Rubber sheet strewn with TiO$_2$ particles: Photocatalytic activity and recyclability

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Abstract

A new method for the preparation of rubber sheet strewn with titanium dioxide particles (TiO$_2$-strewn sheet) is presented. This simple and low cost method is based on the use of TiO$_2$ powder (Degussa P25) being strewn onto the sheet made from rubber latex (60% HA) through a steel sieve. The characteristic of the TiO$_2$-strewn sheet was studied by using scanning electron microscopy/energy dispersive X-ray spectrometer (SEM/EDS) and X-ray diffractometer (XRD) techniques. The photocatalytic activity of TiO$_2$-strewn rubber sheet was evaluated using Indigo Carmine (IC) dye as a model for organic dye pollutant in water. The results showed that the TiO$_2$-strewn sheet could degrade IC dye solution under UV light irradiation. The effects of pH, initial concentration, and the intensity of UV light on the photodegradation were also investigated. Kinetics of the photocatalytic degradation was of the first-order reaction. The used TiO$_2$-strewn sheet can be recovered and reused. The recycling uses did not require any cleaning between successive uses and no decline in the photodegradation efficiency was observed compared with freshly prepared TiO$_2$-strewn sheet.

Key words: immobilized titanium dioxide; TiO$_2$ rubber composite; dye degradation; photocatalytic degradation; indigo carmine

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Introduction

Over the past decade, the application of semiconductor photocatalysts to treat environmental contaminants has overwhelmingly prevailed as another alternative for the pollution treatment technology. Amongst the various semiconductor photocatalysts, TiO$_2$ has been considered as one of the most promising photocatalysts due to its stability, non-toxicity, low cost, and high efficiency in the photocatalysis process (Nagaveni et al., 2004; Zhu et al., 2004; Senthikumaar and Porkodi, 2005; Yuan et al., 2007; Parida et al., 2008; Wu and Cho, 2008). However, a disadvantage of the use of TiO$_2$ powder form as a photocatalyst in large scale processes is the difficulty in separating it from reaction systems, which precludes the recovery and reuse of the catalyst (Ge et al., 2006; Zhang et al., 2006; Choi et al., 2007; Ryu et al., 2008; Shi et al., 2008). The loose powder form of photocatalyst can cause serious human health problems (Yuan et al., 2005; Habibi et al., 2007). To avoid the use of photocatalyst in powder form, several efforts have been made to coat TiO$_2$ as thin films on various substrates (Wang et al., 1998; Kwon et al., 2004; Lositi et al., 2005; Sankapal et al., 2005; Yang et al., 2006), as well as employing several techniques such as chemical vapor deposition (CVD)

(Ding et al., 2001), spray pyrolysis deposition (Weng et al., 2005), flame synthesis (Partsinis, 1996), sol-gel dip coating, (Sen et al., 2005; Yogi et al., 2008). However, the above methods have some disadvantages for industrial applications. The chemical vapor deposition, spray pyrolysis deposition, and flame synthesis methods require special and rather expensive apparatus and complex procedures for the deposition of TiO$_2$ film, while the sol-gel dip coating method needs repeated coatings to get a thick film and requires a high annealing temperature for crystallization. Furthermore, the heating process precludes the fabrication of TiO$_2$ films on substrates with low thermal stability such as plastics and polymers (Yang et al., 2006). An alternative to immobilize TiO$_2$ photocatalyst on organic substrates is to immobilize it along with magnetic materials. This way, TiO$_2$ photocatalyst can be recovered by applying magnetic field to collect photocatalyst particles from the used slurry. Among the first magnetic materials in this application were Fe$_3$O$_4$ and γ-Fe$_2$O$_3$ (Beydoun et al., 2000, 2001; Beydoun and Amal, 2002; Chen et al., 2001; Gao et al., 2003). Recently, NiFe$_2$O$_4$, a superparamagnetic material, was used with good results (Xu et al., 2008). All these methods have not yet been finalized and are still under investigation presently. Industrial application still awaits the most suitable immobilized photocatalyst. Therefore, a simple, less expensive, and more effective method for the

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preparation of immobilized TiO$_2$ powder onto a substrate was investigated in our laboratory.

Recently our group reported the efficiency of the titania rubber sheet prepared from the method of embedding TiO$_2$ particles in rubber sheets (Sriwong et al., 2008, 2010) but that was still inferior to the sheet prepared by the novel method to be reported in this article. The difference can be traced to the fact that, in the new method, TiO$_2$ particles externally adhered to the surface of the sheet and were only covered with very thin clear film of latex while with the previous method TiO$_2$ particles were embedded within the rubber matrix. In comparing the two methods, the TiO$_2$ particles in the new method had a better contact with dye molecules in the solution and, hence, the higher degradation efficiency *(vide infra)*.

In this study, the TiO$_2$-strewn rubber sheet was prepared by strewing TiO$_2$ powder (Degussa P25) onto the sheet of rubber latex (60% HA). The efficiency of Indigo Carmine (IC) degradation by this sheet under UV light was evaluated. The effects of various parameters such as pH, initial concentration, and the intensity of UV light were also studied. Indigo Carmine was used as a model dye in this research due to the fact that it is usually used in the textile industry for dyeing of cloths (blue jeans) and other blue denim, in the food industry (typical products includes milk dessert, sweets, biscuits), and in the cosmetics industry. Indigo Carmine has been regarded as a highly toxic indigoid class of dye. It can cause skin or eye irritation and permanent injury to the cornea and conjunctiva. Moreover, IC dye can be fatal if consumed as it is carcinogenic in nature and can lead to reproduction, developmental of neuron, and acute toxicity (Mittal et al., 2006; Othman et al., 2006, 2007; Barka et al., 2008). The structure of IC dye molecule is a sodium salt which the parent fragment bears negative charges as illustrated in Fig. 1. In addition, the reaction kinetics and recycling uses of the TiO$_2$-strewn rubber sheet on the photodegradation for IC dye solution were presented.

1 Materials and methods

1.1 Chemicals and equipments

Rubber latex (60% HA, Chana Latex Co., Ltd., Thailand), Indigo Carmine dye (Fluka, USA), and titanium dioxide (Degussa P25, Degussa AG, Germany) were used. The surface morphologies of rubber sheets were characterized by using scanning electron microscopy (SEM) (JSM 5800LV, JEOL, Japan). The crystalline phases of TiO$_2$ were identified and confirmed by X-ray diffraction (XRD) technique (X'Pert MPD, Phillips, the Netherlands).
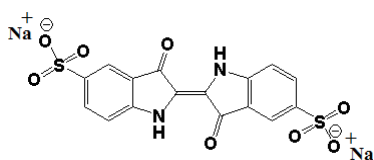
Fig. 1   Molecular structure of indigo carmine (IC) dye.

1.2 Preparation of TiO$_2$-strewn sheet

The TiO$_2$-strewn sheet was prepared from P25 TiO$_2$ powder and rubber latex. Rubber latex (10 mL) was poured into a Petri dish mould (3.5-inch diameter) and was left at room temperature about 2 hr for gelation to form. Then, 0.07 g of P25 TiO$_2$ was strewn onto the surface of the rubber sheet by using a 60-mesh sieve and allowed to dry at room temperature for 6 hr. Afterwards, the strewn rubber sheet was taken out from the mould and dried at 100°C for 1 hr. After cooling to room temperature, the sheet surface was lightly sprayed with distilled water to wash out some of the P25 TiO$_2$ particles that were left unbound until the strewn surface was free of loose particles. The sheet then was dried at 100°C for 10 min and ready for use, as shown in Fig. 2.

1.3 Photocatalytic study

In the photocatalytic studies, the TiO$_2$-strewn sheet was placed in a Petri dish (4-inch diameter) containing 60 mL of IC dye solution of known concentration. The solution was then stirred for 15 min in the dark to allow the adsorption-desorption equilibrium in the closed compartment for photoreaction. Subsequently, the irradiation was initiated using UV light (fluorescent blacklight 20 W, GE, USA) and magnetically stirred. At a given time interval (every 1 hr), 3 mL of dye solution was collected. The concentrations of IC dye after photodegradation were analyzed using a UV-Vis spectrophotometer (Specord S100, Analytik Jena, Germany). Controlled experiments were also performed to ensure the proper interpretation of results. The photoreaction compartment was fitted with five blacklight fluorescent tubes at fixed positions and evenly distributed in the compartment. These blacklight tubes can be turned on individually for one, three, or five tubes to provide low, medium, or high intensity of UV light. Normally, the highest intensity (five tubes) was employed to shorten the experimental time.

Fig. 2   Photograph of TiO$_2$-strewn sheet.

2 Results and discussion

2.1 Characterization of TiO₂-strewn sheet

The solidified rubber sheet served as a substrate upon which P25 TiO₂ powder was deposited. Drying at 100°C for 1 hr removed moisture from the rubber sheet to some extent. The heat drying process softened the sheet and caused subtle melting at the surface which helped increase the binding of TiO₂ particles to the sheet. On a close inspection with the naked eye one can see a colorless thin film covering the TiO₂ particles. The SEM images of the pristine rubber sheet and the TiO₂-strewn sheet are comparatively shown in Fig. 3. The surface morphology of the pristine rubber sheet is very smooth without any particles adhering to the surface (Fig. 3a). On the contrary, for the strewn sheet, TiO₂ particles can be seen spread evenly over the sheet surface causing high surface unevenness and roughness (Fig. 3b, c).

The energy dispersive X-ray spectrometer (EDS) analysis was carried out to determine the presence of elements in the TiO₂-strewn sheet. The EDS spectrum in Fig. 4a shows that only three elements were present in the sheet, i.e., carbon, oxygen, and titanium, as evidenced from their corresponding K lines. Figure 4b1 shows a SEM micrograph of an island of TiO₂ nanoparticles submerged in rubber.
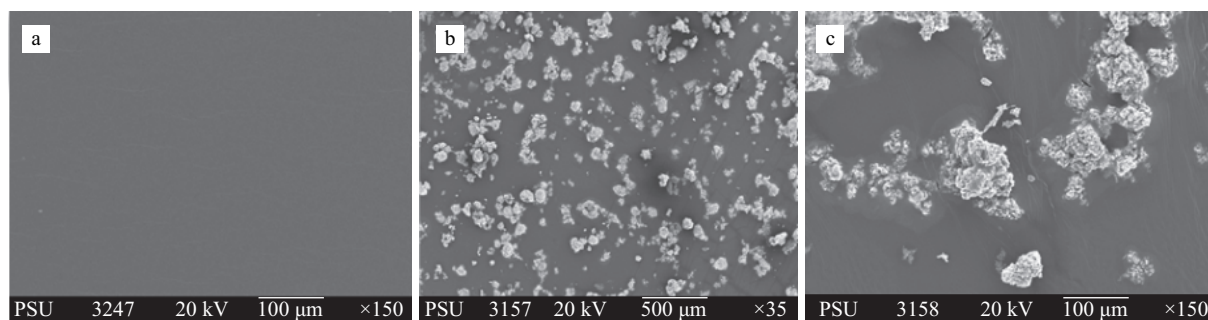

Fig. 3 SEM images of surface morphology of pristine rubber sheet (a), TiO₂-strewn sheet at 35× magnification (b), and TiO₂-strewn sheet at 150× magnification (c).
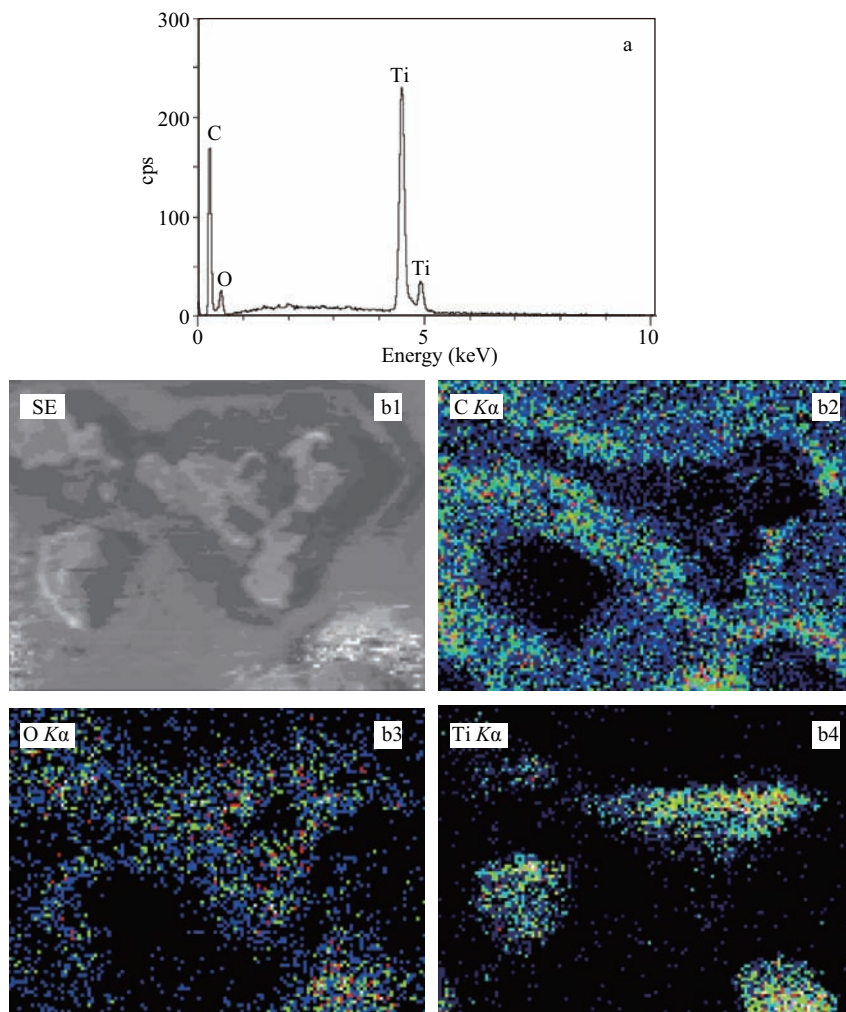

Fig. 4 EDS spectrum (a), and elemental mapping of TiO₂-strewn sheet (b).

This is supported by Fig. 4b2 which shows distribution of carbon atoms on the sheet surface surrounding the TiO$_2$ island (the island is seen as a black area in this figure). Oxygen and titanium atoms are seen in the area occupied by the TiO$_2$ island, Fig. 4b3 and b4, respectively. Titanium atoms are distributed over a narrower area within the TiO$_2$ island than the oxygen atoms distribution. In summary, the EDS data indicate that TiO$_2$ particles are located on the rubber surface with parts of the TiO$_2$ islands protruding from the surface (area of lighter color in Fig. 4b4).

The X-ray diffraction patterns of TiO$_2$ in the powder form and the immobilized form on a rubber sheet surface are illustrated in Fig. 5. The diffraction peaks of anatase and rutile phases are marked with 'A' and 'R', respectively. From Fig. 5, the well crystallized anatase and rutile forms were observed in the TiO$_2$-strewn sheet indicating successful addition of TiO$_2$ powder onto the rubber sheet surface (lines a and b in Fig. 5). A broad scattering peak (2θ = 19°) of the X-ray beam by the low Z matrix of rubber also shows up in the patterns of TiO$_2$-strewn sheet. The surface of TiO$_2$-strewn sheet contains TiO$_2$ particles causing the average rubber matrix of the sheet to increase and, therefore, less scattering of the X-ray beam (Sriwong et al., 2008).

2.2 Photocatalytic degradation of IC by TiO$_2$-strewn sheet

2.2.1 Testing the photocatalytic activity of the TiO$_2$-strewn sheet

Results from the photocatalytic degradation of IC dye solution by the TiO$_2$-strewn sheet under UV light irradiation are shown in Fig. 6. The IC dye was degraded by the TiO$_2$-strewn sheet whereas in the case of pristine rubber sheet no observable loss of the dye could be detected. These results implied that the photocatalytic activity of the TiO$_2$-strewn sheet comes from the TiO$_2$ particles in the rubber sheet. As an example, the spectral changes of IC dye solution at 7.5×10^{-5} mol/L concentration degraded by TiO$_2$-strewn sheet under UV light as a function of irradiation time is shown in Fig. 7. Note that the intensity of the maximum peak at 610 nm decreases with increasing irradiation time due to the degradation of the IC dye molecules.

Since the P25 TiO$_2$ nanoparticles were on the sheet surface and contacted directly with dye molecules in the solution, the mechanism of dye degradation by P25 in this case was essentially the same as that which had been well documented as follows (Houas et al., 2001; Baiju et al., 2007; Khataee and Kasiri, 2010):
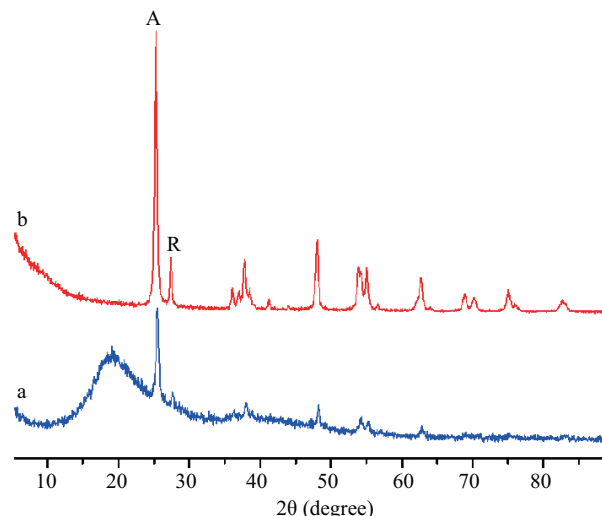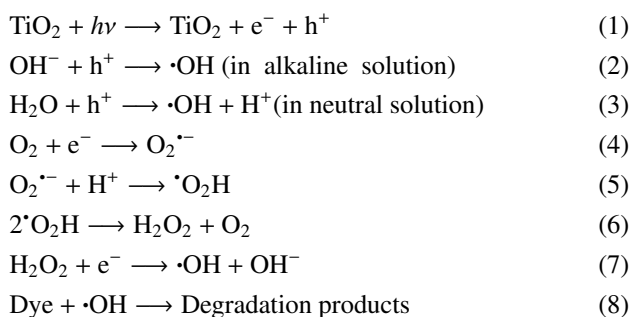
$$TiO_2 + h\nu \longrightarrow TiO_2 + e^- + h^+ \tag{1}$$

$$OH^- + h^+ \longrightarrow \cdot OH \text{ (in alkaline solution)} \tag{2}$$

$$H_2O + h^+ \longrightarrow \cdot OH + H^+ \text{(in neutral solution)} \tag{3}$$

$$O_2 + e^- \longrightarrow O_2^{\cdot -} \tag{4}$$

$$O_2^{\cdot -} + H^+ \longrightarrow \cdot O_2H \tag{5}$$

$$2 \cdot O_2H \longrightarrow H_2O_2 + O_2 \tag{6}$$

$$H_2O_2 + e^- \longrightarrow \cdot OH + OH^- \tag{7}$$

$$Dye + \cdot OH \longrightarrow Degradation\ products \tag{8}$$

Fig. 5 XRD patterns of TiO$_2$-strewn sheet (line a), Degussa P25 powder (line b).
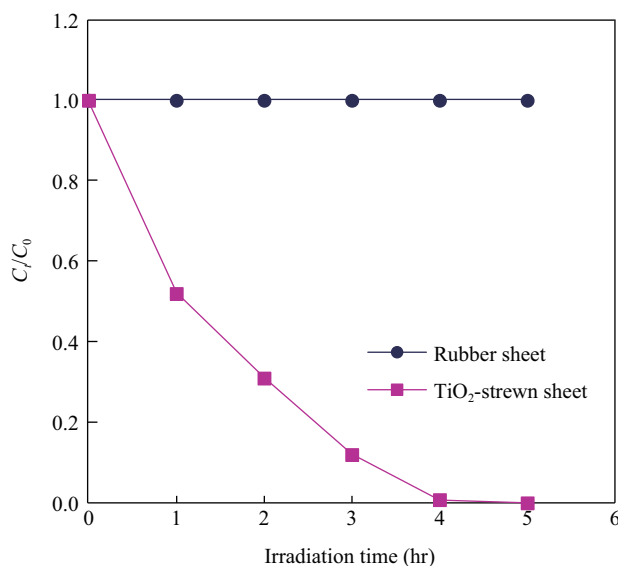

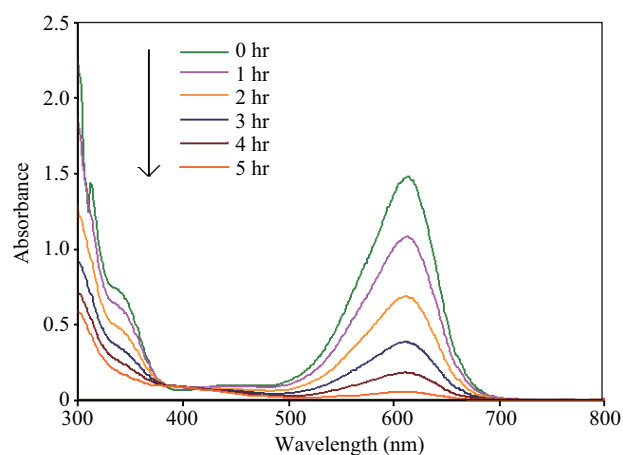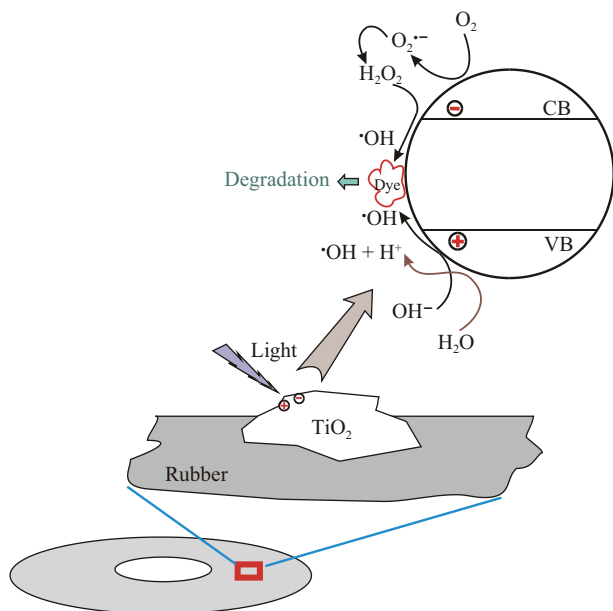**Fig. 6** Photodegradation of IC dye solution under UV light by pristine rubber sheet, and TiO$_2$-strewn sheet.

Fig. 7 Spectral change of IC dye solution (7.5×10^{-5} mol/L) degraded by TiO$_2$-strewn sheet under UV light as a function of irradiation time.

These reactions sequence can be put together as shown in Scheme 1 where the protruding TiO$_2$ surface is first irradiated with UV light causing the electron in the va-

Scheme 1 Degradation of dye by TiO_2-strewn rubber sheet.

Fig. 8 Comparisons of photodegradation efficiencies of IC dye solution $(2.5 \times 10^{-5}$ mol/L) by TiO_2-strewn sheet, Im-Anatase sheet, and Im-P25 sheet.

Fig. 9 Photodegradation efficiencies of TiO_2-strewn sheet as a function of pH (under UV light irradiation 3 hr; dye concentration 2.5×10^{-5} mol/L).

lence band being excited into the conduction band. This generates an electron (e^-) / hole (h^+) pair (Eq. (1)) which, if they can survive from recombination, are highly active species to induce further reactions. The hole in the valence band can oxidize the hydroxide anion (or H_2O) near the surface to yield the very reactive hydroxyl radical ($^\bullet OH$) (Reactions (2) and (3)) meanwhile the electron in the conduction band can reduce the surface adsorbed oxygen molecule to yield the superoxide radical ($O_2^\bullet$) (Reaction (4)) which later yields the active $^\bullet OH$ radicals (Reactions (5)–(7)). The reactive $^\bullet OH$ radical is the main species that degrades the dye molecules (Reaction (8)).

The photocatalytic degradation efficiency of TiO_2-strewn sheet found in this work is higher than that of titania rubber sheets (referred to as Im-Anatase sheet and Im-P25 sheet) as we have reported recently (Sriwong et al., 2010). These efficiencies discrepancy are shown comparatively in Fig. 8. The different efficiencies might be attributed to the location of the TiO_2 particles. TiO_2 particles of the TiO_2-strewn sheet that are externally located at the surface should have more chance to contact with IC dye molecules than those of both Im-Anatase sheet and Im-P25 sheet which are embedded rather deeply under the surface of rubber. Furthermore, in the preparation, only 0.07 g of TiO_2 was used for the TiO_2-strewn sheet while 0.1 g of TiO_2 was required to prepare the other two sheets by the method of Sriwong et al. (2008).

2.2.2 Effects of pH on the photocatalytic activity of the TiO_2-strewn sheet

In real-life applications, the sheet may be used under varied pH conditions. Therefore, the prepared TiO_2-strewn sheet was put to test under varying pH (from 3 to 8). The natural pH of IC dye solution was 6.53. The solution was adjusted to other pH by adding either diluted HCl or NaOH solution accordingly. The effects of pH on the photocatalytic degradation of IC dye in the presence of TiO_2-strewn sheet are shown in Fig. 9. It can be seen
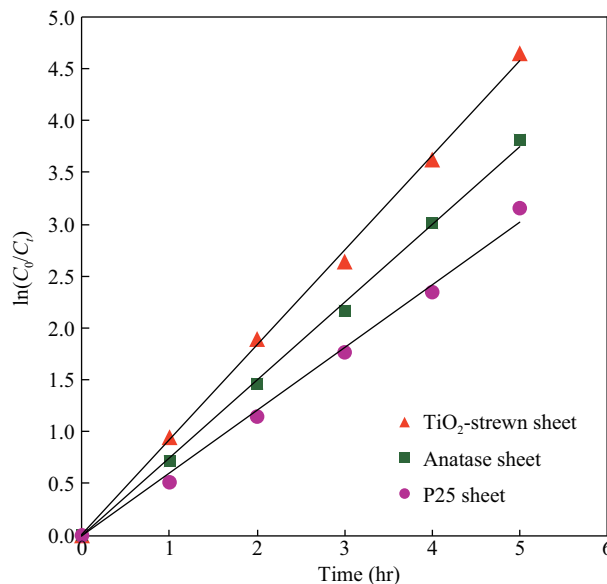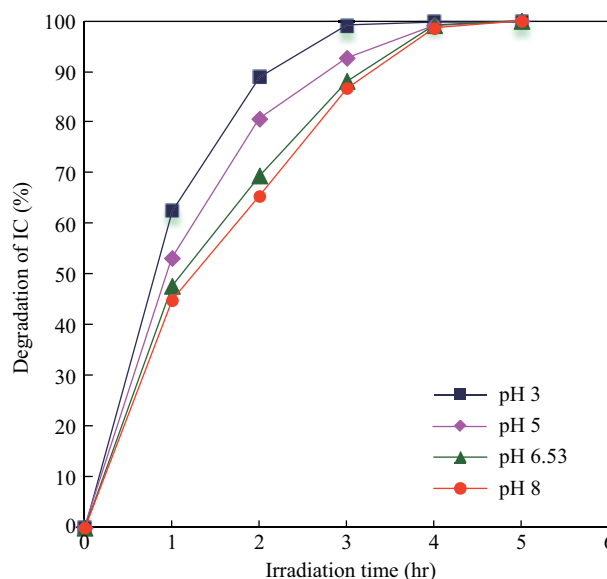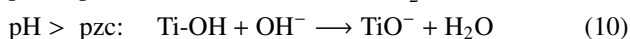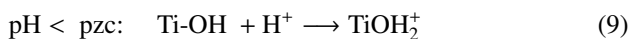
that the degradation efficiency of IC dye decreased with increasing pH. It is known that the metal oxide particles in water exhibit amphoteric behavior and readily react with dye which can be described by the following chemical equilibria (Kiriakidou et al., 1999; Silva et al., 2006; Toor et al., 2006):

$$pH < pzc: \quad \text{Ti-OH} + H^+ \longrightarrow \text{TiOH}_2^+ \qquad (9)$$

$$pH > pzc: \quad \text{Ti-OH} + OH^- \longrightarrow \text{TiO}^- + H_2O \qquad (10)$$

Generally, for the charged surface of TiO_2 particles, a significant dependency of the photocatalytic efficiency on the pH value was observed since the overall surface charge and, hence, the adsorptive properties of TiO_2 particles depended strongly on the solution pH (Senthilkumaar and Porkodi, 2005). According to the point of zero charge (pzc), the surface charge property of TiO_2 changes with

solution pH. The pH$_{pzc}$ for TiO$_2$ has been reported in the range 6.25–6.90. Thus, the TiO$_2$ surface is positively charged in acidic media (pH < pH$_{pzc}$, and negatively charged under alkaline conditions (pH > pH$_{pzc}$ (Sun et al., 2008). Therefore, it is expected that at pH below pH$_{pzc}$, TiO$_2$ particles at the TiO$_2$-strewn sheet surface acquires a positive charge. Since TiO$_2$ particles are located near the sheet surface, hence, the electrostatic interaction between the surface of the strewn sheet and the anionic dye parent fragment (Fig. 1) leads to strong adsorption with a corresponding high photodegradation activities at pH 3. On the other hand, at pH above pH$_{pzc}$, electrostatic repulsion between the negative surfaces of strewn sheet and anionic dye fragment retards the photodegradation activity. The order of activity decreases as pH 3 > pH 5 > pH 6.53 > pH 8.

2.2.3 Effect of initial concentration of IC dye on the photocatalytic activity of the TiO$_2$-strewn sheet

The effect of initial concentration on the photocatalytic degradation was investigated using concentrations 2.5 × 10^{-5}, 5.0 × 10^{-5}, and 7.5 × 10^{-5} mol/L. The kinetics studies of the photocatalytic degradation at different initial concentrations by TiO$_2$-strewn sheet are shown in Fig. 10. It can be seen that with increasing dye concentration, the photocatalytic activities of IC dye decreased. Hence, the photocatalysis process will work faster at lower concentration of pollutants. This behavior has been explained that with a high concentration of dye, the deeper colored solution would be less transparent to the UV light and the dye molecules could also absorb a significant amount of UV light causing less light to reach the catalyst resulting in the OH$^{\bullet}$ radicals forming on the surface of film to decrease, as a result, the reactive number of OH$^{\bullet}$ radicals attacking the dye molecules decreases and thus photodegradation efficiencies decreases (Konstantinou and Albanis, 2004). The straight lines in Fig. 10 confirm the first-order reaction of the degradation process with the rate constants 0.9138 hr^{-1}, 0.7077 hr^{-1}, and 0.5590 hr^{-1} for the dye concentration
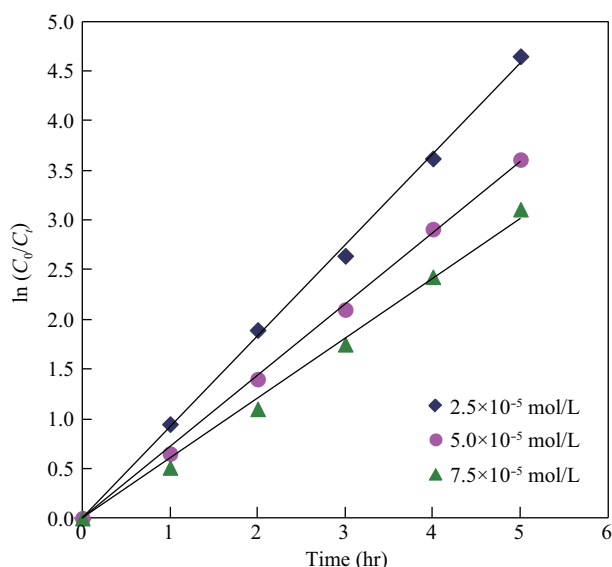
2.5 × 10^{-5}, 5.0 × 10^{-5}, and 7.5 × 10^{-5} mol/L, respectively.

2.2.4 Effect of UV light intensity on the photocatalytic activity of the TiO$_2$-strewn sheet

The effect of UV light intensity on the photocatalytic degradation of IC dye was investigated by varying light intensity designated as: low, medium, and high. With increasing light intensity, the photocatalytic activities increased as shown in Fig. 11. It has been reported by several groups (Toor et al., 2006; Liu et al., 2006; Wang et al., 2007) that the photodegradation rate increased with the increase of irradiation light intensity. High UV light intensity increases the photon influx entering the dye solution and consequently excites the TiO$_2$ particles at the sheet surface resulting in more OH$^{\bullet}$ radicals being formed. As the reactive number of OH$^{\bullet}$ radicals increases, the photodegradation efficiencies also increase.

2.2.5 Recyclability of the TiO$_2$-strewn sheet on the photocatalytic degradation of IC dye solution

In this work, the TiO$_2$-strewn sheet can be used repeatedly for the photodegradation of IC dye solution. The sheet, after being used, remained clean and required no cleaning for subsequent uses. Photographs of new sheets and used sheets are shown in the Fig. 12. The clean sheet surface results from repulsive force between the negative charge at the surface of the sheet and the negative charge on IC dye parent fragment. The hydrophobic properties of rubber sheet substrate may also contribute to the non-accumulation of dye molecules on the sheet surface. As a result, the sheet surface remains clean and the intermittently cleanings are not necessary. The sheet was tested for recyclability up to ten times the results of which are shown in Fig. 13. The photodegradation efficiencies of the sheet remained high throughout the recyclability test. One noticeable feature in Fig. 13 is that the efficiency of the first use was slightly lower than those of the other subsequent uses. This may result from the fact that, when freshly prepared, the rubber surface as well as some of TiO$_2$ particles was still covered with trace of impurities.
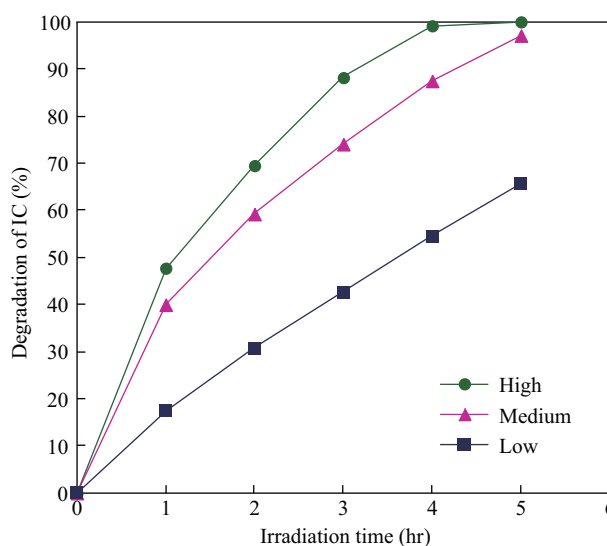

Fig. 10 Reaction kinetics on the photocatalytic degradation of IC dye solution at different initial concentrations by TiO$_2$-strewn sheet.

Fig. 11 Effects of UV light intensity on the photocatalytic degradation of IC dye solution by TiO$_2$-strewn sheet.
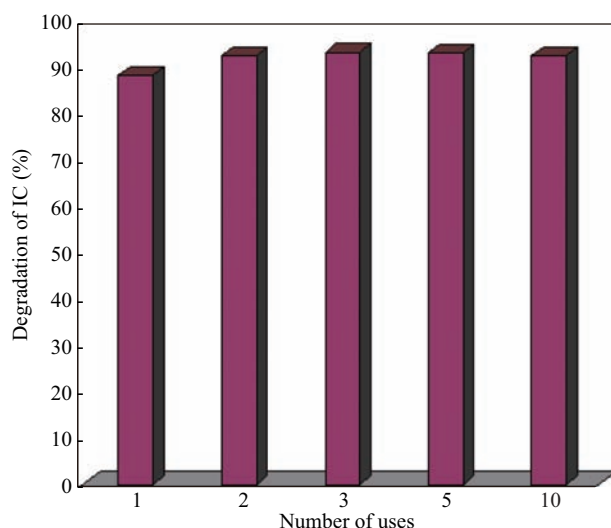
Fig. 12   Photographs of TiO$_2$-strewn sheet.

Fig. 13   Photodegradation efficiencies of TiO$_2$-strewn sheet from the recyclability test (under UV light, 3 hr, concentration 2.5×10^{-5} mol/L).

During the first use these impurities were destroyed in the photodegradation along with IC dye molecules in the solution. Hence, after the first use, the sheet surface appeared to be cleaner, i.e., less covered with impurities, with a higher number of TiO$_2$ particles contact with the dye solution and showed higher activity in the following use.

3 Conclusions

A novel, simple and low cost method for the preparation of TiO$_2$-strewn sheet is presented. The sheet still retains the photocatalytic property of TiO$_2$ particles by showing the photodegradation of IC dye solution under UV light illumination. From the SEM result, the TiO$_2$-strewn sheet contained densely titanium dioxide particles impregnated on the surface of the sheet rendering high surface uneveness and surface roughness from which high photocatalytic efficiency was originated. Dependencies of photocatalytic degradation of IC dye on the pH of dye solution, initial concentration of dye solution, and intensity of UV light were investigated. Although the TiO$_2$-strewn rubber sheet showed less activity than the loose powder of the same catalyst (Sriwong et al., 2008), it had one clear advantage

over the loose powder in that it can be easily recovered after used and can be reused many times. The recyclability of the strewn rubber sheet should be attractive to the water treatment industry as it helps keep the operation cost low.

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