Effect of Photoetching Process onto Immobilized PANI/TiO$_2$ Films Towards Photocatalytic Degradation of RR2 dye

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Abstract. Polyaniline (PANI) and P-25 Titanium dioxide (TiO$_2$) was fabricated as immobilized P-25TiO$_2$/PANI/ENR/PVC film and reported on the photocatalytic study. PANI and TiO$_2$ was immersed into the organic solvent and being coated onto glass plates under influenced of ENR/PVC polymeric binder by using a dip-coating method. It was found that, the removal of RR2 dye nearly good as suspension system after the pre-irradiation process. Based on COD and BET results, it showed that the optimum time of etching process was 7 hours irradiation time. This pre-irradiation process enhanced the removal of dye due to leached out of excessive binder and also exhibit visible light active after insertion of PANI into the immobilized system.

1 Introduction

The use of immobilized photocatalysts has been proposed as a method to overcome suspended system since 1993 [1]. Immobilization involves the use of inert supports, such as glass, activated carbon, silica-based materials and polymeric materials. However, the main drawbacks of using immobilized system for the photocatalytic degradation process are low stability during continuous applications. Moreover, the limitation of mass transfer due to the reduction of specific surface area also reduced its potential applicability to waste water treatment [2]. To solve those problems Nawi and Zain, (2012) and Nawi et al. (2012) had proven that immobilized TiO$_2$ system using ENR/PVC blend as the organic binder improved its photocatalytic activity once most of the organic binders were etched out using light irradiation. This pre-irradiation process allowed the regeneration of the surface area to within 86% of the pristine TiO$_2$ particles. The enhanced surface properties of the immobilized photocatalyst system generated a photocatalytic performance as good as the slurry method of the TiO$_2$ particles during the photocatalytic degradation of an aqueous MB dye solution [3].

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In this study, a conjugated polymer polyaniline (PANI) was selected as amongst of versatile heterogeneous-conjugated polymers that exhibit good stability toward environment. Furthermore, it represents as a hole scavenger and improve photocatalytic activity when electrons are added into photocatalyst conduction band under visible light irradiation [4]. Regardless of having a good performance in photocatalytic activity, there are still no focus attention on sustainability and re-usability of the system on the longer operation time which can minimize the secondary cleaning process and also operational cost.

2 Methodology

The P-25TiO2/PANI/ENR/PVC solution was prepared by addition of PANI soluble in chloroform prepared by slight modification of method described by Palaniappan et al. (2006) [5]. This soluble PANI was added onto an optimized ENR/PVC binder prepared exactly as reported of the work of Nawi et al. (2012). Then 6 g of P-25 TiO2 was added into the mixture and followed by another sonication process for 8 h in order to homogenize the mixture. Complete homogenization was usually indicated by good homogeneity of the PANI/TiO2 nanoparticles inside the solution with additives of PVC/ENR as binders. Finally, the homogenized formulation was sealed up tightly and stored in an ambient atmosphere to avoid unnecessary evaporation. For immobilized purposes, P-25TiO2/PANI/ENR/PVC solution was coated onto glass plate by using a dip coating technique. The amount composite loading coated onto glass were fixed according to the parameter study. Meanwhile during irradiation, fluorescence lamp and sunlight was used as source of energy for the photocatalytic study. SEM micrographs and EDX elemental analyses were carried out by using scanning electron microscope (SEM) (LEO SUPRA 50 VP Carl-Ziess SMT) and energy dispersive X-ray spectrometer (EDX) (Oxford INCA 400 Energy). Meanwhile Chemical Oxygen Demand (COD) reagent contained about 0.1 g mercury sulphate will mix 2mL of each sample aliquot with 3 mL COD reagent. On the other hand, another test tube containing ultrapure water and the COD reagent was also prepared to serve as a blank solution. The mixture was then vigorously shaken before being refluxed in the HACH Cod reactor at 140°C for two hours. After the refluxing process, the mixture was cooled down to room temperature. The COD concentration was measured with a HACH DR2000 spectrophotometer at 620 nm [6].

3 Results and Discussion

ENR/PVC blend organic polymer was a good binder to fix the catalyst onto the glass plate. However, this binder could decompose by the photocatalytic reaction and leach out a dissolved organic matter into the treated water. In this regards, COD test was carried out to determine the amount of leachable organics from the plates. Table 1 shows the pre-irradiation process using P-25TiO2/PANI/ENR/PVC system over the span of 10 h. As suspected, organic binders were etched out and was measured based on COD concentration. Based on Nawi and Zain, (2012), most of the contribution of COD values came from the ENR polymer. Furthermore, as reported by Nawi and Zain, (2012), it was observed that removal of ENR was high at the early stage of the irradiation period and achieved zero COD values after 4 h of irradiation respectively. This was due to the ENR binder which was unstable state during its modification with a peracid. Nevertheless, P-25TiO2/PANI/ENR/PVC system needed longer time to remove the leachable organic from the irradiated plate. Table 1 shows that the degradation of the polymer blend occurred significantly during the first 3 h of irradiation and it started to slow down until it achieved zero value at 7 h onwards. Hence, it can be concluded that the optimum period of the pre-irradiation process was 7 h and it was suspected at this period of time most of the organic binders were etched out from the system.
Table 1: The COD value of treated sample upon irradiation time by using P-25TiO2/PANI/ENR/PVC plate.

| Etching time (h) | 0   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  |
|------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| COD (mg/L)       | 183 | 82  | 47  | 38  | 24  | 11  | 0   | 0   | 0   | 0   |

3.1 SEM-EDX and BET analysis

Based on the effect of the pre-irradiation process, the non-irradiated and irradiated plates were subjected to SEM analysis in order to observe the surface morphology of the coatings before and after 7 h of light irradiation. Figure 1 presents the SEM micrographs for freshly prepared P-25TiO2/PANI/ENR/PVC plate and the 7 h pre-irradiated plate under fluorescent lamp source. It can be seen that, the surface morphology of freshly prepared P-25TiO2/PANI/PVC was quite compact and dense due to TiO2 particles that were enwrapped by the organic binders. The image also shows the particles were less porous due to most of the particles were bounded together. After the plates were subjected to 7 h irradiation, the particles were clearly visible with less bounded and become more porous since the organic binders were degraded and removed upon light irradiation. This observation is consistent with the COD concentration values as at 7 h and onwards gave zero COD which indicates that most of the binders were degraded and removed from the immobilized system [7-12].

Fig.1. SEM images at 1,000X; a) before irradiate , (b) after 7 hrs irradiation

Table 2: The surface area from initial to 7 hours irradiation and amount of % C content and within the P-25TiO2/PANI/ENR/PVC with time irradiation.

| Etching time (h) | Weight % C | Surface area (m²/g) |
|------------------|------------|---------------------|
|                  | 0          | 16.55               |
|                  | 7          | 5.96                |

Table 2 illustrates the decrease of % C content within the P-25TiO2/PANI/ENR/PVC with time of irradiation. Upon 7 hour of irradiation, % C decreased from 16.85% to 5.95%. This decrease in C content can be due to the degradation of ENR, PVC or PANI. As indicated in Table 2, partial removal of the organic binders had increased the surface area from the initial 28 m² g⁻¹ to 34 m² g⁻¹.
3.2 Photocatalytic Activity Study

Figure 2. shows the photocatalytic degradation of RR4 dye under UV and visible light conditions. As has been pointed out by many reports [14–18], doping of PANI into the TiO2 catalyst enabled the resulted composite to be visible light active. Figure 2. shows the results obtained under both unfiltered and UV filtered (visible light irradiation) lamps for various photocatalyst systems in the degradation of RR4 dye. For comparison purposes, the results of photocatalytic degradation of RR4 by an equivalent amount of P-25TiO2 powder in the slurry system are also shown in the Fig. The P-25 TiO2 slurry system only required 15 minutes to decolorize RR4 dye under unfiltered 45-W fluorescent lamp. However, once the fluorescent lamp was attached with a UV filter, the P-25 slurry system was essentially inactive where only 20% of RR4 was removed and this was mainly due to the adsorption process. Nevertheless, the immobilized P-25TiO2/ENR/PVC-7h exhibits some visible light activity whereby the removal of RR4 dye after 60 minutes of irradiation was 35%. As suspected the P-25TiO2/PANI/ENR/PVC-7h was clearly visible light sensitive where 85% of RR4 dye was decolorized after 60 minutes of irradiation.

![Graph](image-url)

**Fig. 2.** Photocatalytic degradation of 30 mg L⁻¹ RR4 dye under visible light irradiation for various photocatalyst systems: (a) TiO2 slurry UV filtered; (b) P-25TiO2/PANI/ENR/PVC; (c) P-25TiO2/PANI/ENR/PVC-7h; d) P-25TiO2/ENR/PVC-7h and (e) P-25TiO2 slurry

4 Conclusion

Photocatalytic degradation of RR2 dye by using P-25TiO2/PANI/ENR/PVC plate under 7 hours pre-irradiation time has been successfully improved the photocatalytic activity of the system whereby its photocatalytic activity was almost as good as the suspended system. The increment of the photocatalytic activity was in line with the increased BET surface area due to removal of excessive binders toward etching process prolong for 7 hours. Additionally, it had also clearly proven that the immobilized P-25TiO2/PANI/ENR/PVC-7h photocatalyst systems were clearly visible light sensitive due to insertion of PANI conjugated polymer.
We would like to thanks the Ministry of Higher education (MOHE) for providing generous internal financial support under FRGS grant: FRGS/1/2019/STG0/UNIMAP/02/2 in conducting this study under Universiti Malaysia Perlis and Universiti Teknologi MARA (UiTM), Arau for providing all the facilities.

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