

METHYL ORANGE DEGRADATION USING TiO₂ POWDER AND IMMOBILIZED TiO₂ PHOTOCATALYSTS

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Abstract: Methyl orange is one of the anionic dyes and is a major pollutant from textile industry that enters both aquatic and atmospheric systems. In this research, methyl orange was degraded using TiO₂ powder and immobilized TiO₂ on glass. Titanium tetra-isopropoxide (TTIP) was used for preparation of TiO₂ powder using soft chemistry method, and it was immobilized on glass via paste-gel coating method. The prepared photocatalysts were characterized by XRD and SEM. Highly crystalline anatase TiO₂ powder photocatalyst was obtained. Meanwhile, immobilized TiO₂ was less crystalline and agglomerated onto the glass surface. TiO₂ powder had higher degradation rate (71%) compared to immobilized TiO₂ (52%) due to its chemical stability and larger amount of photocatalyst contacted with methyl orange during the degradation process.

Keywords: Methyl orange, TiO₂, nanotubes, immobilized, photocatalyst

Introduction

Anionic dyes are a type of dye broadly used in paper, printing, pharmaceutical, cosmetics, and textile industries. However, low biodegradability and the appearance of the azo group (N=N) on anionic dyes molecule have contributed to the environmental issue. The most important and biggest class organic dyes are azo dyes characterized by the appearance of azo groups (N,N) bound to the aromatic rings. It has been predicted that because of their versatility and chemical stability, more than 50% of all dyes usually used are azo dyes. Treatments available for the wastewater discharged from different industries are physical, chemical, and biological methods (Youssef *et al.*, 2016).

The results of the degradation can be carcinogenic and mutagenic causing long-term health problems. Dye pollutant exposure has serious health effects. The molecule structure is stabilized by the strong electron-withdrawing character of the azo group and it will produce secondary waste products that are believed to be the cause of adverse effects to human health and toxic towards aquatic life. It also has teratogenic and carcinogenic effects on public health (Lu *et al.*, 2012). The crucial sources of ecological pollution are textile industries, printing, dyeing,

and dyestuff manufacturing. The direct release of the wastewater into receiving water body and the strongly colored effluents disposed from the industries may cause harm to both human beings and aquatic organisms due to their mutagenic, toxic, and carcinogenic effects (Huang *et al.*, 2017).

The considerable application for the elimination of these dyes is Advanced Oxidation Process (AOP). This method is based on the generation of highly reactive hydroxyl radicals which are very strong oxidizing agent and have one unpaired electron (Devi *et al.*, 2009). Various AOPs (fenton oxidation, uv/ozone oxidation, photocatalysis) have been investigated for effective treatments of textile wastewater. The use of AOPs such as hydrogen peroxide, hydroxyl radicals, atomic oxygen, ozone, and per hydroxyl radicals that require removal of target pollutant until mineralization have achieved promising results. Very strong oxidizers which are radicals and their reactions with organics are characterized by ozone and hydroxyl radicals which are the high reaction rates. An important role in degrading organics since its atomic oxygen and ozone are less than that of oxidation potential is hydroxyl radical (•OH). Nonetheless, few dyes are not

easily removed by ozonation alone. Besides, to increase the oxidative removal activity, analysis was conducted to make the treatment of high-concentration contaminations in waste water more efficient by adding UV irradiation (Lu *et al.*, 2012). However, AOP used nowadays is not enough to be used in the treatment of water. Besides, the TiO₂ powder is difficult to gain as it requires separation in the preparation and cannot be collected after use. Therefore, the TiO₂ coated on glass was introduced to increase the efficiency of the treatment of water.

Experimental

TiO₂ was prepared by sol-gel precipitation route using titanium tetraisopropoxide (TTIP) as precursor. TTIP was dissolved in distilled water, and absolute ethanol was added to the solution. Hydrochloric acid (100 mL, 0.2 M) was used to adjust the pH solution. The solution obtained was kept under constant stirring on a magnetic stirrer for 40 minutes at room temperature. Then, the solution was dried at 80°C for 24 hours to evaporate organic substance and water. Then the sample was divided into two parts. The first part was calcined at 500°C for 24 hours to obtain TiO₂ powder. The second part was deposited on the glass slide and dried at 80°C and calcined at 500°C for 24 hours to produce immobilized TiO₂.

The photocatalytic activity of prepared samples was studied for degradation of MO. TiO₂ powder and immobilized TiO₂ were added into 100 ml of 20 ppm MO dye solution in photoreactor. Prior to photocatalytic degradation, aliquot of 5 ml of dye sample was withdrawn without the presence of any samples and recorded as blank. Mixture of TiO₂ powder with MO solution was exposed to UV bench lamp (302 nm, 230V ~ 50 Hz) for 3 hours and was magnetically stirred throughout the experiment. 5 ml of solution sample was taken out for every 30 minutes. Then absorption spectra of the samples were recorded via UV-Vis spectrophotometer (Perkin Elmer Lambda 35 UV-Vis) and the percentage of MO degradation was calculated using the formula in Equation 1:

$$\text{Degradation (\%)} = \frac{C_0 - C_t}{C_0} \times 100$$

Equation 1

Where C₀ is the initial absorption of dye, and C_t is the absorption of dye after the reaction at *t* time.

X-Ray powder diffraction (XRD) analysis of photocatalyst samples was scanned in step of 0.2°/second over the range of 2θ from 20 up to 80° using a Bruker D8 Diffractometer. ZEISS SUPRATM 35VP scanning electron microscope (SEM) was used to investigate the morphology of the sample.

Results and Discussion

Figure 1 shows the degradation of MO using TiO₂ powder and immobilised TiO₂ nanotubes for 3 hours. It can be seen that the degradation of MO using TiO₂ powder was higher (71%) than immobilised TiO₂ (52%) after 3 hours. This is probably due to the chemical stability and the amount of catalyst involved in the photocatalytic reaction. Immobilised TiO₂ which is TiO₂ coated on glass slide was little compared to the TiO₂ powder. Therefore the adsorption of MO on the TiO₂ active site was lower, thereby reducing the degradation of MO. Before degradation occurs, MO will be adsorbed on the photocatalyst surface. The charge carriers formed by exposing photocatalyst to UV light photons can migrate and trigger redox reactions with the adsorbed MO. The molecular oxygen present in the photodegradation system can catch the electrons and generate superoxide ions (O₂⁻) by reducing the electrons. On the other hand, hydroxide radical (•OH) and hydrogen ion (H⁺) are formed by the oxidation process of hole with water molecules. The active oxygen species such as hydroxyl radicals are considered to be the pivotal oxidizing species in photocatalytic activity to degrade MO (Ahmad *et al.*, 2016).

On top of that, a decrease in the photocatalytic activity for immobilised TiO₂ is due to electron and hole recombination, which will retard the formation of active oxygen

species. Furthermore, the aggregation of nano TiO₂ particles will increase the opacity and light scattering of thick nano titania film, thereby reducing further the photodegradation activity

(Barton *et al.*, 2016). However, the advantage of TiO₂ coated on glass is it can be reused and can be applied for the self-cleaning of substances such as microscopic slide where the area is coated.

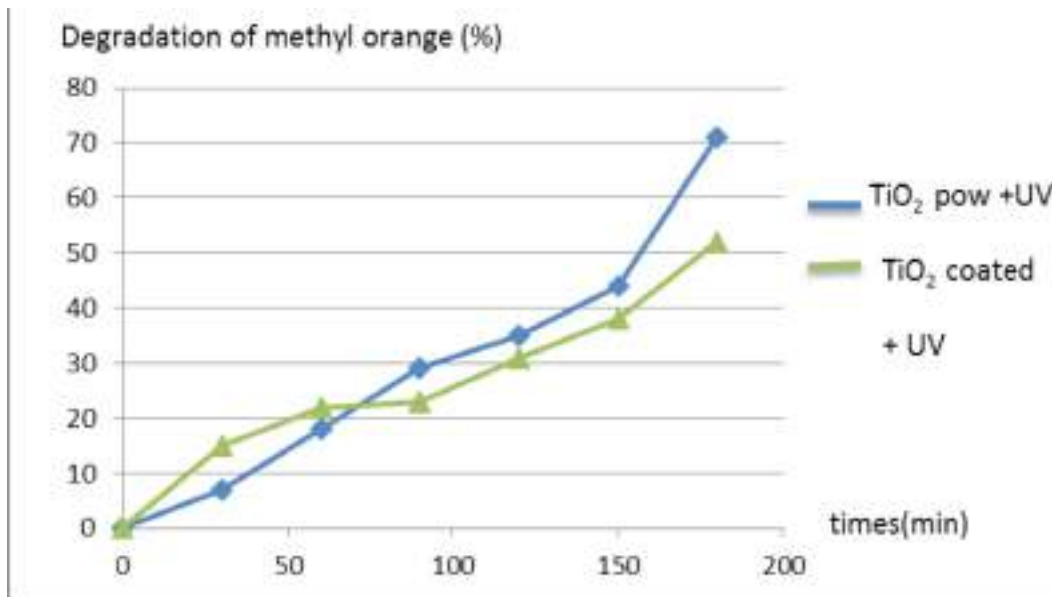


Figure 1: Degradation of MO using TiO₂ powder and TiO₂ coated on glass (immobilized TiO₂) photocatalysts

Figure 2 shows the XRD pattern of TiO₂ powder photocatalyst, where the highest intensity of the peaks was found to be at ~25°, attributed to anatase TiO₂ phase. It has been reported that anatase phase exhibits better photocatalytic activity than other phases of TiO₂ (Tanaka *et al.*, 1991). Several reasons have been proposed to explain why the most photocatalytically active samples have been found within the series of anatase samples. For instance, higher energy position of the anatase conduction band could be

the reason because it increases the driving force for the electron transfer to O₂ to form active superoxide radicals. This radical is extremely reactive and will readily attack organic pollutant molecules and degrade them into CO₂ and H₂O (Razali *et al.*, 2009). Furthermore, less dense structure of anatase causes higher mobility of the charge carriers to proceed with further reaction for the formation of active radical. These could be the reasons for the higher degradation of MO using TiO₂ powder photocatalyst.

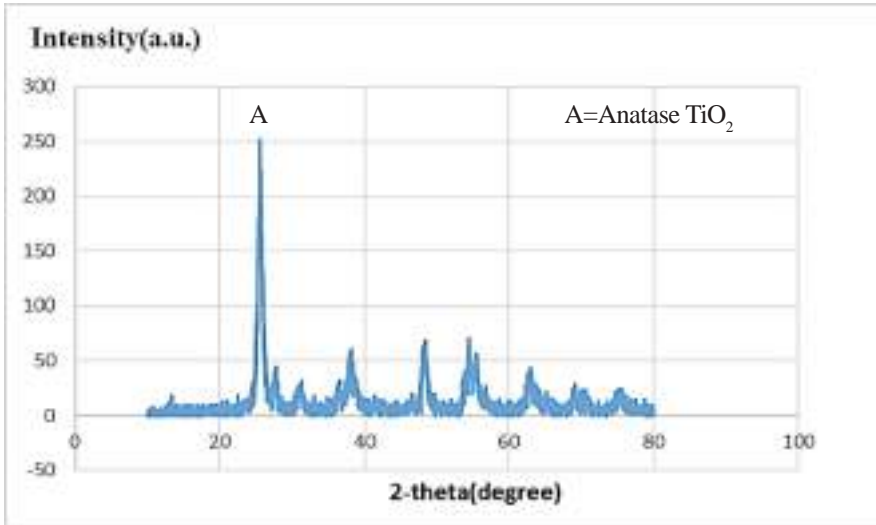


Figure 2: XRD pattern for TiO₂ powder photocatalyst

Figure 3 shows the XRD pattern of TiO₂ coated on glass. A wide diffraction band at $\sim 25^\circ$ instead of sharp peak as compared to TiO₂ powder can be described by the appearance of amorphous TiO₂ in the film and related to the substrate glass slide (Barton *et al.*, 2016). The amorphous properties of the sample create the defect sites such as oxygen vacancy and consequently reduce the performance of the coated photocatalyst (Hanaor *et al.*, 2011).

Figure 4 shows the SEM micrographs of TiO₂ powder and TiO₂ coated on glass slide. The powder sample gave irregular shape with non-uniform size (Figure 4a). On the other hand, result of the SEM measurements on the TiO₂ coated on glass showed that there were dust particles and crack samples (Figure 4b). The cracks can be attributed to the lessening of coating adhesion to the slide of glass in some parts due to the presence of dust particles on the slide.

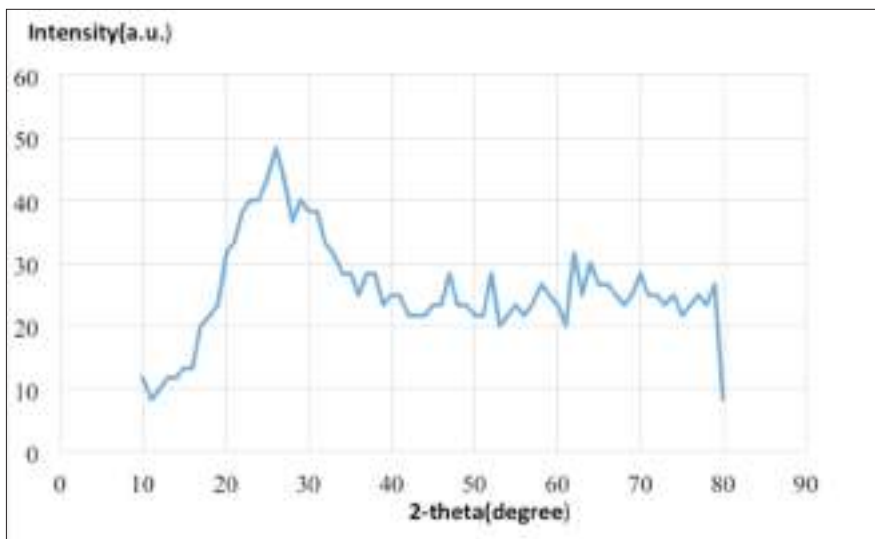


Figure 3: XRD pattern for TiO₂ coated on glass photocatalyst

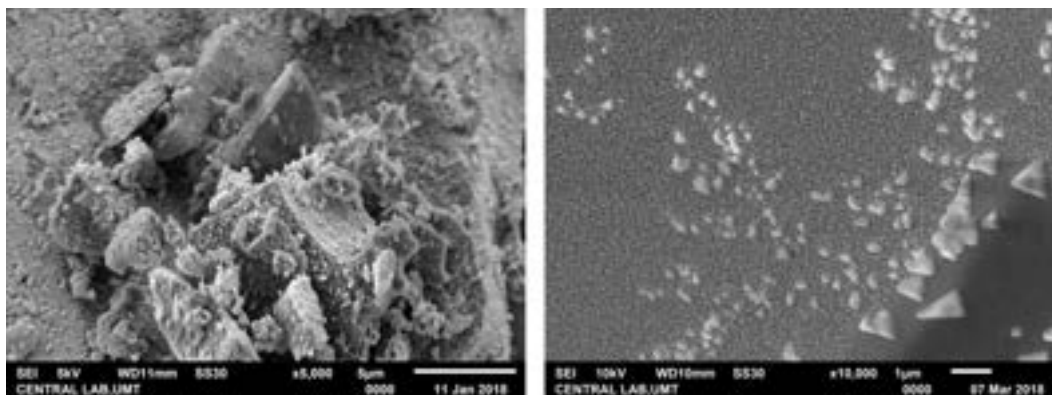


Figure 4: SEM images of (a) TiO₂ powder and (b) TiO₂ coated on glass photocatalyst

Conclusion

This research showed that methyl orange can be degraded using TiO₂ photocatalyst. From the result, it was revealed that TiO₂ powder photocatalyst has higher percentage degradation compared to TiO₂ coated on glass, where TiO₂ powder increased methyl orange degradation as much as 71% after three hours reaction, while TiO₂ coated on glass only decreased to 52%. However, TiO₂ coated on glass can be collected, recycled, and reused.

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