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Research Article

New TiO_2/DSAT Immobilization System for Photodegradation of Anionic and Cationic Dyes

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A new immobilized TiO_2 technique was prepared by coating TiO_2 solution onto double-sided adhesive tape (DSAT) as a thin layer binder without adding any organic additives. Glass plate was used as support material to immobilized TiO_2/DSAT. Two different charges of dyes were applied, namely, anionic reactive red 4 (RR4) and cationic methylene blue (MB) dyes. Photocatalytic degradation of RR4 and MB dyes was observed under immobilized TiO_2/DSAT with the degradation rate slightly lower and higher, respectively, compared with TiO_2 in suspension mode. It was observed that DSAT is able to provide a very strong intact between glass and TiO_2 layers thus making the reusability of immobilized TiO_2/DSAT be up to 30 cycles. In fact, a better photodegradation activity was observed by number of cycles due to increasing formation of pores on TiO_2 surface observed by SEM analysis.

1. Introduction

Advanced oxidation processes (AOPs) are one of the promising ways to eliminate dangerous pollutants into harmless treated products. Photocatalysis is one of the widely applied processes in advanced oxidation. Titanium dioxide (TiO_2) is the most commonly used semiconductor in photocatalysis process due to its high activity, being inert to the biological and chemical environment, nontoxicity, and low cost. Conventional method in the photocatalytic studies is suspension of TiO_2 in aqueous solution, which provides high surface to volume ratio [1]. However, the suspension of TiO_2 powder caused treated wastewater in slurry form and required the filtration process. Due to its small particles, they stay suspended in water, clogging filter membranes, and penetrate through porous filter materials [2]. Realizing this issue, TiO_2 immobilized techniques are implemented onto the support materials such as glass, silica gel, and metals. Numerous additives are also added in TiO_2 as a binder to improve durability, temperature resistance, and strong absorbance affinity towards pollutants [3–6].

Recently, researchers used organic additive to promote proper adhesion in immobilized TiO_2 substrate. Polyvinyl alcohol (PVA), polyethylene glycol (PEG), polyvinyl chloride (PVC), and polyvinylpyrrolidone (PVP) are examples of polymers that have been employed by previous researchers in their studies [7–10]. The immobilizations by using different coating techniques have been applied by some workers to produce smooth coating as well as thin layer like spinning, doctor blade, dipping, brushing, and spraying [11–15]. It is important to determine an ideal mixing ratio of TiO_2 and its binder. Polymer added in TiO_2 composite which acts as a binder induces a strong intact among the immobilized TiO_2 matrix thus making it reusable over times. However, excessive amount of polymer makes TiO_2 embedded in polymer matrix which causes reduction between TiO_2 and pollutant surface

contact and eventually reduces photocatalysis process. The lower the amount of polymer mixing ratio is, the better the performance of photocatalytic process will be observed, but it makes TiO_2 leach out easily. To the best of our knowledge, no work used double-sided adhesive tape (DSAT) in replacing a polymer binder under TiO_2 immobilization system. Since commercial DSAT is water proof, durable, and strong intact with any materials and is made from nonhazardous substances [16], it is highly potential to be used as a thin layer binder for TiO_2 immobilized system.

In this work, TiO_2 photocatalyst was immobilized on glass plate support material by using DSAT as a new binding technique. The photocatalytic activity of the immobilized photocatalyst was investigated by monitoring the degradation of RR4 and MB dyes as well as their durability and reusability.

2. Methods

2.1. Preparation of Immobilized TiO_2. Typically, TiO_2 solution was prepared by mixing 13 g of TiO_2 (P25, Deggusa, 80 : 30 of anatase : rutile) with 100 mL of distilled water in 250 mL reagent bottle. The solution was undergoing shaking process for 30 minutes using orbital shaker model PSU-20i, Grant-bio, to make it homogenised. TiO_2 solution was then coated (immobilized) by using brush technique and DSAT was stacked onto glass plate with dimensions of 13 × 4.8 cm ($L \times H$) priorly coated with TiO_2. The glass cell with immobilized TiO_2 was then dried in the oven at 100°C for 20 minutes. A dried immobilized TiO_2 sample was cleaned by using distilled water under irradiation of 55 W fluorescent lamp model Qusun E27, 6400 K in aerated condition for 1 hour prior to photocatalytic degradation.

2.2. Photocatalytic Degradation. 25 mL of 120 mg L^{-1} of anionic RR4 dye was poured into a glass cell with dimensions of 150 mm × 10 mm × 80 mm ($L \times B \times H$). Immobilized TiO_2 was then entered into glass cell containing RR4 dye and irradiated with a 55-watt fluorescent lamp at specific time interval until it turns colourless. An aquarium pump model NS 7200 was used as an aeration source to supply oxygen. Photocatalytic degradation of MB was repeated by replacing RR4 with 12 mg L^{-1} of MB, following the same procedure. Percentage of colour remaining after photodegradation process was determined based on absorbance values measured by using HACH DR 1900 spectrophotometer at 517 and 661 nm for RR4 and MB, respectively. Two control tests were carried out for both RR4 and MB dyes by following photocatalytic degradation setup without any presence of TiO_2. DSAT was included in the first test while another test was performed without both TiO_2 and DSAT, namely, photolysis.

2.3. Reusability and Strength. The study of reusability was carried out following the photocatalytic degradation procedure by repeating the same procedure up to 30 times by using RR4 and MB dyes. Sample was alternately clean with ultrapure water under 55 W fluorescent lamp in aerated condition for 1 hour prior to repetitions process of photocatalytic degradation. The strength study was carried out by measuring the remaining weight in immobilized TiO_2/DSAT sample after sonication process with ultrasonic bath Cress Ultrasonic, Model 4HT-1014-6.

2.4. Scanning Electron Microscopy (SEM). The study on surface morphology and cross section of immobilized TiO_2/DSAT was carried out by using SEM analysis model Leica Cambridge S360.

3. Result and Discussions

The photocatalytic degradation rate of anionic RR4 under immobilized TiO_2/DSAT shows a significant improvement with increasing amount of loading catalyst as can be seen in Figure 1(a). The optimum catalyst loading of immobilized TiO_2/DSAT was observed at 0.2 g and degradation rate of RR4 was *ca.* 0.040 min^{-1}. The optimum catalyst loading under suspension mode was also observed at 0.2 g and the rate of RR4 removal was *ca.* 0.048 min^{-1} and it is just slightly higher than immobilized TiO_2/DSAT. The plots percentage of RR4 and MB remaining at different catalysts loading is provided in Supplementary Figures 1 and 2, respectively, in Supplementary Material available online at http://dx.doi.org/10.1155/2015/232741. A slightly lower photocatalytic activity of RR4 under immobilized TiO_2/DSAT system compared to the suspension mode was considered as a good photoresponse under immobilized system since the photodegradation of immobilized TiO_2 is always much lower than suspension mode. Based on reports by other researchers, photodegradation rate of immobilization system is more than two times slower than the suspension mode [17, 18]. However, different result will be obtained if another pretreatment process was applied prior to photocatalysis, namely, photoetching (cleaning process) that was successfully studied and reported by Nawi et al. [19]. Photoetching is responsible for removing the organic additive. They reported that the photodegradation of immobilization system was better than the suspension mode. Nevertheless, the system was found to be less effective for commercialization since this photoetching is a time-consuming process which took 8 hours to complete. Figure 1(b) shows the effect of catalyst loading towards photodegradation of cationic MB under suspension TiO_2 and immobilized TiO_2/DSAT. The optimum loading of immobilized TiO_2/DSAT was recorded at 0.3 g where photodegradation rate of MB was *ca.* 0.069 min^{-1} and the rate is higher than optimum photodegradation rate for TiO_2 suspension by 22% (0.054 min^{-1}).

High photocatalytic degradation under immobilized TiO_2/DSAT sample compared to suspension TiO_2 is due to two main factors. Since TiO_2 sample is negatively charged, positive charges in cationic MB make the sample have higher adsorption capacity with MB dye. Higher surface contact of photocatalyst with MB increases the adsorption capacity thus making the adsorption become dominant. Generally, good photodegradation of dye is a combination of adsorption and photocatalysis processes in equilibrium condition [20]. In this study, photocatalytic removal of MB in suspension mode has higher surface area where the adsorption is dominant

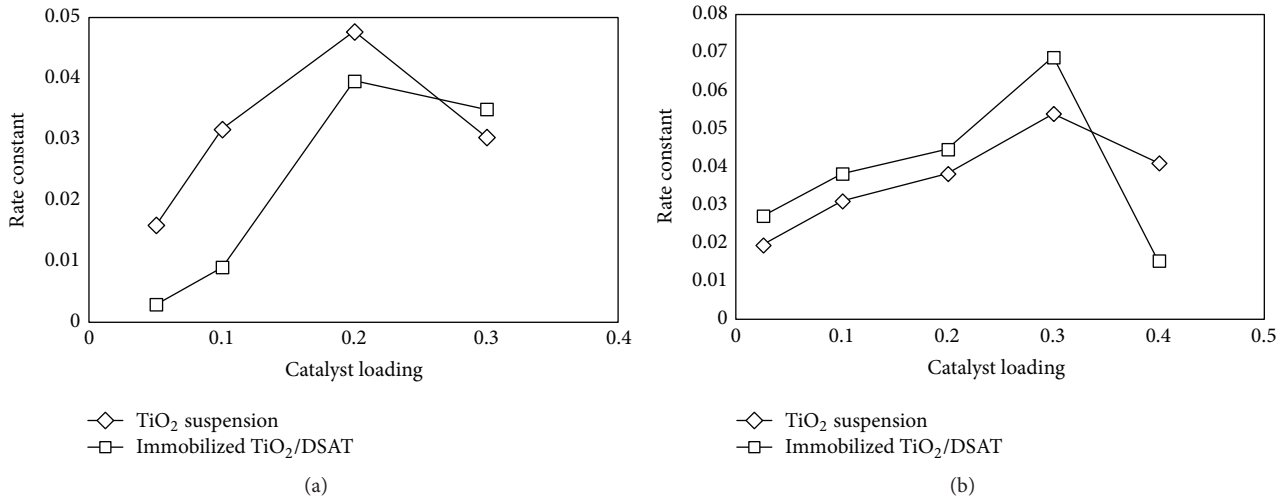

Figure 1: Photocatalytic degradation rate of immobilized TiO_2/DSAT and suspension TiO_2 under (a) RR4 removal and (b) MB removal.

in the entire process thus making TiO_2 particle less able to perform photocatalysis process due to the scattering effect of adsorbed MB dye on the surface of TiO_2 particle. In case of immobilized TiO_2/DSAT sample, the surface area is less compared with suspension; moreover, the sample is more stable due to static condition, thus making the balance between adsorption and photocatalysis processes for enhanced photodegradation of MB. Second, immobilized TiO_2/DSAT samples have undergone cleaning process prior to photodegradation of dyes. Cleaning process is proven to activate the photocatalyst. Nawi and Zain [21] reported that photocatalytic degradation of MB will become higher after washing of immobilized TiO_2/PVC sample compared with sample without washing. Besides, an organic binder that is present in this TiO_2 immobilization system which is DSAT makes this cleaning process become even more essential to oxidize the organic compound. In this study, sample in suspension mode was carried out without washing, thus making the photocatalysis in suspension mode become lower as compared with immobilized TiO_2/DSAT which are under washing condition. As a comparison study, we have applied immobilized TiO_2/DSAT to degrade MB without washing process. A photocatalytic degradation rate of MB under immobilized TiO_2/DSAT without washing is drastically reduced to $0.463\,min^{-1}$ and it is even lower than the rate under TiO_2 in suspension mode ($0.054\,min^{-1}$). A control test has been conducted without the presence of TiO_2 under both dyes to prove the importance of TiO_2 photocatalyst in this study. As expected, there is no photocatalysis reaction occurring during the experiment. From Figure 2, the percentages of RR4 and MB remaining after photolysis are both beyond 90%. This happened due to the absence of TiO_2 in the reaction since photocatalysis activity will only occur when the light from fluorescent lamp strikes the TiO_2 surface thus degrading the organic pollutant. However, 45% of MB was removed for control test with presence of DSAT. This happened due to the adsorption dominant properties of MB which results in the MB itself being adsorbed onto the DSAT

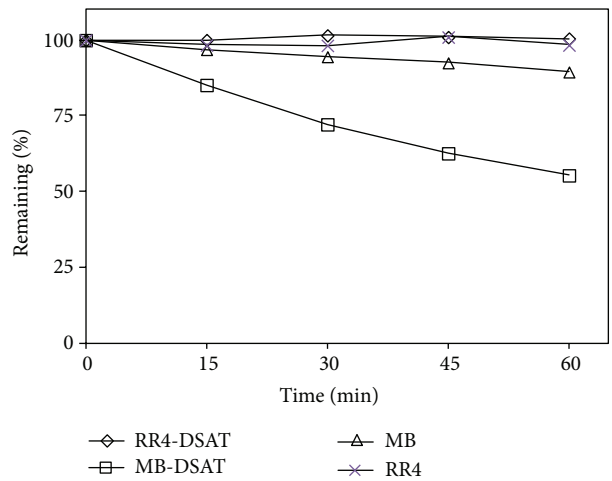

Figure 2: Control tests of RR4 and MB dyes.

surface. This phenomenon explained the results in higher photodegradation of cationic MB dye compared to anionic RR4 dye under immobilization system.

Immobilized TiO_2/DSAT sample has shown a very good photoactivity upon reusability. Figure 3 shows the photocatalytic degradation rate of RR4 and MB upon cycles. It was observed that the photocatalytic degradation rate of immobilized TiO_2/DSAT is getting increased under RR4 as well as MB dye after 20 times of cycles. Beyond 20 until 30 cycles, the degradation rates remained constant for both RR4 and MB dyes. This might be due to the fact that, after the 20th cycle, the formations of porous structure on TiO_2 surface have already exceeded its limit as proven by SEM image in Figure 4(b). Figure 4 shows the surface morphology and cross section images for immobilized TiO_2/DSAT for 1st cycle and 30th cycle. It can be seen that the photodegradation improvement is due to the formation of porous TiO_2 particles on surface of immobilized TiO_2/DSAT after 30th cycle (Figure 4(b)) compared with 1st cycle of immobilized

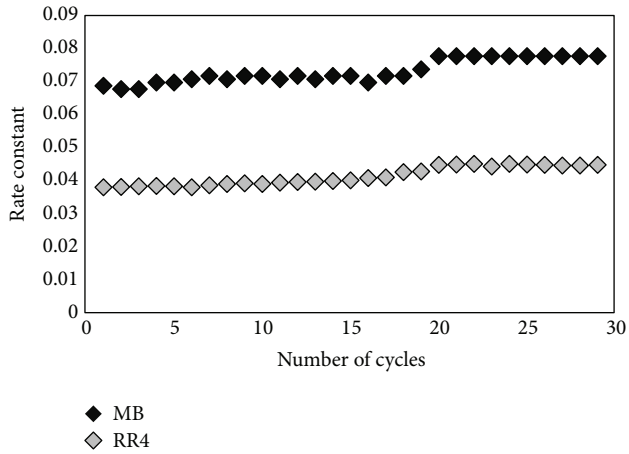

Figure 3: Photocatalytic degradation rate of RR4 and MB under reusability effect.

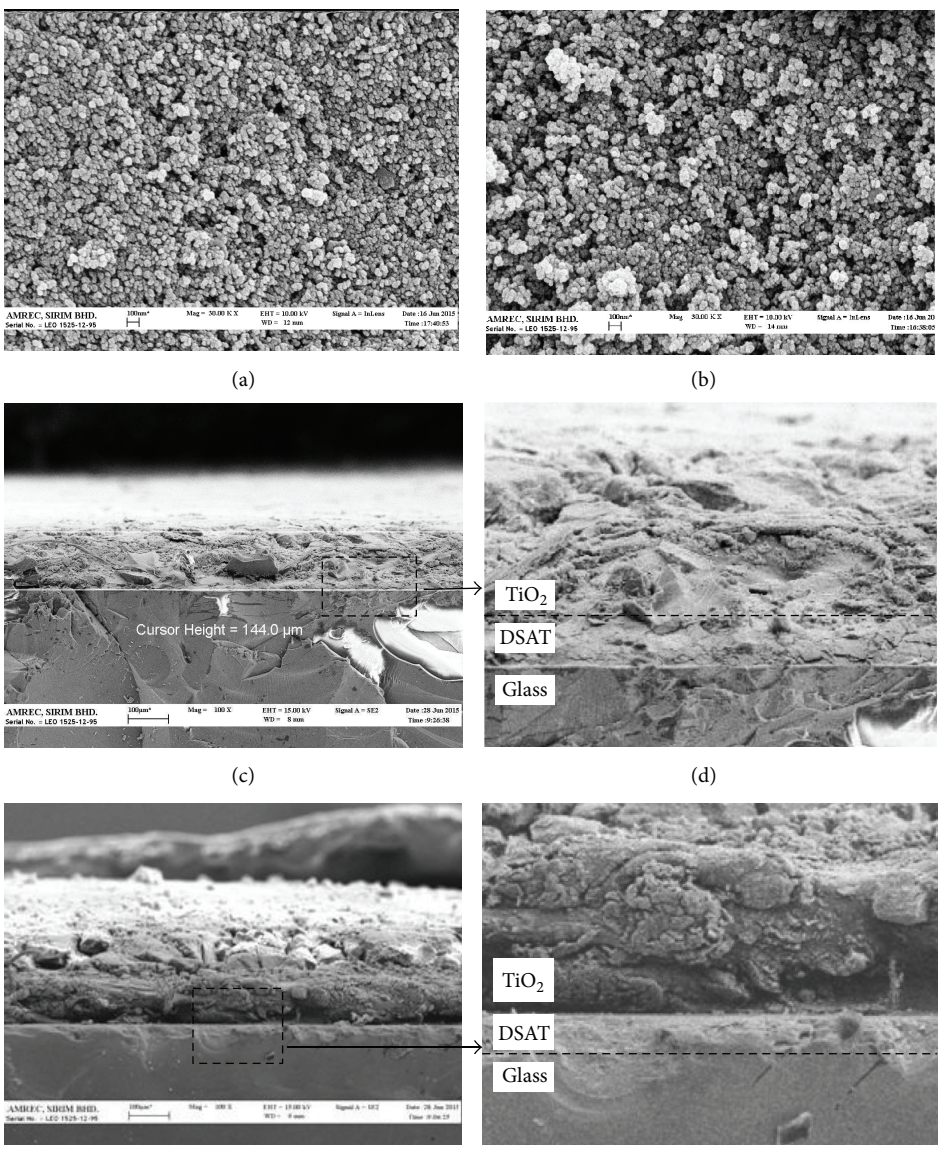

Figure 4: SEM images surface morphology of immobilized TiO_2/DSAT (a) for 1st cycle of photodegradation process of RR4 and (b) after 30 cycles under photodegradation process of RR4. Cross section images of (c) immobilized TiO_2/DSAT under heating process; (d) magnification image for immobilized TiO_2/DSAT under heating process; (e) immobilized TiO_2/DSAT without heating process; and (f) magnification image for immobilized TiO_2/DSAT without heating process.

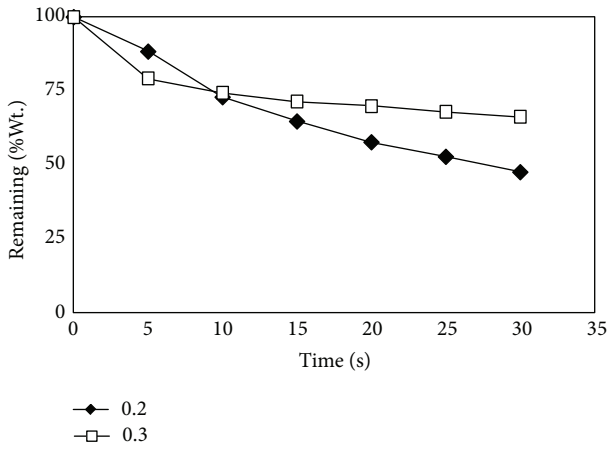

Figure 5: Effect of strength test on immobilized TiO_2/DSAT samples.

TiO_2/DSAT (Figure 4(a)). The formation of pores on TiO_2 surface after 30th cycle is due to oxidation of organic binder (DSAT) during cleaning process. From the cross section images of immobilized TiO_2/DSAT in Figures 4(c) and 4(d), it is obviously shown that TiO_2 sample is embedded in DSAT layer thus making the immobilized TiO_2/DSAT become very strong intact and these cross section images (Figures 4(d) and 4(e)) explain the effect of sample reusability in Figure 3. The heating process after coating TiO_2 on top of DSAT layer during sample preparation is the main cause that makes DSAT condition become semimelted and eventually allowed TiO_2 layer to embed into DSAT. This explanation is supported by comparing of immobilized TiO_2/DSAT without heating process. Figures 4(e) and 4(f) show the cross section images of immobilized TiO_2/DSAT without heating process and the TiO_2 layer is just attached on top of DSAT surface without strong intact. However, TiO_2 layer in immobilized TiO_2/DSAT only remains 50–60 wt.% after 30 minutes of sonication process at strength test as can be seen in Figure 5. It is well expected because no binder was applied on the entire immobilization system. But the immobilized TiO_2 by using DSAT as a thin layer binder significantly improved the photocatalytic degradation rate of cationic and anionic dyes and it is almost the same as TiO_2 suspension or even higher than TiO_2 suspension in certain condition (Figure 1(b)).

4. Conclusion

An immobilized TiO_2 sample was successfully carried out by using DSAT as a thin layer binder. The optimum catalyst loading under photodegradation of RR4 and MB was observed at 0.2 and 0.3 g, respectively. The photodegradation rate of RR4 removal was observed at slightly lower suspension TiO_2 while higher rate of photodegradation under MB was observed. Higher removal rate under MB in immobilized TiO_2/DSAT sample is due to the equilibrium conditions between adsorption and photocatalysis processes and the effect of washing process generated the surface of immobilized TiO_2/DSAT into active photocatalyst. The reusability of immobilized TiO_2/DSAT also is getting improved up to 30 cycles and this cannot be achieved by TiO_2 in suspension mode. A good reusability of immobilized TiO_2/DSAT was revealed whereby TiO_2 was embedded into semimelted DSAT in heating process during sample preparation.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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