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The Effect of Binders Towards Immobilized PANi-TiO2 System during Photocatalytic Energy Conversion

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Abstract: Three types of binder PVA, PVC and PVA/PVC mixtures have been evaluated for PANi-TiO2 immobilized system. These binders have been varied to several weights of loading for optimization purposes. As a result, it shows that higher loading of binders improved the photodegradation of RR4 dye but the mechanical properties of each immobilized system started to decreases. This behavior occurs due to the immobilized particles coated on the plate easy to peel off despite weak attachment toward to the continuous photodegradation operation system. Therefore 4 times of dipping PVA and PVC layers was selected as the optimum loading of binders to the PANi/TiO2 system during photocatalytic degradation of Reactive Red 4 with the rate constant of 0.5568 K/min for PVA and 0.5742 K/min for PVC. Meanwhile for PVA/PVC mixture binder system at 4 times dipping showed the highest rate constant of photodegradation of RR4 dye with 0.6026 K/min. In addition, SEM analysis has also been carried out for further investigation.

Key words: *Polyaniline-TiO2, Immobilized, Photocatalysis, Energy Conversion*

INTRODUCTION

Researchers have provoked the need to create effective evacuation operations, which are known as advanced oxidation processes (AOPs) [2]. Among all the Advance Oxidation Processes (AOPs), Titanium Dioxide (TiO_2) photocatalytic oxidation holds a great responsibility to solve this issue [3]. TiO_2 is the most effective, stable, non-harmful and cheap catalyst in heterogeneous photocatalytic processes for the evacuation of dyes over an extensive variety of pHs [4]. TiO_2 photocatalyst uses sunlight and air to create numerous reactive species, including the effective and non-specific oxidant hydroxyl radicals, to mineralize the natural pollutants to harmless substances [3].However, there are two main drawbacks of TiO_2, firstly it has generally wide band gap which permit it to retain just 3-4% solar energy and furthermore slurry system of TiO_2 just can be utilized as a part of a restricted time of application and none recyclable [1]. So as to proficiently use the solar energy in the photocatalytic reactions, a few endeavors have been made to increase the photoresponse of TiO_2 to the visible region and extend the photocatalytic productivity of TiO_2 under visible-light irradiation, for example, by metal and nonmetal doping, noble metal deposition, producing composites with narrow semiconductors and surface dye sensitization. Among these alteration techniques, surface dye sensitization has possessed the capacity to enhance the immobilization of TiO_2 powder under visible light [5].

Nowadays, consideration is paid to conducting polymers, which are utilized as photosensitizers to change TiO_2 behavior. Conducting polymers been used to modify TiO_2 to degrade natural pollutants. As a conducting polymer, polyaniline (PANi) has special electrical, optical and photoelectric properties [6]. PANi also has good chemical stability, non-toxicity, low cost synthesis and high instinctive redox properties [7]. More attention has been given to the combination of PANi and TiO_2 with another polymer such as polyvinyl chloride (PVC), and polyvinyl alcohol (PVA). Under the certain state, polymers with carboxyl or hydroxyl groups will bond chemically with the hydroxyl group on the surface of TiO_2. PVA has great film-forming capacity and useful in immobilization of TiO_2. Its low market cost is another variable that many analysts utilized this polymer in their work [8].

II. MATERIALS

Titanium (IV) Isopropoxide (TTIP) 97% and Polyvinyl Alcohol (PVA) 75% hydrolyzed which is used to synthesis Titanium dioxide and as polymeric binders respectively that supplied by Sigma Aldrich. In

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addition, aniline, ammonium peroxydisulfate (APS) and polyvinylpyrrolidone (PVP) were also purchased from Sigma Aldrich as a monomer, an oxidant and an emulsion stabilizer respectively. Reagent grade sodium dodecyl sulfate (SDS), acetic acid (BDH, India) and ethanol were used without further purification. Chloroform and Reactive Red 4 (RR4) dye which is also known as Cibacron Brilliant Red with 50% dye content was provided by Aldrich Chemicals.

III. SYNTHESIS OF POLYANILINE

Soluble PANi can be produced by several methods such as aqueous, dispersion, emulsion and electrochemical polymerization techniques [9]. Among all this, emulsion polymerization is the most preferable which can improve the processability of PANi. Soluble PANi was produced by emulsion polymerization using SDS as a surfactant, APS as an oxidant and chloroform used as solvents [10]. At the beginning, 6.0 g acetic acid 0.5 g of PVP were added into 200 ml aqueous solution that contains 0.02 ml of aniline and mixing done by stirring the solution about 10 minutes and followed by the addition of 50 ml of chloroform solvent into the mixture where the mixture was labelled as solution A. For another solution, 0.600 g APS oxidant was dissolved in 50 ml aqueous solution and the mixture of 1.0 g SDS surfactant in 50 ml chloroform was added and stirred for 10 minutes. This mixture was labelled as solution B. Finally, the solution B was added drop by drop into solution A and polymerization occurred for 8 hours.

IV. FORMATION OF PANi/TiO_2/ IMMOBILIZED SYSTEM USING DIFFERENT BINDERS

The adhesion strength of PANi/TiO_2 composite adheres to the glass substrate was influenced by the type of binder as supporting material. Therefore, PANi/TiO2 composite was directly blending together with the binders and being sonicated for one hour prior homogeneity of the solution. In order to select a promising adhesion polymer for the immobilized system, a series of loading binder and the comparison of a number of dipping layers were carried out. **Table 1.0** shows the varied amount of binders with fixed amount PANi/TiO2 used in this experiment.

Table 1.0: Different concentration of binders at different amount of dipping solution

No of dipping / Concentration	3 dips	4 dips	5 dips	6 dips
PVA	3.00×10^{-3}M	4.00×10^{-3}M	5.00×10^{-3}M	6.00×10^{-3}M
PVC	3.75×10^{-4}M	5.04×10^{-4}M	6.25×10^{-4}M	7.50×10^{-4} M
PVA/PVC	1.69×10^{-3}M	3.38×10^{-3}M	5.07×10^{-3}M	6.76×10^{-3}M

V. EXPERIMENTAL

The experimental set up for the photocatalytic study of immobilized PANi/TiO_2/binder is shown in Figure 1. A homemade photoreactor equipped with 50 watts of fluorescent lamp was used as the source of energy. This fluorescent lamp was assembled in the custom made glass container with the PANi/TiO_2/binder plate was placed onto the glass container. The beaker was filled with 60 mL of RR4 solution at specific dye concentration. The photocatalytic activity of the prepared system was determined based on the photodegradation of RR4 dye. Then the sample readings were taken at 1 hour interval for up to 5 hours using the HACH DR/2000 spectrophotometer at a wavelength of 517 nm for reactive red 4 dye.

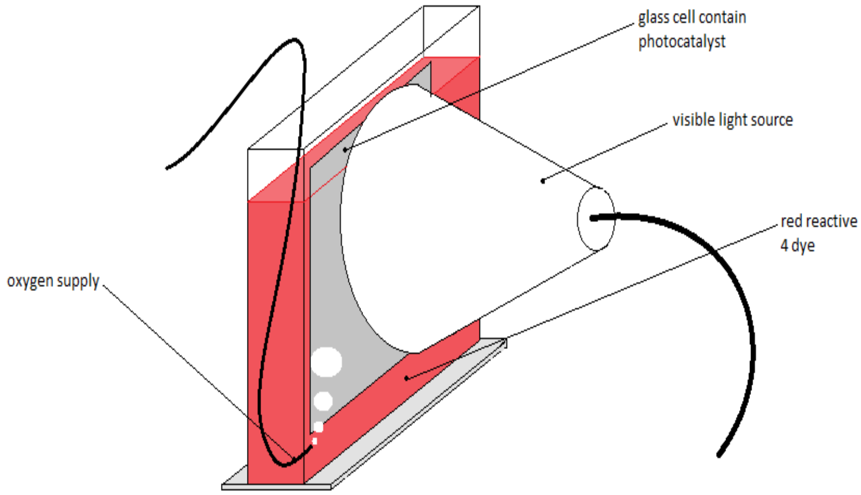


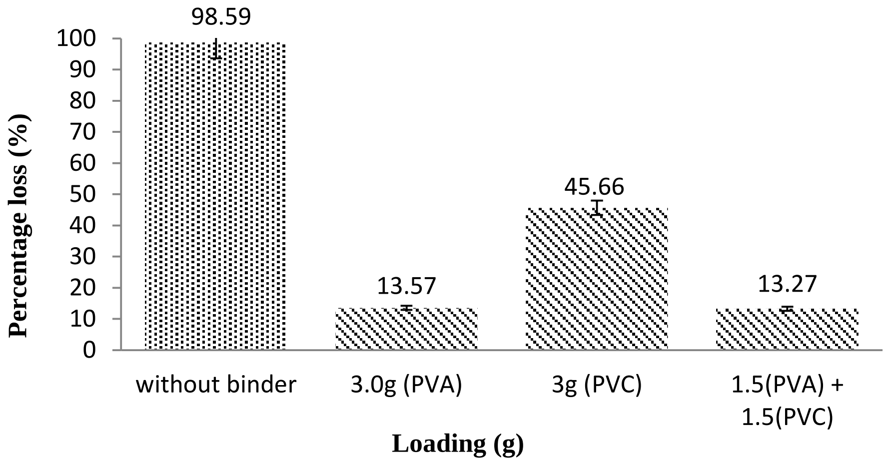
Figure 1: Experimental set up of photocatalytic degradation of RR4 dye.

VI. RESULTS AND DISCUSSION

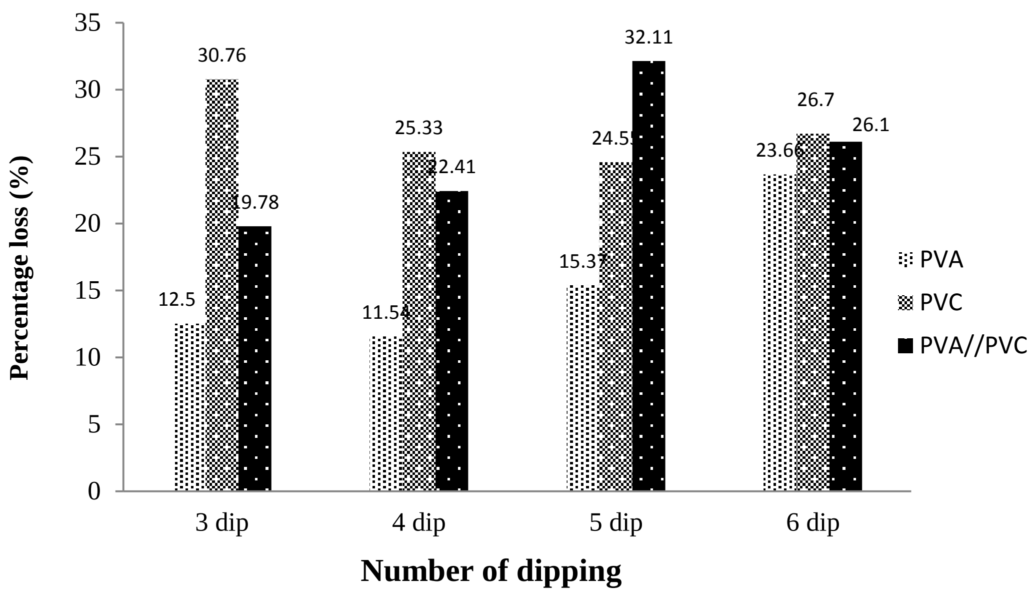
Adhesion study

As preliminary result of adhesion strength of the immobilized system, Figure 2(a) showed the weight loss of sonicated plates of PANi/TiO_2 without binder as a control and PANi/TiO_2 with different binder loading at single dipping coating layer. Clearly shows that without the binder influence, the major weight loss occurred for the control plate with 98.59% of weight loss. While second highest weight loss was recorded by 3g of PVC with 45.66 % followed by minimal losses of 3g of PVA and mixture of 1.5g of PVA/1.5g of PVA with 13.57 % and 13.27 % respectively. As suspected, PVC weight loss occurs due to weak bonding of C-C while PVA losses due to swelling effect of the PVA particles after a certain period of time. Interestingly, the crosslinking of molecule structures of PVA and PVC had reduced the weight loss of particles coated onto the glass plate.

On that regards, a series of different dipping of the composite with the different amount of binder loading were shown in Figure 2(b). Thus, from Figure 2(b), each binder revealed a different interaction of adhesion properties toward the number of dipping layers. It shows that PVA binder loss the strength with the addition of PVA amount to the system while PVC binder showed good stability towards an addition of PVC for each system. However, the percentage of weighing losses of PVC was higher than PVA with the average losses were 26.88 %. Despite of that, the mixture of PVA/PVC binder was applied to the system with the same condition, the adhesion properties of immobilized PANi/TiO_2 were improved for 3 and 4 dipping layers of PVA/PVC binder with the percentage weight losses were below 23%.



(a)



(b)

Figure 2: (a) Single dipping of without binder, PVA, PVC and weight ratio 1: 1 of PVA/PVC polymer onto photocatalyst immobilized system at different number of dipping. ; (b) Percentage weight loss of photocatalyst at different binder and without binder coated onto glass substrate

VII. PHOTOCATALYTIC ACTIVITY OF RR4 DYE AND PHYSICAL CHARACTERISATION

The photocatalytic activity of immobilized at different binders system was showed in Figure 3. It shows that the rate constant of PVA and PVC binders was 0.556 K/min and 0.5742 K/min respectively. Under these systems, the photodegradation of RR4 dye take longer time and both binders might lose it adhere properties due to their weaknesses. Interestingly, the best photocatalytic activity of RR4 dye was recorded by the PANi/TiO_2 system using the mixture of PVA/PVC binder. The rate constant achieved was 0.6026 K/min and the system was sustainable with prolonging photodegradation process. This promising result occurs due to a good interaction of polymeric binder of PVA and PVC. As suspected during PVA and PVC polymers were blended together, some of the parts of polymer were crosslinked together and new bonding was formed whereas improved the structural properties of the blended polymer.

While Figure 4 shows the SEM image of PANi/TiO_2 blended into PVC/PVA binders. The morphological structure analysis was analysed and studied due to the relation between the microstructure of the system towards strength and photoreactivity. Structure analysis using scanning electron microscope was able to view the detailed image of particles up to microstructure. Based on Figure 4, PANi/TiO_2 particles were agglomerated onto the PVC/PVA binders. The morphology of the system prepared showed uneven surfaces. However, the polymeric binder helps to improve the adhesion properties of the system and prolong the photodegradation process without major losses of particles coated onto the immobilized plate.

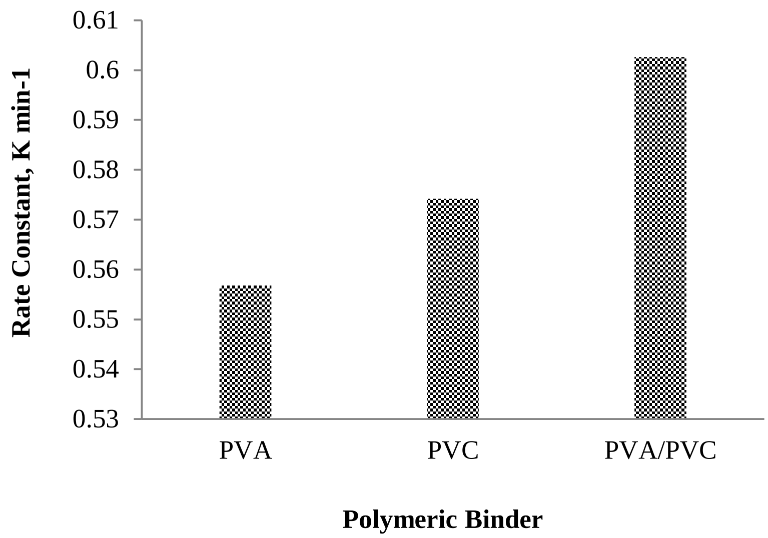


Figure 3: Four times dipping of binder, PVA, PVC and weight ratio 1: 1 of PVA/PVC polymer

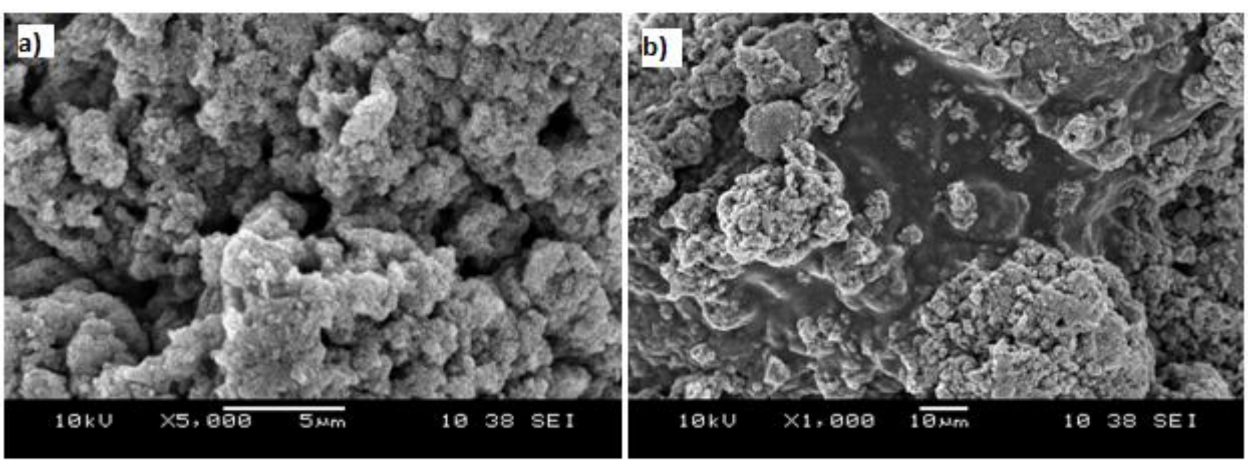


Figure 4: (a) SEM image of PANi/TiO_2 coated with PVA/PVC polymer at 5000x magnification; (b) SEM image of PANi/TiO_2 coated with PVA/PVC polymer at 1000x magnification

VIII. CONCLUSION

The immobilized PANi/TiO_2 system was successfully prepared at different type of binders. PANi/TiO_2 system under PVA/PVC mixture showed the highest rate constant of photodegradation of RR4 dye with 0.6026K/min followed by PVC and PVA binder with the rate constant of 0.5742K/min and 0.5568K/min respectively. Based on the results, that higher loading of binders were not preferable due to weak attachment of PANi/TiO_2 composite toward to the prolong operational system. As can be seen, the stability of the system was achieved in the PVA/PVC mixtures binder at 4 dips loading due to good interaction of polymeric binder of PVA and PVC in the matrix. This result was supported by the SEM image of the PANi/TiO_2 whereby the particles were closely held together in aggregated form into the PVA/PVC matrix which improved the adhesion properties of the system.

IX. ACKNOWLEDGEMENT

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