

TiO₂ Nanoparticles-Coated Polypropylene Copolymer as Photocatalyst on Methylene Blue Photodegradation under Solar Exposure

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Abstract: Problem statement: Pollutions of water bodies by dye wastes from textile industries and other sources have become critical consideration. A photocatalytic technique using semiconductor materials such as Titanium Dioxide (TiO₂) activated by lights has been considered as one economical method to solve this problem. **Approach:** We attached titanium dioxide on the surface of polymer grains as photocatalytic agents using a cylinder milling method. Photodegradation processes were observed in decomposition of Methylene Blue (MB) solutions, as waste model, under solar illumination. Several parameters were optimized such as the milling temperature, the milling period, number of coated grain layers on the surface of the waste. The repeatability of using the coated grains was also expected. **Results:** Two layers of TiO₂ coated grains resulted the optimum decomposition rate of the MB solution. The milling temperature of 100°C and the milling period of 90 min produced the optimal decomposition rate. After five times repetition, the TiO₂ coated grains still function well by decomposition up to 97% MB compound. **Conclusion:** These materials have the potential in large scale wastewater treatment in the tropical regions and nearly do not require a complicated late handling in the process of separating the catalyst for treated water as well as requires very small energy, expect the sunlight energy.

Key words: TiO₂ nanoparticles, polypropylene copolymer, photodegradation, methylene blue, thermal milling method

INTRODUCTION

Rapid growths of industries have limited a great number of water resources due to pollutions. Waste water treatment techniques are continually developed to solve these problems (Fiore and Babineau, 1977; Hashimoto *et al.*, 2005). Compared to well known techniques such as conventional waste water installations, photocatalytic approach is likely to exhibit some advantages, namely: (1) strong oxidation properties, (2) do not create toxic compounds, (3) the chemical bond is stable to light and (4) the cost is relatively cheaper (Xu *et al.*, 1999; Yu *et al.*, 2009).

The photocatalytic process occurs when a specific semiconductor material is induced by lights. The photon energies of greater than the semiconductor band gap will excite electrons from the valence to the conduction band and create holes in the valence band. The produced electrons and holes then react with specific molecules in water to generate free radicals for decomposing organic pollutants (Hoffmann *et al.*,

1995; Fujishima *et al.*, 2000; Barjasteh-Moghaddam and Habibi-Yangjeh, 2011).

Titanium dioxide (Titania or TiO₂) has been understood as a good semiconductor in photocatalytic process because of high oxidation efficiency, producing nearly perfect decomposition process for organic contaminants, cheap and easily available and nearly not generating by-products (Tayade *et al.*, 2007; Qamar and Muneer, 2009; Sikong *et al.*, 2010). Unfortunately, photocatalytic tests using TiO₂ in laboratories reported by many authors have been mainly carried out by directly dispersing the TiO₂ powder into waste waters and exposing either by artificial UV lights or sunlight (Rao *et al.*, 2004). Economically, it requires a large enough electrical energy to generate artificial UV lights continuously for such a treatment purpose. The use of sunlight is also not so effective because of the TiO₂ band gap is large enough (around 3.2 eV) so that the only UV band can excite the electrons. The UV portion in the sunlight itself is nearly about 5% (Xu *et al.*, 2006; Liu *et al.*, 2006). In addition, even though the

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photocatalytic process was completed, another problem arises. Further process is required to remove the used TiO_2 from the treated water. Therefore this technique is hardly applied in larger scale, such as for industrial effluents or polluted rivers/lakes treatments.

A variety of catalyst modifications have been tried to solve the above problems such as using low grade TiO_2 to widen the absorption range due to narrowing the effective band gap (Arutanti *et al.*, 2009). At the present study, we propose a thermal milling method for attaching TiO_2 nanoparticles of this grade on the surface of the polymer grains having a low mass density, transparent and thermoplastics. The low grade TiO_2 is cheaper and was observed to have a narrow effective band gap compared to that of pure TiO_2 . These particles will become the active catalyst not only in the UV band but also in much longer wavelengths (Nurmawati *et al.*, 2009; Abdullah *et al.*, 2010). The selection of polymer grains having a lower specific density and transparent is intended to float on the water and to allow part of the lights were not absorbed by TiO_2 on the front surfaces of grains to activate TiO_2 on the opposite surfaces, or even the TiO_2 on the next grains. In addition, floating grains would be easily separated at the end of treatment. The selection of thermoplastic polymers is intended to allow the TiO_2 particles to be easily attached on the grain surfaces at temperatures near below the polymer melting point because the polymer surfaces become softer. Because of the grain size is large enough (several millimeters), a simple process could be performed to separate the catalysts from the treated waters. The catalyst materials developed in this way may have a great potential for use in large scale waste water treatments, such as for treating textile mill effluents, polluted river or lake using very little energy, except the energy from sunlight.

MATERIALS AND METHODS

Technical grade TiO_2 nanoparticles (Bratachem, Indonesia) were attached on the surface of Polypropylene Copolymer (PC) grains (side of around 3 mm, from local suppliers). This PC, a transparent thermoplastic material, has a density of 0.817 g cm^{-3} and melting points between $130\text{-}170^\circ\text{C}$. To investigate the role of photocatalyst for decomposing organic compounds in waste water, we used the model of waste from Methylene Blue (MB) (Sakura, Indonesia) dissolved in water.

Coating of the TiO_2 nanoparticles on the surface of PC grains was performed by milling a mixture of the TiO_2 nanoparticles and the PC grains in a cylinder mill. The cylinder was placed in an electric oven equipped with a temperature and a time controllers.

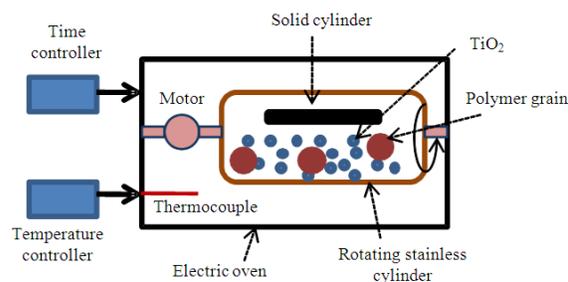


Fig. 1: Illustration of milling process used in this work

Figure 1 illustrates the milling process. The milling process was performed at different temperatures and time durations. The coated grains were then washed with water to remove the TiO_2 particles that were weakly attached on the grain surfaces and dried at 50°C for 30 min.

To avoid excessive use of the catalyst material, the experiment was started with optimizing the amount of catalysts per unit surface area of waste, represented by the number of coated grain layers placed on the waste surface. A glass container with a surface area of 30 cm^2 required 4.5 g of coated grains to form a single layer. Thus, 4.5 g, 9.0, 13.5 and 18 g of coated grains formed respectively 1-4 layers.

We optimized the milling parameters: temperature and time duration. The milling temperature was optimized in the range between $90\text{-}130^\circ\text{C}$ by fixing time duration. Coated grains produced at such temperatures were tested in the MB solutions. The optimum temperature was then used to optimize the milling period (varied between 30-120 min). In addition, the experiments have also been conducted to test the usability of the catalyst.

Testing was performed by distributing the coated grains into 250 mL MB solution ($2.60 \times 10^{-5} \text{ M}$) in the glass containers. The catalysts floated on the waste surface because of lower density. The experiments were conducted in the open air under solar exposure for a few days and small amount of the solution was sampled periodically for inspecting the effect of exposure time on the photodegradation results. The experiments were conducted in Bandung city, West Java, Indonesia. This city is located at the geographical coordinates of $173^\circ 36'$ east longitude $6^\circ 4'$ south latitude and at around 800 m above sea level (Isnaeni *et al.*, 2011).

Absorbance of the solution was measured using an ocean optic USB2000 spectrometer and its concentration was calculated based on the calibration curve belongs to MB standard solution. The sunlight

intensities were measured periodically using an LX-1102 light meter. The effect of exposure time on change of chemical bonding in the MB was observed using an FTIR Shimadzu Prestige 21. The color test was determined using a color filter 25 photometer nano Macherey Nagel. The pH of the solution was measured using a pH sensor connected to a Mixer MGA (Meter Graph Analysis) from Addestation Company. The surface morphology of the catalysts before and after applied to waste treatment were observed using an SEM Jeol JSM-6510LA Scanning Analytical Microscope.

RESULTS

The light intensity and the amount of catalyst are two main factors that controlling the process of photodegradation (Rashed and El-Amin, 2007; Rajeswari and Kanmani, 2009). We fixed both variables to optimize temperature and duration of milling.

The effect of milling temperature on transmittance and density of TiO₂ coated grains are shown in Fig. 2. The milling duration was fixed at 60 min. Below 90°C both density and transmittance of the coated grains nearly unchanged. As temperature increased above 90°C, the amount of TiO₂ attached to the grain surfaces increased because the grain surfaces became softer. The presence of TiO₂ reduced the transmittance since the particles absorbed lights so that as the milling temperature increased above 90°C, the transmittance decreased.

We also changed the milling duration for a specific temperature. We fixed the temperature at 100°C after identifying that it was the optimum milling temperature based on Fig. 2. Effect of milling duration on transmittance and the density of the coated grains are shown in Fig. 3. As the milling duration increased, the density increased while the transmittance decreased. The optimum condition was identified at the milling duration of about 90 min. At this condition the transmittance and density were 52% and 0.827 g cm⁻³, respectively.

In this study, we used MB solutions as the wasting models. As shown in Fig. 4, the MB has a maximum absorption at wavelengths of around 664 nm. We measured the absorbance at 664 nm for solutions at different MB concentrations to develop a calibration curve. The calibration curve was then used for determining the concentrations of the solutions at any conditions.

The absorption of MB solutions at several known concentrations and the corresponding fitting (calibration curve) are shown in Fig. 5. The best fitting was obtained using a linear equation of $A = 0.47C$, with A is the absorbance of the MB solution at a wavelength of 664 nm and C is the concentration of the MB solution.

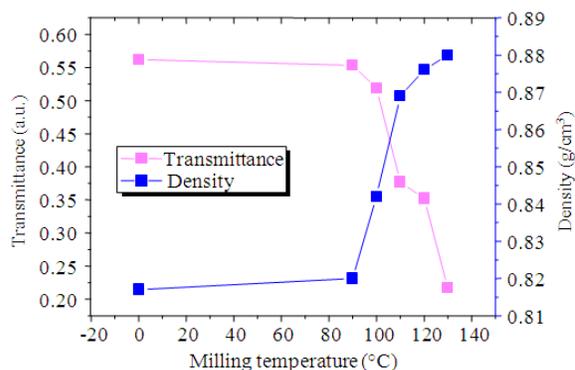


Fig. 2: Effect of milling temperature on the transmittance and the density of TiO₂ coated grains (milling duration = 60 min)

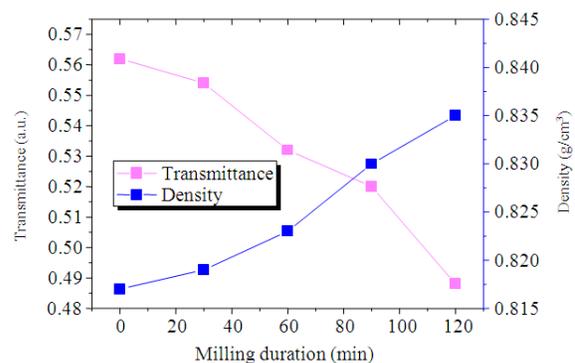


Fig. 3: Effect of milling duration of transmittance and density of TiO₂ coated grains (milling temperature = 100°C)

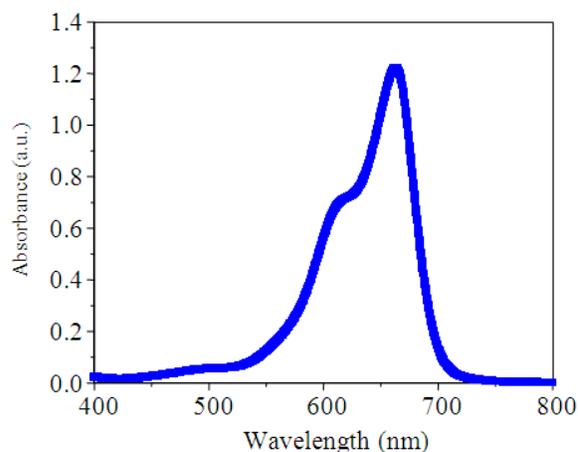


Fig. 4: Absorption spectrum of MB (concentrated = 2.60×10^{-5} M)

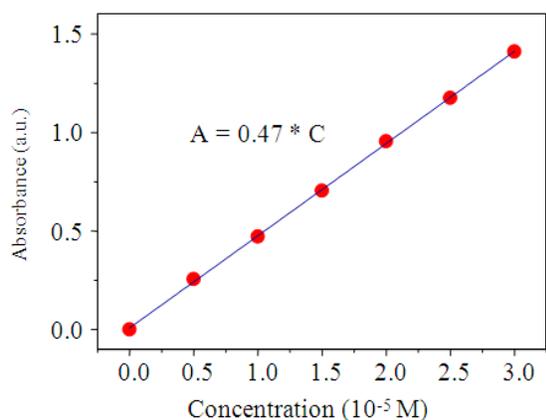


Fig. 5: Symbols are the absorbances of MB solutions at some know concentrations. The line is the fitting (calibration) curve

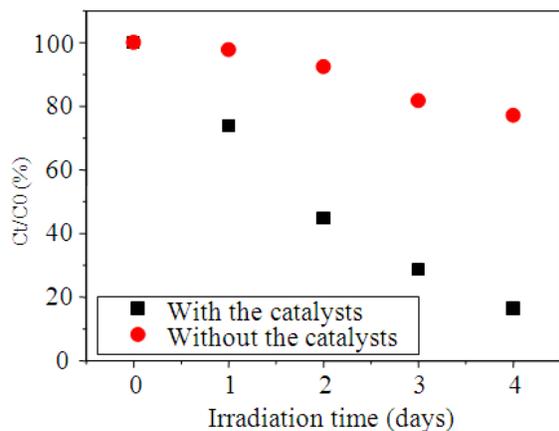


Fig. 6: Effect of TiO_2 coated grains (milling temperature = $90^\circ C$, milling time = 60 min, mass = 4.5g) on MB photodegradation ($C_0 = 2.60 \times 10^{-5}$ M)

At the initial stage of this study, we investigated whether the TiO_2 coated grains are effective as photocatalytic agent. We therefore compared the photodegradation effect on the wastes using plain grains and TiO_2 coated grains, both were treated simultaneously in the open air. Fig. 6 shows decomposition results using both plain grains and coated grains. It is clearly shown that the TiO_2 coated grains showed the photocatalytic effect. During this test, we also measured the physical parameters in open air such as humidity, air temperature and solar intensity. The results are shown in Fig. 7. During conduction of this study, the Bandung city was in the rainy season so that solar radiations were very small in most days.

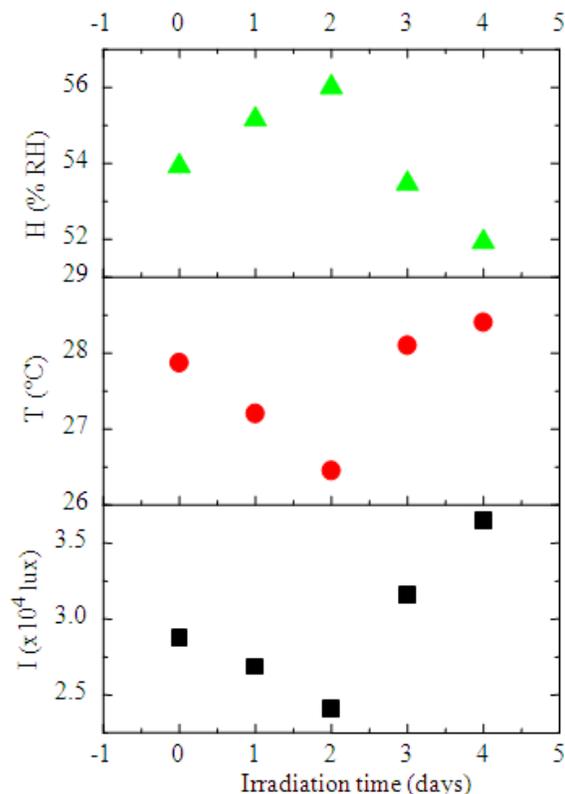


Fig. 7: Physical parameters in open air during experiments for obtaining data in Fig. 6: (top) air humidity, (middle) air temperature and (bottom) solar intensity

DISCUSSION

Based on Fig. 6 we concluded the TiO_2 coated grains have accelerated decomposition of organic compounds. The coated grains decomposed the MB solutions around five times faster than the plain grains. Slow decomposition process observed in solution containing pollen grains was due to direct decomposition of MB compound by sunlight. However, in some compounds, direct sunlight is unable to decompose organic compounds so that without catalyst, no decomposition process will be observed. The solar exposure allows the excitation of electrons to the conduction band and generates holes in the valence band of semiconductor catalyst. Holes react with water to produce OH^\cdot free radicals from oxidizing the organic compounds. Hence, increasing the exposure time, more pairs of electrons and holes are formed to produce more hydroxyl OH^\cdot for oxidizing the MB compounds. A similar pattern was reported by other researchers (Ping-Feng *et al.*, 2006; Hafizah and Sofyan, 2009).

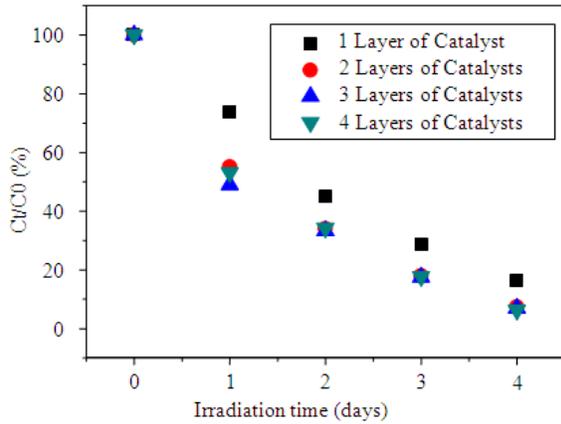


Fig. 8: Effect of number of grain layers (milling temperature = 90°C, milling time = 60 min) on MB photodegradation ($C_0 = 2.60 \times 10^{-5}$ M)

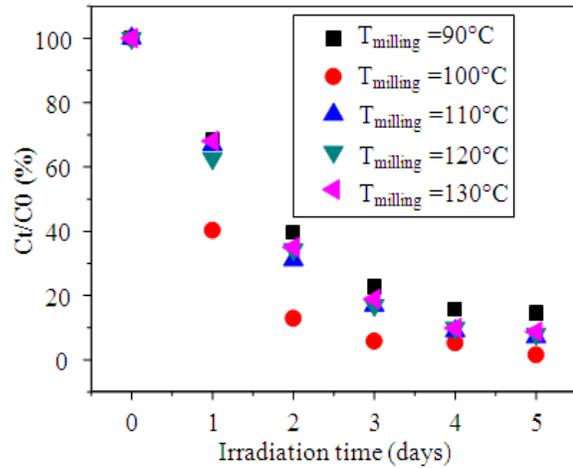


Fig. 10: Effect of milling temperature for producing TiO_2 coated grains on MB photodegradation (milling time = 60 min, $C_0 = 2.60 \times 10^{-5}$ M)

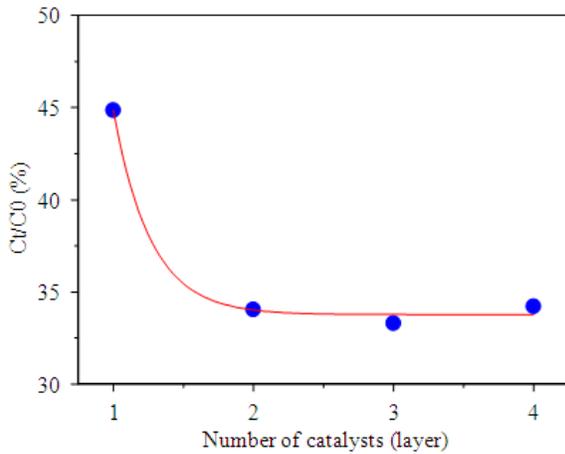


Fig. 9: Fractions of MB concentration left in solutions after two days illumination at various numbers of grain layers

Because the photocatalytic processes were conducted at the open air, the processes were influenced by the weather conditions, such as humidity, air temperature and sunlight intensity. Generally, different days showed different weather conditions. Fig. 7 shows the average weather conditions (humidity, air temperature and sunlight intensity) recorded in four successive days. The data were taken hourly during the daytime. Clearly, significant differences from the weather conditions were recorded for different days.

The TiO_2 coated grains have allowed the sunlight penetrating the first grain layer and reaches the next layers below. The effect of number of layers on the MB photocatalytic decomposition is shown in Fig. 8.

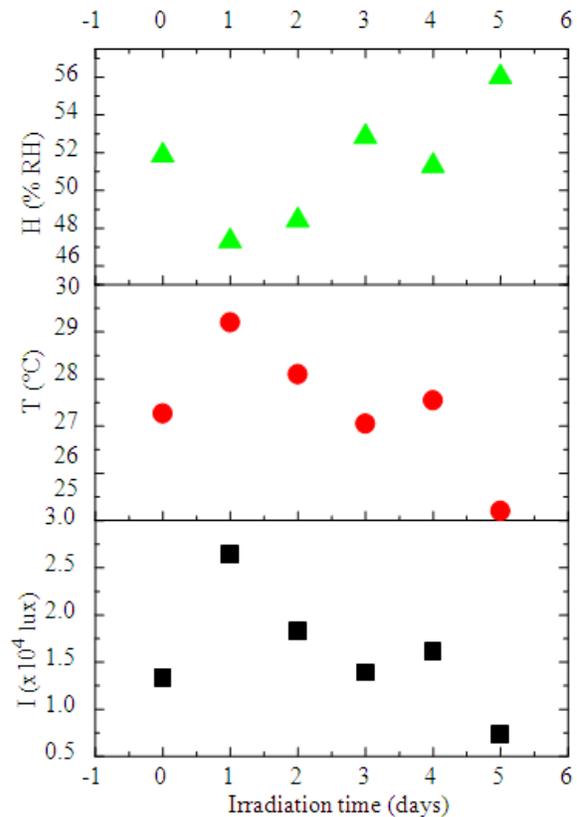


Fig. 11: Physical parameters in open air during experiments for obtaining data in Fig. 9: (top) air humidity, (middle) air temperature and (bottom) solar intensity

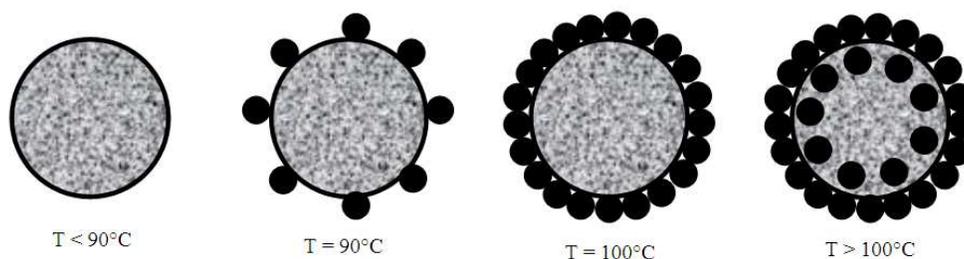


Fig. 12: Illustration of the result of coating on PC grains at different milling temperatures

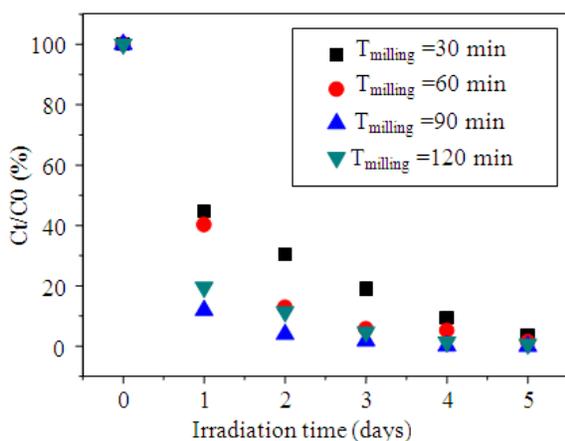


Fig. 13: Effect of milling duration (milling temperature = 100°C) on MB photodegradation ($C_0 = 2.60 \times 10^{-5} \text{ M}$)

We used the coated grains produced at a milling temperature of 90°C and milling time of 60 min. We observed two layers are the optimum number for decomposing the MB effectively. Further increasing the layer number above two layers does not change the decomposition rate.

Figure 9 shows the effect of number of layers on the decomposition of MB after two days' exposure using the coated grains produced at a milling temperature of 90°C and milling time of 60 min. We may state the sunlight energy can reach the grain up to the second layer and after that, nearly no light reaches the grains. The process of MB decomposition involves only electron-hole pairs produced at the first two layers. Starting from the third layer, nearly no electron and hole was generated, so that such layer did not contribute to the photodegradation process.

Based on Fig. 2, the TiO_2 coated grains showed a reduction in transmittance when the milling temperature passed 90°C and showed an incremental of density at the same temperature range. We inspected the effect of milling temperature on the rate of photodegradation.

We used coated grains made at the milling temperatures of 90, 100, 110, 120 and 130°C and the decomposition results are shown in Fig. 10. During this test, the physical parameters in the open air are shown in Fig. 11. It is clear in Fig. 10, the decomposition rate increased when the temperature increased from 90-100°C, after which it decreased when the temperature was increased to 110°C. Above 110°C, the decomposition rate unchanged, same as the decomposition rate when using coated grains produced at 110°C. This observation can be explained as follows. Below 90°C, the surfaces of PC grains are still hard and nearly no TiO_2 particle was attached on the grain surfaces. Therefore, after the milling process, the grain density and transparency were nearly the same as those of plain grain, as shown in Fig. 2.

At a milling temperature of 90°C, a fraction of grain surface was coated with TiO_2 particles and another fraction was still open. Therefore, the density of the coated grains was higher than that of the plain grains and the transparency was lower than that of the plain grain because TiO_2 absorbed light (Fig. 2). Since only a fraction of grain surface was coated with TiO_2 , the amount of TiO_2 exposed by sunlight (especially at the front and back surfaces of the first grain layer on waste surface) was small so that the number of releasing electrons and holes which activating radicals in water was small too. Therefore, the decomposition rate of MB was small, as shown in Fig. 10.

At a milling temperature of 100°C, the surfaces of grains were completely covered by one layer TiO_2 . Compared to coated grains made at 90°C, the density was higher because more TiO_2 was attached on the grain surfaces and transparency was lower because more TiO_2 absorbed light (consistent with Fig. 2). Because more TiO_2 was attached to the front and back surfaces of the grains, more electrons and holes were released on the grain surfaces to activate radicals in the waste. Therefore, the decomposition of MB solution became faster than the decomposition of waste containing grains that were coated at 90°C (consistent with Fig. 10).

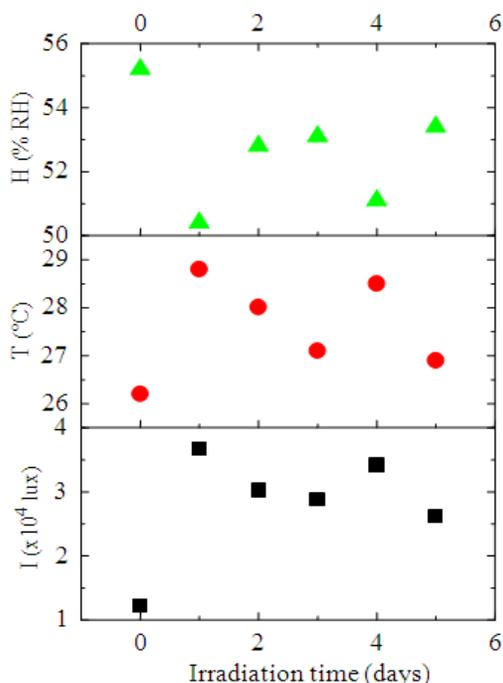


Fig. 14: Physical parameters in open air during experiments for obtaining data in Fig. 13: (top) air humidity, (middle) air temperature and (bottom) solar intensity

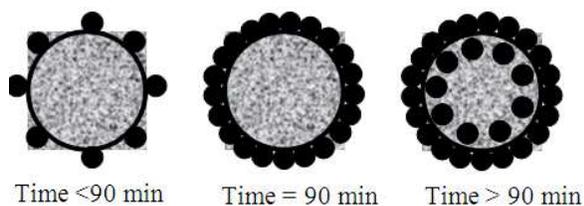


Fig. 15: Illustration of the results of coating on PC grains at different milling durations

Above 100°C, the surfaces of PC grains during the milling process were very soft. Some TiO₂ entered the inner part of the grain, forming more than one TiO₂ layers. It implied the density of coated grains became much higher and the transmittance became much lower because of more TiO₂ absorbed light and transmitting only very little light (consistent with Fig. 2). Because the TiO₂ entering the inner part of the grain will be covered by the polymer material, even those particles are exposed by the light, the produced electrons and holes were unable to reach the grain surfaces for activating radicals in waste. Only TiO₂ on the outermost surface of the grains will be effective for generating electrons and holes for decomposition

purpose. Because so many TiO₂ distributed in the inner part of the grain, the TiO₂ on the opposite surface of the grain may not receive any light. Consequently, only the TiO₂ on the outermost front layer on the grain surface will produce electrons and hole in the decomposition process. This implied the decomposition rate decreased compared to the results when using grains that were coated at 100°C (consistent with Fig. 10). Further increasing the milling temperature above 100°C will increase the number of TiO₂ entering the inner part of the grain so that further increased the density and decreased in the transparency (consistent with Fig. 2). Since only the outermost front layer will be effective for generating electrons and holes for photodegradation purpose, the decomposition rate unchanged and became the same as that obtained when using grains that were coated at 110°C (consistent with Fig. 10). Figure 12 illustrates the result of milling at different temperatures.

We also investigated the effect of milling duration on the decomposition rate. Fig. 13 shows the effect of milling duration on the decomposition rate of the MB compound where the milling temperature was fixed at 100°C. The corresponding physical parameters in open air during the test was performed is shown in Fig. 14. The difference of the decomposition rate for each solution started to be different after the first day of exposure. After solar exposure for two days, the concentrations of the MB solution (compared to initial concentration) containing coated grains that were milled for 30, 60, 90 and 120 min were, respectively, 30, 13, 4 and 11%. It demonstrated that coated grains that were milled for 90 min showed the most effective catalytic process. This observation can be mentioned as follows. The milling time of shorter than 90 min resulted in partially coated grains. At 90 min milling, the grain surface was completely covered by one layer of TiO₂. Longer than 90 min, some TiO₂ entered the inner part of the grain so that reduced the effectiveness of photodegradation process. This mechanism is illustrated in Fig. 15.

Based on the descriptions above, we concluded the optimum operating conditions where the milling temperature of 100°C and the milling duration of 90 min. In addition, using two catalyst layers yielded the best of photodegradation rate.

Increasing at the exposure time was followed by reducing in the waste color to become clear solution, also indicated the reduction in the MB concentration. The reduction in concentrations was followed by a reduction in absorbance. Figure 16 shows the effect of exposure time on the UV spectra of the MB solution. During this test, the parameters in open air (humidity, temperature and solar intensity) are shown in Fig. 17.

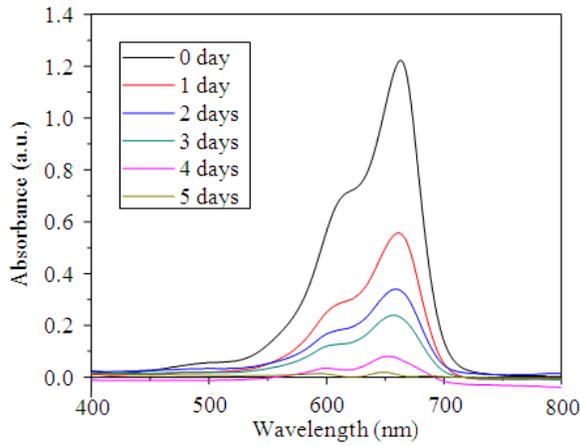


Fig. 16: MB absorption spectra during the photodegradation process (milling temperature = 90°C, milling time = 60 min, coated grain mass = 4.5g, C₀ of MB = 2.60×10⁻⁵ M)

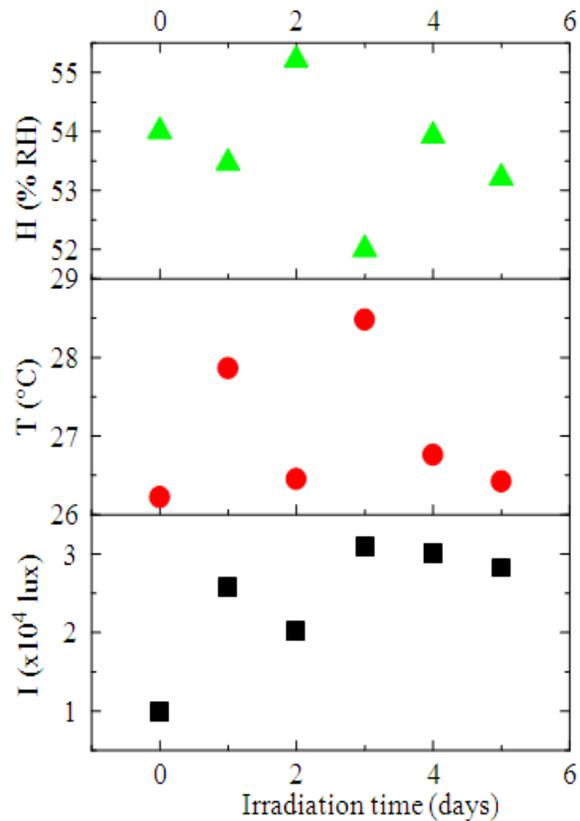
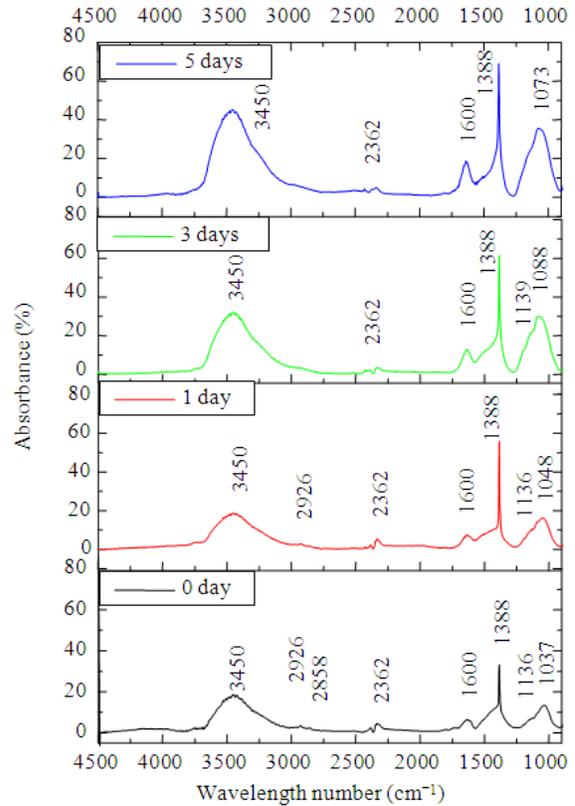
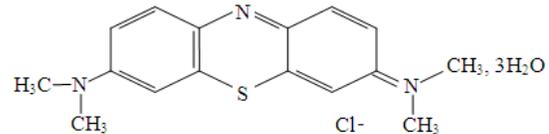


Fig. 17: Physical parameters in open air during experiments for obtaining data in Fig. 16: (top) air humidity, (middle) air temperature and (bottom) solar intensity



(a)



(b)

Fig. 18: (a) IR absorption spectrum of MB solution during the photodegradation process using TiO₂ coated grains and (b) chemical bonding structure of the MB

After five days exposure, the absorbance approached zero, indicating nearly all MB was decomposed and leaved only clear solution. Calculating using the calibration curve we obtained, after five days' exposure the concentration of MB and color reduced by 99.5 and 94.5%, respectively.

Figure 18a shows the IR spectra of the MB solution degraded using the TiO₂ coated grains. This figure indicates the influence of exposure duration on the chemical bonding characteristics of the MB compounds (Fig. 18b). Before photodegradation process, the IR absorption of the MB compounds showed prominent peaks at wave numbers of around 1000 cm⁻¹ and 2362

cm^{-1} , 1388 cm^{-1} , 1600 cm^{-1} , 3450 cm^{-1} , which respectively identified the vibrations of ester group (C-O), aromatic group (C = C), alkene group (C = N) and -OH bridge. In addition, there were also some weak absorption peaks in the range between $2800 - 3000 \text{ cm}^{-1}$ and 1136 cm^{-1} , indicating the presence of (N-CH₃) vibration (Sheppard, 2003). The wave numbers and corresponding bonding types are shown in Table 1.

Increasing the exposure period increased in the absorption spectra at wave numbers of around 1000 cm^{-1} , 1388 cm^{-1} , 1600 cm^{-1} and 3450 cm^{-1} . The same peaks were identified by Yu and Chuang (2007).

Increasing the exposure time caused the increase in absorption of wave numbers 3450 cm^{-1} , indicating the increase in concentration of hydroxyl radical OH in the solution MB. This is confirmed by the increase in pH as shown in Fig. 19.

Figure 20 shows the SEM images of TiO₂ coated grains before and after application to photodegradation. The TiO₂ nanoparticles were well attached on the surface of the grains before and after application to photodegradation of the MB. After application of photodegradation process, some TiO₂ was likely covered with MB chains. However, most part of the coated surface returned back to initial condition after photodegradation process. This gives an opportunity to use the catalyst repeatedly (Aliah *et al.*, 2011).

Table 1: Vibration modes of chemical bonds of MB and the corresponding wave numbers

No.	Chemical bond	Wave number (cm ⁻¹)
1	v (C-O)	1037, 1048, 1088, 1073
2	v (N-CH ₃)	1136
2	v (multiple ring C = C)	1388
3	v (C = N)	1600
4	v _{as} (C = O)	2362
5	v _s (CH ₃)	2858, 2926
6	v (O-H)	3450

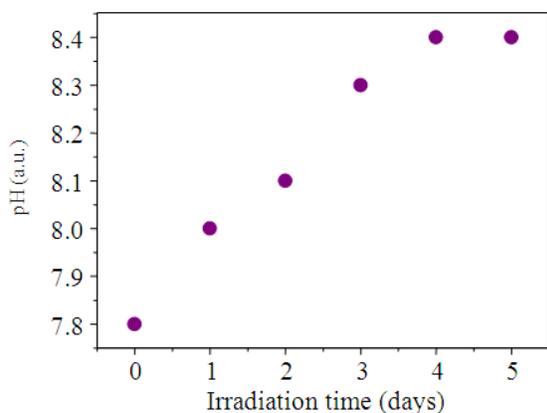


Fig. 19: Changes in the pH of MB solution during the photocatalytic degradation

To investigate the stability of the catalyst, photodegradation testing was repeated many times. We repeated the use of catalyst until five times each of which was exposed for five days. Figure 21 shows the effect of exposure time on the MB concentration for each repetition. The reductions in the MB concentrations after five days' exposure are summarized in Fig. 22.

Based on Fig. 21 all test solutions degraded at nearly the same rate i.e., at an average of about 0.675 days^{-1} . This suggests that after five times repetition, the catalyst still function well for decomposing the MB compound.

After five days' exposure, the catalyst used at the fifth repetition was able to decompose the MB compounds up to 97% of the initial concentration (Fig. 22). Thus, the TiO₂ coated grains become an alternative reusable catalyst for decomposition of the MB solution or other organic pollutants.

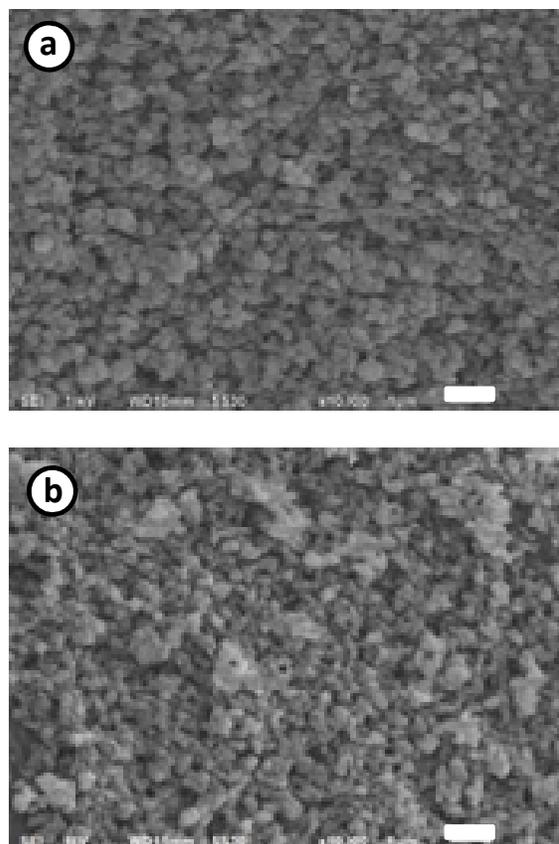


Fig. 20: SEM images of TiO₂ coated PC grains prepared at optimum milling parameters: (a) before, (b) after application to MB photodegradation. The bar length is 1 μm

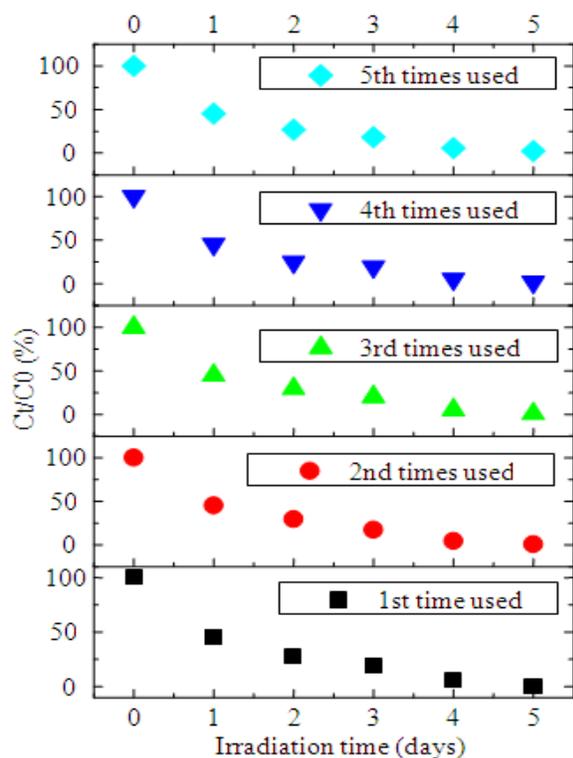


Fig. 21: Photodegradation of MB for usability examination

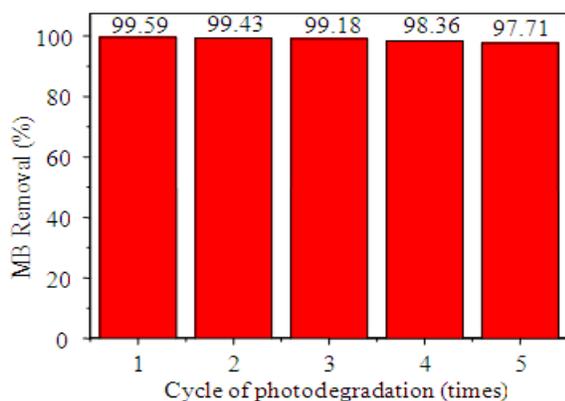


Fig. 22: The stability of TiO₂/PP photocatalysts for recycling MB photodegradation

CONCLUSION

Thermal milling techniques have been successfully used for coating the surface of the PP polymer with the TiO₂ nanoparticles. The TiO₂ coated polymers have been applied as photocatalysts in the process of MB degradation. A number of experiments have been

conducted to investigate the optimum preparation parameters and the optimum amount of catalyst in the process of MB photodegradation. The optimum milling temperature was 100°C and the optimum milling period was 90 min. The use of catalysts the TiO₂ coated polymers as much as two layers and cover the surface of test solutions yielded the optimal photodegradation rate. This catalyst material is reusable, clean and zero energy. Thus, the material could potentially be applied within a large scale water treatment with repeatable usage.

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