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# Photocatalytic activity of rubber sheet impregnated with $TiO_2$ particles and its recyclability

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**Abstract**

The preparation of rubber sheet impregnated with titanium dioxide particles is presented. This method is simple and low cost based on the use of commercial $TiO_2$ powder directly mixing with rubber latex (60% HA) and distilled water. The morphology and roughness of the sheet surface increased with increasing amount of distilled water. Sheet impregnated with anatase (Imp-An) showed uniform, small grains with dense structure and well surface coverage more than one with P25 (Imp-P25). Their photocatalytic activities were evaluated using methylene blue (MB) as a model organic dye compound. These impregnated sheets could degrade MB solution under UV-light irradiation. Comparing with the commercial $TiO_2$ samples in powder form (anatase from Carlo Erba and Degussa P25) the efficiencies of photocatalytic degradation of MB fall in the decreasing order as: P25 (powder) > anatase (Carlo Erba) (powder) > Imp-An sheet > Imp-P25 sheet. However, the impregnated sheet has an advantage over the loose powder that the catalyst sheet can be recovered after used and can be reused.


*Keywords:* Immobilized titanium dioxide; Titanium dioxide photocatalyst; Titanium dioxide thin film; Methylene blue degradation; Photocatalytic degradation

## 1. Introduction

In the industrialized world the major cause of environmental deterioration came from industrial pollutants and water contaminants. One form of the latter is the releasing of dyes by the dyeing and printing industries into the natural water systems. The release of this colored wastewater in the eco-system is a dramatic source of aesthetic pollution, eutrophication and perturbation in aquatic system [1,2]. The known water treatment processes nowadays are rather inefficient for this ever increasing problems. This leads to search for more effective method, low cost, and ease of use to degrade the dye into environmentally compatible products [3–6]. During the past decade, attention has been focused on heterogeneous photocatalysis for the treatment of recalcitrant chemical present in the wastewater. Among the semiconductors, $TiO_2$ is the most widely used photocatalyst because of its good activity, chemical stability, commercial availability, and inexpensiveness. It is generally used as a photocatalyst for environmental applications such as air purification, water disinfection, hazardous waste remediation, and water purification [7–9]. However, the application of powdered $TiO_2$ in wastewater treatment is limited since a post-treatment separation is required to recover the catalyst powder. Mobile photocatalyst powder presents another setback that it also causes an adverse human health problems [10–12]. In order to avoid the use of photocatalyst powder, efforts have been made to coat $TiO_2$ thin films on various substrates such as glass [13], ITO glass [14], plastics [15], and polymers [16]. $TiO_2$ thin films have been prepared by various techniques such as chemical vapor deposition [17], precipitation [18], flame synthesis [19], and sol–gel dip coating [20,21]. These

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techniques, however, need expensive equipment and complex procedures.

In this work, $TiO_2$ powder was impregnated in the rubber sheet, as a means to immobilize $TiO_2$ particles, by direct mixing of commercial $TiO_2$ powder with latex and distilled water. The efficiencies of methylene blue degradation under UV-light irradiation were evaluated. Methylene blue (MB) was used as a model dye in this work due to its being one of the most important basic dyes used in major dyeing and printing industries. MB has also been used in several research articles involving photocatalyst efficacy. The selection of MB in this work would provide direct comparison with those studies as well.

## 2. Experimental

### 2.1. Chemicals and equipment

The main chemicals are titanium dioxide (Anatase, AR grade, Carlo Erba, Milano, Italy); titanium dioxide (P25, Degussa AG, Frankfurt, Germany); methylene blue ($C_{16}H_{18}ClN_3S$, Seelze, Germany); rubber latex (60% HA, Chana Latex Co. Ltd., Songkhla, Thailand). The surface morphologies of all impregnated rubber sheets were studied (not shown) by using scanning electron microscopy (SEM) (JEOL-JSM 5800LV, Japan). The X-ray diffraction (XRD) patterns were obtained on a X' Pert MPD control with Ni filtered Cu K$\alpha$ radiation (Phillips, Netherlands) for identifying crystalline phase and confirming structure of impregnated $TiO_2$ particles. The absorption spectra of MB solutions were recorded using UV–vis spectrophotometer (SPECORD S100, Analytik Jena, Germany).

### 2.2. Preparation of $TiO_2$-impregnated sheets

#### 2.2.1. Impregnated anatase sheet (Imp-An)

The Imp-An sheet was prepared by mixing 0.1 g of commercial $TiO_2$ anatase powder (Carlo Erba) in 3 ml distilled water and stirred for 3 min after which 5 ml of rubber latex (60% HA) was added and then stirred for another 5 min. The mixture was poured into a petri dish (3.5 in. diameter) and left to dryness at room temperature for 15 h after which it was taken out (from petri dish), reversed, and dried at room temperature about 2 h. The sheet thickness was about 1 mm. (These compositions, i.e. the amount of distilled water, rubber latex, and $TiO_2$ powder, were the optimum values we arrived at after systematically varying each component. However, to avoid lengthy presentation the details of these experiments are omitted.) In the photocatalytic study, the sheet was placed in MB solution upside down so that the initial bottom surface which contains more $TiO_2$ particles will face up.

#### 2.2.2. Impregnated P25 sheet (Imp-P25)

The Imp-P25 sheet was prepared using the same method as the Imp-An sheet but using commercial $TiO_2$ P25 powder as a starting material. In this preparation, 5 ml of distilled water, 5 ml of rubber latex, and 0.1 g of P25 were used. (These compositions were obtained similarly as described above.)

### 2.3. Photocatalytic study

In the photocatalytic studies, the impregnated rubber sheets were placed in a petri dish (4 in. diameter) containing 60 ml of MB solution ($2.5 \times 10^{-5}$ M). The solution was then stirred for 1 h in the dark to allow adsorption equilibrium in a tightly closed wooden compartment (0.9 m × 0.9 m × 0.9 m) to avoid interference from ambient light. Subsequently, the irradiation was started by using UV-light (5 tubes of blacklight, 20 W, F20T12-BLB, GE, USA) and magnetically stirred at 400 rpm. The five blacklight tubes were attached in a fixed positions and distributed evenly in the compartment. At given irradiation time intervals (every 1 h), 4 ml of MB solution sample was collected. The degradation of MB solution was analyzed spectrophotometrically from the changes in absorbance of the absorption maximum at 665 nm. The concentration of MB solution was determined quantitatively through the calibration graph constructed from solutions of MB at various concentrations. (The calibration graph was a straight line with $R^2 = 0.9983$.)

In the comparative experiments to measure the photocatalytic activity of the loose powders the same setup was employed as above but using 0.1 g of loose commercials $TiO_2$ powders instead of the impregnated sheet. The solution samples must be centrifuged to obtain clear solutions before analysis.

## 3. Results and discussion

### 3.1. Preparation and characterizations of rubber sheets

In this work, the impregnated rubber sheets were prepared by direct mixing of commercial $TiO_2$ powder with rubber latex and distilled water. The effect of parameters such as the amount of distilled water, the amount of rubber latex, and the amount of commercial $TiO_2$ powder were studied to optimize the preparation of impregnated rubber sheets for the maximum photocatalytic degradation of MB solution under UV-light irradiation. The surface morphology of impregnated rubber sheet sample was governed by the amount of distilled water, rubber latex, and commercial $TiO_2$ powder. These variables, in turn, affected the viscosity of mixture and the period of time for drying the sheet. The viscosity of mixture decreased with increasing amount of distilled water resulting in fast deposition of $TiO_2$ particles to bottom of the mixture and finally increasing the $TiO_2$ particles at the bottom surface of the dried sheet. However, the opposite effect was observed when increasing amount of rubber latex or $TiO_2$ powder as this would cause the viscosity of mixture to increase with the increasing amount of each. Therefore, in the case of using large amount of distilled water for the preparation of sheet would result in