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Photocatalytic Study of New Immobilized TiO_2 Technique Towards Degradation of Reactive Red 4 Dye

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Abstract. The study on TiO_2 for wastewater remediation has gained interest among researchers. However, the application of this photocatalyst is limited due to non-recyclability of conventional TiO_2. Thus, immobilization technique has been developed to solve this issue. Hence, a comparison study between two types of immobilized photocatalysts namely titanium dioxide (TiO_2) and TiO_2 mixed with polyvinyl alcohol (PVA) has been conducted in this work to observe the significant effect of PVA polymer in photocatalysis reaction of reactive red 4 (RR4) dye. Double sided adhesive tape (DSAT) was used as thin layer binder in this immobilization system. The result shows that the photocatalytic performance of TiO_2-PVA/DSAT was higher than that of TiO_2/DSAT under both normal UV and visible light irradiations due to the conjugated unsaturated polymer from PVA serve as electron donor for TiO_2 thus increase the photocatalysis process. Besides, TiO_2-PVA/DSAT was also found to possess much better adhesion strength to the support material compared to TiO_2/DSAT. Based on the findings, this TiO_2 immobilization system is expected to be beneficial in the industrial wastewater treatment. Thus, further study to improve the photocatalytic activity of this immobilized TiO_2 will be in our future work.

1 Introduction

Advanced oxidation processes (AOPs) have seen to be growing interest recently. The practical application of AOPs is commercially known as photocatalysis. Titanium dioxide (TiO_2) is the best known phototcatalyst and has been employed in almost studies. Immobilization of TiO_2 has been introduced to replace the existing suspension system. This is due to the main drawback from the suspension system that is formation of sludge which requires further purification steps thus resulting in difficulties to recycle the photocatalyst. Since past decades, researchers have taken various approaches to modify the TiO_2 for a better performance of photocatalysis reaction. Thus, many different methods that have been developed to prepare the immobilized TiO_2.

Adding polymer as matrices has been widely used by researchers in immobilized TiO_2 preparation to produce photocatalyst with better strength, adsorption capability and surface morphology. Some examples of the widely used polymers are polyvinyl chloride (PVC) [1], polyethylene glycol (PEG) [2] and polyvinyl alcohol (PVA) [3]. Under certain state, polymers with carboxyl or hydroxyl groups particularly, will bond chemically with the hydroxyl groups on the surface of TiO_2.

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PVA which possess good film-forming ability is a hydrophilic polymer and potentially useful in immobilization of TiO_2 [4-6]. Its low market price is another factor that many researchers employed this polymer in their work. Yang et al. [7] prepare C-PVA/TiO_2 composites by calcinating the mixture of TiO_2 sol and C-PVA solution for photocatalytic degradation of rhodamine B. Meanwhile, H-PVA/ TiO_2 composite was synthesized by Song et al. [8] under sol–gel and thermal treatment process with tetrabutyl titanate as titanium source.

In this paper, a comparison study between two types of immobilized photocatalyst which were TiO_2/DSAT and TiO_2-PVA/DSAT has been carried out successfully. The photocatalytic activities of both photocatalysts were investigated by studying the degradation of reactive red 4 (RR4) dye under two different light sources namely normal and visible light. Besides, the adhesion strength of the photocatalysts was also compared through sonication procedure.

2 Experimental

2.1 Materials

TiO_2 powder used (P25, 20% rutile and 80% anatase) was supplied by Evonic-Aeroxide. PVA was provided by R&M Chemicals. The model pollutant used was Reactive red 4 (RR4) dye which was purchased from Sigma-Aldrich. Deionized water was used to prepare all experimental solutions throughout this study.

2.2 Fabrication of immobilized TiO_2/DSAT and TiO_2-PVA/DSAT plates

The TiO_2 coating formulation was prepared by mixing TiO_2 with water while the TiO_2-PVA coating formulation was prepared by adding a specific amount of PVA solution into the TiO_2 formulation. Clean glass plates (130 mm × 50 mm) were prepared as support material to immobilize both photocatalyst formulations by brush-coating method. DSAT was stuck onto one side of the plates to cover an area of 65 mm × 47 mm prior to coating. The plates were each coated with fixed amount of both immobilize photocatalysts.

2.3 Photocatalytic study

A custom made glass cell with dimension of 50 mm × 10 mm × 80 mm (L × B × H) was used as a container to fill in 20 mL of the 200 mg L^{-1} RR4 sample together with the coated plate. An aerator made from aquarium pump model NS 7200 was connected to the glass cell via PVC tubing and a glass Pasteur pipette to supply oxygen and bubbles constantly throughout the experiment. The plate was placed inside the cell. A 55 W Qusun E27, 6400K fluorescent lamp was used to irradiate the normal light source on to the plate. Hoya ultraviolet (UV) filter was used to the normal light to get visible light source. Samples of the irradiated solutions were taken at every 15 min interval to determine their concentration by using HACH DR1900 ultraviolet-visible (UV-vis) spectrophotometer.

2.4 Immobilized TiO_2/PVA adhesion strength test

To test the adhesion strength of the immobilized TiO_2/PVA, the plate was sonicated for 30 seconds with Cress Ultrasonic, Model 4HT-1014-6. The sonicated plate was then taken out after every 5 seconds interval and its weight was recorded. The differences of weight before and after every 5 seconds intervals for up to 30 seconds sonication of the catalyst were measured in order to evaluate the percentage of the catalyst particles adhered onto the surface of the glass plates.

3 Results and Discussion

3.1 Effect of light sources

Figure 1 shows the comparison between photocatalytic activity of TiO_2-PVA/DSAT and TiO_2/DSAT when irradiate under normal and visible light. Photocatalytic efficiency of TiO_2-PVA/DSAT was found to be greater than TiO_2/DSAT under normal light irradiation with first order rate constant was ca. 0.0485 and 0.0309 min^{-1} respectively. Meanwhile, TiO_2-PVA/DSAT shows a more active visible light photocatalysis towards the degradation of RR4. Both types of immobilized photocatalysts are able to degrade RR4 under visible light rather great with 26% and 16% of RR4 colour remaining for TiO_2/DSAT and TiO_2-PVA/DSAT.

This happened due to the RR4 self-sensitization feature and the adsorption properties of the TiO_2 itself since other researchers reported certain kind of dyes may become a sensitizer during the photodegradation and the process could happened under visible light even the bandgap energy of the involved photocatalyst is higher than 3.0 eV [9-10]. Hence, photodegradation study using other pollutants is compulsory.

Methylene blue (MB) dye is used as a model pollutant to affirm the photoactivity of TiO_2/DSAT and TiO_2-PVA/DSAT sample under visible light. Figure 2 shows the photodegradation of 36 mg L^{-1} MB using TiO_2/DSAT and TiO_2-PVA/DSAT under visible light. As expected, no photocatalytic degradation of MB observed under TiO_2/DSAT since the bandgap energy of pristine TiO_2 sample is insufficient for energy from visible light to activate an excitation of electron hole pair.

In contrary, photodegradation activity was observed under under TiO_2-PVA/DSAT with complete decolorization were recorded at 300 minutes, it was clearly proven that TiO_2-PVA/DSAT sample is active under visible light irradiation. The conjugated unsaturated structure of PVA might be the main reason for the activity of the immobilized TiO_2-PVA/DSAT under visible light.

The mechanism is similar with the photosensitized mechanism of the dye sample towards TiO_2 under visible light. Visible light will cause the excitation of the sensitizer molecules adsorbed onto the surface of TiO_2 while consequently excite electrons to the conduction band (CB) of TiO_2. Electrons will be transferred from the sensitizer to the electron acceptor substrate present on TiO_2 surface by the CB which acts as a media while the valence band (VB) will remains unaffected in a standard photosensitization process. The visible light activity of the immobilized polymer/TiO_2 sample happens due to series of chain reactions that will be formed by the excited electrons in CB of TiO_2.

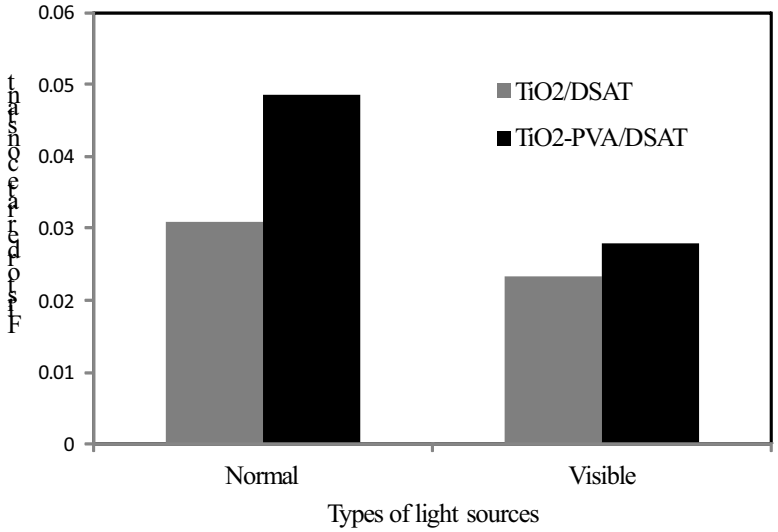

Figure 1. First order rate constant for immobilized TiO_2-PVA/DSAT and TiO_2/DSAT under normal and visible light.

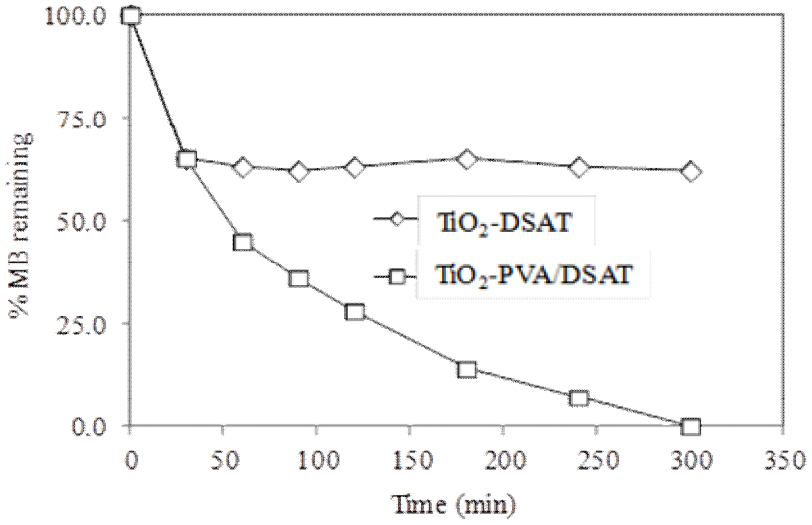

Figure 2. Decolorization of 36 mg L^{-1} MB dye using immobilized TiO_2-DSAT and TiO_2-PVA/DSAT under visible irradiation.

3.2 Adhesion strength test

This test identifies the adhesion strength of the immobilized TiO_2-PVA/DSAT and TiO_2/DSAT onto the support material. Figure 3 shows percentage of each photocatalyst weight remained after 30 seconds of sonication. Immobilized TiO_2-PVA/DSAT shows much better adhesion strength towards the glass plate compared to the TiO_2/DSAT. There is still as much as 87% of catalyst remaining for immobilized TiO_2-PVA/DSAT while only 47% catalyst left on TiO_2/DSAT after sonication. This was due to the significant effect of PVA that binds well chemically with TiO_2 matrices which results in stronger adhesion strength toward the support material. Since there is no binder present in immobilized TiO_2/DSAT, a great amount of its photocatalyst was removed during sonication.

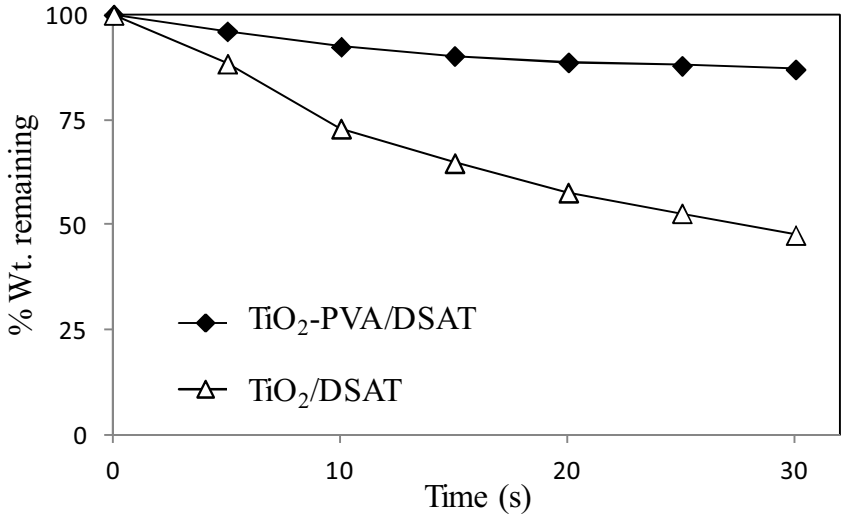

Figure 3. Percentage of immobilized TiO_2-PVA/DSAT and TiO_2/DSAT weight remained after sonication.

4 Conclusion

Photocatalytic efficiency of immobilized TiO_2-PVA/DSAT and TiO_2/DSAT has been successfully carried out under normal and visible light with RR4 as the model pollutant. It was found that photocatalytic activity of immobilized TiO_2-PVA/DSAT was not affected by different light sources. When test under ultrasonication, the adhesion of immobilized TiO2-PVA/DSAT was a lot better than TiO_2/DSAT towards the support material. Thus, this polymer bound immobilized TiO_2 photocatalyst was expected to be employed for industrial application for its durability. The study towards improvement of TiO_2-PVA/DSAT immobilized photocatalyst will be further investigated.

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