Inquiro, the UAB undergraduate science research journal

Volume 2007 | Number 1 Article 8

2007

Photocatalytic Degradation of Industrial Dyes in UV-irradiated Suspensions of Titania-Coated Glass Microballoons

Kristen E. Kerr

M. L. Jones

M. Koopman

K. K. Chawla

W. Ricci

See next page for additional authors

Photocatalytic Degradation of Industrial Dyes in UV-irradiated Suspensions of Titania-Coated Glass Microballoons

Authors
Kristen E. Kerr, M. L. Jones, M. Koopman, K. K. Chawla, W. Ricci, and M. Lalor

Photocatalytic Degradation of Industrial Dyes in UV-irradiated Suspensions of Titania-Coated Glass Microballoons

Kristen E. Kerr, M.L. Jones, M. Koopman, K.K. Chawla, W. Ricci, M. Lalor

The photocatalytic degradation of two common dyes used in the textile industry, PRO Forest Green H-Reactive H-E4BD (initial concentration: 0.0918 g/L of distilled water) and Procion Red MX-5B (initial concentration: 0.0227 g/L of distilled water) was examined through the introduction of titania (TiO_2)-coated glass microballoons (GMBs) into the dye solutions. Under solar ultraviolet (UV) radiation, the degradation of the dye solutions was monitored both qualitatively, through observation and photography, and quantitatively, through spectrophotometry analysis, comparing values to a control sample of dye solution also exposed to solar UV radiation but without titania-coated GMBs. The photodegradation experiments were carried out using one of two different forms of agitation: an aeration bubbler apparatus and a magnetic stirrer plate. The relative success of each of the two forms of agitation and their effect on the photocatalytic capabilities of titania-coated GMBs was used for comparison. The following results of the two samples agititated using the magnetic stirrer were observed: after 2 h, 30 min of UV exposure the PRO Forest Green H-Reactive H-E4BD dye sample was clear in appearance and had an absorbance of 0 at 630 nm, and after 3 h of UV exposure the Procion Red MX-5B dye sample also appeared clear and had an absorbance of 0.006 at 510 nm. After 6 h and 10 min of UV exposure and agitation using the aeration bubbler apparatus, the PRO Forest Green H-Reactive H-E4BD dye sample had an absorbance of 0.345 at 630 nm, and the Procion Red MX-5B dye sample had an absorbance of 0.030 at 510 nm. Both of the dye samples appeared lighter in color in comparison to their respective initial concentrations. Scanning electron microscopy (SEM) showed that the titania coatings on the GMBs were more affected by the magnetic stirrer than by the aeration bubbler apparatus.

INTRODUCTION

Wastewater produced from the textile industry is distinguished by the presence of color from various dyes. In fact, every day about 400 tons of dyes are discarded as waste from various industries world wide (Moreira et al., 2005). As a result of this aesthetically displeasing colorful effluent, the pollution produced is readily noted (Byrappa et al., 2006). Therefore, there is interest in discovering techniques to degrade this colored wastewater to comply with United States wastewater discharge permits (NPDES) before it causes harmful environmental effects (Garcia-Maontano et al., 2005) such as worsening the quality and reducing the gas solubility of water systems (Asad et al. 2006). In order to break down organic contaminants such as textile dyes, techniques of photocatalytic degradation using titania (TiO_2) as a catalyst have been successfully applied in previous studies such as those performed by Akarsu et al. (2006) and Lachheb et al. (2002). TiO_2 exists in three different forms: anatase, brookite, and rutile. Among these three polymorph forms, anatase-TiO2 has gained the most attention due to its successful use as a catalyst (Akarsu et al., 2006). In the presence of ultraviolet (UV) light, titania, acting as a photocatalyst, is activated, leading to the oxidation of organic material through the excitation of an electron from its valence band to the conduction band. This process results in positively charged holes in the valence band which are able to oxidize organic compounds (Ren et al., 2006). Azo dyes, such as Procion Red MX-5B and Reactive Green H-E4BD, are synthetic dyes widely used in the textile industry. This type of textile dye has created a particular problem in the environment due to the stability of its molecular structures and its resulting resistance to many different standard techniques of degradation (So et al., 2002).

Glass microballoons (GMBs) often have density values below 1.0 g/cm3, the density of water, and are used in syntactic foam composites for a variety of applications. GMBs can be coated with various materials, such as titania, and thus, have a range of potential uses (Koopman et al., 2003). As a result of the photocatalytic properties of titania, titania-coated GMBs are candidate materials in the treatment of wastewater produced by the textile industry by breaking down the dye, and therefore its color, in the polluted effluent. Furthermore, by using HGMs as a medium for bearing titania, both the recovery and reuse of this photocatalyst is made possible.

MATERIALS AND METHODS

Two commercially used textile azo dyes were obtained. One of the dyes, Procion Red MX-5B, was purchased from Sigma-Aldrich Co., and the other dye, PRO Forest Green H-Reactive H-E4BD was purchased from Pro Chemical and Dye. Stock solutions were prepared using distilled water. Titania-coated HGMs were obtained from Trelleborg Emerson & Cuming, Inc. The HGMs had a true particle density (TPD) of 0.38 g/cm3 without the titania coating and a TPD of 0.44 g/cm3 after the titania coating had been added.

50 mL of PRO Forest Green H-Reactive H-E4BD dye with a concentration of 0.0918 g/L of distilled water was placed into 4 different beakers. Two of the beakers contained no GMBs and served as controls; one of these beakers was placed under solar UV-radiation, and one was placed in dark conditions. The third beaker contained 1.0605 g of titania-coated GMBs, was placed under solar UV-radiation, and was agitated using an aeration bubbler apparatus. The fourth beaker contained 1.0604 g of titania-coated GMBs, was placed under solar UV-radiation, and was agitated using a magnetic stirring plate.

Then, 50 mL of Procion Red MX-5B dye with a concentration of 0.0227 g/L of distilled water was placed into 4 separate beakers. The two controls mimicked the previous experiment. The third beaker containing 1.0641 g of titania-coated GMBs was placed under solar UV-radiation, and agitated using an aeration bubbler apparatus. The fourth beaker contained 1.0645 g of titania-coated GMBs, was placed under solar UV-radiation, and was agitated using a magnetic stirring plate.

For both the dye experiments, samples were taken after various intervals of UV-exposure, centrifuged using an IEC Clinical Centrifuge to isolate the dye solution from any suspended GMBs, and then evaluated using a Cary 100 UV-Visible Spectrophotometer. Additionally, scanning electron microscopy (SEM) was used to analyze the effects of agitation on the titania coatings of the HGMs.

RESULTS

Both PRO Forest Green H-Reactive H-E4BD and Procion Red MX-5B dye samples appeared clear in color as a result of UV-irradiated GMBs and agitation by a magnetic stirrer (Figs. 1 and 2). Spectrophotometry measurements showed that the samples containing titania-coated GMBs agitated by the magnetic stirrer had absorbance values of 0, or essentially 0, after UV exposure. On the other hand, the samples containing the titania-coated GMBs agitated by the aeration bubbler apparatus also showed a decrease in absorbance after UV exposure (with absorbance values of 0.345 for the PRO Forest Green H-Reactive H-E4BD dye and 0.030 for the Procion Red MX-5BD) in comparison to

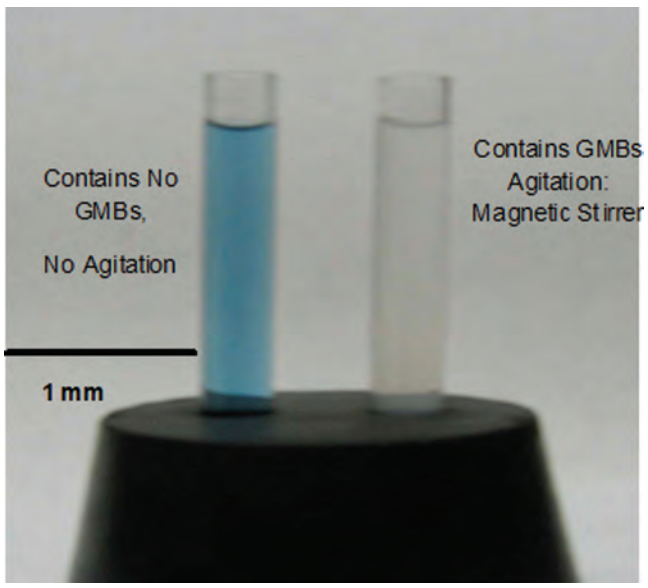


Figure 1. Effect of titania-coated glass microballoons (GMBs) on PRO Forest Green H Reactive H-E4BD Dye (initial concentration: 0.0918 g of dye/ L of distilled water) after 3 h, 30 min UV exposure

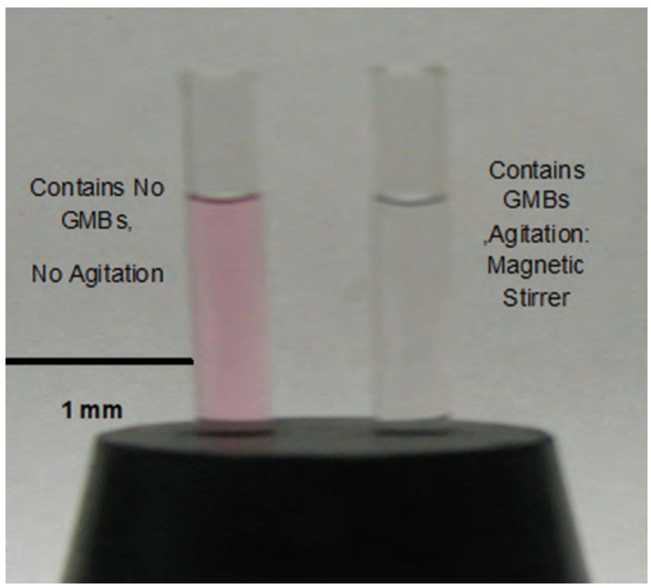


Figure 2. Effect of titania-coated glass microballoons (GMBs) on Procion Red MX-5B Dye (initial concentration: 0.0227 g of dye/ L of distilled water) after 3 h, 40 min UV exposure

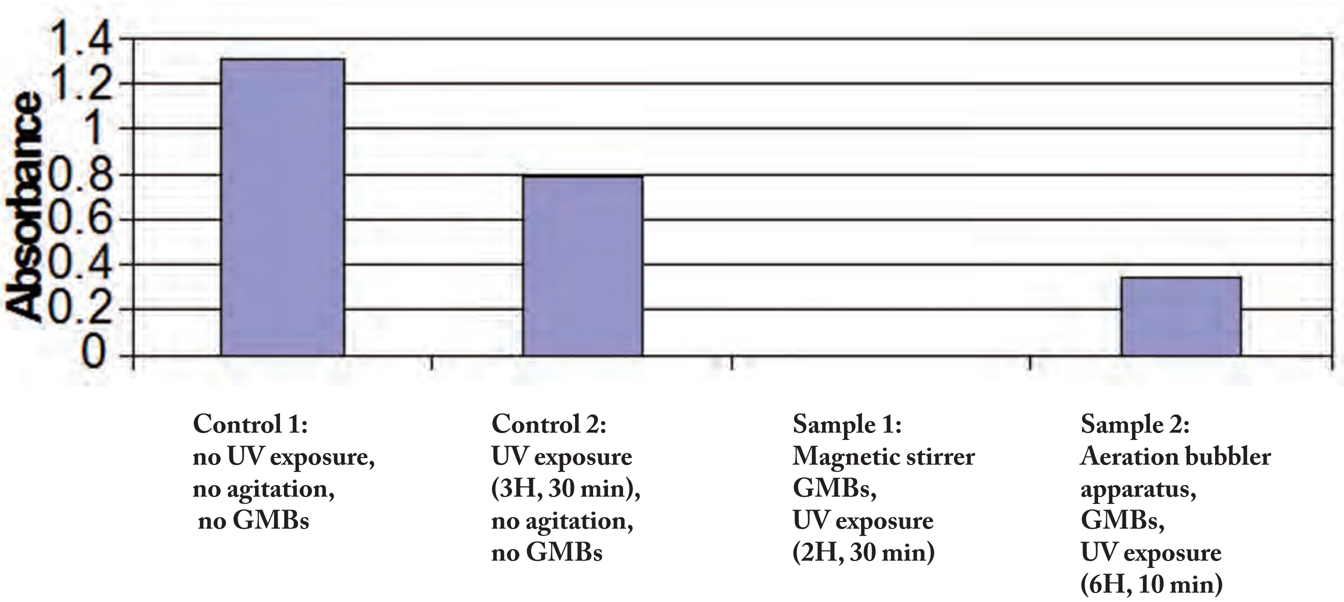


Figure 3. Photospectrometry Analysis of the Effect of UV-irradiated Titania-Coated Glass Microballoons (GMBs) on PRO Forest Green H-Reactive H-E4BD Dye (Initial Concentration: 0.0918 g of dye/ L of distilled water) at a wavelength of 630

the controls, but this decrease was not as significant as the decrease observed in the sample agitated by the magnetic stirrer. Furthermore, a decrease in absorbance was observed for the control samples exposed to UV-radiation that did not contain titania-coated GMBs; however, this decrease was less profound than either of the samples that contained titania-coated GMBs (Figs. 3 and 4). SEM analysis was performed on the GMBs in the samples agitated by both the magnetic stirrer and by the aeration bubbler apparatus at the conclusion of the experiments. The GMBs used in the dye samples agitated by the magnetic stirrer appeared to have suffered a loss of titania coating (Figure 5).

DISCUSSION AND CONCLUSIONS

Our experiments show successful use of titania as a photocatalyst in the form of coating of GMBs, which is in accord with work on titania in the form of suspended nano-particles (Akarsu et al.,2006, Lachheb et al., 2002). This success was evidenced by the decolorization of common textile dyes. Interestingly, however, the success in the form of the complete decolorization of both the PRO Forest Green H-Reactive H-E4BD dye and the Procion Red MX-5B dye was more profound when the magnetic stirrer was used as a source of agitation than when these two dyes were simply aerated. The samples agitated by the magnetic stirrer were both found to have an absorbance of 0 (or essentially 0) as a result of the dye in each sample breaking down. As a result of the increase in collisions of particles from the agitation of the magnetic stirrer, the ensuing increase in reaction rate of the titania-driven photocatalytic degradation must be considered as a possible reason for the more rapid effects noted in the samples exposed to the magnetic stirrer. Also, in accordance to the findings of Preis et al. (1997), the overall success of the magnetic stirrer as a source of agitation can be attributed to the slurry of titania coatings formed from the breakage of GMBs during the turbulent conditions created by the magnetic stirrer; SEM analysis confirms that the titania coatings of the GMBs were damaged as a result. In slurry form, the titania coatings have a larger surface area exposed both to the dye particles in solution and to the effects of UV-irradiation. Consequently, the dye solutions seem to be more effectively degraded as a result of the tumultuous effects of the magnetic stirrer. Like the findings of Preis et al. (1997), which showed that titania attached to GMBs was less photocatalytically active than titania

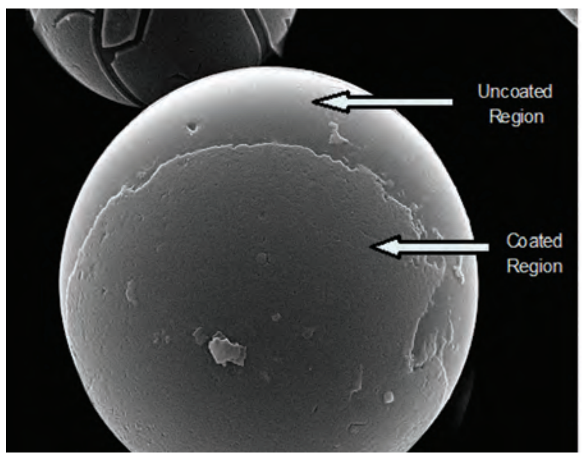
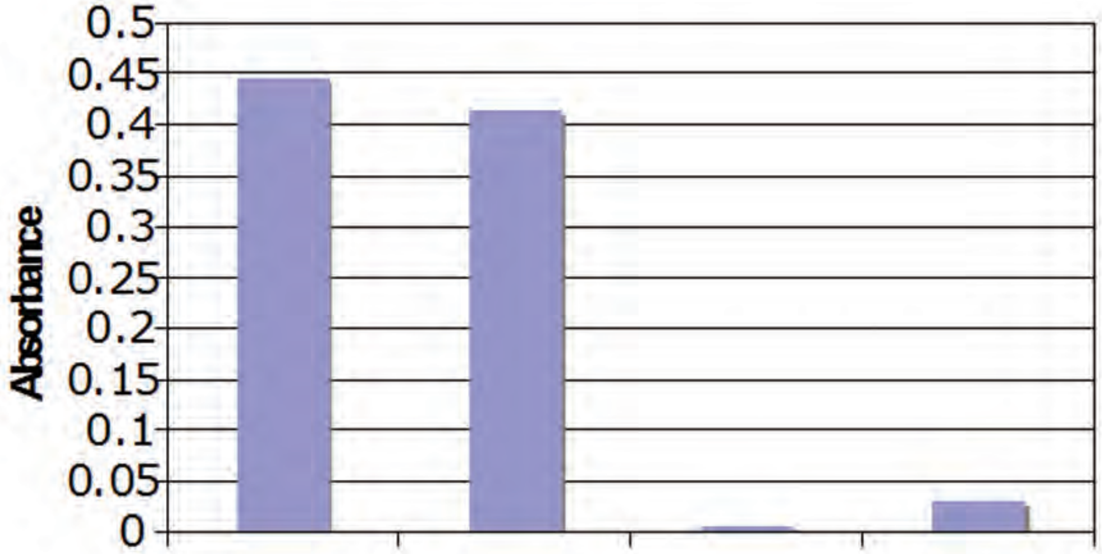


Figure 4. Scanning Electron Microscopy (SEM) Analysis of Titania-Coated GMBs From Sample Agitated Using the Magnetic Stirrer (magnification: 4020x, working distance: 19.2 mm)



Control 1:
no UV exposure,
no agitation,
no GMBs

Control 2:
UV exposure
(3H, 40 min),
no agitation,
no GMBs

Sample 1:
Magnetic stirrer
GMBs,
UV exposure
(3H)

Sample 2:
Airation bubbler
apparatus,
GMBs,
UV exposure
(6H, 10 min)

Figure 5. Photospectrometry Analysis of the Effect of UV-irradiated Titania-Coated Glass Microballoons (GMBs) on Procion Red MX-5B Dye (Initial Concentration: 0.0227 g of dye/ L of distilled water) at a wavelength of 510 nm

slurries, this experiment suggests that the intact titania-coated GMBs in the samples agitated using the aeration bubbler apparatus produced less successful results than the slurry of titania particles generated by the turbulent effects of the magnetic stirrer. However, the conclusions of Preis et al. (1997) also offered that the use of titania-coated GMBs produces the cost-effective advantage of photocatalytic treatment without constant agitation, unlike slurries of titania particles which require continuous stirring to have an effect. Furthermore, without the act of agitation, Preis et al. (1997) concluded that the titania coating would be less likely to become separated from its substrate. Therefore, although the dye samples agitated using the aeration bubbler apparatus were not as successfully broken down as the samples agitated using the magnetic stirrer, the results obtained are more notable in terms of possible industrial applications due to the implied cost-effectiveness and simplicity of design. Moreover, the findings of this experiment echo other studies in terms of the degradation abilities of titania as a photocatalyst and stress the success of GMBs as an effective substrate in the photocatalytic degradation of common textile dyes.

These experiments are conclusive of the photocatalytic effects of titania and the use of GMBs as its substrate. For the purpose of gaining more knowledge of the behavior of titania-coated GMBs and their potential role in the breakdown of textile dyes on a larger industrial scale, various parameters must be tested such as: varying pH levels, initial dye concentrations, and amount of catalyst present.

ACKNOWLEDGMENTS

The authors would like to thank the National Science Foundation for the Research Experience for Undergraduates (REU) program grant. Thanks are also due to Dr. William Nonidez (Department of Chemistry, University of Alabama at Birmingham).

REFERENCES

- Akarsu, M., M. Asilturk, F. Sayilkan, N. Kiraz, E. Arpac, and H. Sayilkan (2006). A novel approach to the hydrothermal synthesis of anatase titania nanoparticles and photocatalytic degradation of Rhodamine B. Turk J. Chem., 30. 333-343.
- Asad, S., M. A. Amoozegar, A. A. Pourbabaee, M. N. Sarbolouki, and S. M. M. Dastgheib (2007). Decolorization of textile azo dyes by newly isolated halophilic and halotolerant bacteria. Bioresource Technology, 98. 2082-2088.
- Byrappa, K., M. H. Sunitha, A. K. Subramani, S. Ananda, K. M. L. Rai, B. Basavalingu, and M. Yoshimura (2006). Hydrothermal preparation of neodymium oxide coated titania composite designer particulates and its application in the photocatalytic degradation of procion red dye. J. Mater. Sci., 41. 1369-1375.
- Garcia-Montano, J., F. Torrades, J. A. Garcia-Hortal, X. Domenech, and J. Peral (2005). Degradation of Procion Red H-E7B reactive dye by coupling a photo-Fenton system

with a sequencing batch reactor. Journal of Hazardous Materials, 134. 220-229.

- Koopman, M., G. Gouadec, K. Carlisle, K. K. Chawla, and G. Gladysz (2004). Compression testing of hollow microspheres (microballoons) to obtain mechanical properties. Scripta Materialia, 50. 593-596.
- Lachheb, H., E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard, and J. Herrmann (2002). Photocatalytic degradation of various types of dyes (Alizarin S, Crocein Orange G, Methyl Red, Congo Red, Methylene Blue) in water by UV-irradiated titania. Applied Catalysis B: Environmental, 39. 75-90.
- Moreira, R., T. P. Sauer, L. Casaril, and E. Humeres (2005). Mass transfer and photocatalytic degradation of leather dye using TiO2/UV. Journal of Applied Electrochemistry, 35. 821-829.
- Preis, S., M. Krichevskaya, and A. Kharchenko (1997). Photocatalytic oxidation of aromatic aminocompounds in aqueous solutions and groundwater from abandoned military bases. Wat. Sci. Tech., 35. 265-272.
- Ren, M., R. Ravikrishna, and K. T. Valsaraj (2006). Photocatalytic Degradation of Gaseous Organic Species on Photonic Band-Gap Titania. Environ. Sci. Technol., 40. 7029-7033.
- So, C. M., M. Y. Cheng, J. C. Yu, and P. K. Wong (2002). Degradation of azo dye Procion Red MX-5B by photocatalytic oxidation. Chemosphere, 46. 905-912.