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Photocatalytic performance of Anatase/Rutile TiO_2 composite against different organic dyes

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Abstract

Organic waste dyes from textile industries are considered to be significant environmental wastewater. In general, wastewater treatment using photocatalytic degradation via a semiconductor is an advanced technology, due to the high photocatalytic efficiency of the semiconductor, the environmentally friendly nature of the process, the low-cost of materials needed and the free energy available for consumption from sunlight. Recently, an anatase/rutile titanium dioxide (TiO_2) composite has been widely studied, due to its unique optical property as a photocatalyst, which is more effective than the pure phase. In this work, an anatase/rutile titania mixed phase composite was prepared by a simple mechanical method. The degradation mechanisms of specific organic dyes are different, resulting in a difference of degradation performance. This research was conducted in order to study the photocatalytic performance of an anatase/rutile titanium dioxide (TiO_2) composite, prepared from commercial TiO_2 by ball-mill techniques, against three types of dyes including methylene blue (MB), methyl orange (MO), and Rhodamine B (RhB). Phase ratios of the composites were evaluated by X-ray diffraction (XRD) and confirmed by Raman spectroscopy. Their morphologies were monitored by a scanning electron microscope (SEM). We have reported the optimized condition of various anatase/rutile titanium dioxide phase ratios necessary, for a high synergistic effect of each organic dye type. The photocatalytic activities of the titania catalyst, for all three dyes degradation under visible light irradiation were also scrutinized. The results revealed that the prepared anatase/rutile TiO_2 composites, can provide significant enhancement in photocatalytic efficiency for MB, MO and RhB textile dye degradation.

Keywords: Anatase/Rutile composite, Dye degradation, Photocatalytic performance, Titanium dioxide

1. Introduction

In relation to the dyes wastewater generated by textile industries, it is generally known that some azo-dyes and degradation products are highly carcinogenic. The treatment technologies of organic dye pollutants such as the methods of adsorption, biodegradation, chemical chlorination and ozonation have all been recently developed. However, the main drawbacks of these methods are the generation of another concentrated dyes-containing phase. The alternative process, leading to the total degradation and mineralization of most organic dye pollutants in water, is the oxidation method using photocatalytic titania particles under UV irradiation [1-3]. Electron-hole pairs from titania particles activated by UV irradiation can react with oxygen and water molecules, becoming reactive oxygen specimens that degrade pollutants such as organic dye compounds or bacterial membranes [4-8]. It is generally known that the photocatalytic performance of the anatase phase under UV irradiation is more highly effective than the rutile phase. Meanwhile, degradation of organic dyes induced under visible light can be proceeding on the modification of titania particles with metal ion or mixed phase of anatase and rutile titania [9-11]. Typically, the commercially mixed-phase of rutile and anatase in TiO_2 Degussa P25, known as P25, is also well known in producing the highest activity of photocatalysis under both UV radiation and visible light sources. Moreover, TiO_2 P25 is often used as reference material in photocatalytic applications [11]. The advantage of the high photocatalytic activity generated by the P25 photocatalyst is derived from the synergistic effect, of the anatase/rutile mixed-phase in relation to charge transferance at the interface phase, suppressing electron-hole pair recombination [12]. However, the conventional method to prepare P25 always uses expensive raw materials and complex procedures [5]. In this work, the photocatalytic degradation of three various dyes has been investigated using anatase titania and the mixed phase of anatase and rutile titania by the ball-mill technique. The 90% anatase and 10% rutile phase ratio was selected for the titania mixed phase sample. Meanwhile, the ball-milling technique was chosen because it has considerable advantages including cost effectiveness, ease of manufacture in mass production and the use of low-cost raw materials. The effects of crucial parameters, such as diverse light irradiation (UV and visible light sources) and a mixed-phase catalyst compared to a pure titania phase were investigated. Methylene blue, methyl orange and Rhodamine B are three organic dyes used to study their degradation, together with an evaluation of the photocatalytic activity produced by the titania samples.

2. Materials and Methods

The anatase TiO_2 laboratory grade (Ajax Finechem, Australia) was used as the anatase phase and precursor for the TiO_2 rutile phase. The rutile phase was obtained by the calcination of anatase phase at 1,200 °C for 3h. The TiO_2 mixed-phase was prepared by mixing 90% anatase and 10% rutile by weight. 10 g of TiO_2 powder was loaded into the milling cells with a mixture of 2 and 5 mm diameter zirconia balls, followed by filling with 40 ml of ethanol media. The milling time was operated at 18 h. The phase ratio of TiO_2 samples was confirmed by X-ray diffraction (X'Pert PRO ANalytical) and Raman spectrometer (Thermo Scientific DXR). TiO_2 samples (tiatania) particle size and their morphology were observed by SEM (FE-SEM, JEOL JEM 6340J). The photocatalytic efficiency by the modified TiO_2 samples was investigated by the degradation of three dyes; Methylene blue (MB), methyl orange (MO) and rhodamine B (RhB) in aqueous solution (1 mg dm^{-3}). For photocatalytic degradation, 150 mg of TiO_2 samples were added to a 150 ml dye solution and stirred under dark conditions for 10 min to achieve equilibrium, before being irradiated with a UV lamp (10 W UVA and 14W UVB Phillips T5) or visible light from 3M LED light sources. Aliquots suspension samples of 5 ml were collected from the beaker, withdrawn at 10 min intervals, except for the MO solution under UV irradiation, for which dye aqueous was withdrawn at 1 min intervals. The concentrations of dyes in each solution were monitored by a UV-Vis spectrophotometer (Thermo Electron Corporation). The degradation rates of the three dyes were calculated from the decrease of the maximum absorption peak of each tested organic dyes solution. The maximum absorption peaks of RhB, MO, and MB were determined at 554, 464 and 663 nm, respectively.

3. Results and Discussion

Photocatalyst characterization

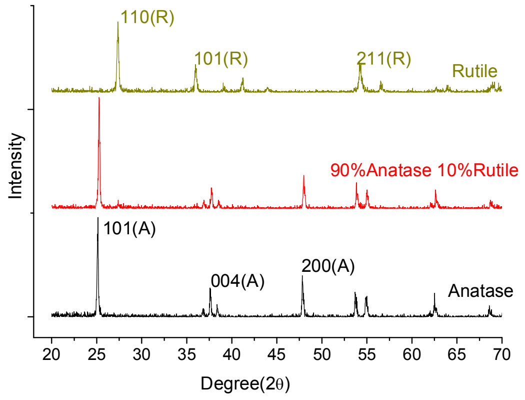

Fig. 1 XRD patterns of anatase, rutile, and mixed phase titania samples.

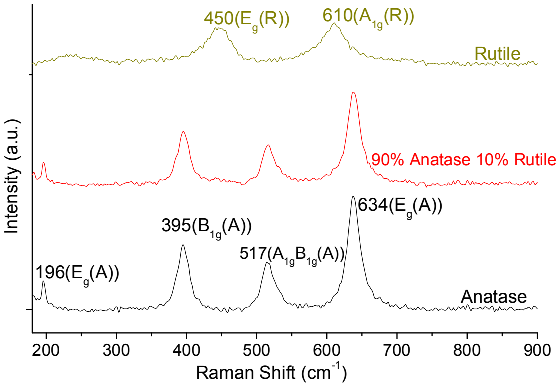

Fig. 2 Raman spectra of anatase, rutile, and mixed phase titania samples.

Fig. 1 exhibits the XRD patterns of rutile and anatase samples. The XRD pattern of the anatase phase, mixed phase 90% anatase/10% rutile and rutile phase is at the bottom line, middle line and the top line, respectively. The anatase phase pattern shows a strong peak of (101) plane situated at around 25° and weak dips of (200), (205), and (211) plane peaks at around 48°, 55°, and 56° respectively. The main diffracted peak of rutile (110) plane is located at around 27° whilst the other weak peaks are around 36° and 55°, which corresponds to the rutile (101) and (211) planes, respectively [13]. For the mixed phase pattern, only a weak peak of rutile is seen at around 27°, indicating a small percentage of rutile in the mixed titania composite. Fig. 2 shows the corresponding Raman spectra confirming the mixed phase of the samples. All of the Raman bands can be attributed to the O–Ti–O bending and Ti–O stretching vibrations mode of the anatase and rutile titania [5, 13]. The Raman spectra shows various bands of the vibrations mode of a pure rutile phase, a pure anatase phase and a mixed phase comprised of anatase and rutile. The rutile spectra exhibits the bands of E_g and A_{1g} vibration modes at 450 and 610 cm^{-1}, respectively. The mixed phase titania shows the main bands at around 395, 517, and 634 cm^{-1} ascribed to anatase B_{1g}, $A_{1g}+B_{1g}$, and E_g vibration modes, respectively. The presence of rutile in the mixed phase spectra is indicated by an additional band of the E_g vibration mode and the A_{1g} band in the shoulder of the anatase E_g band at around 610 cm^{-1}.

SEM images of titania samples are shown in Fig. 3 with the same magnification at 10,000X. The morphologies of anatase, anatase/rutile mixed phase and rutile after ball-mill mixing are shown in Fig. 3 (a)-(c), respectively. The average anatase titania particle size is approximately 200 nm, while the particle size of rutile titania is in the range of 1 to 4 μm. In the SEM image of the mixed phase, it is clearly evident that both anatase and rutile phases are present in the mixture, due to the distinct difference in size and morphology between the two phases.

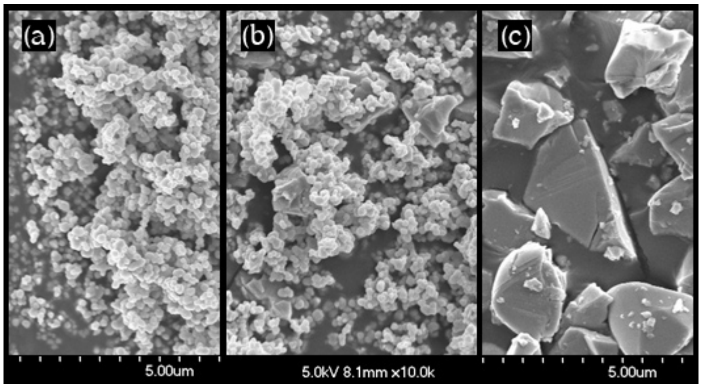

Fig. 3 SEM micrographs of titania samples anatase (a), anatase/rutile mixed phase (b), and rutile (c) after ball-mill mixing.

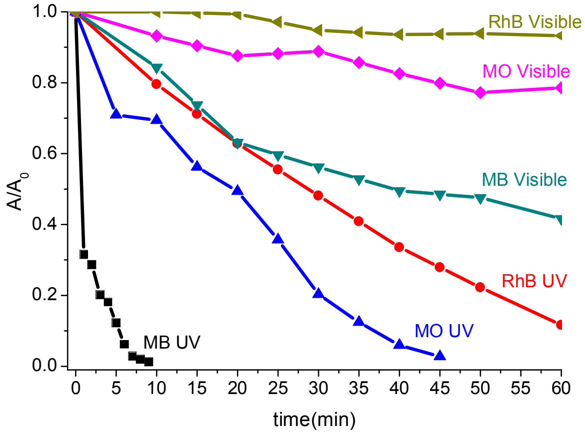

Fig. 4 The degradation curve of MB, MO and RhB using a 100% anatase titania photocatalyst under UV and Visible light irradiation.

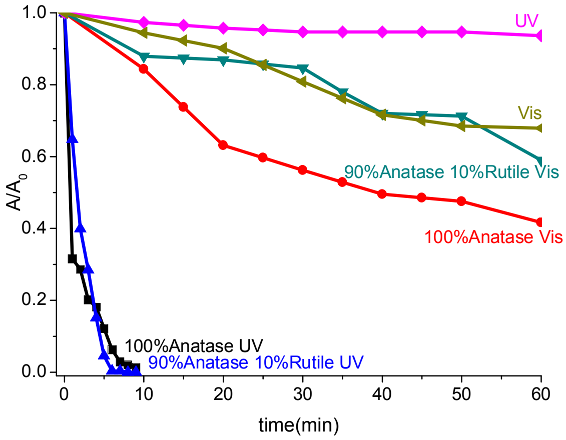

Fig. 5 The photocatalytic degradation of MB commercial textile dye using various titania samples and without the presence of a photocatalyst under UV/Visible light source irradiation.

Photocatalytic degradation of dyes

The photocatalytic degradation of the three dyes by a 100% anatase titania photocatalyst under UV/visible light irradiation (Fig. 4), shows higher photocatalytic activity under UV irradiation was achieved for all three dyes; more so than visible light. The total and complete photocatalytic degradation of RhB and MO by a 100% anatase phase under UV radiation was obtained within 90 min and 10 min respectively. Meanwhile, the photocatyst of 100% anatase titania, when activated by visible light irradiation, can be seen to also degrade all three textile dyes. The photocatalytic degradation mechanism of 100% anatase titania under visible light irradiation could be prompted by the inducement of a self-sensitization mechanism. Dye molecules absorb the visible light and initiate a charge transfer from the excited state of dyes to the anatase titania conduction band, leading to the creation of a reactive oxygen species at the titania surface [2]. RhB is a class of the xanthene dyes family which by itself doesn't degrade under UV and visible light irradiation, nor by the presence of a photocatalyst without illumination [2]. The degradation rate of RhB with 100% anatase phase under UV irradiation is much higher than that under visible light. The photocatalytic degradation of MB in Fig. 5 indicates that direct photolysis of the MB thiazin dye was slightly degraded under UV and visible light irradiation, without the presence of a titania photocatalyst.

The MB degradation rate by a mixed phase titania photocatalyst was found to be higher compared to the absence of a titania and pure anatase catalyst. The mixed phase should provide higher degradation rates due to the existence of the rutile phase, with a bandgap around 3.01 eV that could absorb the correlated photon in the region of visible light [12, 14]. This feature suggests that the main mechanism responsible for MB degradation under visible light should be a self-sensitization mechanism. The great degradation activity of MB can be obtained within 10 min under UV irradiation and within 90 min from visible light. The results suggest that the main degradation mechanism of MB under UV conditions is contained within a photocatalization mechanism, with the corresponding degradation strongly dependant upon the reactive species created from the reaction. The photocatalytic degradation of the three dyes in the presence of 90% anatase/10% rutile phase titania, under either UV or visible light irradiation is shown in Fig. 6. The degradation activity results of the mixed phase show a similar trend to the results of the 100% anatase titania, except for the result of RhB under visible light, which is found to be greater than that under UV irradiation. The absorption spectra of RhB by a titania photocatalyst under UV and visible light at different irradiation times are clearly shown in Fig. 7. The RhB degradation mechanism occurring via titania photocatalysis under UV and visible light illumination is different, as illustrated in Fig. 7(a) and (b). Under visible light, RhB could be degraded by a decolorization mechanism, resulting in fragmented product forms. RhB degradation under visible light using a mixed phase catalyst, shows the maximum absorption peak shift from a wavelength of 554 nm. Fig. 7 (d), and (e) display scenarios of RhB degrading into fragmented products comprised of triethylrhodamine and ethylrhodamine, whilst also showing different maximum absorption peaks at 538.5 and 509.5 nm, respectively [2]. The decolorization of RhB by a reductive mechanism can exist by way of a self-sensitization mechanism. RhB degradation under UV irradiation results in degradation by OH, due to the absence of any fragmented product peak. The result reveals that the main RhB degradation mechanism under UV irradiation is still dominated by a photocatalytic mechanism. MO is a class of azo dye and consists of azo bonds (-N=N-) or nitrogen to nitrogen double bonds. Azo bonds in azo-dye molecules are typically reactive bonds, that can directly react with electrons or the positive holes of activated titania particles. The cleavage of azo-bonds also occurs by the action of reactive species from photocatalytic mechanisms, including hydroxyl radicals [8]. The degradation results of MO suggest that the titania anatase phase is more active than the rutile phase under UV irradiation. The major mechanism for MO degradation under UV irradiation could be led by a photocatalytic mechanism. The lower MO degradation occurring through direct photocatalytic and self-sensitization mechanisms under visible light, could be due to the weak adsorption arising between titania and the MO dye, which prevents charge transfers between the MO dye and the titania surface.

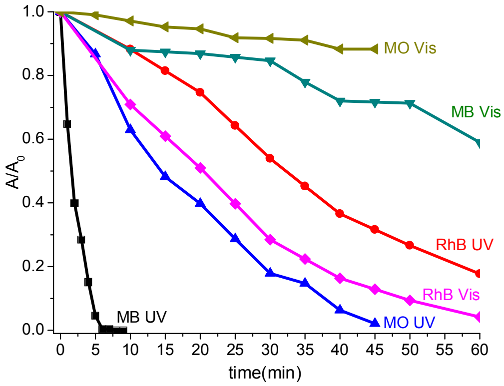

Fig. 6 The degradation curves of three dyes using 90% anatase/10% rutile phase titania under UV and Visible light irradiation.

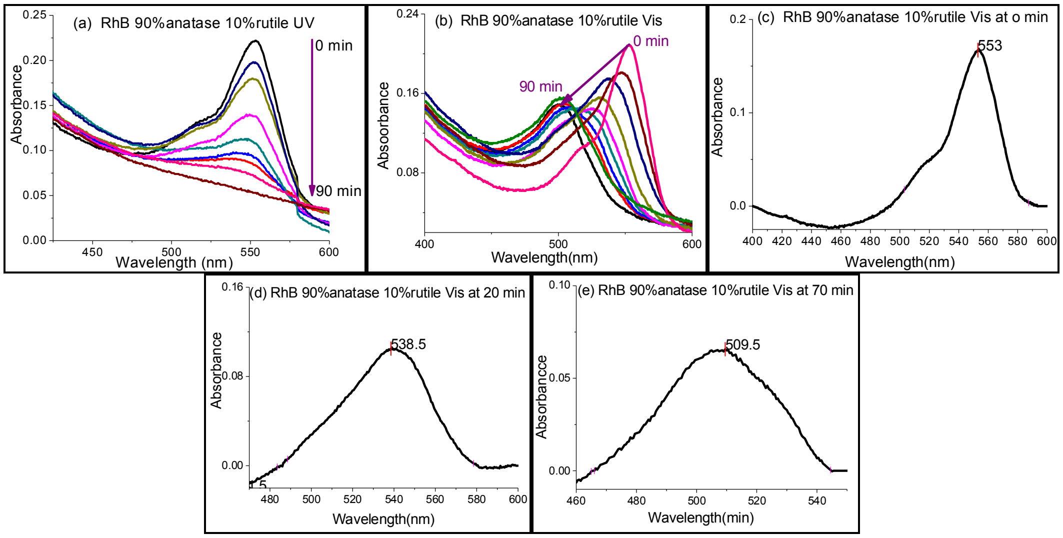

Fig. 7 The UV-Vis absorption spectra of RhB with mixed phase titania samples (a) RhB changes in degradation time under UV radiation (b) RhB changes in degradation time under visible light radiation (c) absorption spectra of RhB (d) absorption spectra of triethylrhodamine and (e) absorption spectra of ethylrhodamine having λ_{max} at 555, 539, 510 nm, respectively

4. Conclusion

Three different classes of textile dyes; MB, MO, and RhB, can be decolorized by titania photocatalysts (obtained by the ball-milling technique) under a UV/Visible light source. The ball-milling method has been put forward to synthesize a visible-driven titania photocatalyst from commercial grade titania. Due to the usage of low-cost materials associated with the ball-mill method, it is considered to be very suitable for industrial purposes. All three different dyes can be totally degraded and mineralized under UV irradiation, with both 100% anatase and a mixed phase of 90% anatase and 10% rutile. Higher photocatalytic activity degradation can be obtained under UV irradiation for all three dyes. The results suggest that the photocatalytic activities with various path mechanisms strongly depend on the type of dye (due to the different molecular structures of dyes), the UV/Visible light source, and the phase of the titania. This knowledge of the photocatalytic mechanism pathways of dye degradation can be beneficial, when designing for optimum efficiency, any equipment or dye pollutant removal reactors, or processing systems for the treatment of wastewater.

5. Acknowledgement

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6. References

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