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A Study on RR4 Dye as a Sensitizer in Enhancing Photoactivity of Immobilized Photocatalysts

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Abstract. In this work, anionic RR4 dye was used to sensitize TiO_2/PVA and TiO_2/PEG immobilized system in enhancing photocatalytic degradation of cationic methylene blue (MB) dye. 0.3g of TiO_2 and polymer binder was coated onto a clean glass plate by using brush technique to develop optimum immobilize TiO_2 system. A comparison study between immobilized TiO_2/PVA (Im/TiO_2/PVA) and Immobilized TiO_2/PEG (Im/TiO_2/PEG) system with and without RR4 sensitizer were carried out under 45 W fluorescent lamp and visible light irradiation. The photocatalytic degradation of MB was significantly enhanced for both RR4 dye sensitized Im/TiO_2/PVA and Im/TiO_2/PEG with 1st order rate constant was ca. 0.035 and 0.030 min-1 respectively under 45-W fluorescent lamp. Same observation as well under visible light irradiation whereby enhanced of those RR4 sensitized immobilized photocatalysts were recorded as compared with immobilized photocatalysts without RR4 as sensitizer. The photocatalytic enhancement under Im/TiO_2/PVA/RR4 and Im/TiO_2/PEG/RR4 are due to the ability of RR4 dye to become electron (e-) donor for conduction band (CB) of TiO_2, thus making TiO_2 CB riches with electron, eventually this e- is used to remove MB by producing hydroxyl radical.

1 Introduction

The growth of industry in worldwide has discharge variety of contaminants and tremendously increase the generation of byproducts which lead to environment severe. One of the biggest effluents generated from the industries are dyes. These dyes are toxic and give serious hazard to human and aquatic life [1]. Therefore, researcher from all over the world has been working on various approaches in order to solve these issues. Advance oxidation process (AOP) [2], ozonation [3], Fenton technology [4], and photocatalysis [5] has been extensively used by previous researcher to mitigate variety of pollutants in various environmental condition. Recently, photocatalysis has grabbed many attentions from researcher to overcome these issues. Among all of semiconductor photocatalyst, titanium dioxide (TiO_2) is considered very close to the ideal semiconductor for photocatalysis due to its high stability, low cost, readily available and most important it is safe toward both humans and environment [6].

However there are two main disadvantages of TiO_2, firstly it has relatively wide band gap which allow it to absorb only 3-4% energy of the solar spectrum [7] and secondly the suspension mode application of TiO_2 only can be used in a limited time of application, leeched out easily and none

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recyclable [7]. Therefore, many efforts have been done in order to increase the sensitivity of TiO_2 towards visible light region and improve its ability as photocatalyst such as by using dye sensitizer, doping with metallic and non-metallic species, heterojunction system and utilization thin film [7]. Mital et al. [8] reported that dye sensitization is expected to increase the efficiency of the excitation process and also expand the wavelength range of the excitation for the photocatalysis. This is done through excitation of the sensitizer followed by charge transfer to the semiconductor. Charge transfer can be formed in the semiconductor particles by exciting the dye attached to the photocatalyst surface. The excited state of the dye will eject e- to the semiconductor particles. Thus, this sensitization will increase the range of wavelength response of the photocatalyst in order to operate under normal sunlight.

Recently, immobilization of TiO_2 powder has been used by researcher in order to overcome issues arise from suspension mode of TiO_2 as it can be used in a long-term applications [7]. Despite, immobilize TiO_2 system also has its drawbacks such as less surface area for photocatalytic reactions as well as cracking and peeling off of the catalyst layer thus reduce the degree of degradation [7]. Therefore, water soluble polymer such as PEG and PVA is used as a binder to the TiO_2 system to improve its adhesiveness. From the best of knowledge, no study observed on using RR4 as dye sensitizer for MB removal and to compare with PVA and PEG as binder, moreover DSAT method is a new approach used to overcome some issues arise from previous method.

Therefore the aim of this study is to determine the effectiveness of RR4 as sensitizer for photodegradation of MB dye under different polymer binders in immobilized TiO_2. Cationic MB dye was used to evaluate the photocatalytic activity of immobilized photocatalysts under 45 W fluorescent lamp and visible light irradiations.

2 Experimental

2.1 Preparation of TiO_2 immobilized system

TiO_2 solution was prepared by adding 6.5g of TiO_2 powders into 50mL distilled water. The solution will then added with 1mL of PVA polymer in a reagent bottle followed by mechanical stirring until homogenized. The white solution of TiO_2 was then coated onto a clean glass plate with dimension of 50mm x 10mm x 80mm (Length x Wide x Height), which has been taped before with double sided adhesive tape (DSAT). The formulation was then dried in the oven for 10 minutes forming immobilized/TiO2/PVA (Im/TiO_2/PVA), coating process was repeated until 0.3 g loading of Im/TiO_2/PVA was achieved. Im/TiO_2/PVA samples was undergoing washing process by exposing immobilized sample with 45 W of fluorescent lamp under aerated condition for 1 hour prior sensitized with RR4 dye. The preparation procedure of immobilized sample will be repeated using other polymer which is PEG forming Im/TiO_2/PEG sample. This experimental method was modified from Wan et al. [8].

2.2 Preparation of RR4 sensitizer TiO_2 immobilized and photocatalytic study

Both of Im/TiO_2/PVA and Im/TiO_2/PEG plates were immersed into glass cell contained distilled water for washing purpose in 40 minutes prior sensitized with RR4 dye for about 2 hours forming Im/TiO_2/PVA/RR4 and Im/TiO_2/PEG/RR4. Then, those immobilized sample were tested for its photocatalytic activity by applying the plate in a glass cell containing methylene blue (MB). The process was carried out by immersing immobilized sample plate into a glass cell filled with 12 mg L^{-1} of MB dye and irradiated with 45-W fluorescent lamp named as normal light and 45-W fluorescent lamp covered by UV cut-off filter for visible light irradiation. An aquarium pump model NS 750 is used as an aeration source to ensure enough oxygen supply. The dimension of glass cell used in this study is 50mm x 10mm x 80mm (Length x Wide x Height). The decolourization degree of MB dye was determined at 15 minutes time interval until complete decolourization is achieved. The color

reduction value of MB was determined by measuring the absorbance using HACH DR 1900 spectrophotometer with 661 nm wavelength.

3 Results and Discussions

3.1 Place Photocatalytic study of Im/TiO_2/PVA and Im/TiO_2/PEG under 45-W fluorescent lamp

The photocatalytic degradation of 12 mg L^{-1} MB using Im/TiO_2/PVA and Im/TiO_2/PEG with and without RR4 sesitized was illustrated in Figure 1a. Previously, limited study has been conducted on this subject matter. Therefore, this results demonstrate that the increment of photocatalytic activity for RR4 sensitized immobilized samples were observed where the complete decolorization of MB dye can be shorten into 45 and 60 minutes for Im/TiO_2/PEG and Im/TiO_2/PVA respectively, compared to the irradiation time for sample without RR4 sensitizer which both samples are takes more than 90 minutes to complete the decolorization process. This phenomenon supposed to be from the additional of RR4 dye as sensitizer where a significant photocatalytic activity enhancement might be due to the two major factors from RR4 dye. Firstly, RR4 was observed can increased the adsorption ability of the immobilized photocatalyst. As can be seen in Figure 1a, the big different percentage decolorization of MB was observed at first 15 minutes for both Im/TiO_2/PVA/RR4 and Im/TiO_2/PEG/RR4 where the trend for MB color removal was in line with the adsorption study of MB using those immobilized photocatalysts as can be seen in Figure 1b.

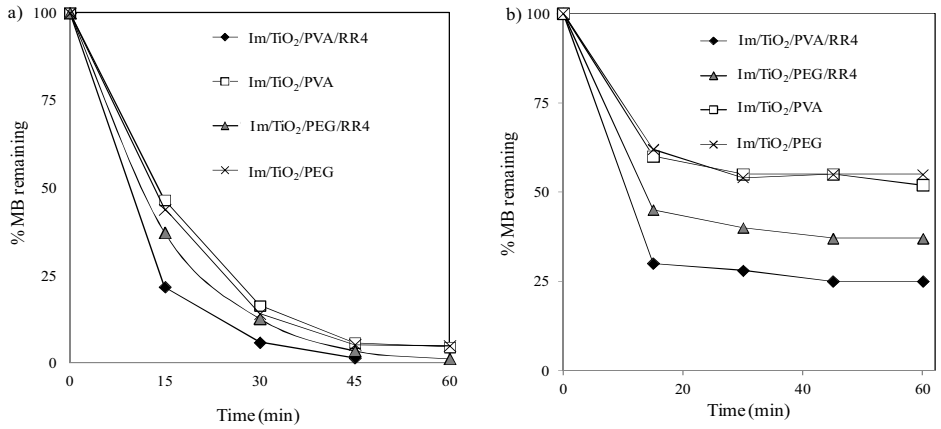

Figure 1. a) Photocatalytic degradation of MB under 45 W fluorescent lamp and b) adsorption study using various immobilized photocatalysts.

Secondly, RR4 dye was observed to become electron (e-) donor thus make the wide range of lights (UV and visible lights) to excite an e-hole pair and become e- donor for conduction band (CB) of TiO_2, thus making TiO_2 CB riches with electron, eventually this e- is used to remove MB by producing hydroxyl radical. Figure 2a shows the photodegradation study of MB under visible light irradiation. Those Im/TiO_2/PEG/RR4 and Im/TiO_2/PVA/RR4 shows a good photo response under visible light where complete decolorization of 12 mg L^{-1} MB was 60 and 75 minutes respectively while no photocatalytic activity was observed under Im/TiO_2/PEG and Im/TiO_2/PVA. According to Mital et al. [9] in their study showed that dye sensitization is expected to increase the efficiency of the excitation process of e-hole pair and also expand the wavelength range towards visible light region. This is done through excitation of the sensitizer followed by charge transfer to the semiconductor. Charge transfer can be formed in the semiconductor particles by exciting the dye attached to the photocatalyst surface. The excited state of the dye will eject e- to the semiconductor particles. Thus, this sensitization will increase the range of wavelength response of the photocatalyst in order to

operate under normal sunlight. Therefore as a surface modification for TiO_2, dye sensitizer can be effective in broadening the range of absorption of this semiconductor. Figure 2b shows the schematic diagram the propose mechanism of photocatalysis process in presence of RR4 dye as sensitizer.

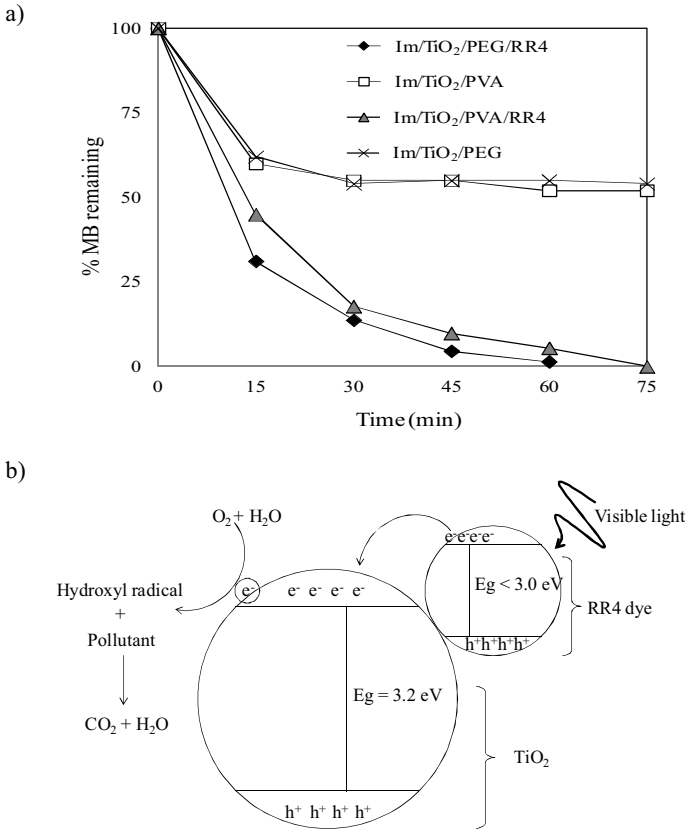

Figure 2. a) Photocatalytic degradation of MB dye under visible light irradiation and b) propose mechanism of photocatalysis in presence of RR4 dye sensitizer.

4 Conclusions

A study on RR4 dye as sensitizer for TiO_2 using immobilization technique was successfully applied namely Im/TiO_2/PVA/RR4 and Im/TiO_2/PEG/RR4. The photocatalytic activity of samples under RR4 sensitizer is significantly enhanced due to the ability of RR4 to become absorbance and electron donor for visible light irradiation. No photocatalytic activity under visible light irradiation was observed for those immobilized photocatalysts without presence of RR4 sensitizer. Hence, the influent of sensitize RR4 in immobilized TiO_2 makes this photocatalyst become more effective.

References

[1] M.A. Nawi, S. Sabar, and Sheilatina, Photocatalytic decolourisation of Reactive Red 4 dye by an immobilised TiO2/chitosan layer by layer system, J. of Colloid and Interface Science, **372**, 80–87 (2012).

[2] M. Pera-Titus, V. Garcia-Molina, M.A. Banos, J. Gimenez and S. Esplugas. Degradation of chlorophenols by means of advance oxidation process: A general review, Appl. Catal. B., **47**, 219–256, (2004).
[3] K. Ikehata and M.G. El-Din, Aqueous pesticides degradation by ozonation and ozone-based advances oxidation processes: A review (part II), Ozone-Sci. Eng., **27**, 173–202, (2005).
[4] K. Ikehata and M.G. El-Din, Aqueous pesticides degradation by hydrogen peroxide/ultraviolet irradiation and fenton type advance oxidation processes: A review, J. Environ. Eng. Sci., **5**, 81–135, (2006).
[5] J.M. Britto and M.D. Rangel, Advanced oxidation process of phenolic compounds in industrial wastewater, Quim. Nova, **31**, 114–122, (2008).
[6] M.N. Chong, B. Jin, C.W.K. Chow and C. Saint, Recent developments in photocatalytic water treatment technology: A review, Water Res., **44**, 2997–3027, (2010).
[7] M.A. Nawi, A.H. Jawad, S. Sabar and W.S. Wan Ngah, Immobilized bilayer TiO_2/chitosan system for the removal of phenol under irradiation by a 45 watt compact fluorescent lamp, Desalination, **280**, 288–296, (2011).
[8] W.I. Nawawi, S.K. Ain, R. Zaharudin, A.H. Jawad, M.A.M Ishak, K. Ismail and S. Sahid, New TiO_2/DSAT immobilization system for photodegradation of anionic and cationic dyes, International Journal of Photoenergy, **2015**, 1-7, (2015).
[9] G. S. Mital and T. Manoj, A review of TiO_2 nanoparticles, Chinese Science Bulletin, **56**, 1639-1657, (2011)