous particle. In the meantime, only 5% of MB was removed by pure TiO_2 adsorption. These results suggest that the adsorption effectiveness of the catalyst can be enhanced by the addition of mesoporous (vetiver) particle.

Fig. 3 presents the changes of MB wavelength under the photocatalytic activity of pure TiO_2. In a typical photocatalytic experiment, before the UV-A irradiation, the mixture of catalyst and MB solution was mixed by magnetic stirrer in dark for 12 hours for complete adsorption. After the dark adsorption, UV-A light was turned on for photocatalysis to occur. As presented in Fig. 3, after 12 hours without UV-A light, the absorbance intensity of MB decreased approximately 4%. This result is in agreement with the adsorption test presented in Fig. 2. After that, under the activation of UV-A light, MB was removed rapidly. After 6 hours of irradiation, the MB absorbance intensity dropped from 4% to 50%.

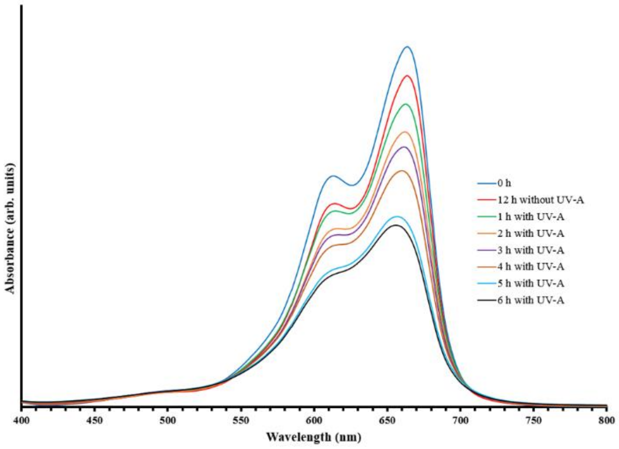

Fig. 3. The change of MB wavelength under the photocatalytic activity of pure TiO_2.

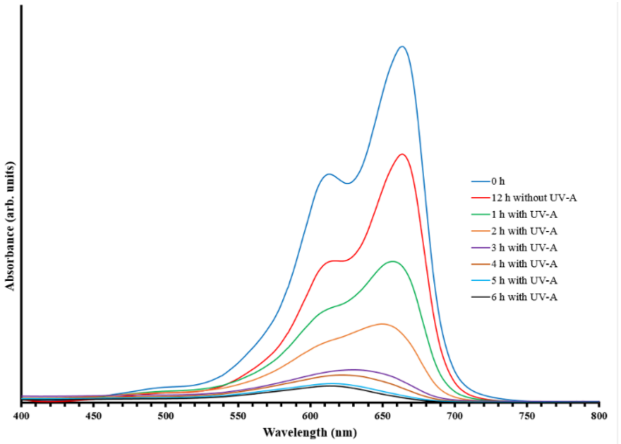

Fig. 4. The change of MB wavelength under the photocatalytic activity of TiO_2-coated mesoporous particle.

Fig. 4 shows the changes MB of MB wavelength under the photocatalytic activity of TiO_2-coated mesoporous particles.

After the dark adsorption process for 12 hours (without UV-A light), the MB absorbance intensity decreased by 20%, in agreement with data in Fig. 2. Furthermore, when the UV-A light was turned on, the absorbance intensity of MB declined significantly from 20% to 98% after 6 hours.

In addition, it has to be noted that under the effect of UV-A irradiation, the peak shifts in MB wavelength were observed (Fig. 3 and Fig. 4). This result indicates the occurrence of photocatalysis and the generation of by-products.

Fig. 5 illustrates the comparison in MB removal efficiency between pure TiO_2 and TiO_2-coated mesoporous particle. The result indicates that TiO_2-coated mesoporous particle showed higher efficiency of MB removal in term of both adosrption and photodegradation. The increased photocatalytic activity of TiO_2-coated mesoporous particle compared to pure TiO_2 is due to the co-mechanism of adsorption and photocatalysis. The adsorption mechanism enhanced the probability for the oxidizing species to interact with MB molecules adsorbed on the surface of the catalyst, leading to the increase of photodegradation effectiveness. After the adsorbed MB molecules were oxidised, free MB molecules in the aqueous phase were adsorbed, which created a cycle of adsorption and photocatalysis.

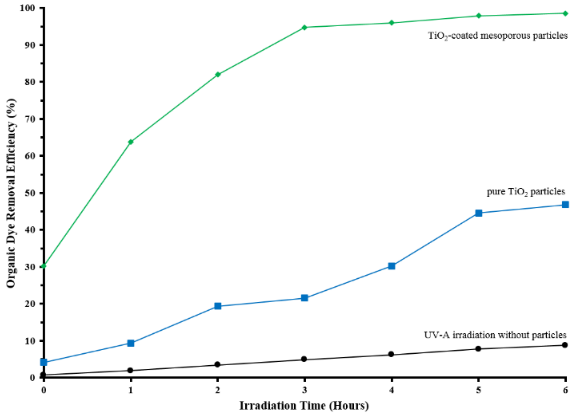

Fig. 5. The removal efficiency of MB under the photocatalytic activity of TiO_2-vetiver, pure TiO_2, and UV-A irradiation.

In addition, it can be seen that the MB removal efficiency of TiO_2-coated mesoporous particle reached the optimum of 96% after 4 hours of UV-A irradiation. The next 2 hours of irradiation provided an insignificant of MB removal efficiency (2%). This observation is due to the low concentration of MB. After 4 hours of irradition, MB was removed to the low concentration, at which the probability of oxidizing species to interact and react with MB molecules was limited. Therefore, the reaction occurred slowly during the last 2 hours.

The blank experiment (UV irradiation only) was also conducted, which presents approximately 8% of MB removal efficiency.

IV. CONCLUSIONS

In this work, mesoporous particles were prepared by calcining vetiver leaves at 600℃ for 3 hours. Afterwards, produced particles were used to synthesise TiO_2-coated mesoporous particles by sol-gel method followed by the calcination at 450℃ for 5 hours. The X-ray Diffraction (XRD) result indicates the anatase crystallinity of TiO_2-coated mesoporous particles. On the other hand, the MB adsorption test and degradation test reveals that TiO_2-coated mesoporous particles showed higher efficiency in adsorption and photocatalytic activity compared to those of pure TiO_2. This result suggests that the addition of produced mesoporous (vetiver) particles improved the MB adsorption efficiency, and enhanced the general photocatalytic activity of the catalyst.

ACKNOWLEDGMENT

The authors would like to thank to Siam Kubota Corporation Co., Ltd. and Naresuan University's research funding for the financial support.

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