

UNIVERSITI TEKNOLOGI MARA

**PHOTOCATALYTIC
ENHANCEMENT OF
IMMOBILIZED Ag-TiO₂/ENR/PVC
BY REVERSED
PHOTODEPOSITION METHOD FOR
PHOTODEGRADATION OF
METHYLENE BLUE DYE**

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ABSTRACT

This study proposed a reversed photodeposition technique to increase the reaction of modified semiconductor with the organic pollutant. This technique requires the introduction of Ag onto the surface of immobilized TiO₂, in contrast to the standard method of applying photodeposition on TiO₂ to produce Ag doped TiO₂ prior to immobilization. The immobilization approach employed a dip-coating technique using a coating solution consisting of Degussa P-25 TiO₂, epoxidized natural rubber (ENR-50) and polyvinyl chloride (PVC) as the organic binder. This study focused on the coating of Ag on TiO₂/ENR/PVC materials forming ATEP plates. The coating was carried out at different concentrations (100-500 ppm) using reversed (R) and standard (S) approaches at various photodeposition times (1-6 h). The photocatalytic efficacy of the immobilized ATEP(R) and ATEP(S) was investigated in the degradation of 12 mg L⁻¹ methylene blue (MB) dye. XRD and FESEM study revealed that the photoetching of ENR/PVC in the reversed approach exposed more TiO₂ crystals. The composition of Ag in the reversed approach was higher at wt% = 28.3 than wt% = 0.1 in the standard approach, as confirmed by EDX analysis. Additionally, Ag exhibits a strong surface plasmonic resonance (SPR) effect, giving a decrease in PL intensity in the reversed sample suggesting the deposition of Ag lowered the e⁻/h⁺ recombination. UV-Vis DRS analysis demonstrated that the reversed sample has reduced the band gap energy at E_g = 2.30 eV compared to the standard sample with E_g = 2.62 eV and shifted the adsorption edge into the visible region. 3D profiler revealed that the surface porosity of ATEP-300 (R 5h) was higher with surface roughness, R_a = 6556.93 nm than R_a = 5138.02 nm for ATEP-400 (S 1h). PEC analysis confirmed that the ATEP-300 (R 5h) sample showed better separation of charge transfer in light conditions thus increasing its conductivity. The rate constant, k, for the optimal ATEP-300 (R 5h) was higher at 0.0495 min⁻¹ compared to the ATEP-400 (S 1h) with k = 0.0463 min⁻¹ after 60 min degradation of MB dye with the percentage removal for ATEP-300 (R 5h) = 96.39% and ATEP-400 (S 1h) = 94.41%. This difference was attributed to the more porous structure of TiO₂ and the strong SPR impact of Ag in the reversed sample. The scavenger trapping test showed that the main reactive species involved in the degradation of MB dye was •OH. The reversed samples demonstrate a better photocatalytic efficiency than the standard samples with the optimum sample exhibits stability for 6 cycles. From the ICP-OES result, the percentage of Ag used in the reversed method was 8 times lesser compared to the standard method which proved that the reversed method successfully minimized the usage of Ag dopant.

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Wastewater management has become a concern these days due to the inability to treat effluent properly. Wastewater may contain hazardous materials such as toxic chemicals, heavy metals, dyes, and organic compounds (Saravanan et al., 2021). Industries such as printing factories and textile manufacturers heavily used dye in their production which led to the accumulation of dye in water bodies. Nearly 10,000 different synthetic dyes can be found in the market and over 700,000 tons are produced annually worldwide and almost 200,000 tons of synthetic dyes are released into the mainstream because of the ineffective dyeing method used in textile industries (Al-Mamun et al., 2019).

Several technologies have been proposed for wastewater treatment such as adsorption, photo-fenton process, ozonation and electrochemical filtration. However, a few drawbacks make these treatments not viable in treating wastewater. For example, the adsorbent used in the adsorption process may lose its efficacy over time and the generation of large amounts of ferrous iron sludge in the photo-fenton process makes the process less efficient while ozonation produces hazardous byproducts and requires higher energy (Zajda & Aleksander, 2019; Das et al., 2024).

Advanced oxidation process (AOP) refers to a set of chemical treatment procedures designed to remove organic and inorganic materials in wastewater by oxidation process through reactions with hydroxyl radicals ($\bullet\text{OH}$). Photocatalysis is one of the techniques under AOP that shows strong potential for the effective removal of dye pollutants in wastewater (Natarajan et al., 2018). This process involved the semiconductor and production of $\bullet\text{OH}$ as the main oxidant to oxidize model pollutants (Nosaka et al., 2016). Photocatalysis produces no secondary waste and is readily available and easily accessible despite it needs low cost to operate (Al-Nuaim et al., 2023). These advantages make it received extensive attention from researchers.

Titanium dioxide (TiO_2) is a potential semiconductor due to its non-toxicity, stability, availability, photochemically active and low cost (Lu et al., 2019; Dharma et al., 2022). One of the most critical characteristics influencing its functionality is its band