

Degradation of indigo carmine by rubber sheet impregnated with TiO₂ particles

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ABSTRACT: The photocatalytic degradation of indigo carmine was investigated by using rubber sheet impregnated with titanium dioxide particles. The characteristics of the impregnated sheet were studied using scanning electron microscopy and X-ray diffraction. The degradation was monitored by measuring the change of dye concentration as a function of irradiation time under UV light. The anatase impregnated sheet showed higher degradation efficiency than the P25 impregnated sheet. The effects of solution pH, dye initial concentration, and intensity of UV light on the photodegradation were investigated. Kinetics of photocatalytic degradation was of a first-order reaction. The used TiO₂-impregnated sheets can be recovered and reused with no decline in the photodegradation efficiency.

KEYWORDS: immobilized titanium dioxide, titanium dioxide photocatalyst, photocatalytic degradation, dye degradation

INTRODUCTION

Applications of semiconducting catalysts for environmental protection and remediation have attracted much attention in recent years. Heterogeneous photocatalysis using semiconducting materials is efficient and broadly used for environmental applications such as air purification, water disinfection, hazardous water remediation, and water purification^{1–4}. This process is based on the incidence of radiation of an adequate wavelength on semiconducting materials to shift an electron from the valence band to the conduction band thus producing an electron-hole pair that is responsible for the start of the degradation catalysis of organic compounds. Among the semiconducting materials, one of the most used is titanium dioxide due to its commercial availability, low cost, chemical stability, photostability, and high efficiency in photocatalytic processes^{5–7}. A disadvantage of the use of TiO₂ in powder form as a photocatalyst in large scale processes is the difficulty in separating it from the reaction system, precluding its recovery and reuse. The loose photocatalyst powder can also cause human health problems^{8,9}. In order to avoid the use of photocatalyst powders, efforts have been made to coat TiO₂ thin films on various substrates such as glass^{10–12}, plastics¹³, and polymers¹⁴. However, these substrates are expensive and have some limitations

in applications. Photocatalyst TiO₂ thin films have been prepared by various techniques such as chemical vapour deposition¹⁵, spray pyrolysis deposition¹⁶, flame synthesis¹⁷, sol-gel dip coating^{18–20}. However, these methods also have some disadvantages for industrial applications. Chemical vapour deposition, spray pyrolysis deposition, and flame synthesis all require costly apparatus and complex procedures for the deposition of TiO₂ films. The sol-gel dip coating method needs repeated coating to produce a thick film and a high annealing temperature for crystallization. Furthermore, the heating process precludes the fabrication of TiO₂ films on substrates with low thermal stability such as plastics and polymers¹⁴. To overcome these obstacles, simple, less expensive, and more effective methods to prepare immobilized TiO₂ powder on a certain type of substrate are under investigation worldwide.

In our previous work²¹, we reported the preparation of rubber sheet impregnated by commercial TiO₂ powders and their photocatalytic activity in the degradation of methylene blue (MB), a cationic dye usually used as a model to test for photocatalytic activity. In the present work, the scope was extended to cover indigo carmine (IC) which is an anionic dye usually used in the textile, food, and cosmetics industries. Indigo carmine is regarded as a highly toxic dye that may lead to tumours at the site of application, cause

skin or eye irritation, and permanent injury to cornea and conjunctiva, and can be fatal if consumed. The toxicity tests of IC dye revealed long-term toxicity in mice and short-term toxicity in pigs²²⁻²⁴.

In this report, the degradation of IC dye was investigated by using rubber sheets impregnated with commercial TiO₂ particles. The effect of various parameters such as solution pH, dye initial concentration, and intensity of UV light were studied. After being used, the sheet remained clean and ready for reuse. The sheet was tested for reuse up to ten times with no decrease in degradation efficiency.

MATERIAL AND METHODS

Materials

Titanium dioxide P25 was a gift donated from Degussa AG (Frankfurt), anatase was purchased from Carlo Erba (AR grade). Indigo carmine (C₁₆H₈N₂Na₂O₈S₂, MW = 466.36 g/mol) was purchased from Fluka and rubber latex (60% HA) from Chana Latex Co. Ltd. (Songkhla, Thailand). The dye and latex were used as received.

Preparation and characterization of TiO₂-impregnated rubber sheet

The preparation of both impregnated anatase sheet (Im-Anatase) and impregnated Degussa P25 sheet (Im-P25) has been described previously²¹. The surface morphology of TiO₂-impregnated rubber sheets were characterized by scanning electron microscopy (SEM) (JEOL-JSM 5800LV, Japan) while X-ray diffraction (XRD) (X' Pert MPD, Ni filtered Cu K α radiation, Phillips) was used for the identification of crystalline phase of TiO₂ particles embedded in the sheets.

Photocatalytic study

The same experimental set up was employed for the photocatalytic studies as described previously²¹. The concentration of IC dye solution was 2.5×10^{-5} M. Five fluorescent blacklight tubes served as the source of UV light. These blacklight tubes were turned on 1, 3, or 5 tubes at a time to provide, respectively, low, medium, or high intensity of UV light. In most of the experiments, high intensity was used to shorten the experiment times. The concentration of IC dye after photodegradation was analysed by using a UV-Vis spectrophotometer (Specord S100, Analytik Jena) by measuring the change in absorbance at 610 nm. The control experiment was carried out by irradiating an aqueous solution of IC dye and replacing the TiO₂-impregnated rubber sheet with a pristine rubber sheet where no observable loss of dye was observed.

RESULTS AND DISCUSSION

Characterization of TiO₂-impregnated rubber sheet

The impregnated rubber sheet was prepared by mixing TiO₂ powder with latex and a certain amount of distilled water. Then, the mixture was poured into the Petri-dish mould. When the latex sheet solidified, it was taken out of the mould and flipped upside down before being used so that the bottom surface would face upward and contact with the dye solution. This flipped-up bottom surface was characterized. The SEM images of the surface and cross-section of Im-Anatase and Im-P25 sheets are shown in Fig. 1. The surface morphology of Im-Anatase sheet showed evenly and well-spread anatase powder with higher surface roughness than that of the Im-P25 sheet. This results from the physical difference of anatase and P25 powders. The former has a higher agglomeration and density than P25, which exists as light and fluffy-like particulates. When added to the latex, the anatase particles sank to the bottom faster and accumulated close to the bottom surface. The P25 particles, however, sank to the bottom slower so the number of particles to reach and accumulate at the bottom surface was smaller than in the case of anatase. This is clearly shown in Fig. 1a (right) where a distinct layer of anatase particles can be seen at the surface of the sheet (arrow) while that in P25 is less visible (Fig. 1b, right). The rough surface of Im-Anatase sheet (Fig. 1a, left) resembles the cracks running through a sun-dried mud surface. With these cracks, the anatase powders that gather near the surface will have more chance to contact the dye molecules than those of the Im-P25 which are buried rather deep under the smoother surface of the rubber. This surface difference is responsible for a better performance of Im-Anatase sheet over Im-P25 sheet in the subsequent dye degradation studies.

The X-ray diffraction patterns of TiO₂ in powder form and in the impregnated rubber sheets are illustrated in Fig. 2. The anatase peaks appear at $2\theta = 25.50^\circ$ (101) and 48.0° while those of rutile appear at $2\theta = 27.50^\circ$ (110) and 54.5° . Well crystallized anatase can be observed in the Im-Anatase sheet indicating successful impregnation of anatase powder into the rubber sheet (compare Figs. 2a and 2c). The same result is seen for Im-P25 sheet as shown in Fig. 2d (compare with Fig. 2b). The XRD of pristine rubber sheet has been shown previously to have only a large broad scattering peak near $2\theta = 19^\circ$ ²¹ due to the fact that the rubber matrix is composed of low atomic number (low *Z*) elements. This broad scattering peak

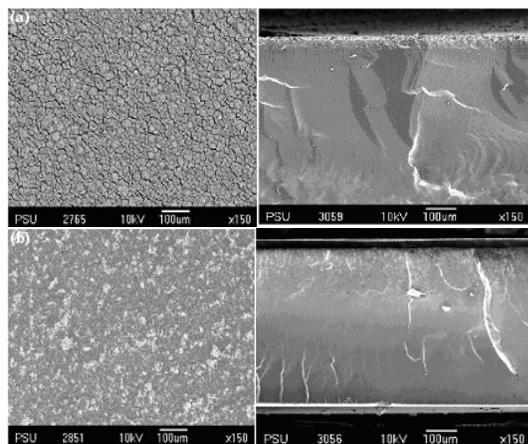


Fig. 1 SEM images of surface (left) and cross-section (right) of (a) Im-Anatase sheet and (b) Im-P25 sheet.

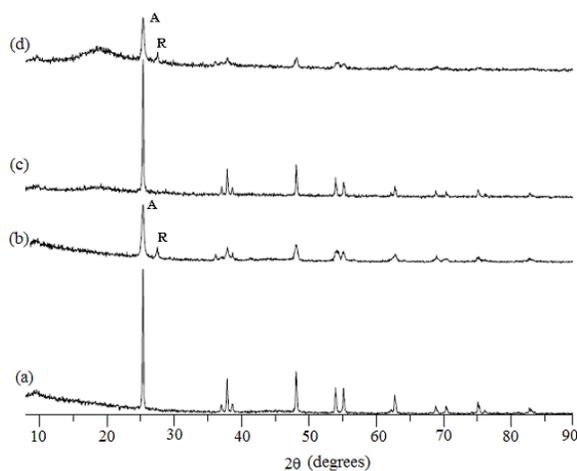


Fig. 2 XRD patterns of (a) commercial anatase powder, (b) Degussa P25 powder, (c) Im-Anatase sheet, and (d) Im-P25 sheet. A: anatase phase; R: rutile phase.

also appears in the patterns of both impregnated sheets but with smaller intensity due to inclusion of TiO₂ particles in the impregnated sheets. The surface of Im-Anatase sheet has a higher content of TiO₂ particles than that of Im-P25 causing the average Z-value of matrix in the former to increase. This results in lower X-ray scattering in the case of Im-Anatase.

Photocatalytic degradation of indigo carmine (IC) by TiO₂-impregnated rubber sheet

The photodegradation efficiencies of IC by Im-Anatase sheet and Im-P25 sheet under UV light irradiation are shown in Fig. 3. The Im-Anatase sheet has higher surface roughness than the Im-P25 sheet (Fig. 1). The cracked surface of Im-Anatase sheet

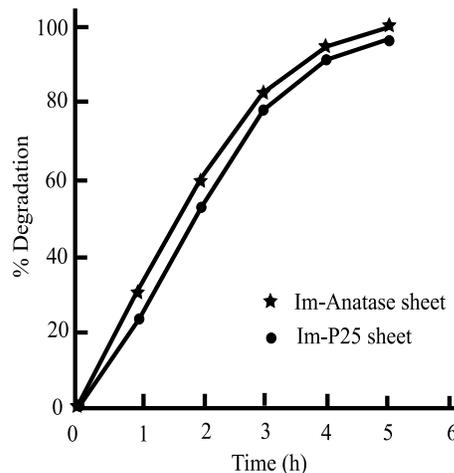


Fig. 3 The efficiencies of photocatalytic degradation of IC dye by impregnated rubber sheets under UV irradiation.

has grooves running all over the surface. These grooves give the sheet at least two advantages: (i) after falling into the groove, the dye molecules cannot easily escape from the surface, and (ii) along the groove surface, the oxygen atoms have a better chance to protrude from the latex texture and their negative charges can attract or repel charges of the dye molecular fragment (Fig. 4). The smoother surface of Im-P25 with TiO₂ particles embedded deeper in the surface will have weaker electrostatic forces to interact with the dye molecules. Therefore, the higher surface roughness can help to gather more dye molecules onto the sheet surface and more photocatalytic reaction can take place. This is reflected by the slightly better performance of Im-Anatase over Im-P25 as shown in Fig. 3.

The kinetics of the degradation was studied and the data were tested with the first-order kinetic expression^{2,28},

$$\ln[C_t] = \ln[C_0] - k_{app}t,$$

where [C₀] is the initial concentration of dye, [C_t] is the concentration at time *t*, and *k_{app}* is the apparent rate constant. The straight lines obtained when ln[C_t] was plotted against *t* confirmed the first-order kinetics of dye degradation. The rate constants for IC dye degradation were found to be 0.717 ± 0.004 h⁻¹ and 0.595 ± 0.004 h⁻¹ for the Im-Anatase and Im-P25 sheets, respectively (*n* = 3).

Effect of pH

All of the experiments were carried out at the natural pH of IC dye solution which is 6.4. However, in real life situations the effluents from factories may cover

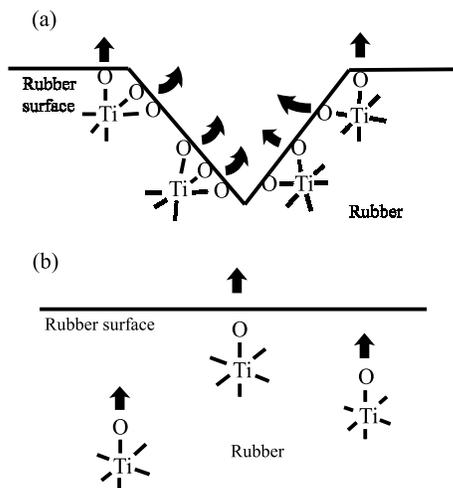
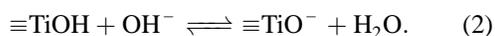
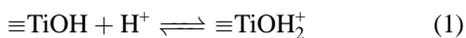


Fig. 4 Effect of rough and smooth surfaces: (a) Im-Anatase (b) Im-P25. Arrows represent electrostatic forces from the negatively charged oxygen atoms.

a wide range of pHs. To assess the efficiencies of degradation by the TiO₂ impregnated rubber sheet, solutions of several pH values (3, 5, 6.4, and 8) were investigated. Both Im-Anatase and Im-P25 showed parallel behaviour (Figs. 5a and 5b) with the efficiencies decreasing as the pH values increased in the order: (pH) 3 > 5 > 6.4 > 8.

Generally, for a charged surface containing TiO₂ particles, a significant dependence of the photocatalytic efficiency on the pH value is observed, since the overall surface charge and hence the adsorptive properties of TiO₂ particles depend strongly on the solution pH²⁹⁻³¹. It is known that the metal oxide particles in water exhibit amphoteric behaviour and readily reacts with dye by a mechanism which can be described by the following chemical equilibria²⁹⁻³¹:



The charge of TiO₂ depends on the solution pH. The pH at the point of zero charge (pH_{PZC}) for TiO₂ has been reported to be in the range 6.25–6.90³². Thus, the TiO₂ surface is positively charged in acidic media (pH < pH_{PZC}), and negatively charged under alkaline conditions (pH > pH_{PZC}). This argument, valid for the powder form in contact with solution, should also be applicable when the powder is in a rubber sheet. The effect, however, should be less pronounced for the impregnated sheet than in the powder form. In the case of the impregnated sheet, the TiO₂ particles closer to

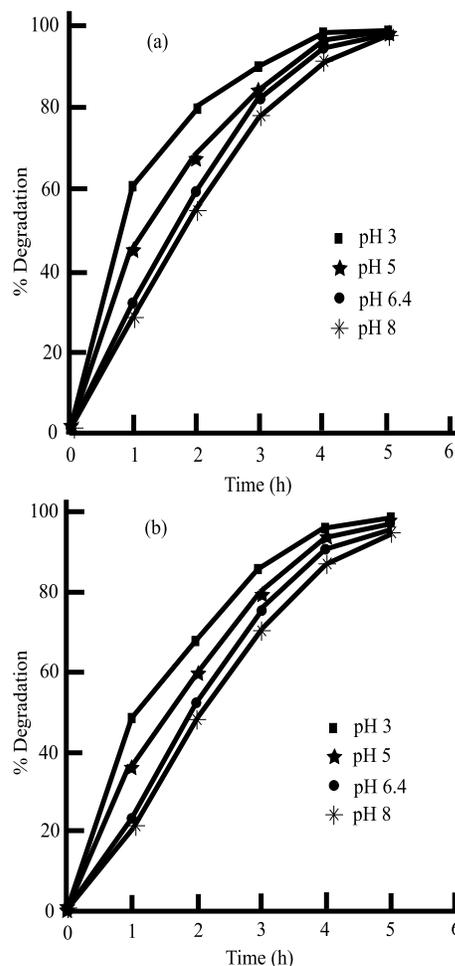


Fig. 5 Effect of pH on the photodegradation efficiency of IC dye by (a) Im-Anatase sheet and (b) Im-P25 sheet.

the surface may have part of oxygen atoms protrude from the rubber surface (Fig. 4). (This assertion is justified by the fact that the photocatalytic reaction did indeed take place but with less efficiency than in the loose powder form.) Therefore, it is expected that at a pH below pH_{PZC}, the surface of impregnated sheet acquires a positive charge, indicated by (1), and hence attracts the negatively charged IC dye skeleton resulting in a large number of dye molecules being attracted (or adsorbed) onto the sheet surface. As the dye concentration at the surface increases the photodegradation activity also increases, as observed at pH 3. At a pH above pH_{PZC}, electrostatic repulsion between the negative charge at the surface of impregnated sheet, as shown in (2), and anionic dye skeleton retards the accumulation of dye molecules at the surface resulting in decrease of the photodegradation activity.

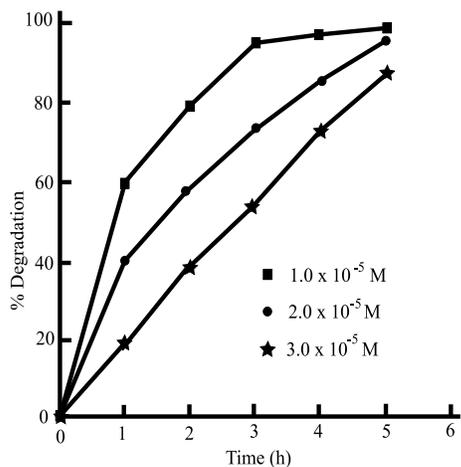


Fig. 6 Effect of IC dye initial concentration on the photocatalytic efficiency of Im-Anatase sheet.

Effect of dye initial concentration

The effects of the initial concentration of IC dye on the photocatalytic efficiency was investigated with concentrations 1.0×10^{-5} M, 2.0×10^{-5} M, and 3.0×10^{-5} M (Fig. 6). It was found that on increasing the dye concentration the degradation efficiencies of dye decreases. Hence, the photo-oxidation process will work faster at a low concentration of pollutants. These results are in agreement with previous reports^{2,31,33} that photodegradation of textile dye Reactive Red 2, C.I. Acid Yellow 17, and Direct Yellow 12 decreased with increasing concentrations. At high concentrations of dye, the deeper coloured solution would be less transparent to UV light and the dye molecules may absorb a significant amount of UV light causing less light to reach the catalyst and thus reducing the OH^\bullet radical formation. Since OH^\bullet radicals are of prime importance in the attack of the dye molecules, lowering the amount OH^\bullet radicals would cause the photodegradation efficiency to decrease³⁴.

Effect of UV light intensity

On increasing the light intensity, the degradation efficiency of dye increases. It has been reported that the photocatalytic reaction rate depends largely on the irradiation absorption of the photocatalyst leading to an increase in the degradation rate with increasing light intensity during photocatalytic degradation^{31,33,35}. The high UV light intensity increases the photon influx entering the dye solution and consequently excites the TiO_2 particles in the sheet resulting in more OH^\bullet radicals being formed at the surface of the film. As the reactive number of OH^\bullet radicals

attacking the dye molecules increases, the photodegradation efficiency also increases. The activity increases with increasing intensity of UV light.

Recyclability of the TiO_2 -impregnated rubber sheets on the photocatalytic degradation of IC dye

Both types of sheet were tested for their recyclability up to 10 times. The sheets showed no sign of deterioration or decrease in performance. We thus anticipate that the sheets could be used much more than 10 times. One striking result was that the sheet surface remained rather clean after being used. As a result, the sheet surface need no cleaning between uses and so could be used immediately for the next cycle. The reason for this can be traced back to the repulsive force between the negative charge on the skeleton of the dye fragment and the oxygen atoms on the catalyst surface. This repulsion greatly diminishes the accumulation of dye fragments on the sheet surface.

The highest performance was only obtained after the third use and remained at that high efficiency until the tenth use (Fig. 7). This trend can be expected to continue even after the tenth use. The lower results of the first few uses may result from the fact that the rubber surface was covered with traces of impurities during the preparation and the impurities were destroyed during the first and the second uses by the photodegradation reaction together with IC dye molecules in the solution.

The recyclability of the impregnated rubber sheet should be attractive to the water treatment industry as it helps keep the operational cost low. The low cost of raw materials (photocatalyst powder and rubber latex) enables a one time investment which will last over a long period of uses.

Comparison between MB and IC degradation by TiO_2 impregnated rubber sheet

In another study we carried out (unpublished) the rate constants of MB degradation by TiO_2 impregnated rubber sheet were found to be $1.086 \pm 0.002 \text{ h}^{-1}$ for Im-Anatase and $0.764 \pm 0.006 \text{ h}^{-1}$ for Im-P25 sheets ($n = 3$). These figures indicate that the rubber sheets exhibit higher photocatalytic activities towards MB than IC dye. Our results agree with other studies which showed that MB degradation efficiency was higher than other dyes containing the $-\text{SO}_3^-$ group³⁰. It has also been shown elsewhere that under similar conditions the rate of degradation of MB is faster than that for IC^{25,36}.

When the rubber sheet was used with MB, a significant amount of dye adhered to the sheet surface. However, the surface could be cleaned easily and

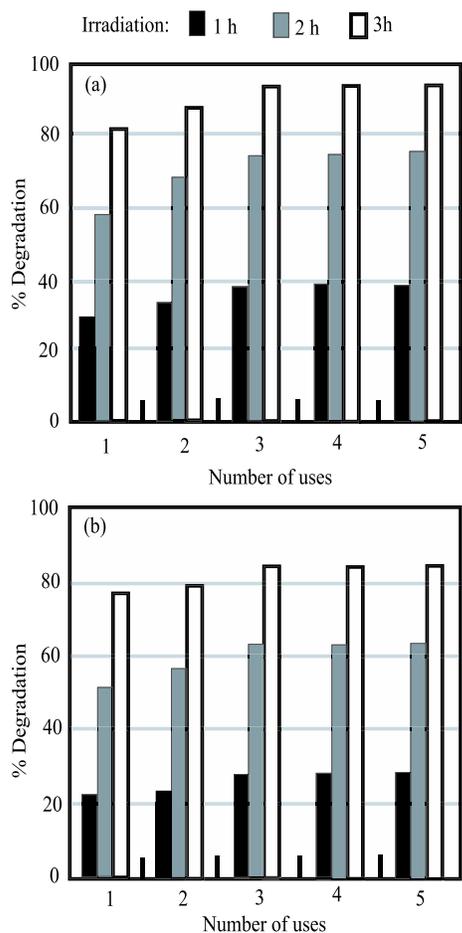


Fig. 7 The efficiencies of IC dye degradation by (a) Im-Anatase sheet and (b) Im-P25 sheet after repeated use under UV light irradiation for 1–3 h.

reused²¹. The number times the sheet could be reused for MB dye appeared to be less than for IC dye.

The trend on pH for MB was the opposite of the IC behaviour, i.e., the efficiency for MB degradation increased with increasing pH. These differences can be explained based on the charge type on the dye fragment. MB is a cationic dye whereas IC is anionic. The positive charge of the MB fragment attracts the negatively charged oxygen atom of TiO₂ impregnated in the rubber surface promoting accumulation of dye molecules onto the surface. As more molecules flock together on the catalyst surface, a higher rate of degradation should result. In the IC case, the negative charge on the dye skeleton repels with the impregnated TiO₂ in the rubber surface discouraging accumulation of dye molecules on the sheet surface. As a result the surface remains clean, but the degradation rate was less than the MB case.

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